

Er³⁺-doped aluminophosphosilicate glasses obtained by
the sol-gel method: structural study and luminescence
properties

Ph.D. thesis

Beatriz Helena Costa

Universidade Estadual Paulista
Campus de Araraquara
Programa de Pós-Graduação em Química

Araraquara
2024

Beatriz Helena Costa

Er³⁺-doped aluminophosphosilicate glasses obtained by the sol-gel
method: structural study and luminescence properties

Thesis presented to the Institute of
Chemistry, São Paulo State University,
to obtain the Ph.D in Chemistry

Advisor: Dra. Silvia Helena Santagneli

Araraquara

2024

Beatriz Helena Costa

Vidros aluminofosfosilicatos dopados com Er^{3+} obtidos pelo método sol-gel: estudo estrutural e propriedades luminescentes

Tese apresentada ao Instituto de Química, Universidade Estadual Paulista, como parte dos requisitos para obtenção do título de Doutora em química

Orientadora: Dra. Silvia Helena Santagneli

Araraquara

2024

C837d	Costa, Beatriz Helena Er³⁺-doped aluminophosphosilicate glasses obtained By the sol-gel method: structural study and luminescence properties / Beatriz Helena Costa – Araraquara: [s.n.], 2024 149 p.: il. Thesis (doctor) – Universidade Estadual Paulista, Instituto de Química Advisor: Silvia Helena Santagneli 1. Glass. 2. Sol-gel process. 3. Nuclear magnetic Resonance. 4. Erbium. 5. Luminescence. I. Title.
-------	---

Sistema de geração automática de fichas catalográficas da Unesp. Biblioteca do Instituto de
Química, Araraquara. Dados fornecidos pelo autor(a).

Essa ficha não pode ser modificada

Expected impact

The present work significantly contributes to the development of new glassy materials within the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ ternary system. It introduces a new sol-gel route to overcome the limitations of the conventional melting method. This advancement opens the way for the application of the MCVD method in the production of optical fibers. The achievement of homogeneous and transparent glasses at relatively lower temperatures, combined with good optical properties, opens new possibilities for applications in photonics and telecommunications, especially in the fabrication of optical devices doped with rare-earth ions.

Societal Impact

The possibility of developing new materials for use in optical amplifiers has the potential to improve telecommunications systems and other technological fields. This advancement could lead to more efficient and affordable technologies, benefiting sectors such as high-speed internet and the creation of new data transmission channels to meet the increasing annual demand. Additionally, the reduction in energy consumption and environmental impact, as it enables lower manufacturing temperatures and the use of eco-friendly solvents, thereby contributing to sustainability.

Economic Impact

The development of advanced materials, such as those investigated in this study, can lower manufacturing costs through the sol-gel route, which allows lower processing temperatures. Furthermore, the potential application of these materials in optical devices could lead to innovations in the telecommunications industry, aiming to expand market opportunities and enhance the competitiveness of both national and international industries.

Academic Impact

This work significantly contributes to materials science and glass chemistry by introducing a new approach to the synthesis of aluminophosphosilicate glasses doped

with rare earth ions. It provides a detailed understanding of their structural by solid-state NMR and optical properties. The methodologies employed and the results obtained also offer a solid foundation for future research in the field of photonic materials and sol-gel synthesis.

Sustainable Development Context

By proposing a more energy-efficient synthetic route, with lower temperatures and greater homogeneity in the resulting materials, this work aligns with the United Nations Sustainable Development Goals (SDGs), particularly those related to affordable and clean energy (SDG 7) and industry, innovation, and infrastructure (SDG 9). Additionally, the reduction in energy consumption during the manufacturing stages contributes to mitigating climate change (SDG 13).

Conclusion

This work represents an advancement in the synthesis of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glass system, enabling the production of materials with good optical properties at relatively lower temperatures compared to the conventional melting method, contributing thus to a more sustainable production route. Furthermore, the ability to dope these glasses with rare-earth ions, such as the Er^{3+} ion, demonstrates the potential of these materials for applications in the field of photonics, promoting technological and scientific advancement.

Impacto Esperado

O presente trabalho traz contribuições significativas ao desenvolvimento de novos materiais vítreos baseados no sistema ternário $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$. Ele introduz uma nova rota sol-gel para superar limitações do método convencional de fusão. Este avanço abre a possibilidade para a aplicação do método MCVD na obtenção de fibras ópticas. A obtenção de vidros homogêneos e transparentes a temperaturas relativamente mais baixas com boas propriedades ópticas, abre novas possibilidades para aplicações na área de fotônica e telecomunicações, principalmente na fabricação de dispositivos ópticos dopados com íons terras raras.

Impacto Social

A possibilidade de desenvolver novos materiais para uso em amplificadores ópticos tem o potencial de melhorar o sistema de telecomunicações e outras áreas tecnológicas. Esse avanço possibilitará o acesso a tecnologias que sejam mais eficientes e acessíveis, beneficiando setores como a internet de alta velocidade e a criação de novos canais para transmissão de dados para suprir a crescente demanda anual. Além disso, a diminuição no consumo energético e o impacto ambiental, pois permite a produção desses materiais em temperaturas mais baixas e o uso de solventes mais ecológicos, contribuindo assim para a sustentabilidade.

Impacto Econômico

O desenvolvimento de materiais avançados, como os investigados neste trabalho, pode reduzir custos no processo de fabricação através da rota sol-gel que permite o uso de menores temperaturas de processamento. Além disso, a possibilidade de utilizar esses materiais como dispositivos ópticos pode gerar inovações na indústria de telecomunicações, visando ampliar as oportunidades de mercado e a competitividade da indústria nacional e internacional.

Impacto Acadêmico

Este trabalho contribui significativamente para a ciência dos materiais e química de vidros, introduzindo uma nova abordagem para síntese de vidros aluminofosfosilicatos dopados com íons terras raras. Ele fornece uma compreensão detalhada da sua estrutura por RMN no estado sólido. As metodologias empregadas e os resultados obtidos também oferecem uma base sólida para pesquisas futuras no campo de materiais fotônicos e síntese sol-gel.

Contexto do Desenvolvimento Sustentável

Ao propor uma rota sintética mais eficiente em termos energéticos, com temperaturas mais baixas e maior homogeneidade nos materiais resultantes, o trabalho se alinha com os Objetivos de Desenvolvimento Sustentável (ODS), particularmente os que tratam de energia limpa e acessível (ODS 7) e inovação e infraestrutura (ODS 9). Além disso, a redução de consumo de energia nas etapas de fabricação colabora com a mitigação das mudanças climáticas (ODS 13).

Conclusão

O presente trabalho representa um avanço na síntese de vidros do sistema $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$, o qual permite a obtenção de materiais em temperaturas relativamente baixas quando comparadas ao método convencional de fusão com boas propriedades ópticas, o que contribui para uma rota mais sustentável de produção. Além disso, a capacidade de dopagem desses vidros com íons terras raras, como o íon Er^{3+} , demonstra o potencial desses materiais para aplicações na área da fotônica, promovendo o avanço tecnológico e científico.

CERTIFICADO DE APROVAÇÃO

TÍTULO DA TESE: "Er³⁺-doped aluminophosphosilicate glasses obtained by the sol-gel method: structural study and luminescence properties"

AUTORA: BEATRIZ HELENA COSTA

ORIENTADORA: SILVIA HELENA SANTAGNELI

Aprovada como parte das exigências para obtenção do Título de Doutora em Química, pela Comissão Examinadora:

Prof^a. Dr^a. SILVIA HELENA SANTAGNELI (Participação Presencial)
Departamento de Química Analítica, Físico-Química e Inorgânica / Instituto de Química - UNESP - Araraquara

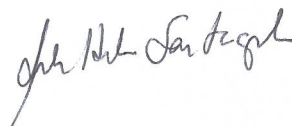
Prof. Dr. MARCOS DE OLIVEIRA JUNIOR (Participação Presencial)
Departamento de Física / Instituto de Física - IFSC - USP - São Carlos

Dr. DOUGLAS FAZA FRANCO (Participação Presencial)
Departamento de Química Analítica, Físico-Química e Inorgânica / Instituto de Química - UNESP - Araraquara

Prof. Dr. THIAGO BRANQUINHO DE QUEIROZ (Participação Virtual)
Centro de Ciências Naturais e Humanas - CCNH / Universidade Federal do ABC - São Paulo

Prof. Dr. DANILO MANZANI (Participação Presencial)
Departamento de Química e Física Molecular / Instituto de Química - USP - São Carlos

Araraquara, 29 de novembro de 2024



In 'Capitães da Areia', Jorge Amado wrote that certain men have stars in place of their hearts, and when they die, their hearts remain in the sky. I can say that my father had a star in place of his heart. My entire journey was guided and cared for by him. Therefore, I dedicate this thesis to keeping him alive in every line I write.

ACKNOWLEDGMENT

First of all, I would like to thank my advisor Dr. Silvia Helena Santagneli, for all her support and for trusting me in carrying out this work. I also thank her for the countless lessons she provided me throughout all these years of research, especially for sharing her knowledge about the solid-state NMR technique with me.

Secondly, I would like to thank Prof. Younès Messaddeq for his support and guidance during my stay as a research intern at Université Laval in Canada. His co-supervision was essential for the execution of this work, and the knowledge I gained there was fundamental to the success of this project.

I would like to thank the members of the examination committee for accepting the invitation to evaluate this work.

I am deeply grateful to Gabriel T. Tayama for all his contributions and for the knowledge shared throughout these years of my Ph.D, especially at the beginning.

Additionally, I would like to thank Victor A. G. Rivera for his support with the luminescence measurements in Canada and for all his help in the discussion part of this work.

I would like to thank Bruno S. D. Onishi for all his support in the scientific discussions over the years, and especially for our friendship.

I appreciate all my lab-mates and professors at the Laboratory of Photonic Materials in Araraquara.

I would like to thank João and Rhayane for our friendship and for making me laugh even on the bad days.

I am grateful to the Institute of Chemistry of the São Paulo State University.

I am very grateful for the friendships I made during my stay at COPL - Université Laval: Anees, Gaston, Rizan, Haleh, Can, Iago, Alizée, Hasnaa, Samar, and Ishfaq.

I express my sincere gratitude to my mom Soraia, my father Tadeu, my brothers Bruno and Marcio, and my aunt and uncle Sônia and Manuel for always supporting and encouraging me in the pathways that I follow.

I would like to thank the financial support from Coordenação de Aperfeiçoamento de Pessoa de Nível Superior (CAPES) for the scholarship (Finance code: 001).

DATA

Personal Information

- Full Name: Beatriz Helena Costa
- Name in bibliography Citation: Costa, B. H.; Beatriz H. Costa; Costa, Beatriz Helena
- Nationality: Brazilian
- Birth city: Mairinque - SP
- Profession: Chemist
- Address: Instituto de Química – Universidade Estadual Paulista “Júlio de Mesquita Filho” – Av. Prof. Francisco Degni, 55 – Jardim Quitandinha – Araraquara -SP. CEP: 14800-060
- E-mail: bh.costa@unesp.br

Academic education

- Bachelor's degree in Chemistry (2018), State University of Londrina (UEL - Universidade Estadual de Londrina), Londrina – PR
- Master's degree in Chemistry (2020), State University of Londrina (UEL - Universidade Estadual de Londrina), Londrina – PR

Work Experience

- Undergraduate research (PROIT) in the chemistry department (UEL), in the field of atmospheric air - Advisor: Prof. Dra. Maria Cristina Solci (2017);
- Scholarship holder of CNPq in master's degree (UEL - 2018 – 2020);
- Scholarship holder of CAPES in Ph.D degree (UNESP - 2020-2024);
- Research Internship and scholarship holder by CAPES PrInt at Université Laval (Québec – Canada) – Advisor: Prof. Dr. Younès Messaddeq (2022-2023);
- Internship supervision – Lucas Toth Elias e Silva - Structural elucidation by NMR spectroscopy of transparent hybrid materials based on aluminum silicate borate for photonic applications by 3D printing (UNESP - 2022-2023)

Participation in scientific events

- XXII B-MRS Meeting. Structural characterization and luminescence properties of Er^{3+} -doped aluminophosphosilicate glass obtained by sol-gel method (2024) – poster presentation;
- 10th International Conference on Optical, Optoelectronic and Photonic Materials and Applications – ICOOPMA. Effects of the thermal treatment on structure and luminescence properties of erbium-doped aluminophosphosilicate glass obtained by sol-gel method (2024) – oral presentation;
- XXI B-MRS Meeting. Influence of Al/P ratio on the luminescence properties of erbium-doped aluminophospho- silicate glasses obtained by sol-gel method (2023) – oral presentation;
- XXXVI Semana da Química - a Química - ta on: os desafios e possibilidades da era pós-pandemia (2021) – seminar participant;
- Semana dos Profissionais de Química (2020) – seminar participant;
- XVIII B-MRS Meeting. Characterization of silicon oxycarbide (SiCO) ceramics derived from organic-inorganic hybrid polymers with different proportions of organic phase (2019) – poster presentation;
- XVIII B-MRS Meeting. Investigation of the electrochemical potentialities of silicon oxycarbide (SiCO) ceramics obtained from organic-inorganic hybrid polymers (2019) – poster presentation;
- XXXV Semana da Química da UEL: Química e materiais: uma interface de inovação para a sociedade (2019) – oral and poster presentations;
- 6th. Bioanalytical School (2018) – seminar participant;

- XXV Encontro de Química da Região Sul. Influência de precursores poliméricos orgânico-inorgânicos com diferentes estruturas na obtenção de cerâmicas de oxycarbeto de silício (SiCO) (2018) – poster presentation;
- VIII Encontro Nacional de Química Ambiental (2017) – seminar participant;
- XXXIII Semana da Química da UEL: Tecnologias em química: inovações na indústria, pesquisa e ensino (2017) – seminar participant;
- XXXI Semana da Química da UEL: A química e a sua multidisciplinaridade (2015) – seminar participant.

Scientific production

- **B. H. Costa**, Gabriel T. Tayama, V. A. G. Rivera, Younès Messaddeq, Silvia H. Santagneli. Effects of the thermal treatment on structural and luminescence properties of Er³⁺-doped aluminophosphosilicate glasses obtained by the sol-gel method. *J. Alloys Compd.* Accepted manuscript. DOI: 10.1016/j.jallcom.2024.177112;
- **Beatriz Helena Costa**, Gabriel Toshiaki Tayama, Silvia Helena Santagneli. Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials *J. Non Cryst. Solids*. Accepted manuscript. DOI: 10.1016/j.jnoncrysol.2024.123105;
- B. S. D. Onishi, **B. H. Costa**, L. Marchiori, B. D. de Freitas, R. S. Pugina, J. R. Bartlett, L. D. Carlos, E. P. Ferreira-Neto, S. J. L. Ribeiro. Organic–inorganic hybrid silica systems: synthesis strategies and optical applications *J. Solgel Sci. Technol.* Accepted review manuscript. DOI: 10.1007/s10971-024-06406-9;
- **Beatriz Helena Costa**, Maria de Almeida Silva, César Ricardo Teixeira Tarley, Emerson Schwingel Ribeiro, Mariana Gava Segatelli. Influence of polymer synthesis route and organic fraction content on structure and porosity of silicon oxycarbide ceramics *Process Appl. Ceram.* Accepted manuscript. DOI: 10.2298/PAC2302118C.

FOREWORD

This Ph.D thesis was written in the chapters/article format in accordance with the norms of “Programa de Pós-Graduação em Química” at the Institute of Chemistry, UNESP – Araraquara -SP.

The content of Chapter 2 was reproduced from a paper published in the Journal of Non-Crystalline Solids (impact factor: 3.2) after peer review. All the co-author's permissions were acquired as well as the Copyright © 2024 from Elsevier. To access the final published work see: <https://doi.org/10.1016/j.jnoncrysol.2024.123105>.

The content of Chapter 3 was reproduced from a paper published in the Journal of Alloys and Compounds (impact factor: 5.8) . All the co-author's permissions were acquired as well as the Copyright © 2024 from Elsevier. To access the final published work see: <https://doi.org/10.1016/j.jallcom.2024.177112>.

The results in Chapter 2 were collected fully at the host institution. The results in Chapter 3 were collected at the host institution and during the studies abroad in COPL at Université Laval, Quebec City - Canada.

Chapter 2 Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials

Authors Beatriz Helena Costa, Gabriel Toshiaki Tayama, Silvia Helena Santagneli

Journal Journal of Non-Crystalline Solids, 2024, 639, 123105

DOI 10.1016/j.jnoncrysol.2024.123105

State Received 25 April, 2024; Received in revised form 19 June, 2024; Accepted 23 June, 2024

Chapter 3 Effects of the thermal treatment on structural and luminescence properties of Er³⁺-doped aluminophosphosilicate glasses obtained by the sol-gel method

Authors Beatriz H. Costa, Gabriel T. Tayama, V. A. G. Rivera, Younès Messaddeq, Silvia H. Santagneli

Journal Journal of Alloys and Compounds, 2025, 1010, 177112

DOI 10.1016/j.jallcom.2024.177112

State Received 2 August, 2024; Received in revised form 7 October, 2024; Accepted 17 October, 2024

ABSTRACT

This study investigates the structural evolution in the ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ system and the effects of heat treatment on the photoluminescent properties of Er^{3+} -doped aluminophosphosilicate glasses obtained via the sol-gel method. Hybrid materials were synthesized using the sol-gel method and further subjected to heat treatment up to 800 °C to obtain vitreous materials. The structural evolution of the hybrid and heat-treated materials was monitored as a function of SiO_2 concentration (10, 30, 50, 70, 90, and 100 mol%) using various characterization techniques, such as solid-state NMR of ^{13}C , ^{29}Si , ^{31}P , and ^{27}Al , infrared (FTIR) and Raman scattering spectroscopies, X-ray diffraction (XRD), and differential scanning calorimetry (DSC). FTIR, Raman, and ^{13}C NMR analyses confirmed the formation of hybrids, indicated by signals from methacrylate groups and carbon chains formed via photopolymerization of the precursors, along with Si-O-Si bond signals, demonstrating the formation of a three-dimensional network connected by silicon tetrahedra. Additionally, NMR results confirmed this three-dimensional network formed by silicon tetrahedra as the SiO_2 proportion in the matrix increased. They also revealed that cross-linking involved homo- and heterocondensation reactions among silicate, phosphate, and aluminum species (Si-O-Si, Si-O-Al, and Al-O-P bonds), with the absence of Si-O-P bonds. After heat treatment, glass formation was observed for samples with $\text{SiO}_2 \geq 90\%$, confirmed by the glass transition temperature (T_g) on DSC curves. NMR results also showed that the thermally treated materials formed AlPO_4 and a homogeneous structure via heterocondensation among aluminum, phosphate, and silicate species, as indicated by the presence of Al-O-P and P-O-Si bonds (not previously seen in the hybrid materials) in an interconnected network of silicon tetrahedra as SiO_2 content in the matrix increased. Materials with lower SiO_2 proportions (10-70 mol%) demonstrated a higher proportion of AlPO_4 formation as showed by Raman spectra.

Due to the formation of cracks during heat treatment, primarily caused by the release of organic components, the synthesis procedure was modified to include a highly controlled heat treatment up to 800 °C, with a heating rate of 1 °C/min and various intermediate plateau, to prevent cracking in the final material. For the photoluminescence study, the $95\text{SiO}_2\text{-}5\text{AlPO}_4\text{:}0.2\text{Er}^{3+}$ composition was selected, focusing on the structural evolution from gel to glass, as well as the optical properties in response to heat treatment. Controlled heat treatment resulted in high-optical-quality (homogeneous, transparent)

glasses. A higher heterocondensation degree was observed through NMR, where higher temperatures led to the appearance of Si-O-Si, Si-O-P, Si-O-Al, and Al-O-P bonds. Photoluminescence studies showed emission at 1540 nm of low intensity due to the high water content on the surface of these materials. This was confirmed by OH group signals in the UV-Vis-NIR spectra and ^1H NMR, which contributed to Er^{3+} ion luminescence quenching.

Furthermore, the photoluminescence of materials treated at 800 °C and after an additional vacuum heat treatment at 900 °C for 30 minutes was studied, with varying Er^{3+} ion concentrations (0.05, 0.1, 0.2, 0.5, and 1.0 mol%). Results indicated that vacuum heat treatment promoted matrix densification and increased condensation among aluminum, phosphate, and silicate species. Additionally, vacuum treatment reduced OH groups in the glass matrix, which enhanced the luminescence intensity at 1.5 μm and increased the emission band's full width at half maximum (~ 100 nm) for the sample containing 0.5 mol% Er^{3+}), suggesting the formation of different chemical environments for Er^{3+} ions. Moreover, luminescence studies showed that at Er^{3+} concentrations above 0.5 mol%, signal intensity decreased, indicating luminescence quenching, likely due to non-radiative losses caused by cluster formation. This new sol-gel synthesis approach provides a way to obtain homogeneous, transparent glasses doped with rare-earth elements, opening the way for developing new optical devices for telecommunications with broadband emission in the near-infrared (NIR), operating in the C+L transmission bands.

RESUMO

Este estudo investiga a evolução estrutural no sistema ternário $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$, assim como os efeitos do tratamento térmico influenciam nas propriedades fotoluminescentes dos vidros de aluminofosfosilicatos dopados com Er^{3+} obtidos via método sol-gel. Os materiais híbridos foram sintetizados utilizando o método sol-gel, e então submetidos ao tratamento térmico até $800\text{ }^\circ\text{C}$ para obtenção dos materiais vitreos. A evolução estrutural dos materiais híbridos e tratados termicamente foi monitorada em função da concentração de SiO_2 (10, 30, 50, 70, 90 e 100 mol.%) a partir de diferentes técnicas de caracterização como: espectroscopias de RMN de estado sólido de ^{13}C , ^{29}Si , ^{31}P e ^{27}Al , infravermelho (FTIR) e espalhamento Raman, difração de raios X (DRX) e calorimetria exploratória diferencial (DSC). A partir das técnicas de FTIR, Raman e RMN de ^{13}C foi verificada a formação dos híbridos a partir da presença de sinais referentes aos grupos metacrilato e da cadeia carbônica formada a partir da fotopolimerização dos precursores, além de sinais referentes as ligações Si-O-Si evidenciando a formação de uma rede tridimensional conectada por tetraedros de silício. Além disso, principalmente os resultados de RMN confirmaram a formação desta rede tridimensional formada por tetraedros de silício em função do aumento da proporção de SiO_2 na matriz, e evidenciou que no processo de reticulação ocorreram reações de homo- e heterocondensação entre as espécies silicato, fosfato e alumínio (ligações Si-O-Si, Si-O-Al e Al-O-P), revelando a ausência de ligações Si-O-P. No entanto, após tratamento térmico, foram obtidos vidros para as amostras com % $\text{SiO}_2 \geq 90\%$, as quais foram confirmadas a partir da temperatura de transição vítrea (T_g) observada nas curvas DSC. Adicionalmente, os resultados de RMN confirmaram que os materiais tratados termicamente apresentaram a formação de AlPO_4 e uma estrutura homogênea a partir da heterocondensação entre as espécies alumínio, fosfato e silicato indicada pelo surgimento de ligações Al-O-P e P-O-Si (não observada anteriormente nos materiais híbridos) em uma rede interconectada por tetraedros de silício conforme o aumento da quantidade de SiO_2 na matriz. Os materiais contendo menores proporções de SiO_2 (10-70 mol.%) evidenciaram a formação de AlPO_4 em maior proporção como mostrado pelos espectros Raman.

Devido ao aparecimento de trincas durante o tratamento térmico que ocorre principalmente durante a liberação dos componentes orgânicos, a síntese dos materiais foi adaptada e foram submetidos a um tratamento térmico extremamente controlado até

800 °C, com taxa de aquecimento de 1 °C min⁻¹ contendo diferentes temperaturas e tempos de patamares, de modo a evitar o aparecimento de trincas no material final. Para o estudo de fotoluminescência foi escolhida a composição 95SiO₂-5AlPO₄:0,2Er³⁺, onde foi estudado a evolução estrutural do gel para o vidro, assim como as propriedades ópticas em função do tratamento térmico. O tratamento térmico controlado permitiu a obtenção de vidros de alta qualidade óptica (transparentes e homogêneos). O aumento no grau de heterocondensação foi observado a partir do estudo de RMN, onde o aumento da temperatura resultou no aparecimento de sinais referentes a formação da ligações Si-O-Si, Si-O-P e Si-O-Al e Al-O-P. O estudo da fotoluminescência desses materiais apresentou emissão em 1540 nm de baixa intensidade devido a alta concentração de água presente na superfície desses materiais. Isso foi confirmado a partir da presença de sinais referentes ao grupo hidroxila (OH) nos espectros UV-Vis-NIR e RMN de ¹H, o qual é responsável pela supressão da luminescência dos íons Er³⁺.

Assim, foi realizado o estudo da fotoluminescência dos materiais tratados em 800 °C e submetendo a um tratamento térmico sob vácuo a 900 °C por 30 minutos contendo diferentes concentrações de íons Er³⁺ (0,05; 0,1; 0,2; 0,5 e 1,0 mol.%). Os resultados obtidos indicaram que o tratamento térmico sob vácuo promoveu uma densificação da matriz, assim como um maior grau de condensação entre as espécies alumínio, fosfato e silicato. Adicionalmente, o tratamento térmico sob vácuo ocasionou na diminuição de grupos OH na matrix vítrea, o que promoveu o aumento na intensidade do sinal de luminescência em 1,5 µm, assim como o aumento da largura meia altura da banda de emissão (~100 nm) para amostra contendo 0,5 mol.% de Er³⁺, sugerindo a formação de diferentes ambientes químicos para os íons Er³⁺. Além disso, o estudo de luminescência mostrou que para concentrações maiores de 0,5 mol.% de Er³⁺ a intensidade do sinal diminui, indicando supressão da luminescência, provavelmente devido a perdas não radiativas ocasionadas pela formação de *clusters*. Assim, esta nova abordagem de síntese sol-gel oferece uma maneira de obter vidros transparentes homogêneos dopados com elementos terras raras, possibilitando o desenvolvimento de novos dispositivos ópticos para telecomunicações com emissão de banda larga na região do infravermelho próximo (NIR) operando nas bandas C+L de transmissão de dados.

Resumo expandindo da tese em português

Neste resumo está descrito a metodologia, os resultados e discussões apresentados nos capítulos 2 e 3, com uma breve introdução apresentando a motivação para os trabalhos executados.

Embora os vidros baseados no sistema ternário $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ apresentem características interessantes para hospedarem íons terras raras, tornando-os desejáveis para aplicações em fotônica, o método comumente utilizado para obtê-los, fusão seguido de choque térmico, requer temperaturas muito altas e, ainda apresenta muitos problemas durante a preparação, como separação de fase e/ou cristalização, principalmente para composições ricas em SiO_2 . Dessa forma, novas abordagens para a obtenção de vidros homogêneos são essenciais para o avanço da área. Assim, o método sol-gel se mostra uma rota interessante, uma vez que permite obter vidros a base de $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ em temperaturas relativamente baixas quando comparado ao método de fusão. A sua preparação a partir de precursores no estado líquido permite uma boa homogeneização dos precursores, inclusive na dopagem com íons terras raras. No entanto, mesmo o método sol-gel, dependendo dos precursores e/ou metodologia de preparação, os vidros também podem apresentar segregação de fase, como observado em alguns trabalhos na literatura. Então uma nova rota sol-gel foi abordada neste trabalho para tentar evitar esses problemas e, conseqüentemente, obter materiais homogêneos e transparentes.

Considerando os pontos apresentados acima, o objetivo do trabalho apresentado no capítulo 2 foi primeiramente o estudo dos materiais híbridos contendo diferentes concentrações de SiO_2 , Al_2O_3 e P_2O_5 , e tratados termicamente, de modo a investigar a evolução estrutural do material híbrido e tratado termicamente conforme o aumento da proporção de SiO_2 na matriz.

Os materiais híbridos no sistema $x\text{SiO}_2[(\text{Al}_2\text{O}_3)_{50}-(\text{P}_2\text{O}_5)_{50}]_{100-x}$ com diferentes proporções de SiO_2 ($x = 10, 30, 50, 70, 90$ e 100 mol.%) foram sintetizados e caracterizados. Primeiramente, o complexo $\text{Al}(\text{MAEAA})_2$ foi preparado em atmosfera inerte sob agitação magnética por 4 h em uma glovebox adicionando MAEAA ao tri-sec-butoxido de alumínio em uma razão molar de 2:1. Em seguida, o sol de Al-P (Sol-1) foi preparado pela adição de uma solução de HEMAP em metanol ao complexo $\text{Al}(\text{MAEAA})_2$ em uma razão de 1:1, sob agitação magnética por 12 h, e o solvente foi evaporado utilizando sistema de bomba de vácuo e dessecador. O Sol-2 foi preparado pela

hidrólise do TEOS, utilizando uma solução 65% em massa EtOH/H₂O e HNO₃ como catalisador ácido sob agitação por 30 min. Em seguida, o MPTMS e 1% em massa do fotoiniciador TPO foram adicionados deixando a mistura agitar por mais 30 min. Finalmente, uma solução de condensação composta por 65% em massa EtOH/H₂O catalisada por NH₄Ac foi adicionada e deixou-se agitar por mais 45 min. O Sol-1 e Sol-2 foram misturados na proporção de modo a obter a composição desejada, resultando em uma solução homogênea polimerizável. Após polimerização sob lâmpada de Hg (4 mW/cm² por 5 min), as amostras foram fechadas com parafilme e secas por 5 dias em estufa a 50 °C. Os materiais híbridos foram submetidos a tratamento térmico até 800 °C por 1 h com uma taxa de aquecimento de 1°C min⁻¹. Os híbridos secos a 50 °C foram caracterizados por análise termogravimétrica (TGA) e espectroscopias de infravermelho com transformada de Fourier (FTIR), Raman e ressonância magnética nuclear no estado sólido (SSNMR) de ¹³C, ²⁹Si, ³¹P e ²⁷Al, respectivamente. Os materiais tratados foram caracterizados por calorimetria diferencial exploratória (DSC), difração de raios X (XRD) e espectroscopias FTIR, Raman e SSNMR de ²⁹Si, ³¹P e ²⁷Al.

A partir dos espectros de FTIR e Raman foi possível verificar a efetividade da polimerização dos híbridos obtidos, porém ainda foi observado presença de monômeros remanescentes (grupos C=C) que não reagiram. Além disso, foi possível observar o aumento na intensidade do sinal referente ao estiramento Si-O-Si conforme o aumento da proporção de SiO₂ no material indicando a formação de uma rede tridimensional conectada por tetraedros de silício. Os resultados de FTIR e Raman foram corroborados com os espectros de RMN de ¹³C que confirmaram a efetividade da polimerização e a presença de grupos relacionados a estrutura do metacrilato que apresentavam sinais mais intensos conforme o aumento da proporção de Al-P no material, além da presença de grupos remanescentes que não sofreram polimerização.

Uma investigação estrutural mais detalhada foi realizada utilizando diferentes experimentos uni- e bidimensional de RMN de estado sólido para os núcleos de ²⁹Si, ²⁷Al e ³¹P. Nos espectros de RMN de ²⁹Si dos materiais híbridos foram observados três diferentes ambientes para espécies silicatos (unidades Q², Q³ e Q⁴) que conforme o aumento da proporção de SiO₂ no material (até 90%) há o aumento de unidades Q³, sugerindo a formação de oxigênios não ligados e formação de grupos silanóis (Si-OH). A formação dos grupos Si-OH foi associada ao processo de desidratação/densificação incompleta da rede e/ou a heterocondensação entre espécies de silicato e alumínio que podem ocorrer durante o tratamento térmico. Já para a amostra contendo 100% SiO₂ foi

observado uma maior proporção de unidades Q^4 indicando a formação de uma rede tridimensional conectada por tetraedros de silício. Nos espectros de RMN do ^{31}P foram observados quatro sinais referentes a diferentes ambientes de espécies ortofosfatos (unidades $\text{P}_{0\text{Al}}^0$, $\text{P}_{1\text{Al}}^0$, $\text{P}_{2\text{Al}}^0$ and $\text{P}_{3\text{Al}}^0$) as quais mostraram que durante a formação do material híbrido não ocorreu a heterocondensação entre espécies silicato e fosfato, sendo que as espécies fosfatos estavam preferencialmente ligadas as espécies de alumínio, independente do aumento da proporção de SiO_2 no material. Por outro lado, os espectros de RMN-MAS do ^{27}Al mostraram a presença de dois picos largos, referentes aos sítios de Al(IV) e Al(VI) . Entretanto os dados de ^{27}Al TQMAS mostraram a contribuição de duas espécies de Al(IV) , atribuídos a formação de Al(PO)_4 e Al(SiO)_4 . A presença dos dois sítios ficou ainda mais evidente nos espectros com o aumento da proporção de SiO_2 , onde foi possível observar o aumento na intensidade e um deslocamento do pico para maiores valores de desvio químico, indicando a formação de ligações Al-O-Si . Por outro lado, o pico referente aos sítios de Al(VI) mostrou que as espécies de Al -hexacoordenado não sofreram mudanças em seu ambiente químico com o aumento da proporção de SiO_2 , sugerindo que a maioria das espécies fosfatos se ligam ao alumínio hexacoordenado. Além disso, para entender melhor o ambiente químico dos diferentes sítios de Al foram realizados experimentos $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR, onde o acoplamento dipolar Al-P calculado (M_2) a partir das curvas REDOR confirmou a formação de unidades de AlPO_4 , assim como a formação de ligações Al-O-P e Al-O-Si , enquanto que para a espécie Al(VI) o valor de M_2 permaneceu praticamente constante independente da proporção de SiO_2 . Esses resultados corroboraram com os resultados observados pelos espectros de RMN de ^{29}Si e de FTIR.

A decomposição dos compostos orgânicos foi estudada a partir de análise termogravimétrica, e as curvas TGA e DTG dos materiais híbridos mostraram a presença de quatro eventos térmicos referentes a evaporação de solvente residual, reações de condensação, degradação de compostos orgânicos e a degradação de compostos orgânicos residuais e/ou água. Basicamente os dados revelaram que os eventos referentes a degradação dos compostos orgânicos aumentavam conforme Al-P era adicionado na matriz, o que corroborou com o aumento da massa residual em função do aumento de SiO_2 . Esta observação está diretamente relacionada as reações de heterocondensação inorgânica, com formação de ligações Si-O-Si , Si-O-Al e Al-O-P que estão em acordo com os resultados de RMN de ^{29}Si , ^{27}Al e ^{31}P .

Após o tratamento térmico, os difratogramas de DRX para todos os materiais tratados à 800 °C eram característicos de materiais não-cristalinos apresentando apenas um halo em 23° referente a SiO₂ amorfa. As curvas DSC para amostras contendo 10 e 30% SiO₂ apresentaram um pico de cristalização, o qual foi identificado como a cristalização de AlPO₄, enquanto que as amostras contendo 90 e 100% SiO₂ foi possível observar um evento endotérmico entre 1168-1200 °C, o qual foi atribuído a relaxação estrutural da matriz (transição vítrea). Por outro lado, nas composições abaixo de 90% de SiO₂ não foi possível observar eventos referentes a transição vítrea, dessa forma não foram classificadas como materiais vítreos após tratamento térmico. Os espectros de FTIR e Raman dos materiais tratados a 800 °C apresentaram bandas referentes as ligações Si-O-Si, as quais tornavam-se mais intensas conforme o aumento da proporção de SiO₂. Adicionalmente, nos espectros Raman foi possível observar um sinal entre 1000-1200 cm⁻¹ referente ao estiramento P-O que foi atribuído às unidades AlPO₄, cuja intensidade aumentava com a proporção de Al-P no material, o que corroborou com os resultados de DSC para amostras contendo 10 e 30% SiO₂ que apresentaram um pico de cristalização.

A evolução estrutural dos híbridos para os materiais tratados termicamente foi também investigada por RMN de estado sólido, utilizando como sonda estrutural os núcleos de ²⁹Si, ²⁷Al e ³¹P. Os espectros de RMN de ²⁹Si dos materiais após o tratamento térmico apresentaram também três sinais referentes às unidades de silício (unidades Q², Q³ e Q⁴). O tratamento térmico resultou no aumento do grau de homocondensação das espécies de silício conforme o aumento da proporção de SiO₂, confirmado pelo aumento das unidades Q⁴, indicando a formação da rede tridimensional conectada por tetraedros de silício. Adicionalmente, nos dados do ³¹P foi possível observar sinais referentes às espécies de ortofosfatos comumente encontradas em vidros aluminofosfosilicatos, como P_{3Al}⁰, P_{4Al}⁰ e P_{3Al,1Si}⁰ e, ainda verificar que o tratamento térmico promoveu a hetecondensação entre espécies silicatos e fosfatos confirmada pela formação de ligações Si-O-P que não foram anteriormente observadas nos materiais híbridos, mas podem ocorrer em altas temperaturas. Já os espectros de ²⁷Al apresentaram três sítios de alumínio (Al(IV), Al(V) e Al(VI)), confirmados pelos experimentos de ²⁷Al TQMAS. Assim como observado nos materiais híbridos, o sinal referente ao Al(IV) também apresentou a contribuição de dois diferentes sítios (Al-O-P e Al-O-Si) mesmo após o tratamento térmico. No entanto, ao contrário do que foi observado nos híbridos, conforme o aumento da proporção de SiO₂ houve uma diminuição do sinal de Al(IV), o que corroborou com os resultados do ²⁷Al{³¹P} REDOR nos quais observa-se a diminuição dos valores de M₂

conforme o aumento da proporção de SiO_2 , indicando a diminuição de espécies fosfatos ligadas ao átomo de Al-tetracoordenado. Por outro lado, no ambiente químico do sítio de Al(VI) não houve mudanças independente da quantidade de SiO_2 , assim como observado para os materiais híbridos. O estudo no sistema mostrou que após o tratamento térmico pôde-se observar um aumento nas unidades Q^4 e aumento de Al-tetracoordenado, indicando que o aumento de SiO_2 promoveu a formação de uma rede mais interconectada ligada por tetradros de silício e ainda, a presença de ligações Si-O-Al(IV) confirmada pelo deslocamento do sítio Al(IV), mesmo comportamento observado nos materiais híbridos. A formação das ligações Si-O-Al foi confirmada a partir dos valores de M_2 calculados, obtidos a partir do ajuste da curva de evolução do acoplamento dipolar resultante dos experimentos de $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR. Portanto, esta nova rota sol-gel permitiu fabricar novos materiais homogêneos e, que poderiam ser dopados com íons terras raras para o desenvolvimento de novos dispositivos ópticos.

Os vidros a base de SiO_2 , Al_2O_3 e P_2O_5 são interessantes para hospedar íons terras raras, uma vez que a presença de unidades AlPO_4 permite o aumento de solubilidade destes íons na matriz. Dessa maneira, como a nova rota sol-gel empregada no capítulo 2 possibilitou a obtenção de materiais homogêneos, o capítulo 3 relata a investigação da luminescência dos materiais a partir da dopagem com íons Er^{3+} . No entanto, como o tratamento térmico utilizado no capítulo 2 ainda não possibilitava a obtenção de amostras vítreas com alta qualidade óptica devido ao aparecimento de trincas e alta porosidade, no capítulo 3 a síntese foi parcialmente modificada, assim como o procedimento de tratamento térmico para obtenção de amostras contendo alta concentração de SiO_2 (95 mol.%).

A síntese dos géis foi realizada de maneira semelhante ao capítulo 2, porém para o capítulo 3 na preparação do Sol-2 optou-se por não adicionar MPTMS e TPO como precursor e fotoiniciador, respectivamente, de modo a evitar a fotopolimerização e consequentemente diminuir a quantidade de compostos orgânicos a serem liberados durante o tratamento térmico para tentar diminuir a formação de poros e o aparecimento de trincas no material final. Sendo assim, o Sol-1 foi preparado da forma descrita no capítulo 2, porém para a preparação do Sol-2 foi realizada a hidrólise do TEOS sob agitação magnética por 30 min. Em seguida aumentou-se o pH da solução com a adição de $0,171 \text{ mol L}^{-1} \text{ NH}_4\text{Ac}$ em uma solução de 65 % EtOH/ H_2O (m/m), a qual permaneceu sob agitação por 10 min. Por fim, foi realizado a mistura do Sol-1 e Sol-2, a qual permaneceu sob agitação por mais 35 min. Após agitação, os solventes utilizados durante

a síntese foram evaporados com um rotaevaporador e então, esse Sol foi adicionado em potes plásticos e levado para uma estufa a 50 °C por 7 dias, seguido de 80 °C por mais 5 dias para evaporação residual dos solventes, obtendo-se assim géis rígidos. Foram sintetizados géis contendo alta proporção de silício (95SiO₂:5AlPO₄ em mol.%), os quais foram submetidos ao tratamento térmico em diferentes temperaturas (80, 550, 600, 700 e 800 °C). Além disso, o material tratado à 800 °C também foi submetido a um tratamento térmico a 900 °C por 30 min sob vácuo.

O estudo da fotoluminescência dos íons Er³⁺ foi realizado após dopagem dos materiais tratados em 800 °C e 900 °C (sob vácuo) com diferentes concentrações de íons Er³⁺ (0,05; 0,1; 0,2; 0,5 e 1,0 mol.%). Os materiais foram caracterizados por diferentes técnicas como FTIR, Raman, XRD, RMN de ²⁹Si, ²⁷Al e ³¹P, MEV, Fisiossorção de N₂, Densidade, Índice de refração, UV-Vis-NIR, e medidas de luminescência e tempo de vida, utilizando um laser de excitação em 980 nm.

A evolução da densidade dos materiais mostrou que, com o aumento da temperatura de tratamento, os poros formados pela liberação de solventes residuais e compostos orgânicos foram colapsando devido a formação das ligações Si-O, Al-O e P-O, à medida que a matriz se tornava mais compacta. Os espectros de FTIR e Raman dos materiais apresentaram sinais semelhantes aos da SiO₂ pura, especialmente nas amostras tratadas a temperaturas mais elevadas. Porém ainda era possível observar, mesmo após o tratamento em 800 °C, bandas referentes a grupos OH e silanóis (Si-OH), associado a desidratação/densificação incompleta da rede. No entanto, para a amostra tratada a 900 °C sob vácuo, nos dados de FTIR e ¹H MAS RMN observou-se a redução dos grupos OH, indicando maior grau de condensação entre as espécies de silicatos, fosfatos e alumínio, que foi confirmado a partir dos dados de RMN. Os difratogramas de DRX confirmaram o estado amorfo dos materiais, com a presença de um halo em 23° referente a sílica amorfa.

A morfologia dos materiais foi investigada por meio de microscopia eletrônica de varredura (MEV). As imagens mostraram que com o aumento da temperatura de tratamento térmico, poros surgiram na superfície do material devido à liberação de solventes residuais e à degradação dos compostos orgânicos. Porém em 800 °C a porosidade foi reduzida e diminuiu drasticamente após o tratamento térmico sob vácuo em 900 °C. O estudo da evolução de formação vítrea foi monitorado por RMN, onde os espectros de RMN de ²⁹Si apresentaram três sinais referentes as unidades Q², Q³ e Q⁴, sendo que com o aumento da temperatura de tratamento foi possível observar uma maior

formação de Q^4 , principalmente após o tratamento sob vácuo a 900 °C, indicando a formação de uma rede tridimensional interconectada por tetradros de silício. Já os espectros de ^{31}P mostraram a presença de quatro diferentes ambientes químicos de P ($\text{P}_{2\text{Al}}^0$, $\text{P}_{3\text{Al}}^0$, $\text{P}_{4\text{Al}}^0$, e $\text{P}_{3\text{Al},1\text{Si}}^0$), sendo que o aumento da temperatura de tratamento térmico promoveu o aumento nas unidades $\text{P}_{4\text{Al}}^0$ e $\text{P}_{3\text{Al},1\text{Si}}^0$, especialmente após tratamento térmico sob vácuo, indicando um maior grau de condensação, ou seja, a formação de ligações Al-O-P e Si-O-P. Nos espectros de ^{27}Al foi possível observar dois sinais referentes a formação de Al(IV) e Al(VI), assim como o deslocamento do valor de desvio químico (δ_{cs}) do sítio de Al(IV) em função do aumento da temperatura, indicando que as unidades fosfatos estavam preferencialmente se ligando ao átomo de Al, ou seja, a formação das ligações P-O-Al foram favorecidas. O tratamento térmico à vácuo favoreceu a formação do AlPO_4 na matriz e promoveu a densificação do material através da eliminação da água superficial e das reações de condensação entre as espécies de Si, Al e P. O processo de eliminação da água superficial foi confirmado a partir dos dados de ^1H MAS RMN, nos quais a redução de grupos hidroxilas na matriz foi observada. Estes resultados foram consistentes com a redução de grupos OH observada nos dados de FTIR, favorecendo reações de homo e heterocondensação entre as espécies silicato, fosfato e alumínio como observado nos resultados de RMN.

A partir dos espectros UV-Vis-NIR dos materiais tratados até 800 °C foi possível observar o desaparecimento de sinais referentes aos compostos orgânicos que foram liberados em função do aumento da temperatura, porém ainda era possível observar os sinais referentes aos grupos OH advindos de água e silanóis, os quais diminuíram significativamente após tratamento térmico sob vácuo. Além disso, os valores de área superficial obtidos a partir das isotermas de fisiossorção de N_2 para os materiais tratados a 800 °C e 900 °C (sob vácuo) mostraram a densificação da matriz devido a drástica diminuição do valor de área superficial, assim como a diminuição de valores de volume e diâmetro de poros, corroborando com os dados de FTIR e RMN. A densificação das amostras também refletiu nos valores de índice de refração da amostra tratada em 900 °C sob vácuo, onde os valores foram maiores do que para a amostra tratada a 800 °C, sugerindo que o tratamento térmico sob vácuo promoveu a diminuição de oxigênios não ligados (NBO) na matriz, confirmado pelos dados de RMN, o que indicou um alto grau de condensação entre as espécies silicatos, fosfatos e alumínio.

Por fim, a investigação das propriedades luminescentes dos materiais tratados a 800 °C e 900 °C (sob vácuo) dopados com íons Er^{3+} foi realizada utilizando um laser diodo de 980 nm. Todos os materiais apresentaram uma banda de emissão centralizada em 1540 nm, porém após o tratamento térmico a banda de emissão observada mostrou um aumento de intensidade de 180 vezes maior do que as amostras tratadas em 800 °C. Esse comportamento pôde ser justificado pela quantidade de água ainda presente nas amostras tratadas em 800 °C, o que é responsável pela atenuação do sinal a partir de perdas não-radiativas dos íons Er^{3+} . Adicionalmente, os resultados mostraram que a intensidade da emissão em 1540 nm e os valores de tempo de vida aumentaram com a concentração de íons Er^{3+} adicionada na matriz, porém foi possível observar uma supressão de luminescência para concentrações acima de 0,5 mol.% de Er^{3+} . Além disso, a amostra dopada com 0,5 mol.% de Er^{3+} tratada a 900 °C sob vácuo apresentou uma banda de emissão com largura à meia altura de aproximadamente 100 nm, atribuída à diversidade dos ambientes químicos dos íons Er^{3+} . Essa característica, que abrange as bandas C + L (1530-1625 nm) utilizadas em telecomunicações, tornam este material um candidato promissor para amplificadores ópticos. O estudo da luminescência também permitiu calcular os valores de seção transversal de absorção e emissão, assim como calcular o ganho de sinal de luminescência que sugeriu que uma largura de banda de amplificação entre 1510 e 1550 nm pode ser alcançada com uma inversão de população superior a 60%. Esta seção transversal de amplificação abrange o canal de 1530–1565 nm (banda C) na janela de telecomunicações ópticas.

Dessa forma, podemos concluir que os vidros aluminofosfossilicatos dopados com Er^{3+} de alta qualidade óptica foram sintetizados pelo método sol-gel. O tratamento térmico sob vácuo promoveu a densificação da matriz, reduzindo a presença de grupos OH, resultando em um aumento na intensidade da luminescência, especialmente na amostra contendo 0,5 mol.% de Er^{3+} . O tratamento à vácuo também aumentou o índice de refração da matriz, e o método sol-gel permitiu a síntese de vidros em temperaturas relativamente baixas e promoveu a formação de diferentes ambientes químicos hospedeiro para os íons Er^{3+} , ocasionando no alargamento da banda de emissão em 1,5 μm , abrindo possibilidades para novos dispositivos ópticos em telecomunicações.

LIST OF SYMBOLS AND ABBREVIATIONS

EDFA – Erbium-doped fiber amplifiers
MCVD – Modified Chemical Vapor Deposition
 T_g – Glass transition temperature
 T_m – Melting point
RE – Rare earth
RI – Refractive index
NMR – Nuclear Magnetic Resonance
SSNMR – Solid State Nuclear Magnetic Resonance
 B_0 – Static field
 B_1 – Induced field
 ω – Larmor frequency
 γ – Gyromagnetic constant
 B_{eff} – Effective field
 T_1 – Spin-spin relaxation
 T_2 – Spin-lattice relaxation
 H_J – J-coupling
 H_{CS} – Chemical Shielding
 H_D – Dipolar interaction
 H_Q – Quadrupolar effect
 M_2 – Second moment
REDOR - Rotational echo double resonance
MAS – Magic Angle Spinning
PL – Photoluminescence
 S_1 – Singlet Excited State
 S_0 - Singlet Ground State
 T_1 - Triplet Excited State
 τ – Lifetime
TEOS - Tetraethyl orthosilicate

MPMTS - 3-(Trimethoxysilyl) propyl methacrylate

HEMA - Hydroxyethyl methacrylate phosphoric acid ester

MAEAA - 2-(methacryloyloxy)ethyl acetoacetate

MeOH – Methyl alcohol

EtOH – ethyl alcohol

HNO₃ – Nitric acid

NH₄Ac – Ammonium acetate

TPO - Diphenyl(2,4,6- trimethylbenzoyl)phosphine oxide

TGA – Thermogravimetric analysis

DTG - Derivative Thermogravimetric

DSC – Differential scanning calorimetry

XRD – X-Ray diffraction

FTIR-ATR - Attenuated Total Reflectance Fourier Transformed Infrared

ν_{ro} – spinning speed

TMS - Tetramethylsilane

TQMAS – Triple-Quantum

PMMA - Poly(methyl methacrylate)

T_{max} - Maximum weight loss temperature

LIST OF FIGURES

Fig. 1.1. Optical fiber telecommunication windows from http://fowiki.com/b/understand-fiber-attenuation/	38
Fig. 1.2. (a) Crystalline and (b) non-crystalline silica structures adapted from Zachariasen, 1932.	40
Fig. 1.3. Representative structure of ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ (a) non-doped and (b) Er^{3+} -doped adapted from Xu et al., 2015.	42
Fig. 1.4. Composition diagram for obtaining of the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ through the melt-quenching method from Zhou et al., 2022.	43
Fig. 1.5. Representative scheme of the sol-gel synthetic route for obtaining glasses. ...	45
Fig. 1.6. Reaction between the β -diketone 2-methacryloxyethylacetoacetate (MAEAA) and aluminum alkoxide.	47
Fig. 1.7. Representative scheme of Zeeman effect as applied to a spin $\frac{1}{2}$ nucleus adapted from Hussain, 2015.	49
Fig. 1.8. Magic Angle Spinning (MAS) representation adapted from Eckert, 2018.	50
Fig. 1.9. Energy diagram for the Er^{3+} ions adapted from Sigoli et al., 2022.	56
Fig. 1.10. Deactivation mechanism of the emitting states of Eu^{3+} and Tb^{3+} caused by O-H oscillators found in H_2O molecules adapted from Sigoli et al., 2022.	57
Fig. 2.1. Photos of aluminophosphosilicate materials $x\text{SiO}_2[(\text{Al}_2\text{O}_3)_{50}-(\text{P}_2\text{O}_5)_{50}]_{100-x}$ before (left) and after (right) heat treatment with different SiO_2 content (a) $x = 100$, (b) $x = 90$, (c) $x = 70$, (d) $x = 50$, (e) $x = 30$ and (f) $x = 10$ (mol.%). The background of all the photos illustrates the UNESP blue logo.	71
Fig. 2.2. (a) $^{29}\text{Si}\{^1\text{H}\}$ CP-MAS and (b) ^{29}Si MAS deconvolution spectra of hybrid polymers with different SiO_2 content ($x = 10, 30, 50, 70, 90$ and 100 mol.%). The solid black line represents the experimental spectrum and the red line represents the deconvolution envelope.	75
Fig. 2.3. (a) ^{31}P and (b) ^{27}Al MAS NMR spectra of hybrid materials with different SiO_2 content ($x = 10, 30, 50, 70, 90$ and 100 mol.%). The solid black line represents the experimental spectrum and the red line represents the deconvolution envelope.	77
Fig. 2.4. $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR curves for (a) tetracoordinated Al(IV) and (b) hexacoordinated Al(VI) species for $x = 30, 50$ and 70 (mol.%) of SiO_2 content. Solid curves are fits of the data points to eq. (1) within the data range $\Delta S/S_0 \leq 0.2$	80

Fig. 2.5. TGA curves of hybrid materials with different SiO ₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%).	82
Fig. 2.6. DSC curves for the heat-treated materials with different SiO ₂ contents (x = 10, 30, 50, 70, 90 and 100 mol.%).	82
Fig. 2.7. (a) FTIR-ATR and (b) Raman spectra for the heat-treated materials with different SiO ₂ contents (x = 10, 30, 50, 70, 90 and 100 mol.%).	83
Fig. 2.8. (a) ²⁹ Si MAS NMR spectra for the heat-treated materials with different SiO ₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%). The solid black line represents the experimental spectrum and the dashed red line represents the deconvolution envelope. (b) Q ⁿ units evolution as a function of SiO ₂ content.	85
Fig. 2.9. (a) ³¹ P and (b) ²⁷ Al MAS NMR spectra for the materials after heat treatment with different SiO ₂ content. The solid black line represents the experimental spectrum and the solid red line represents the deconvolution envelope.	87
Fig. 2.10. ²⁷ Al{ ³¹ P} REDOR curves for (a) tetracoordinated (Al(IV)) and (b) hexacoordinated (Al(VI)) species for the materials after heat treatment with different SiO ₂ contents. Solid curves are fits of the data points to eq. (1) within the data range $\Delta S/S_0 \leq 0.2$	88
Fig. 2.S1. (a) FTIR-ATR and (b) Raman spectra for the hybrid materials with different SiO ₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%).	101
Fig. 2.S2. (a) ¹³ C{ ¹ H} CP-MAS spectra and (b) structural assignment for the hybrid materials with different SiO ₂ content (x = 10, 30, 50, 70, 90 and 100 in mol%).	102
Fig. 2.S3. ²⁷ Al TQMAS NMR spectra for the hybrid materials with different SiO ₂ concentration (x = 10, 30, 50, 70 and 90 mol.%).	104
Fig. 2.S4. XRD spectra for the heat-treated materials with different SiO ₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%).	105
Fig. 2.S5. ²⁷ Al TQMAS NMR spectra for the heat-treated materials treatment different SiO ₂ concentration (x = 10, 30, 50, 70 and 90 mol.%).	106
Fig. 3.1. Representative scheme of the sol-gel synthesis route for obtaining the dried aluminophosphosilicate gel.	111
Fig. 3.2. Thermal treatment curve for debinding process of Er ³⁺ -doped aluminophosphosilicate gels.	112
Fig. 3.3. Aluminophosphosilicate samples heat-treated at different temperatures (a) gel dried at 80 °C, (b) 550 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C and (f) 900 °C (under vacuum).	114

Fig. 3.4. SEM images for the APS(T)-0.2 samples, where T is the heat treatment temperature.	116
Fig. 3.5. ^{29}Si MAS NMR spectra for the APS(T) samples heat-treated at different temperatures. The solid black line represents the experimental spectrum, and the solid red line represents the deconvolution envelope.	117
Fig. 3.6. (a) ^{31}P and (b) ^{27}Al MAS NMR for the APS(T) samples heat-treated at different temperatures. The solid black line represents the experimental spectrum, and the solid red line represents the deconvolution envelope.	119
Fig. 3.7. Area's evolution as a function of the heat treatment temperature of (a) Q^n units in ^{29}Si MAS NMR, (b) PmAln units in ^{31}P MAS NMR and (c) Al units in ^{27}Al MAS NMR.	120
Fig. 3.8. (a) ^1H MAS NMR spectra and (b) OH signal in ^1H MAS NMR spectra for the APS(T) samples heat-treated at different temperatures.	122
Fig. 3.9. Refractive index (± 0.0001) values for the APS800-0.2 and APS900-0.2 samples heat-treated at 800 and 900 °C in air and under vacuum, respectively, and for pure fused SiO_2 glass.	123
Fig. 3.10. UV-Vis-NIR absorption spectra for the (a) APS(T)-0.2 samples and (b) APS800-0.2 and APS900-0.2 glasses heat-treated at 800 °C in air and 900 °C in vacuum, respectively.	124
Fig. 3.11. Non-normalized intensity emission spectra heat-treated (a) in air at 800 °C and (b) under vacuum at 900 °C. Normalized lifetime decay curves heat-treated (c) in air at 800 °C and (d) under vacuum at 900 °C for APS materials containing different Er^{3+} content (0.05 to 1.0 mol.%).	125
Fig. 3.12. (a) Absorption and emission cross-sections of APS900-0.5 and (b) Gain spectra of the APS900-0.5 sample determined from Fig. (a).	129
Fig. 3.S1. (a) FTIR and (b) Raman spectra for the APS(T)-0.2 samples, where T is the heat treatment temperature.	142
Fig. 3.S2. XRD patterns for the APS(T)-0.2 samples, where T is the heat treatment temperature.	142
Fig. 3.S3. Adsorption and desorption nitrogen gas isotherms obtained by N_2 physisorption analysis for the APS800 and APS900 samples heat-treated at 800 °C in air and 900 °C in vacuum.	144
Fig. 3.S4. UV-Vis-NIR spectra for the APS900 samples doped with different Er^{3+} content (0.05 to 1.0 mol.%) heat-treated at 900 °C under vacuum.	145

Fig. 3.S5. (a-b) Absorption and emission cross-sections of the Er^{3+} ions and (c-d) Gain spectra by the McCumber theory of the APS900 samples doped with 0.2 and 1.0 mol.% of Er^{3+} 146

LIST OF TABLES

Table 2.1. Band positions and assignments of FTIR and Raman spectra for hybrid materials.	74
Table 2.2. Deconvolution results (chemical shift δ_{iso} and fractional areas of the Q^2 , Q^3 and Q^4 units) of the ^{29}Si MAS NMR spectra obtained for the compositions from 50 to 100 mol.% SiO_2 content of the hybrid materials. Estimated errors are ± 0.2 ppm for Chemical Shift and $\pm 2\%$ for Areas.	76
Table 2.3. Deconvolution results (chemical shift δ_{iso} and fractional areas of the $P0\text{Al}0$, $P1\text{Al}0$, $P2\text{Al}, 0$ and $P3\text{Al}0$ units) of ^{31}P NMR spectra obtained for the compositions from 10 to 90 mol.% SiO_2 content of the hybrid materials. Estimated errors are ± 0.5 ppm for Chemical Shift and $\pm 1\%$ for Areas.	77
Table 2.4. ^{27}Al isotropic chemical shift (δ_{iso}) (± 0.2 ppm), fractional areas ($\pm 2\%$) and nuclear electric quadrupolar coupling values (C_Q) (± 0.5 MHz) extracted from the Czsimpl model and second moment ($M_{2(\text{Al-P})}$) ($\pm 10\%$) of the hybrid materials.	79
Table 2.5. Deconvolution results (chemical shift δ_{iso} and fractional areas) of the ^{29}Si MAS NMR spectra obtained for compositions from 30 to 100 mol.% SiO_2 content of the materials heat-treated at 800°C . Estimated errors are ± 0.2 ppm for Chemical Shift and $\pm 2\%$ for Areas.	85
Table 2.6. Deconvolution results (chemical shift δ_{iso} and Fractional Areas of the $P3\text{Al}0$, $P4\text{Al}, 0$ and $P3\text{Al}, 1\text{Si}0$ units) of the ^{31}P NMR spectra obtained for the compositions from 10 to 90 mol.% SiO_2 content of the materials heat-treated at 800°C . Estimated errors are ± 0.5 ppm for Chemical Shift and $\pm 1\%$ for Areas.	87
Table 2.7. ^{27}Al isotropic chemical shift (δ_{iso}) (± 0.2 ppm), fractional areas ($\pm 2\%$) and nuclear electric quadrupolar coupling values (C_Q) (± 0.5 MHz) extracted from the Czsimpl function and Al-P dipolar coupling ($M_{2(\text{Al-P})}$) ($\pm 10\%$) of the materials heat-treated at 800°C	89
Table 2.S1. Calculated and experimental residual mass (%) values for the hybrid materials with different SiO_2 content ($x = 10, 30, 50, 70, 90$ and 100 mol.%).	101
Table 3.1. Density (ρ) and Er^{3+} concentration values for APS(T)-0.2 samples, where T is the heat treatment temperature and x corresponds to the molar composition of erbium.	115

Table 3.2. BET surface area (S_{BET}), the average pore volume (V_p), and the average pore diameter (r_p) for the APS800 and APS900 samples heat-treated in air and under vacuum, respectively.	123
Table 3.3. Lifetime (ms) and FWHM (nm) values for the APS(T)-x (x is the molar composition of erbium) samples heat-treated at 800 °C in air and 900 °C under vacuum.	126
Table 3.4. Lifetime and FWHM values for Er^{3+} -doped silicate glasses containing Al and/or P obtained by the sol-gel method reported in this research and in the literature.	127
Table 3.5. Absorption ($\sigma_{\text{abs}}(\lambda)$) and emission ($\sigma_{\text{ems}}(\lambda)$) cross-sections of the Er^{3+} ions for the APS900-x materials (x is the molar composition of erbium).	129
Table 3.S1. Deconvolution results (chemical shift δ_{iso} and fractional areas) of the ^{29}Si MAS NMR spectra obtained for the APS(T) samples.....	143
Table 3.S2. Deconvolution results (chemical shift δ_{iso} and fractional areas of the P2Al0, P3Al, 0, P4Al, 0 and P3Al, 1Si0 units) of the ^{31}P NMR spectra obtained for the APS(T) samples.	143
Table 3.S3. ^{27}Al isotropic chemical shift (δ_{iso}) and nuclear electric quadrupolar coupling values (C_Q) extracted from the Czsimpl function for the APS samples heat-treated at different temperatures (80, 550, 600, 700, 800 in air and 900 °C in vacuum).	144

TABLE OF CONTENTS

1. Introduction/literature review	37
1.1. GLASSES	39
1.1.1. Ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$	41
1.2. SOL-GEL METHOD FOR OBTAINING GLASSES	44
1.3. SOLID STATE NUCLEAR MAGNETIC RESONANCE (SSNMR)	48
1.4. PHOTOLUMINESCENCE'S PRINCIPLE	53
1.4.1. Rare earth ions luminescence	54
REFERENCES	57
Objectives	65
2. Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials	67
ABSTRACT	67
2.1. INTRODUCTION	68
2.2. EXPERIMENTAL	70
2.2.1. Synthesis of aluminophosphosilicate materials	70
2.2.2. Characterization	71
2.3. RESULTS AND DISCUSSION	73
2.3.1. Structural study of the hybrid materials	73
2.3.2. Thermal properties of the hybrid materials.....	80
2.3.3. Characterization of the heat-treated materials	82
2.4. CONCLUSIONS	90
CREDIT AUTHORSHIP CONTRIBUTION STATEMENT	91
DECLARATION OF COMPETING INTEREST	91
ACKNOWLEDGMENTS	91
REFERENCES	91
SUPPLEMENTARY MATERIAL	100
3. Effects of the thermal treatment on structural and luminescence properties of Er³⁺-doped aluminophosphosilicate glasses obtained by the sol-gel method	108
ABSTRACT	108
3.1. INTRODUCTION	109
3.2. EXPERIMENTAL	110
3.2.1. Synthesis of the Er ³⁺ -doped aluminophosphosilicate samples	110
3.2.2. Heat treatment	111
3.2.3. Characterization	112
3.3. RESULTS AND DISCUSSION	114

3.4. CONCLUSION	130
CREDIT AUTHORSHIP CONTRIBUTION STATEMENT	130
DECLARATION OF COMPETING INTEREST	131
ACKNOWLEDGMENTS	131
DATA AVAILABILITY	131
APPENDIX A. SUPPORTING INFORMATION	131
REFERENCES	131
SUPPLEMENTARY MATERIAL.....	141
4. General conclusions and perspectives	148

CHAPTER 1

Introduction/ literature review and objectives

1. Introduction/literature review

The demand for data transmission has significantly increased, particularly after the COVID-19 pandemic, with an annual growth rate of 25%. Nowadays, the demand for data transmission continues to rise at a 25 %, driven by cloud services, streaming, and international data transfer. The capacity of modern telecommunications systems has been increasing, particularly due to advancements in optical fiber communication technologies, which must achieve data rates of 100 or 400 Gb/s for the next generation of Ethernet (RIVERA et al., 2024). As a result, developing new materials to be used as optical amplifiers for telecommunication systems has become extremely necessary to prevent bottlenecks in the next 10 to 15 years. Currently, the most commercially available optical amplifiers operating only in the C-band are based on silica (SiO_2) glass doped with erbium ions, and they are well known in the literature as erbium-doped fiber amplifiers (EDFA). These amplifiers have a lifetime of approximately 10 ms and a bandwidth of 30 to 40 nm (ISKHAKOVA et al., 2021; JALILPIRAN et al., 2023; LIU, 2019). However, despite the good optical, chemical, and mechanical properties of SiO_2 glass, there is a limit to the amount of erbium ions that can be dissolved in the matrix (a maximum of 1000 ppm by weight), which leads to the formation of clusters and, consequently, to signal attenuation due to quenching of luminescence through non-radiative relaxation (ISKHAKOVA et al., 2021; KAJIHARA; KUWATANI; KANAMURA, 2012; KANEKO; KAJIHARA; KANAMURA, 2013).

For this reason, new SiO_2 -based glass compositions are being explored in the literature to achieve high signal intensity and broadband emission in the NIR region, thereby increasing the number of available channels in the telecommunications system in the C+L bands (Fig. 1.1). In this context, the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ has become very interesting, as the addition of Al_2O_3 and P_2O_5 increases the solubility of erbium ions in the silica matrix, reducing the formation of erbium clusters and consequently preventing signal attenuation (GLORIEUX et al., 2018; KUHN et al., 2018; LORD et al., 2020; SHAO et al., 2020; WANG et al., 2019). Furthermore, the glass composition must contain a high amount of SiO_2 , since this optical fiber amplifier will be connected to the optical fibers already in use worldwide. In this context, both the optical amplifier and the SiO_2 fiber must have similar properties.

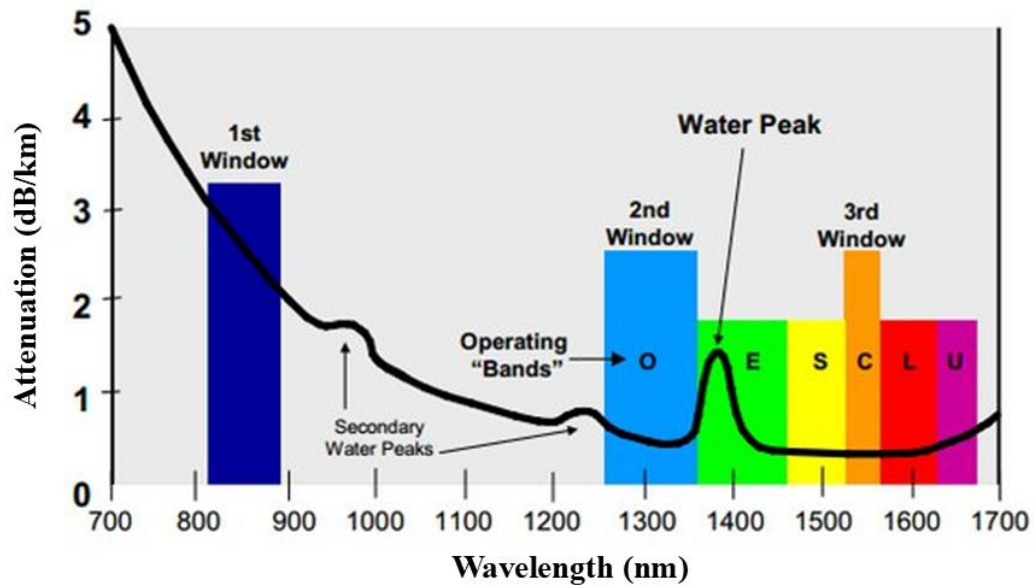


Fig. 1.1. Optical fiber telecommunication windows from <http://fowiki.com/b/understand-fiber-attenuation/>.

The most commonly used method in the literature for obtaining glasses based on the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ is the melt-quenching method. However, this method requires a high melting temperature and can also lead to issues such as phase separation, crystallization, or composition loss, especially if the phosphorus is not bonded to aluminum and/or silicon, as it may degrade at high temperatures (KAJIHARA, 2013; ŁACZKA; CIECIŃSKA, 1994; LIANGEN; ZARZYCKI, 1989; LINDNER et al., 2022; LIVAGE et al., 1992; ROY; JAIN, 2005). In this context, new approaches have been explored for obtaining $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses, such as the use of the sol-gel method (BRINKER; SCHERER, 2013; COOPERSTEIN et al., 2018; REN; ZHANG; ECKERT, 2014; WANG; ZHENG; WANG, 2020). The sol-gel method is interesting because it allows the production of glasses with a wide range of compositions at relatively low temperatures compared to the melt-quenching method and enables the condensation of phosphorus with aluminum and/or silicon, thereby avoiding compositional loss. In addition, this method allows the formation of different chemical environments for the erbium ions, resulting in signal broadening and, consequently, the opening of new channels for data transmission (LAM TRAN et al., 2022). However, the sol-gel method can also present problems such as phase separation, as reported by De Araujo et al. (DE ARAUJO; ZHANG; ECKERT, 2006). In this work, the authors studied the incorporation of SiO_2 into the AlPO_4 matrix using the sol-gel method. The NMR results indicated that Al-O-Si and Si-O-P linkages did not form, suggesting only the presence of AlPO_4 and

SiO₂ sub-domains. In another study by Deshpande et al. (DESHPANDE; ZHANG; ECKERT, 2009), the authors prepared AlPO₄-SiO₂ glasses using the sol-gel method and also demonstrated the absence of Si-O-P linkages, indicating that the overall network organization is far from homogeneous.

Regarding the production of erbium-doped SiO₂ fibers, they are currently obtained using the Modified Chemical Vapor Deposition (MCVD) method at temperatures close to 2000 °C. This method allows the production of preforms with high purity and low water content, the latter being responsible for the quenching of erbium ion photoluminescence at 1.5 μm. However, using this method to obtain glasses with different compositions, such as the ternary SiO₂-Al₂O₃-P₂O₅, can also result in phase separation, crystallization, and compositional loss, similar to the melt-quenching method (GAO et al., 2016; LIKHACHEV et al., 2010; LINDNER et al., 2022; LORD et al., 2020). Therefore, the strategy of using the sol-gel method may enable the preparation of a sol that can be used in the future as a doping solution combined with the MCVD method for the production of erbium-doped aluminophosphosilicate glass preforms. Indeed, this strategy is still underexplored in the literature, with only one study reported by Yang et al. (YANG et al., 2021), in which the authors combined the sol-gel method with the MCVD method and obtained an optical fiber with a composition of 96.7SiO₂-3Al₂O₃-0.3Er₂O₃ (in mol.%) that exhibited good optical properties and homogenous doping, thanks to the sol-gel method.

1.1. Glasses

Glass plays a very important role in the development of new materials that impact society's life, as it can be present in both domestic applications and high technology (MAURO; ZANOTTO, 2014; WONDRAKZEK et al., 2011; ZANOTTO; MAURO, 2017). Due to its versatility, many chemical compositions are possible, including traditional oxide glasses, chalcogenides, fluorides, bromides, oxyfluorides, oxynitrides, metals, hybrids, among others (BENNETT et al., 2016; MAZURIN, 2005; ZANOTTO; MAURO, 2017). The development of new compositions with specific properties is crucial for enabling current applications such as magneto-optical devices, energy storage, and advanced telecommunication systems (MORSE; EVENSON, 2016).

The most modern definition for glass found in the literature was proposed by Zanotto and Mauro (ZANOTTO; MAURO, 2017):

"Glass is a non-equilibrium state of condensed matter thermodynamic, non-crystalline, which exhibits a glass transition. Its structure is similar to its supercooled liquids (SL) and it spontaneously relaxes towards the SL state. Its final fate, for infinitely long time, is to crystallize."

In summary, glass is classified as a non-crystalline solid because its basic units are arranged in a non-periodic three-dimensional network over long, medium, and short ranges. In contrast, in a crystal, the basic units are organized periodically, exhibiting long-range symmetry (YADAV; SINGH, 2015; ZACHARIASEN, 1932). Fig. 1.2 illustrates a commonly used example to differentiate the structure of crystalline and non-crystalline silica.

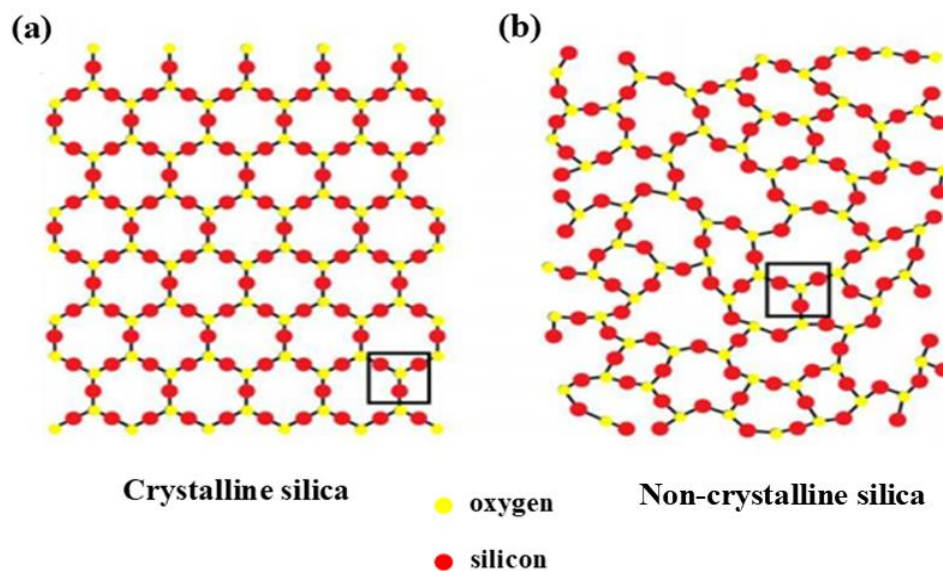


Fig. 1.2. (a) Crystalline and (b) non-crystalline silica structures adapted from Zachariasen, 1932.

Silicon and phosphorus oxides are well-known glass-forming species, while aluminum oxide is considered an intermediate oxide. This means it can be classified either as a network modifier or former, depending on its concentration and/or glass composition (ZACHARIASEN, 1932). Binary glass systems composed of two oxides, such as aluminosilicate, aluminophosphate, and phosphosilicate, have been extensively investigated for applications in fast proton conductors (MATSUDA et al., 2002; NOGAMI et al., 2003), bioactive materials (ROMA; PADILLA, 2003; SARAVANAPAVAN et al., 2003), and optical fibers (SEN; YOUNGMAN, 2004). However, the ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glass systems have gained significant attention for

their numerous applications in optical fibers and waveguide technologies. To employ this type of material in these applications, it is necessary to understand the dependence of its physical properties on composition in terms of structural information.

1.1.1. Ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$

The ternary system is of great interest in different applications as optical telecommunications (LORD et al., 2020; SHAO et al., 2020). The structure of the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ is formed by tetrahedra of silica, aluminum, and phosphorus interconnected by oxygen atoms to form a three-dimensional network. It is known that small Al_2O_3 content can integrate into SiO_2 in a four-fold coordination. However, the Al^{3+} cation causes a modification to the SiO_2 network since each aluminum atom forms a tri-coordinated oxygen, which is thermodynamically less favorable than the clustering of aluminum cations, especially when the aluminum content increases leading to six-fold coordination. This process eventually results in crystal nucleation and growth. On the other hand, phosphorous species are very miscible in silica matrix, leading to the formation of non-bridging oxygens. This occurs due to the incorporation of P=O terminal bonds reduces the connectivity of the three-dimensional SiO_2 network. Thus, the tetracoordinated aluminum species are stabilized by the presence of the non-bridging oxygen species leading to an increase in its glass-forming ability. In addition, miscible regions in the $\text{SiO}_2\text{-AlPO}_4$ matrix are formed since the structures of AlPO_4 and α -quartz are similar which are based on tetrahedral coordination with each cation bonded by four oxygens and each oxygen between two cations (DIGIOVANNI; MACCHESNEY; KOMETANI, 1989).

Nowadays, as data exchange continues to increase, the development of optical fibers doped with rare earth (RE) ions as efficient optical amplifiers is necessary to meet this demand. Increasing the RE ions concentration can typically enhance this efficiency but it can also lead to cluster formation leading to quenching of luminescence. In this sense, the chemical strategy of the RE ions incorporation in the network of the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ (Fig. 1.3) plays a key role on the optical properties of these materials, since both Al and P increase the dissolution of RE ions in silica matrix, which beneficially influences luminescence properties in terms of emission intensity, bandwidth and lifetime (BUBNOV et al., 2009; CAO et al., 2018; KOSINSKI et al., 1988; KUHN et al., 2018; LORD et al., 2020; WANG et al., 2013; XU et al., 2015). Indeed, Likhachev

et al. (LIKHACHEV et al., 2009) reported that the presence of AlPO_4 increased the solubility of the RE ions and consequently enhanced the optical fiber's amplifier efficiency. Moreover, the addition of equal amounts of Al_2O_3 and P_2O_5 results in a decrease in the refractive index (RI) of silica glass, due to AlPO_4 units formation, allowing the fiber core to be doped with a higher content of rare earth, while it keeps a relatively low RI (BOURHIS et al., 2015; GLORIEUX et al., 2018; SHAO et al., 2020; WANG et al., 2019).

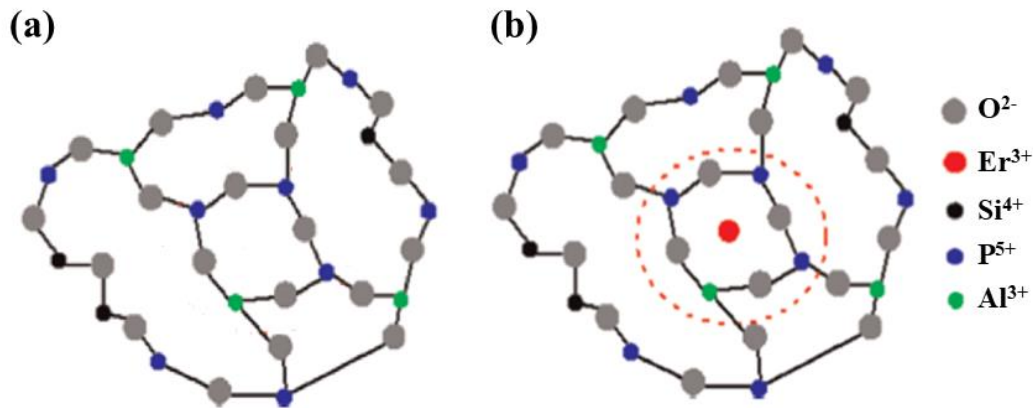


Fig. 1.3. Representative structure of ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ (a) non-doped and (b) Er^{3+} -doped adapted from Xu et al., 2015.

Thus, large quantities of data are collected and sent to the cloud for processing, storage, and sharing for applications ranging from entertainment to health monitoring. In addition, with the advent of artificial intelligence and sensor networks, this quest for bandwidth seems uncontrollable. Optical fiber communications are at a crossroads where innovative research is extremely necessary to meet the bandwidth demand, in order to increase the number of transmission channels available in C+L telecommunication windows between 1530 and 1625 nm (Fig. 1.1). The quest to increase the optical transmission capacity of communication networks stimulates the search for new approaches, and one of the strategies to meet this demand is the development of optical amplifiers that enable signal and/or bandwidth enhancement.

Regarding the obtaining of these types of glasses, the melt-quenching method is the most common glass preparation process. However, its used for the preparation of this ternary system based on $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ presents some disadvantages as impurities and high melting temperatures ($\sim 1700^\circ\text{C}$), depending on the composition. In addition, this method can lead to phase crystallization and/or composition loss since at high

temperatures, phosphorous will be degraded if it is not bonded to aluminum and/or silicate species (ŁACZKA; CIECIŃSKA, 1994; LIANGEN; ZARZYCKI, 1989; LINDNER et al., 2022; LIVAGE et al., 1992; ROY; JAIN, 2005). Fig. 1.4 shows the composition diagram for obtaining the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ through the melt-quenching method studied by Zhou et al. [ZHOU et al., 2022]. In this work, the authors obtained glasses based on $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ and they were able to present the approximate glass forming region on the composition diagram, which shows that the green, blue, and orange dots refer to the composition resulting in homogeneous glass, crack glass, and crystal, respectively. The authors realized that samples containing P_2O_5 higher than 15 wt% could not form homogeneous glass and when the Al_2O_3 content was greater than or equal to 15 wt%, amorphous samples were obtained. In addition, they did not show the compositions where phase separation could happen, and they did not explore compositions with high SiO_2 content (greater than 86 mol.%). Furthermore, in another work in the literature made by DiGiovanni et al. [(DIGIOVANNI; MACCHESNEY; KOMETANI, 1989], the authors investigated some properties (such as refractive index, density, and coefficient of thermal expansion) dependence on composition in the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$. They studied glasses in a wide composition range with high SiO_2 content (from 77.7 up to 94.0 mol.%) obtained through the MCVD method.

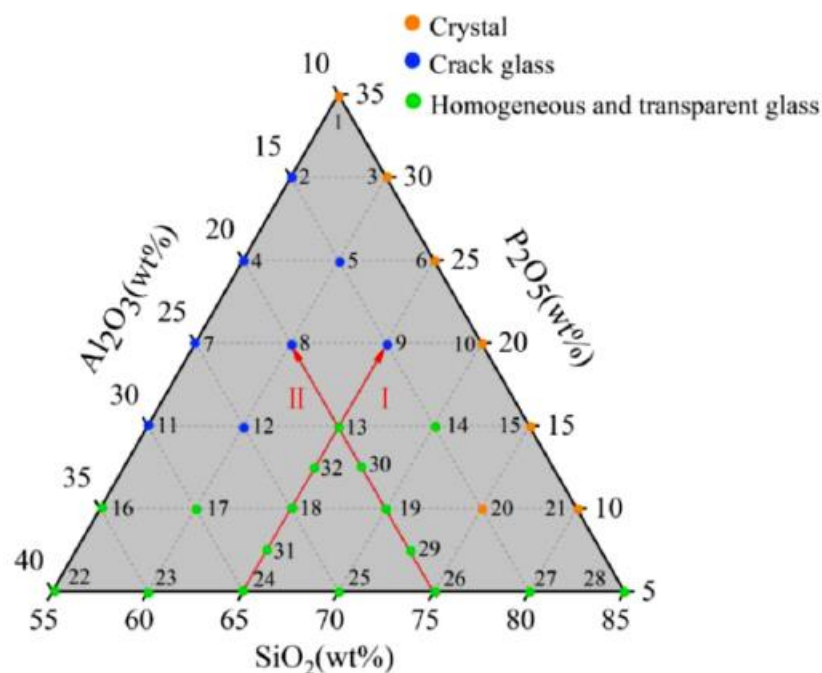
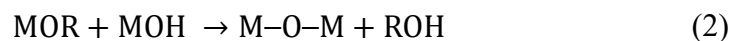
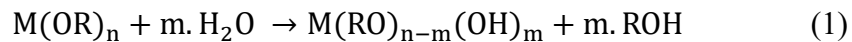


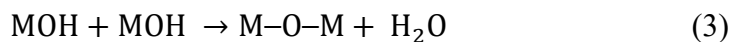
Fig. 1.4. Composition diagram for obtaining of the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ through the melt-quenching method from Zhou et al., 2022.

In this sense, the sol-gel process has become a highly attractive method for preparing $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses with a wide variety of chemical compositions allowing the formation of different chemical environments for erbium ions. The low processing temperature and the mixing of starting materials on a molecular scale offer unique opportunities for compositional and structural adaptation (BRINKER; SCHERER, 2013; TAYAMA et al., 2023; WOIGNIER; PHALIPPOU, 2016). However, some works in the literature as the one reported by De Araujo et al. (DE ARAUJO; ZHANG; ECKERT, 2006) showed especially through solid-state NMR experiments the absence of Al–O–Si and P–O–Si connectivity after SiO_2 incorporation, suggesting phase separation with the formation of AlPO_4 and SiO_2 sub-domains. In another work (DESHPANDE; ZHANG; ECKERT, 2009) the authors tried to add a network modifier such as Na_2O in the $\text{SiO}_2\text{-AlPO}_4$ matrix, however, they could see through NMR experiments that the modifier causes depolymerization of the AlPO_4 network and the formation of Al–O–Si linkages, and on the other hand, there is an absence of P–O–Si linkages indicating that the network organization is far from homogeneous. Thus, a new approach based on the sol-gel route must be developed enabling the immobilization and homogenization of $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$ in the SiO_2 matrix without the use of network modifiers. Therefore, the sol-gel method is a very interesting strategy for P_2O_5 incorporation since phosphorous will undergo condensation with Al and/or Si and will not be degraded when subjected to high temperatures.

1.2. Sol-gel method for obtaining glasses

The sol-gel method is an interesting route for obtaining hybrid and glassy materials, as it allows for mild working conditions, such as low temperatures ($< 200\text{ }^\circ\text{C}$), the use of aqueous and/or organic solvents, and an ambient atmosphere. Typically, this type of synthesis starts with a metal alkoxide, which undergoes hydrolysis (Reaction (1)), followed by the formation of a sol through ololation and oxolation reactions, as shown in Reactions (2) and (3), respectively. Finally, the sol transforms into a three-dimensional network, resulting in a gel (JUDEINSTEIN; SANCHEZ, 1996).





The evolution of the sol to the gel is a crucial step in the sol-gel synthesis for obtaining glasses, and several factors must be considered, including the reactivity of the metal alkoxide, the solvent used, the synthesis temperature, the presence of acidic or basic catalysts, and the use of complexing agents (GUGLIELMI; CARTURAN, 1988; JUDEINSTEIN; SANCHEZ, 1996). In fact, pH plays a crucial role in sol-gel synthesis, as hydrolysis or condensation can be favored depending on the choice of acidic or basic conditions. When acid catalysts are employed, hydrolysis is favored, leading to the formation of a more homogeneous and transparent gel. Conversely, when basic catalysts are used, condensation is favored, resulting in a less uniform gel with the formation of particles or mesoporous agglomerates (ONISHI et al., 2024). In addition, it is necessary to evaporate the solvent and remove the organic compounds from the final material through a controlled drying process and thermal treatment to avoid damaging the material. The drying process involves keeping the solution in the oven at a certain temperature ($\sim 50\text{-}80\text{ }^{\circ}\text{C}$) for at least 2 weeks, allowing the solution to transform into a rigid gel after releasing the residual solvent (usually ethanol and/or water) used during synthesis. Following this, thermal treatment, commonly known as the debinding process, is carried out to remove any organic components still present in the gel. All these steps necessary to obtain a glass sample are represented in Fig. 1.5.

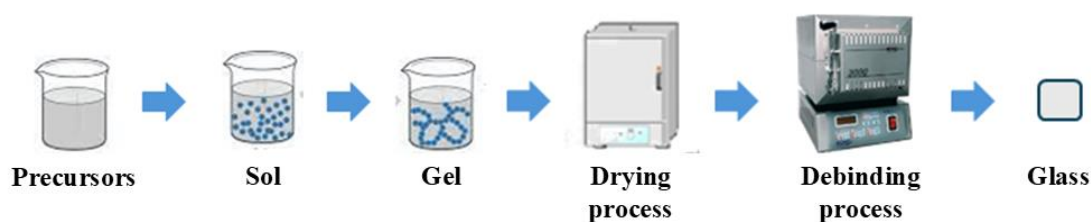


Fig. 1.5. Representative scheme of the sol-gel synthetic route for obtaining glasses.

While the sol-gel route for silicates is well-established, the formation of gels from phosphates becomes quite complicated, as their precursors are stable against hydrolysis and they cannot form P-O-P bonds (phosphate homocondensation). The high electronegativity of phosphorus impedes nucleophilic substitution (hydrolysis) and self-condensation in an acidic medium. Additionally, the small positive charge on phosphorus restricts both homocondensation and hydrolysis in a basic medium (LIVAGE et al., 1992).

Phosphorus alkoxides are highly stable against hydrolysis due to the electronegativity of phosphorus, which prevents the alkoxide groups from being replaced by hydroxyl groups. To overcome this issue, it is necessary to use precursors that already contain hydroxyl groups in their structures and exhibit high reactivity, or to use transition metal alkoxides or halides, which allow heterocondensation reactions due to the nucleophilic attack of hydroxyl groups on the phosphorus precursor (LIVAGE et al., 1992). Thus, this synthesis is limited to heterocondensation using highly reactive metal alkoxides such as zirconium, titanium, aluminum, sodium, and calcium, among others, which are attacked by phosphorus hydroxyls to form the gel (MUTIN; GUERRERO, 2005). However, since the degree of gel formation directly depends on the reactivity of the metal alkoxides, this can lead to undesirable issues in the synthesis, such as a lack of reaction control and sol stabilization. The complexity of phosphorus condensation can result in compositional deviations, as precursors that do not undergo condensation may evaporate during thermal treatment (TODAN et al., 2013).

In the manufacturing of a hybrid material using the sol-gel method, the alkoxide group can be replaced by a non-hydrolyzable and polymerizable functional group, such as (meta)acrylate, vinyl, or epoxy (DRISKO; SANCHEZ, 2012; JUDEINSTEIN; SANCHEZ, 1996; RIBOT; SANCHEZ, 1999). This modification allows the precursor to react through both polycondensation (sol-gel) and the polymerization of the functional group. Additionally, it is important to consider the stability of the polymerizable group against hydrolysis. Several factors can directly affect the reactivity of the precursor, including steric hindrance, the electronegativity of the central atom, and the type of chemical bond between the polymerizable group and the central atom. In the case of elements like titanium, zirconium, cerium, aluminum, and others, their low electronegativity and ability to expand the coordination sphere make both bonds more susceptible to hydrolysis, leading to a loss of functionality and consequent precipitation, meaning that a gel may not be formed (LICHTENBERGER; SCHUBERT, 2010). Thus, to control the reactivity of transition metal alkoxides, the use of complexing agents such as carboxylic acids, β -ketoesters, and β -diketones becomes an interesting strategy. These agents can form bonds with the metal, expanding its coordination sphere, which sterically hinders the nucleophilic attack of water. Additionally, it is ideal to choose complexing agents that contain polymerizable groups in their structures to enable polymerization reactions as well (GANESAN et al., 2011; LICHTENBERGER et al., 2009; LICHTENBERGER; SCHUBERT, 2010; TAYAMA et al., 2020; VELEZ; QUINSON;

FENET, 1999). Fig. 1.6 illustrates a reaction between the β -diketone 2-methacryloxyethylacetoacetate (MAEAA) and aluminum alkoxide.

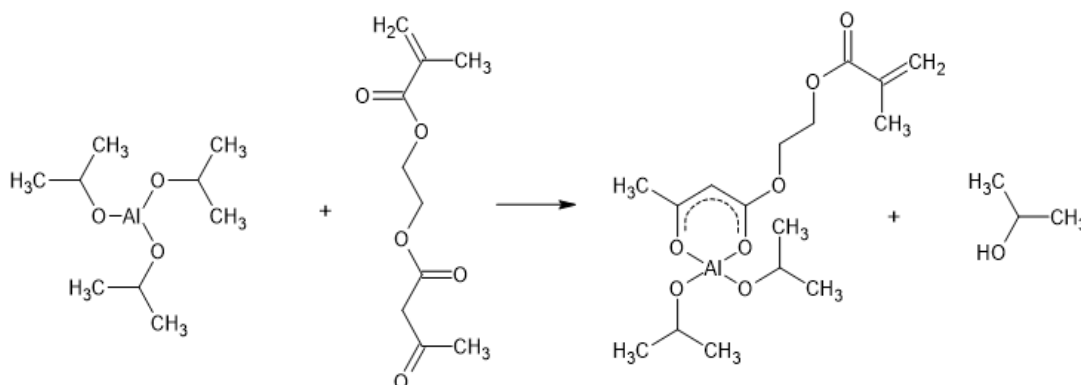


Fig. 1.6. Reaction between the β -diketone 2-methacryloxyethylacetoacetate (MAEAA) and aluminum alkoxide.

Although these hybrid materials obtained via the sol-gel method have been explored for several years, many current studies use this strategy to create hybrids combined with 3D printing. For example, Cooperstein et al. (COOPERSTEIN et al., 2018) achieved silica glasses through the thermal treatment of hybrid materials synthesized via sol-gel. Other studies have reported obtaining organic-inorganic hybrids with high transparency via sol-gel combined with 3D printing, as well as phosphosilicate glasses co-doped with Er³⁺/Yb³⁺ through the thermal treatment of hybrids synthesized via sol-gel and 3D printing (WANG; ZHENG; WANG, 2020). In addition, the debinding process is a highly important step, and the quality of the organic compounds released will directly affect the final product. To obtain a monolithic, crack-free material, a better approach is to decrease the amount of organics in the gel, skipping the polymerization process (ÇETINEL et al., 2011; LIU et al., 2018; WANG et al., 2020; WU et al., 2016).

In summary, at low temperatures (200-300 °C), gaseous decomposition products escape from the inside to the outside of the sample, forming pores on the surface. However, the pressure from the gas expansion is not sufficient to cause cracks. On the other hand, at higher temperatures (400-600 °C), CO₂ formation and heat generation occur due to the oxidation of residual carbon components. At this point, it is important to set an appropriate temperature to ensure that the CO₂ and heat are discharged smoothly without cracking the material (WANG et al., 2020). Thus, for the debinding process, it is crucial to maintain a plateau and a low heating rate to obtain a crack-free glass. Finally,

the last step involves sintering this material under vacuum at higher temperatures (~900-1000 °C) to densify the glass matrix.

Finally, to understand the structure of these types of materials obtained through sol-gel method, the most interesting technique is the Solid State Nuclear Magnetic Resonance (SSNMR). The use of different solid-state NMR experiments on SiO₂-Al₂O₃-P₂O₅-based materials gives insight into the structural evolution from the gel to the thermal treatment material in terms of the condensation between aluminum, phosphate, and silicate species, as well as the homogeneity of the matrix.

1.3. Solid State Nuclear Magnetic Resonance (SSNMR)

Solid State Nuclear Magnetic Resonance (SSNMR) is a technique widely used in the investigation of the structural and molecular dynamics of solid materials, such as polymers, zeolites, ceramics, and glasses. This technique provides detailed information on atomic connectivity, molecular geometry, conformational rearrangements, and the dynamics of intermolecular interactions (BAKHMUTOV, 2016).

The NMR phenomenon was first observed by the physicist Zeeman, who found that light could be altered in the presence of a magnetic field (Fig. 1.7). Initially, in the absence of a magnetic field, the energy levels of the nuclei degenerate. However, when an external magnetic field (B_0) is applied, this degeneracy is broken, resulting in distinct energy levels. The energy difference (ΔE) between the energy levels of the nuclei is associated with the gyromagnetic constant (which is experimentally determined for each nucleus) and the external magnetic field, as shown in Equation (1).

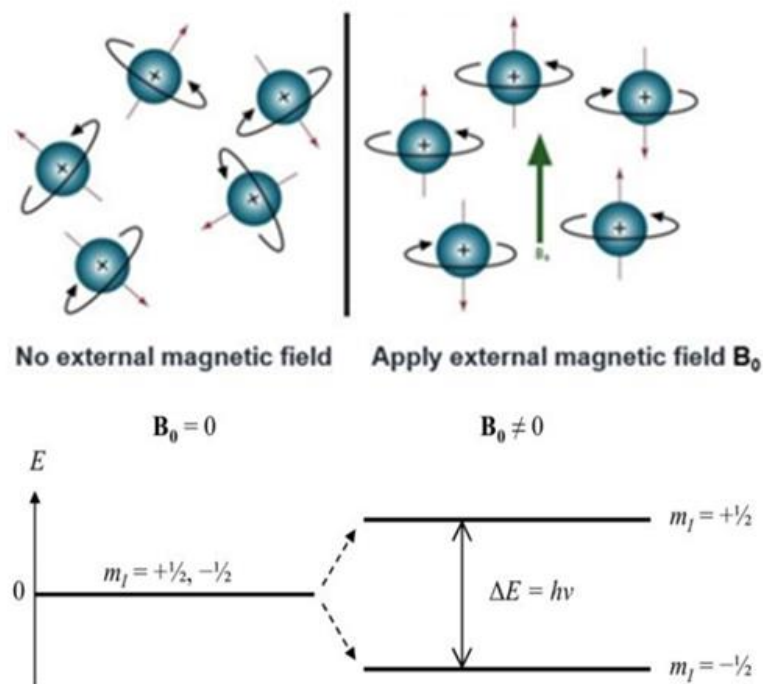


Fig. 1.7. Representative scheme of Zeeman effect as applied to a spin $\frac{1}{2}$ nucleus adapted from Hussain, 2015.

$$\Delta E = \frac{\gamma B_0}{2\pi} \quad (1)$$

This energy difference is related to the Larmor frequency (ω), which corresponds to the precession frequency of the nuclei in a magnetic field, as shown in Equation (2). This frequency is directly proportional to the gyromagnetic ratio and the effective field, which is the sum of the external field (B_0) and the local field generated by electron density (BAKHMUTOV, 2016; ECKERT, 2018).

$$\omega = \gamma B_{\text{eff}} \quad (2)$$

In NMR spectroscopy, nuclear interactions affect the observed signals such as J coupling (H_J), Chemical Shielding (H_{CS}) which is a contribution of isotropic shift (related only to electron density) and anisotropic shift, dipolar interaction (H_D), and the quadrupolar effect (H_Q) as shown in Equation (3) (BAKHMUTOV, 2016; ECKERT, 1996):

$$H = H_J + H_{\text{CS}} (\sigma_{\text{iso}} + \sigma_{\text{ani}}) + H_D + H_Q \quad (3)$$

While in liquids the reorientation of spins with B_0 is very fast due to the free mobility of molecules, the contributions of anisotropic shifts, dipolar interactions, and quadrupolar effects approach to zero. In contrast, in solids, permanent magnetic fields are generated in the sample that have different orientations relative to B_0 , and due to the restricted mobility, the anisotropic interactions such as dipolar interactions and quadrupolar effects are observed in the solid-state spectra, resulting in a loss of resolution. All these interactions are orientation-dependent, as expressed in the term shown in Equation (4) (ECKERT, 2018):

$$\omega = \gamma B_0 (1 - \sigma_{iso} - \frac{1}{3} \Delta\sigma (3\cos^2\theta - 1)) \quad (4)$$

where θ is the angle between B_0 and the fixed direction of the molecule. However, when the value of this angle is 54.7° , this term $(3\cos^2\theta - 1)$ tends to zero, preventing the contribution of bond orientation, and only the chemical shift related to electron density is observed. This angle is known as the magic angle, and when the sample is rotated in the direction of this angle, we have the experiment known as Magic Angle Spinning (MAS), as shown in Fig. 1.8. It makes the magnetic moment of each crystallite of the sample to be at different positions over time, creating a temporal average of rotation in this angle direction. This cancels out the anisotropic contribution and dipolar interaction, ensuring higher spectral resolution (BORISOV; HAZENDONK; HAYES, 2010; ECKERT, 2018).

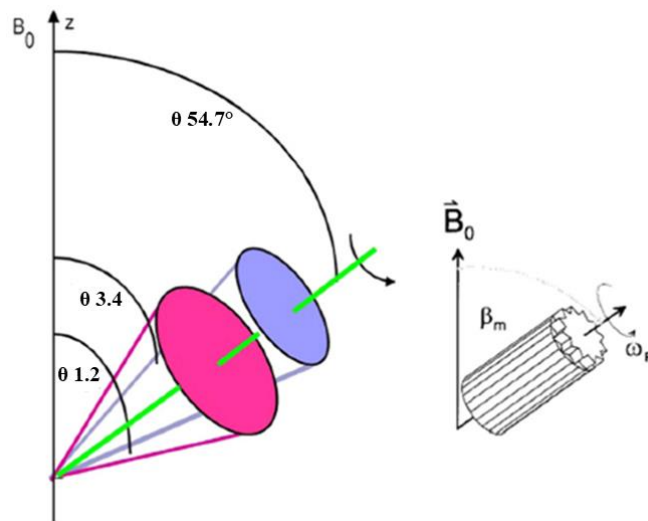


Fig. 1.8. Magic Angle Spinning (MAS) representation adapted from Eckert, 2018.

Since the technique considers nuclear spin, the nucleus must have a spin quantum number different from 0 to be measured by NMR. Additionally, the easiness or complexity of observing a particular nucleus is dictated by several factors, including its natural abundance, spin quantum number, and the size of its nuclear electric quadrupole moment (ECKERT, 2017). Depending on the experiment used, this technique allows the acquisition of short- or mid-range information. For example, when a particular nucleus is being observed, it is possible to obtain information about its neighboring atoms (first coordination sphere) or even those in the second and third coordination spheres. Moreover, it is possible to distinguish whether an atom near the observed nucleus is bonded or just spatially close. For these reasons, NMR is a technique that enables detailed structural studies through different experiments (ECKERT, 2017, 2018).

In NMR, nuclei are sensitive to two types of interactions: those with the external field and those with neighboring nuclei, electronic spin, and electric field gradients. In summary, when there is a population distribution among the energy levels, an induced field (B_1) is applied in the form of a radiofrequency pulse specific to each nucleus. This field induces transitions between the energy levels, and the return to thermodynamic equilibrium is what is measured in the NMR technique. The induced field is therefore responsible for exciting the nuclear spins and promoting the transition between the energy states determined by the external field. On the other hand, interactions with neighboring nuclei include spin-electron and spin-spin interactions (BAKHMUTOV, 2016; ECKERT, 1996).

To conduct the NMR measurements, pulse sequences are used to promote the spin transition between the energy levels by irradiating the sample with radiofrequency pulses. The return of the magnetization to its equilibrium value along the magnetic field direction is governed by two distinct relaxation processes: spin-spin relaxation and spin-lattice relaxation. In the first mechanism, spin-spin relaxation, the nuclear spins interaction causes small local field variations that lead to a loss of coherence in the transverse magnetization components (along the X and Y axes) and is referred to T_2 . The second mechanism, spin-lattice relaxation, denominated as T_1 , refers to the restoration of the equilibrium magnetization M_0 along the direction of the external magnetic field (Z axis) and it involves energy exchange between the spin system and its surroundings (BAKHMUTOV, 2016; BORISOV; HAZENDONK; HAYES, 2010; ECKERT, 2018).

The Single Pulse experiment, in which a 90° pulse is applied and the experiment is repeated to accumulate more scans and enhance spectral resolution, is typically

employed for nuclei with high natural abundance, such as phosphorus (^{31}P). However, it can also be used for nuclei with low natural abundance, like silicon (^{29}Si), although the experiment will take longer due to the need of more scans. The advantage of this experiment is that it allows the quantification of the number of sites associated with the nucleus by integrating the area, as it provides a direct measurement (BAKHMUTOV, 2016; ECKERT, 2018).

Another experiment called Cross Polarization (CP-MAS) is based on the polarization transfer from one species to another. It is typically employed when measuring a nucleus with low natural abundance by using a nucleus with high natural abundance. The pulse sequence is based on a 90° pulse and what is known as a spin-lock pulse, which allows the magnetization to be maintained in the transverse plane for some time. An important aspect of this experiment is that, for the polarization transfer between the nuclei to occur, the Hartmann-Hahn condition (the energy difference between the levels of the two nuclei must be equivalent) must be met. However, unlike the Single Pulse experiment, this is a qualitative experiment, so it is not possible to quantify the sites (BAKHMUTOV, 2016).

A bi-dimensional experiment called Rotational Echo Double Resonance (REDOR) (GULLION; SCHAEFER, 1989) allows the reintroduction of heteronuclear dipolar coupling. This provides structural information, not about chemical bonding but about conformational details (i.e., atoms near one another). In this type of measurement, the dipolar interaction between the two nuclei is introduced. When the dipolar interaction is introduced, it is possible to measure the normalized difference signal $\Delta S/S_0 = (S_0 - S)/S_0$ in the absence (intensity S_0) and the presence (intensity S) of the recoupling pulses. The REDOR curve is generated by plotting $\Delta S/S_0$ as a function of dipolar evolution time NT_r , that is, the duration of one rotor period multiplied by the number of rotor cycles. The heteronuclear second moment (M_2) can be calculated theoretically through the Van Vleck equation (Equation (5)), but the average heteronuclear Van-Vleck second moment can be extracted from a simple parabolic fit of the REDOR curve in the limit of short dipolar evolution times ($\Delta S/S_0 < 0.2$) (BERTMER; ECKERT, 1999; CHAN; ECKERT, 2000; ECKERT, 2017).

$$M_2 = \frac{4}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma_I^2 \gamma_S^2 S(S+1) \hbar^2 \sum_i \frac{1}{r_{IS}^6} \quad (5)$$

Regarding the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$, some works in the literature have used different SSNMR experiments to elucidate its structure (DE ARAUJO; ZHANG; ECKERT, 2006; LOGRADO et al., 2022; TAYAMA et al., 2023; ZHU et al., 2022). The structure of this ternary system is based on a periodic network of coordination polyhedrals with different silicate, phosphate, and aluminum units depending on their chemical environments. Thus, silicate species are usually represented by Q^n units where n is the number of Si-O-Si bonds. Phosphate species are denominated as P_{mAl}^n where n is the number of phosphates bonded to P units (P-O-P) and m is the number of aluminum units bonded to P units (Al-O-P). And the aluminum species in this ternary system usually appear as Al-tetracoordinated (IV), Al-pentacoordinated (V), and Al-hexacoordinated (VI) (ECKERT, 2018; TAYAMA et al., 2023).

In this sense, the SSNMR is a very interesting technique for studying the different chemical environments that can be formed in RE-doped materials to explain their luminescence properties. Therefore, this technique allied to the photoluminescence study of these RE ions can give insight into the structural and optical properties, as well as corroborate with other characterization techniques leading to a detailed understanding of these materials.

1.4. Photoluminescence's principle

Photoluminescence (PL) is a phenomenon based on the photon's emission by a substance after radiation absorption. In summary, there are two main processes in PL: i) the excitation process which happens when electromagnetic radiation is absorbed by a substance leading to an electron promotion from a lower electronic state to a higher one, and ii) the emission process when this excited electron at higher electronic state 'release' photons with a specific energy and decay to a lower electronic state (LAKOWICZ, 2006; VALEUR, 2001).

During the excitation process, the electron stays at a higher electronic state during a period of time before releasing energy and returning to the ground state. This period of time is denominated of lifetime (τ), which is defined as the time of an initial population N_0 reaches the value of $1/e$ and can be measured experimentally considering the emission process according to Equation (6), where $N_{(t)}$ is the concentration of excited species at $t = 0$ (LAKOWICZ, 2006; VALEUR, 2001).

$$N(t) = N_0 \exp\left(-\frac{t}{\tau}\right) \quad (6)$$

However, it is not possible to measure the concentration of excited species. Instead, a measurable parameter is the fluorescence intensity, I , defined as the amount of photons emitted per unit time (s). The relationship between the fluorescence intensity at a time, t , and the decay in the fluorescence intensity is shown in Equation (7) (LAKOWICZ, 2006; VALEUR, 2001).

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (7)$$

The relation between the decay rates considers radiative (k_r) and non-radiative (k_{nr}) processes as described by Equation (8). Besides the radiative transitions between excited and ground states, there are also non-radiative transitions when some energy levels appear between excited and ground states generated by vibrational and rotational motions of the substance structure. When the vibrational levels of the electronic states have similar energy and similar or different multiplicity, non-radiative pathways can occur to reach a lower electronic state. And due to different types of non-radiative pathways, the energy absorbed during the excitation process is not entirely emitted (LAKOWICZ, 2006; VALEUR, 2001).

$$\tau = \frac{1}{k_{nr} + k_r} \quad (8)$$

1.4.1. Rare earth ions luminescence

The lanthanides (Ln), also known as rare earth ions, is a group of chemical elements that include elements from lanthanum (La) to lutetium (Lu). These elements are characterized by their unique electronic configuration, where the 4f orbital is partially filled. Lanthanum, the first of the lanthanides, does not have electrons in the 4f subshell so La has the electronic configuration $[Xe] 6s^2 5d^1$ since the 5d subshell has lower energy. By increasing the number of protons in the nucleus in the lanthanides series, the 4f energy became lower and more stable and penetrating than the 5d orbital. In this sense, cerium (Ce) has the electronic configuration $[Xe] 4f^1 6s^2 5d^1$, but from praseodymium (Pr) to

europium (Eu), they all follow the configuration $[\text{Xe}] 4f^n 6s^2$ ($n = 3-7$). After Eu, the energy required for filling the 5d orbital with an electron is lower than the energy for pairing the electrons in the 4f orbital, so for gadolinium (Gd) the configuration of $[\text{Xe}] 4f^7 6s^2 5d^1$. From terbium (Tb) to ytterbium (Yb), the number of protons in the nucleus increases and the configuration follow as $[\text{Xe}] 4f^n 6s^2$ ($n = 9-14$). Finally, Lu has filled f-orbitals and its configuration is $[\text{Xe}] 4f^{14} 6s^2 5d^1$ (SIGOLI et al, 2022).

These ions typically exhibit a trivalent oxidation state (Ln^{3+}), for which they have an electronic configuration of $[\text{Xe}] 4f^n$ ($n = 0 - 14$). This configuration leads to a wide variety of microstates (electronic levels) since each of the n electrons of the $4f^n$ orbital corresponds to one of the seven 4f wavefunctions and can have a spin of $\pm \frac{1}{2}$. Since the 4f orbitals are shielded by the outer electronic layers as 5s and 5p orbitals, they do not directly participate in chemical bonding resulting in energy levels well-defined and insensitive to the chemical environment. This characteristic explains the luminescent properties in the forbidden 4f-4f transitions of the lanthanides ions such as the multiple narrow and sharp emissions, and long excited-state lifetimes. In summary, these properties are key reasons for their use in a wide range of luminescent applications (MARTINS; ISOLANI, 2005; SIGOLI et al, 2022).

Regarding the emission in the NIR range, the erbium ion becomes very interesting. Fig. 1.9 shows the erbium ion energy diagram, and it is possible to observe a transition between the energy levels $^4\text{I}_{15/2}$ and $^4\text{I}_{13/2}$ with an emission at 1.55 μm . This emission is used in C-band in telecommunication systems for the erbium-doped fiber amplifier which is well-known in the literature (KOTOV; LIKHACHEV, 2019). However, these fiber amplifiers are usually based on SiO_2 , which has a low solubility of RE ions (maximum of 1000 ppm by weight) leading to cluster formation and consequently quenching of the erbium photoluminescence due to the non-radiative relaxation (ISKHAKOVA et al., 2021).

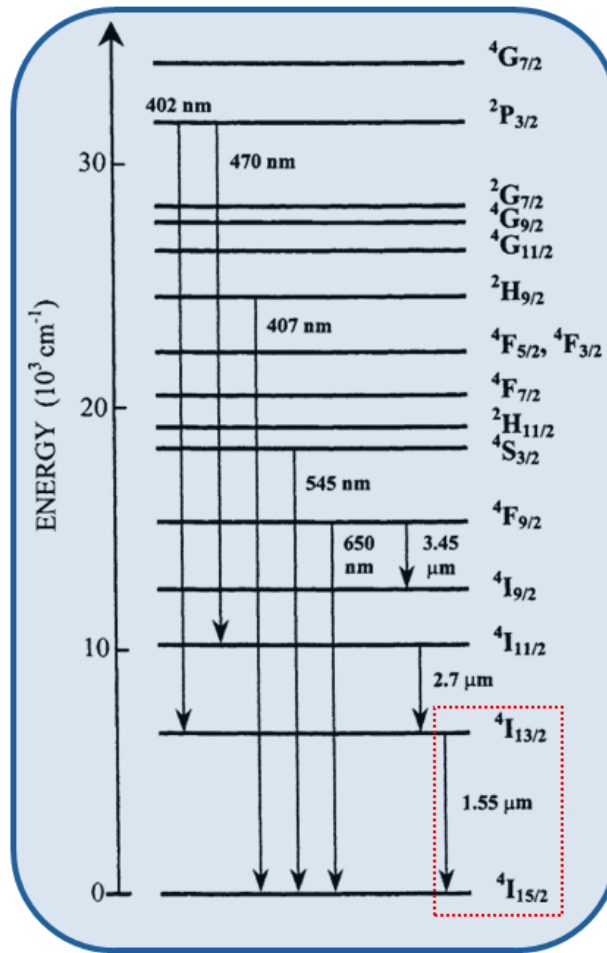


Fig. 1.9. Energy diagram for the Er³⁺ ions adapted from Sigoli et al., 2022.

For this reason, to enhance the solubility of Er³⁺ ions within the glass matrix, the use of the ternary system SiO₂-Al₂O₃-P₂O₅ is particularly advantageous. The sol-gel method is an effective approach in this context, as it facilitates the formation of different chemical environments for Er³⁺ ions and enhances the glass solubility, leading to a broad near-infrared (NIR) emission signal that covers the C+L-bands (1530 to 1625 nm) of telecommunication systems. However, the sol-gel process involves the use of ethanol and/or water as solvents, which results in the presence of OH groups. These OH groups can significantly lead to the quenching of photoluminescence for the Er³⁺ ions through non-radiative relaxation from the 4I_{13/2} energy level due to the vibrational energy of O-H bonds in water molecules. Consequently, the energy from excited Er³⁺ ions may be transferred to the vibrational modes of water molecules rather than being emitted as light, causing signal attenuation (HAYASHI et al., 2006). For example, Fig. 1.10 shows the deactivation mechanism of the emitting states of Eu³⁺ and Tb³⁺ caused by O-H oscillators found in H₂O molecules, which also occurs in the case of Er³⁺ ions. To avoid this issue,

thermal treatment under vacuum is crucial, as it reduces the OH content and promotes densification of the glass matrix through further condensation between silicate, aluminum, and phosphate species, thereby enhancing the emission intensity of the Er^{3+} ions.

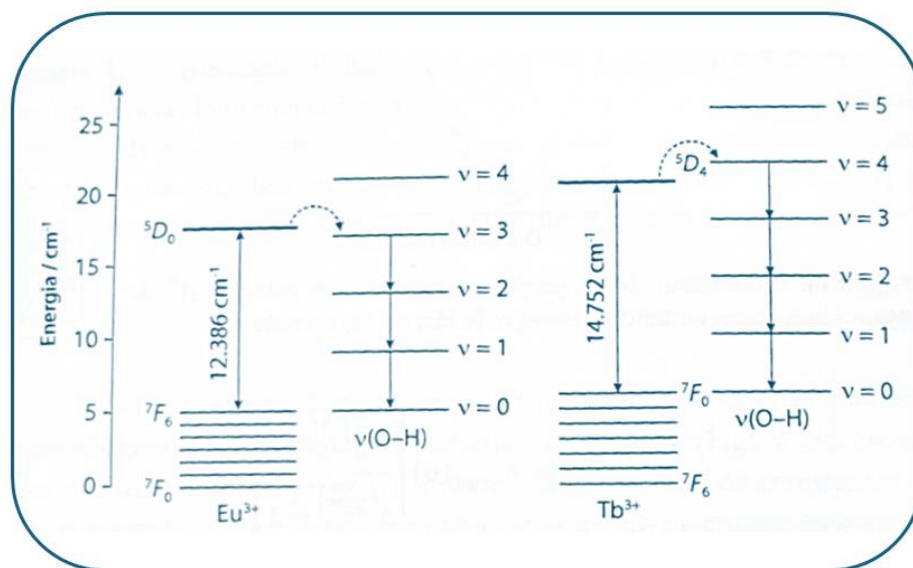


Fig. 1.10. Deactivation mechanism of the emitting states of Eu^{3+} and Tb^{3+} caused by O-H oscillators found in H_2O molecules adapted from Sigoli et al., 2022.

References

BAKHMUTOV, V. I. **Solid-state NMR in materials science: Principles and applications.** [s.l: s.n.].

BENNETT, T. D. et al. Melt-Quenched Glasses of Metal-Organic Frameworks Melt-Quenched Glasses of Metal-Organic Frameworks. 2016.

BERTMER, M.; ECKERT, H. Dephasing of spin echoes by multiple heteronuclear dipolar interactions in rotational echo double resonance NMR experiments. **Solid State Nuclear Magnetic Resonance**, v. 15, n. 3, p. 139–152, 1999.

BORISOV, A. S.; HAZENDONK, P.; HAYES, P. G. Solid-state nuclear magnetic resonance spectroscopy: A review of modern techniques and applications for inorganic polymers. **Journal of Inorganic and Organometallic Polymers and Materials**, v. 20, n. 2, p. 183–212, 2010.

BOURHIS, K. et al. Influence of P_2O_5 and Al_2O_3 content on the structure of erbium-

doped borosilicate glasses and on their physical, thermal, optical and luminescence properties. **Materials Research Bulletin**, v. 63, p. 41–50, 2015.

BRINKER, C. J.; SCHERER, G. W. **Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing**. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, 2013.

BUBNOV, M. M. et al. Fabrication and optical properties of fibers with an Al₂O₃-P₂O₅-SiO₂ glass core. **Inorganic Materials**, v. 45, n. 4, p. 444–449, 2009.

CAO, Y. et al. Influence of an equimolar amount of aluminium and phosphorus on spectroscopic properties of neodymium under local phosphorus environment in silica glass. **Journal of Rare Earths**, v. 36, n. 10, p. 1030–1035, 2018.

ÇETINEL, F. A. et al. Factors affecting strength and shape retention of zirconia micro bending bars during thermal debinding. **Ceramics International**, v. 37, n. 7, p. 2809–2820, 2011.

CHAN, J. C. C.; ECKERT, H. Dipolar Coupling Information in Multispin Systems: Application of a Compensated REDOR NMR Approach to Inorganic Phosphates. **Journal of Magnetic Resonance**, v. 147, n. 2, p. 170–178, 2000.

CHOWDHURY, M. Selection Rules For Processes Involving Photon-Molecule Interaction: A Symmetry-Conservation-Based Approach Bypassing Transition Matrix Elements. **Journal of Chemical Education**, v. 73, n. 8, p. 743, 1 ago. 1996.

COOPERSTEIN, I. et al. Additive Manufacturing of Transparent Silica Glass from Solutions. **ACS Applied Materials and Interfaces**, v. 10, n. 22, p. 18879–18885, 2018.

COSTA, B. H.; TAYAMA, G. T.; SANTAGNELI, S. H. Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials. **Journal of Non-Crystalline Solids**, v. 639, n. June, p. 123105, 2024.

DE ARAUJO, C. C.; ZHANG, L.; ECKERT, H. Sol-gel preparation of AlPO₄-SiO₂ glasses with high surface mesoporous structure. **Journal of Materials Chemistry**, v. 16, n. 14, p. 1323–1331, 2006.

DESHPANDE, R. R.; ZHANG, L.; ECKERT, H. Sol-gel synthesis of sodium-modified AlPO₄-SiO₂ glasses and structural characterization by solid state NMR. **Journal of Materials Chemistry**, v. 19, n. 8, p. 1151–1159, 2009.

DIGIOVANNI, D. J.; MACCHESNEY, J. B.; KOMETANI, T. Y. Structure and properties of silica containing aluminum and phosphorus near the AlPO₄ join. **Journal of Non-Crystalline Solids**, v. 113, n. 1, p. 58–64, 1989.

DRISKO, G. L.; SANCHEZ, C. Hybridization in Materials Science – Evolution ,

Current State , and Future Aspirations. p. 5097–5105, 2012.

ECKERT, H. Solid state NMR as a tool of structure and dynamics in solid state chemistry and materials science: Recent progress and challenges. **Current Opinion in Solid State and Materials Science**, v. 1, n. 4, p. 465–476, 1996.

ECKERT, H. Spying with spins on messy materials: 60 Years of glass structure elucidation by NMR spectroscopy. **International Journal of Applied Glass Science**, v. 9, n. 2, p. 167–187, 5 abr. 2017.

ECKERT, H. Structural characterization of bioactive glasses by solid state NMR. **Journal of Sol-Gel Science and Technology**, v. 88, n. 2, p. 263–295, 2018.

EGAN, J. M.; WENSLOW, R. M.; MUELLER, K. T. Mapping aluminum/phosphorus connectivities in aluminophosphate glasses. **Journal of Non-Crystalline Solids**, v. 261, n. 1, p. 115–126, 2000.

ELLIS, A. M. Spectroscopic selection rules: The role of photon states. **Journal of Chemical Education**, v. 76, n. 9, p. 1291–1294, 1999.

GANESAN, R. et al. Direct nanoimprinting of metal oxides by in situ thermal copolymerization of their methacrylates. **Journal of Materials Chemistry**, v. 21, n. 12, p. 4484–4492, 2011.

GAO, C. et al. Yb-doped Aluminophosphosilicate Laser Fiber. v. 8724, n. c, 2016.

GULLION, Terry; SCHAEFER, Jacob. Rotational-echo double-resonance NMR. **Journal of Magnetic Resonance**, v. 81, n. 1, p. 196–200, 1989.

GLORIEUX, B. et al. Better understanding of the role of SiO₂, P₂O₅ and Al₂O₃ on the spectroscopic properties of Yb³⁺ + doped silica sol-gel glasses. **Journal of Non-Crystalline Solids**, v. 482, p. 46–51, 2018.

GUGLIELMI, M.; CARTURAN, G. Precursors for sol-gel preparations. **Journal of Non-Crystalline Solids**, v. 100, n. 1–3, p. 16–30, mar. 1988.

HAYASHI, H. et al. Effect of hydroxyl groups on erbium-doped bismuth-oxide-based glasses for fiber amplifiers. **Journal of Applied Physics**, v. 99, n. 9, 2006.

ISKHAKOVA, L. D. et al. Analysis of elemental distributions and phase separation in rare-earth-doped silica-based fiber preforms and optical fibers. **Journal of Non-Crystalline Solids**, v. 554, n. December 2020, p. 120616, 2021.

JALILPIRAN, S. et al. Baria-Silica Erbium-Doped Fibers for Extended L-Band Amplification. **Journal of Lightwave Technology**, v. 41, n. 14, p. 4806–4814, 2023.

JUDEINSTEIN, P.; SANCHEZ, C. Hybrid organic–inorganic materials: a land of multidisciplinary. **J. Mater. Chem.**, v. 6, n. 4, p. 511–525, 1996.

KAJIHARA, K. Recent advances in sol-gel synthesis of monolithic silica and silica-based glasses. **Journal of Asian Ceramic Societies**, v. 1, n. 2, p. 121–133, 2013.

KAJIHARA, K.; KUWATANI, S.; KANAMURA, K. Sol-Gel synthesis of rare-earth and phosphorus codoped monolithic silica glasses from a cosolvent-free phase-separating system. **Applied Physics Express**, v. 5, n. 1, p. 0–3, 2012.

KANEKO, K.; KAJIHARA, K.; KANAMURA, K. Cosolvent-free sol-gel synthesis of rare-earth and aluminum codoped monolithic silica glasses. **Journal of the Ceramic Society of Japan**, v. 121, n. 1411, p. 299–302, 2013.

KOSINSKI, S. G. et al. Raman and NMR spectroscopy of SiO₂ glasses CO-doped with Al₂O₃ and P₂O₅. **Journal of Non-Crystalline Solids**, v. 105, n. 1–2, p. 45–52, out. 1988.

KOTOV, L. V.; LIKHACHEV, M. E. **High Power Continuous-Wave Er-doped Fiber Lasers**. [s.l.] Springer International Publishing, 2019. v. 222

KUHN, S. et al. Modelling the refractive index behavior of Al,P-doped SiO₂, fabricated by means of all-solution doping, in the vicinity of Al:P = 1:1. **Optical Materials Express**, v. 8, n. 5, p. 1328, 2018.

ŁACZKA, M.; CIECIŃSKA, M. Preparation, structure and properties of silicate-phosphate glasses obtained by means of sol-gel method. **Journal of Sol-Gel Science and Technology**, v. 3, n. 3, p. 219–227, 1994.

LAKOWICZ, J. R. **Principles of Fluorescence Spectroscopy**. Boston, MA: Springer US, 2006. v. 33

LAM TRAN, T. N. et al. Sol-gel-derived transparent glass-ceramics for photonics. **Optical Materials**, v. 130, n. May, p. 112577, 2022.

LIANGEN, S.; ZARZYCKI, J. Evolution of the structure of gels of the system SiO₂Al₂O₃P₂O₅ submitted to thermal treatment. **Journal of Non-Crystalline Solids**, v. 112, n. 1–3, p. 428–431, 1989.

LICHTENBERGER, R. et al. Modification of aluminum alkoxides with β -ketoesters : new insights into formation , structure and stability OR. p. 130–140, 2009.

LICHTENBERGER, R.; SCHUBERT, U. Chemical modification of aluminium alkoxides for sol – gel processing †. p. 9287–9296, 2010.

LIKHACHEV, M. E. et al. Effect of the AlPO₄ join on the pump-to-signal conversion efficiency in heavily Er-doped fibers. v. 34, n. 21, p. 3355–3357, 2009.

LIKHACHEV, M. E. et al. Erbium-doped aluminophosphosilicate optical fibres. **Quantum Electronics**, v. 40, n. 7, p. 633–638, 2010.

LINDNER, F. et al. FTIR multispectral imaging of P/Al-doped silica glass preforms prepared by MCVD in combination with the high temperature evaporation of AlCl_3 . **Optical Materials Express**, v. 12, n. 1, p. 184, 2022.

LIU, C. et al. Additive manufacturing of silica glass using laser stereolithography with a top-down approach and fast debinding. **RSC Advances**, v. 8, n. 29, p. 16344–16348, 2018.

LIU, X. Evolution of Fiber-Optic Transmission and Networking toward the 5G Era. **iScience**, v. 22, p. 489–506, 2019.

LIVAGE, J. et al. Sol-gel synthesis of phosphates. **Journal of Non-Crystalline Solids**, v. 147–148, n. C, p. 18–23, 1992.

LOGRADO, M. et al. Silica incorporation into sodium aluminum phosphate glasses: Structural characterization by Raman spectroscopy and multinuclear solid-state NMR. **Journal of Non-Crystalline Solids**, v. 579, n. December 2021, p. 121366, 2022.

LORD, M.-P. et al. Erbium-doped aluminophosphosilicate all-fiber laser operating at 1584 nm. **Optics Express**, v. 28, n. 3, p. 3378, 2020.

MARTINS, T. S.; ISOLANI, P. C. Terras raras: Aplicações industriais e biológicas. **Química Nova**, v. 28, n. 1, p. 111–117, 2005.

MATSUDA, A. et al. Proton conductivities of sol – gel derived phosphosilicate gels in medium temperature range with low humidity. v. 155, p. 687–692, 2002.

MAURO, J. C.; ZANOTTO, E. D. Two Centuries of Glass Research : Historical Trends , Current Status , and Grand Challenges for the Future. v. 327, p. 313–327, 2014.

MAZURIN, O. V. Glass properties : compilation , evaluation , and prediction. v. 351, p. 1103–1112, 2005.

MORSE, D. L.; EVENSON, J. W. Welcome to the Glass Age. v. 4, p. 1–4, 2016.

MUTIN, P. H.; GUERRERO, G. Hybrid materials from organophosphorus coupling molecules. p. 3761–3768, 2005.

NAGASHIMA, H. et al. Recent Developments in NMR Studies of Aluminophosphates. **Annual Reports on NMR Spectroscopy**, v. 94, p. 113–185, 2018.

NOGAMI, M. et al. Sol-gel preparation of fast proton-conducting P_2O_5 - SiO_2 glasses. **Journal of Sol-Gel Science and Technology**, v. 26, n. 1–3, p. 1041–1044, 2003.

ONISHI, B. S. D. et al. Organic–inorganic hybrid silica systems: synthesis strategies and optical applications. **Journal of Sol-Gel Science and Technology**, 2024.

REN, J.; ZHANG, L.; ECKERT, H. Sol-gel preparation of mesoporous Al_2O_3 - SiO_2 glasses: Structural evolution monitored by solid state NMR. **Journal of Sol-Gel Science**

and Technology, v. 70, n. 3, p. 482–490, 2014.

RIBOT, F.; SANCHEZ, C. Organically Functionalized Metallic Oxo-Clusters: Structurally Well-Defined Nanobuilding Blocks for the Design of Hybrid Organic-Inorganic Materials. **Comments on Inorganic Chemistry**, v. 20, n. 4–6, p. 327–371, jan. 1999.

RIVERA, V. A. G. et al. Novel insights into the electronic and optical properties of the 1.53- μm emission in Er^{3+} -doped oxide- and oxyfluoride- tellurite glasses for optical communications. **Journal of Alloys and Compounds**, v. 976, n. December 2023, p. 173182, 2024.

ROMA, J.; PADILLA, S. Sol - Gel Glasses as Precursors of Bioactive Glass Ceramics. n. 19, p. 798–806, 2003.

ROY, B.; JAIN, H. Phase Separation and Structural Differences between Alkali Silicate Glasses Prepared by the Sol-Gel and Melt-Quench Methods. **Journal of the American Ceramic Society**, v. 81, n. 9, p. 2360–2370, 20 set. 2005.

SARAVANAPAVAN, P. et al. Bioactivity of gel – glass powders in the CaO-SiO_2 system : A comparison with ternary ($\text{CaO-P}_2\text{O}_5\text{-SiO}_2$) and quaternary glasses ($\text{SiO}_2\text{-CaO-P}_2\text{O}_5\text{-Na}_2\text{O}$). p. 17–19, 2003.

SCHWEIZER, T.; KUBACH, H.; KOCH, T. Investigations to characterize the interactions of light radiation, engine operating media and fluorescence tracers for the use of qualitative light-induced fluorescence in engine systems. **Automotive and Engine Technology**, v. 6, n. 3, p. 275-287, 2021.

SEN, S.; YOUNGMAN, R. E. High-resolution multinuclear NMR structural study of binary aluminosilicate and other related glasses. **Journal of Physical Chemistry B**, v. 108, n. 23, p. 7557–7564, 2004.

SHAO, C. et al. Relationship between glass structure and spectroscopic properties in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Al}^{3+}/\text{P}^{5+}$ -doped silica glasses . **Optical Materials Express**, v. 10, n. 5, p. 1169, 2020.

SIGOLI, Fernando Aparecido; BISPO JUNIOR, Airton Germano; SOUZA FILHO, Paulo Cesar de. Lantanídeos: química, luminescência e aplicações. **Campinas: Átomo**, 2022.

TAYAMA, G. T. et al. Preparation and Structural Characterization of New Photopolymerizable Transparent Aluminum-Phosphate Hybrid Materials as Resins for 3D Printing. **Journal of Physical Chemistry C**, v. 124, n. 46, p. 25621–25631, 2020.

TAYAMA, G. T. et al. Understanding the Microstructure Connectivity in

Photopolymerizable Aluminum-Phosphate-Silicate Sol – Gel Hybrid Materials for Additive Manufacturing. 2023.

TODAN, L. et al. Thermal behavior of silicophosphate gels obtained from different precursors. **Journal of Thermal Analysis and Calorimetry**, v. 114, n. 1, p. 91–99, 2013.

TRICOT, G. et al. Non-homogeneous distribution of Al^{3+} in doped phosphate glasses revealed by $^{27}Al/^{31}P$ solid state NMR. **Solid State Nuclear Magnetic Resonance**, v. 84, n. November 2016, p. 137–142, 2017.

TSUCHIDA, J. et al. Structure of ternary aluminum metaphosphate glasses. **Journal of Physical Chemistry C**, v. 115, n. 44, p. 21927–21941, 2011.

VALEUR, B. **Molecular Fluorescence Principle and Applications**. [s.l.] Wiley, 2001.

VAN WÜLLEN, L.; TRICOT, G.; WEGNER, S. An advanced NMR protocol for the structural characterization of aluminophosphate glasses. **Solid State Nuclear Magnetic Resonance**, v. 32, n. 2, p. 44–52, 2007.

VELEZ, K.; QUINSON, J. F.; FENET, B. Modification study of aluminum sec-butoxide by acrylic acid. **Journal of Sol-Gel Science and Technology**, v. 16, n. 3, p. 201–208, 1999.

WANG, F. et al. Effect of $AlPO_4$ join concentration on optical properties and radiation hardening performance of Yb-doped Al_2O_3 - P_2O_5 - SiO_2 glass. **Journal of Applied Physics**, v. 125, n. 17, 2019.

WANG, J.; ZHENG, B.; WANG, P. 3D printed Er^{3+}/Yb^{3+} co-doped phosphosilicate glass based on sol-gel technology. **Journal of Non-Crystalline Solids**, v. 550, n. June, p. 120362, 2020.

WANG, K. et al. Study on defect-free debinding green body of ceramic formed by DLP technology. **Ceramics International**, v. 46, n. 2, p. 2438–2446, 2020.

WANG, S. et al. Optical and laser properties of Yb^{3+} -doped Al_2O_3 - P_2O_5 - SiO_2 large-mode-area photonic crystal fiber prepared by the sol-gel method. **Laser Physics Letters**, v. 10, n. 11, 2013.

WEGNER, S.; VAN WÜLLEN, L.; TRICOT, G. The structure of aluminophosphate glasses revisited: Application of modern solid state NMR strategies to determine structural motifs on intermediate length scales. **Journal of Non-Crystalline Solids**, v. 354, n. 15–16, p. 1703–1714, 2008.

WOIGNIER, T.; PHALIPPOU, J. Glasses: Sol–Gel Methods. **Reference Module in Materials Science and Materials Engineering**, n. July 2015, p. 1–6, 2016.

WONDRACZEK, L. et al. Towards ultrastrong glasses. **Advanced Materials**, v. 23, n. 39, p. 4578–4586, 2011.

WU, H. et al. Effect of the particle size and the debinding process on the density of alumina ceramics fabricated by 3D printing based on stereolithography. **Ceramics International**, v. 42, n. 15, p. 17290–17294, 2016.

XU, W. et al. Effect of P5+ on spectroscopy and structure of Yb3+/Al3+/P5+ co-doped silica glass. **Journal of Luminescence**, v. 167, p. 8–15, 2015.

YADAV, A. K.; SINGH, P. A review of the structures of oxide glasses by Raman spectroscopy. **RSC Advances**, v. 5, n. 83, p. 67583–67609, 2015.

YANG, Q. et al. Gain and laser performance of heavily Er-doped silica fiber fabricated by MCVD combined with the sol-gel method. **Chinese Optics Letters**, v. 19, n. 11, p. 110603, 2021.

YUNG, S. W. et al. Thermal, optical and structural properties of Tb doped zinc aluminum phosphate glasses. **Ceramics International**, v. 41, n. 1, p. 877–888, 2015.

ZACHARIASEN, W. H. THE ATOMIC ARRANGEMENT IN GLASS. **Journal of the American Chemical Society**, v. 54, n. 10, p. 3841–3851, 1 out. 1932.

ZANOTTO, E. D.; MAURO, J. C. The glassy state of matter: Its definition and ultimate fate. **Journal of Non-Crystalline Solids**, v. 471, n. March, p. 490–495, 2017.

ZHU, Q. et al. The role of phosphate in the glass forming region, structure and mechanical properties for the SiO₂-Al₂O₃-P₂O₅ system contains high-aluminum. **Journal of Non-Crystalline Solids**, v. 583, n. February, p. 121464, 2022.

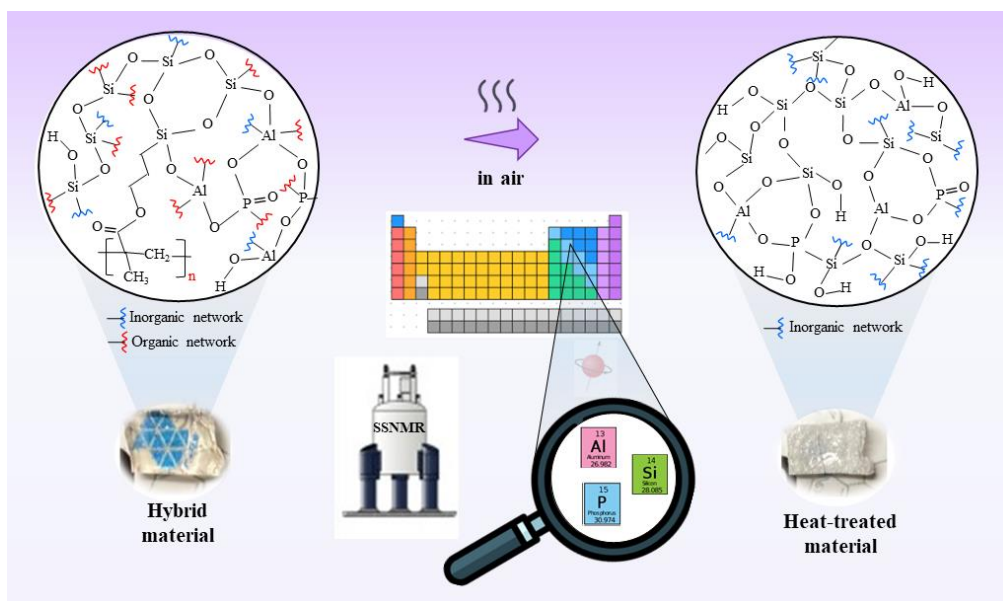
Objectives

The main aim of this thesis is to obtain aluminophosphosilicate glasses doped with Er^{3+} ions through the sol-gel method containing good optical properties for future applications. The specific aims can be summarized as:

- Synthesis of hybrid materials and glasses based on the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$;
- Structural, thermal, and optical characterization through different techniques such as FTIR, Raman, XRD, TGA, DSC, multinuclear solid-state NMR, SEM, UV-Vis-NIR, and M-lines;
- Effects of the thermal treatment on the structural evolution from the gel to the glass;
- Investigation of the Er^{3+} ions photoluminescence properties in the doped glasses;
- Effects of the densification process by thermal treatment under vacuum on the structure and photoluminescence of Er^{3+} ions.

CHAPTER 2

Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials



2. Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials

Beatriz Helena Costa^{a*}, Gabriel Toshiaki Tayama^b, Silvia Helena Santagneli^{a*}

a. Institute of Chemistry, São Paulo State University (UNESP), SP, Araraquara, Brazil

b. Centre d'optique, photonique et laser (COPL), Université Laval, Québec, G1V 0A6, Canada

* Corresponding authors.

E-mail addresses: bh.costa@unesp.br (B.H. Costa), silvia.santagneli@unesp.br (S.H. Santagneli).

<https://doi.org/10.1016/j.jnoncrysol.2024.123105>

Received 25 April 2024; Received in revised form 19 June 2024; Accepted 23 June 2024

Abstract

Aluminophosphosilicate materials of composition (mol.%) $x\text{SiO}_2[(\text{Al}_2\text{O}_3)_{50}-(\text{P}_2\text{O}_5)_{50}]_{100-x}$ were prepared through sol-gel method and heat-treated yielding non-crystalline materials. The structural evolution from the hybrid to heat-treated material as a function of the SiO_2 content was studied by ^{13}C , ^{29}Si , ^{31}P and ^{27}Al solid-state NMR, infrared spectroscopies, X-ray diffraction and differential scanning calorimetry (DSC). NMR analyses showed the AlPO_4 formation in the matrix and heterocondensation, forming Al-O-P and P-O-Si linkages. The heat treatment promoted the formation of a more interconnected SiO_2 tetrahedra network as the SiO_2 content increased. Similar to the hybrid materials, the increase of SiO_2 content induces the replacement of P-O-Al(IV) bonds by Si-O-Al(IV) bonds in the heat-treated materials as confirmed by ^{27}Al NMR and $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR data, which was also supported by Raman analysis. This sol-gel route provides a novel way to fabricate new homogeneous materials, which can be doped with rare earths and applied to new optical devices.

Keywords: Aluminophosphosilicate hybrid material, solid-state NMR, sol-gel

2.1. Introduction

Glasses of the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ are of great interest for active optical devices based on rare-earth (RE) ions' luminescence, such as optical amplifiers and fiber lasers [1,2]. The addition of phosphate and aluminate to the composition of silicate glasses increases the solubility of RE ions and enhances their luminescent properties, by reducing clustering and concentration quenching [3–5]. The equimolar Al_2O_3 and P_2O_5 can decrease the refractive index when compared to binary systems with the same SiO_2 content due to the AlPO_4 -like unit formation [6–8]. Furthermore, the aluminate significantly increases the glasses' mechanical properties, thermal properties, and hydrolytic stability [9,10].

Such glasses are often prepared using the melt-quenching method. It is an approach that is convenient and easy to implement. However, the low purity of the chemical precursors and challenges to homogenize the glass due to its high viscosity can be detrimental to the luminescence properties. Furthermore, the high temperature involved results in an energy-demanding process, which is consequently costly. Another downside for these glasses is the risk of phosphate evaporation, which can introduce compositional deviation in these glasses and pose challenges towards reproducibility [11–14].

In this regard, the sol-gel process is a promising alternative approach to the melt-quenching method [15–17,6]. This chemical route induces the hydrolysis and condensation of molecular precursors, usually metal alkoxides, to result in a three-dimensional inorganic network. Sol-gel uses inexpensive high-purity precursors processed in liquid state, allowing good homogeneity of RE ions [18–20], and facile stoichiometry control. The method employs mild processing conditions, such as low temperature ($< 1200\text{ }^\circ\text{C}$), environmentally friendly solvents and a non-controlled atmosphere. Furthermore, this route can synthesize organic-inorganic hybrid (OIH) material compatible with additive manufacturing [21–24] for 3D printing of glasses [16,25–28].

The structure of RE doped $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses plays a key role in the optical properties of these materials. Solid-state NMR experiments on melt quenched $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses have shown that aluminum bonded to phosphate species can assume different coordinations such as Al(IV) , Al(V) and Al(VI) . Under a low concentration of Al_2O_3 in silica matrix, the Al^{3+} cations are tetracoordinated, however the increase of

aluminum content favors the formation of aluminum clusters as the silica network must undergo modifications to compensate the +3 charge associated with the aluminum. Clustering precedes crystallization, and most aluminosilicate glasses incorporate network modifiers to compensate the charge of aluminum, further stabilizing the tetracoordinated site. In the particular case of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glass system, phosphorous is very miscible in silica matrix, and the presence of the P=O terminal bond reduces the connectivity of the three-dimensional SiO_2 network, introducing non-bridging oxygens. Thus, the non-bridging oxygen species introduced by the phosphorus stabilizes the tetracoordinated aluminum species, further extending its glass-forming ability. Furthermore, P-O-Al bonds can replace P-O-P bonds because of the preferential interaction between Al_2O_3 and P_2O_5 in the network [29–36]. Ultimately, a SiO_2 and an AlPO_4 -rich phase are formed, leading to discontinuities in the matrix. The structures of AlPO_4 and α -quartz are similar (tetrahedral coordination with each cation bonded by four oxygens and each oxygen between two cations) forming regions of miscibility for $\text{SiO}_2\text{-AlPO}_4$ compositions [37]. These studies, however, have been conducted in melt-quenched or CVD-produced glass samples, and there is little information available for sol-gel-produced glasses of this system. A similar $\text{SiO}_2\text{-AlPO}_4$ system prepared by the sol-gel method was studied by De Araujo et al. [38]. In this work, the authors studied the incorporation of SiO_2 (up to 67 mol.%) in Aluminum lactate and Ammonium dihydrogen phosphate. The NMR results indicated the absence of Al-O-Si and P-O-Si connectivity after incorporating TEOS, suggesting the formation of AlPO_4 and SiO_2 sub-domains.

Thus, the present work aims to explore the $x\text{SiO}_2[(\text{Al}_2\text{O}_3)_{50}-(\text{P}_2\text{O}_5)_{50}]_{100-x}$ ($x = 10, 30, 50, 70, 90$ and 100 mol.%) aluminophosphosilicate system using a different aluminum and phosphorus precursor for sol-gel synthesis to obtain homogeneous glasses. The OIH materials were studied by thermogravimetric analysis (TGA) to understand the elimination of organic compounds during heat treatment as a function of SiO_2 concentration. Lastly, the OIH and the heat-treated materials were analyzed using multinuclear solid-state NMR to obtain insight into the structural transformation that occurs during heat treatment.

2.2. Experimental

2.2.1. Synthesis of aluminophosphosilicate materials

All reactants were purchased from Sigma-Aldrich, and used as received. Tetraethyl orthosilicate (TEOS, $\geq 99.0\%$), 3-(Trimethoxysilyl)propyl methacrylate (MPTMS, 98.0%) aluminum-tri-sec-butoxide 97.0% , hydroxyethyl methacrylate phosphoric acid ester (HEMAP, 90.0%), 2-(methacryloyloxy)ethyl acetoacetate (MAEAA, 95.0%), methyl alcohol (MeOH, 99.8%), ethyl alcohol (EtOH, 99.9%), nitric acid (HNO_3 $65\text{-}67\%$), ammonium acetate (NH_4Ac , $\geq 98.0\%$), and MiliQ water were used in the sol-gel synthesis. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 97.0%) was employed as a radical photoinitiator for the photopolymerization process.

Initially, the $\text{Al}(\text{MAEAA})_2$ complex was prepared in a glovebox (N_2 atmosphere with $\text{H}_2\text{O} < 100$ ppm) by adding MAEAA to aluminum tri-sec-butoxide at 2:1 molar ratio under magnetic stirring. The mixture reacted for approximately 4 h, resulting in a modified alkoxide stable under an ambient atmosphere. Then, the Al-P sol (Sol-1) was prepared by adding an HEMAP solution in methanol, to the $\text{Al}(\text{MAEAA})_2$ complex in a 1:1 ratio under magnetic stirring. The solution was stirred for 12 h, and the solvents were evaporated under reduced pressure.

The Sol-2 was prepared according to the method proposed by Cooperstein et al. [16]. TEOS was dissolved in a HNO_3 hydrolysis solution (65 wt. % EtOH in H_2O) under magnetic stirring for 30 min. MPTMS and 1 wt.% of the photoinitiator TPO were added, and the mixture was stirred for another 30 min. Finally, an NH_4Ac condensation solution (65 w.t. % EtOH in H_2O) was added, and the mixture was stirred for 45 min. Sol-1 and Sol-2 were mixed in the required proportion to obtain the desired composition resulting in a polymerizable solution. This solution was polymerized under a Hg lamp ($4 \text{ mW}/\text{cm}^2$) for 5 min inside plastic cuvettes. Once polymerized, the samples were closed with parafilm and dried at 50°C for 5 days.

The hybrid materials obtained were heated from room temperature to 800°C at a heating rate of 1°C min^{-1} . The samples were held at 800°C for 1 h and cooled down to room temperature at a 5°C min^{-1} ratio. Fig. 2.1 shows the aluminophosphosilicate materials of composition $x\text{SiO}_2[(\text{Al}_2\text{O}_3)_{50}-(\text{P}_2\text{O}_5)_{50}]_{100-x}$ before (left) and after (right) heat treatment.

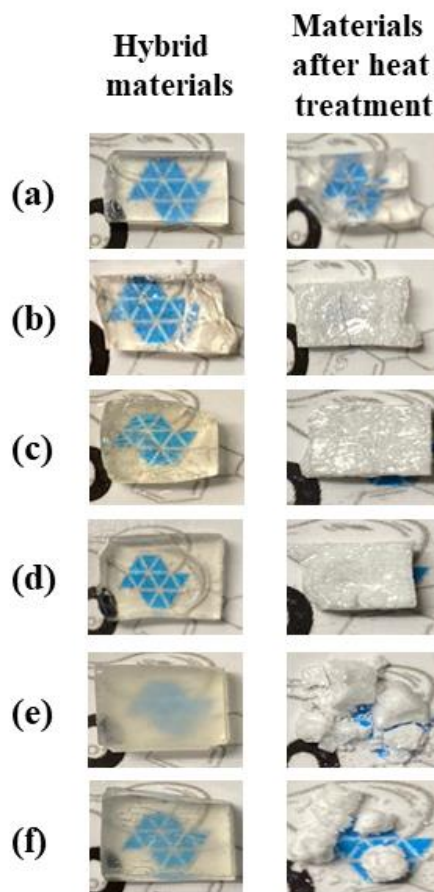


Fig. 2.1. Photos of aluminophosphosilicate materials $x\text{SiO}_2[(\text{Al}_2\text{O}_3)_{50}-(\text{P}_2\text{O}_5)_{50}]_{100-x}$ before (left) and after (right) heat treatment with different SiO_2 content (a) $x = 100$, (b) $x = 90$, (c) $x = 70$, (d) $x = 50$, (e) $x = 30$ and (f) $x = 10$ (mol.%). The background of all the photos illustrates the UNESP blue logo.

2.2.2. Characterization

Thermogravimetric analysis (TGA) was conducted using SDT Q600 (TA Instruments) equipment. Thermal degradation was measured from 30 to 900 °C (heating rate of 10 °C min⁻¹) under dynamic synthetic air atmosphere (flow of 20 mL min⁻¹). Approximately, 10 mg of sample was used for each analysis in the alumina crucible.

The heat-treated samples were analyzed by differential scanning calorimetry (DSC), using a NETZSCH - DSC404 F3 Pegasus. The samples were heated from 500 to 1200 °C in a platinum crucible at a heating rate of 10 °C min⁻¹ under a dynamic nitrogen atmosphere (flow of 20 mL min⁻¹).

X-Ray diffraction (XRD) measurements were performed on a SmartLab SE diffractometer, operating with $\text{CuK}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$), in Bragg Brentano

geometry. XRD patterns were collected between 5 and 70°(2 θ), with a 0.02° step size and a time-counting of 1.2 s, operating at 40 kV and 30 mA at room temperature.

FTIR-ATR spectra for the hybrid and heat-treated materials were collected on a Bruker®, Vertex 70 spectrometer. All spectra were collected with 100 scans, using Attenuated Total Reflectance mode and a spectral resolution of 4 cm⁻¹.

Raman scattering spectra were collected with a LabRAM HR (Horiba Jobin Yvon) spectrometer equipped with a 632.8 nm laser with power of 20 mW. The measurement was performed using an objective lense of 50x and a grating of 50 nm from 400 to 3500 cm⁻¹ with an integration time of 50 s and 5 scans.

Solid-state NMR of ¹³C, ²⁹Si, ²⁷Al, and ³¹P nuclei for hybrid and heat-treated materials were conducted using a Bruker Avance III HD 400WB spectrometer equipped with a 4 mm double and triple resonance probe. The ¹³C and ²⁹Si spectra were measured under $\nu_{\text{ro}} = 10.0$ kHz. The ¹³C{¹H} and ²⁹Si{¹H} CP-MAS measurements were made using a contact time of 3.0 and 3.8 μ s and a relaxation time of 2.5 and 3.0 s, respectively. ²⁹Si single pulse NMR spectra were measured using an excitation $\pi/2$ pulse of 3.8 μ s length and relaxation time of 500 s. All spectra were referenced externally to Tetramethylsilane (TMS). For NMR experiments of the ³¹P and ²⁷Al spectra, they were conducted under 14 kHz. The ³¹P MAS NMR spectra for hybrid and heat-treated materials were recorded using an excitation $\pi/2$ pulse of 3.2 μ s length and a relaxation time of 120 and 240 s, respectively. The chemical shift was referenced against an external 85% H₃PO₄ standard. ²⁷Al MAS spectra were collected using a short pulse of 1.4 μ s for all samples, and a relaxation time of 1 s. ²⁷Al TQMAS spectra were measured with a three-pulse z-filtering sequence [39], using 5.9 and 1.7 μ s length for hard excitation and reconversion pulses and 10.0 μ s length for a soft detection pulse. The recycle delay was set to 1.0 s. Chemical shift are reported relative to a 1 mol L⁻¹ Al(NO₃)₃ aqueous solution. ²⁷Al{³¹P} rotational echo double resonance (REDOR) experiments were performed at a MAS frequency of 14.0 kHz using the standard Schaefer–Gullion sequence [40] with π recoupling pulses on the ³¹P channel and acquisition of rotor-synchronized ²⁷Al spin echoes (the π pulse length was 4.4 μ s in these experiments). The second moments $M_{2(\text{Al-P})}$ characterizing the dipolar interaction between ²⁷Al-³¹P nuclei were obtained by applying a parabolic fit to the REDOR data within the range $S/S_0 \leq 0.2$ and f is a calibration factor, corresponding to the expression [41,42]:

$$\frac{\Delta S}{S_0} = \frac{4}{3\pi^2} (NT_R)^2 f M_{2(Al-P)} \quad (1)$$

For crystalline $Al(PO_3)_3$ a theoretical value $M_{2(Al-P)} = 6.8 \times 10^6 \text{ rad}^2/\text{s}^{-2}$ is expected, and the experimental data obtained on this compound without the calibration factor ($5.8 \times 10^6 \text{ rad}^2/\text{s}^{-2}$) indicate an f – value of 0.85 in our experiments. Applying this calibration factor to the REDOR data obtained, the values of $M_{2(Al-P)}$ [9] can be obtained. Line shape analysis and deconvolutions were made using the DMFIT routine [43].

2.3. Results and discussion

2.3.1. Structural study of the hybrid materials

FTIR and Raman spectra are presented in Fig. 2.S1 (a) and (b) available in the Supporting Information and band assignments are shown in Table 2.1. The infrared spectra agree with those of PMMA-based materials [44]. The broad band observed at 3450 cm^{-1} in the FTIR is assigned to the stretching of the hydroxyl group (OH) of water, as well the band at 2345 cm^{-1} attributed to bond of hydrogen formed with non-bridging oxygen [45]. The weak signal observed at 2975 and 2890 cm^{-1} in the FTIR, but strong in the Raman spectra at 2930 cm^{-1} , is assigned to the C-H stretching [46]. The signals at 1715 and 1725 cm^{-1} observed in the FTIR and Raman spectra are assigned to the stretching of the carbonyl group (C=O) of the methacrylate. Unpolymerized C=C groups result in vibrational bands at 1634 and 1630 cm^{-1} observed in the FTIR and Raman spectra, respectively. The bands observed at 1533 cm^{-1} in the FTIR and Raman spectra, were assigned to the C-C stretching of the ring of the $Al(MAEAA)_2$ complex. The low-intensity signals observed at 1455 cm^{-1} in the FTIR spectra and in the range of 1445 to 1410 cm^{-1} in Raman spectra were assigned to the symmetrical and asymmetrical deformations of CH_2 and CH_3 groups, respectively. The band at 1154 cm^{-1} observed in the FTIR spectra was assigned to the (O=C)-O stretch [46–50]. The band observed at 1066 cm^{-1} was assigned to the Si-O-Si stretching. It can be seen that its intensity decreased as the Al-P concentration increased, in good agreement with its assignment [46]. The signals at 951 and 979 cm^{-1} in FTIR and Raman spectra, respectively, are assigned to Si-OH stretch. The band at 782 cm^{-1} in FTIR spectra is attributed to the stretching of Si-O [51–53]. Finally, the vibrational bands observed at 606 and 857 cm^{-1} in Raman spectra

are assigned to the bending of Si-O-Si and PO_4^{3-} , respectively [52]. These assignments were further confirmed with $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectra of hybrid materials (see Fig. S2 (a) available in the Supporting Information), which are in agreement with the literature [54–57] and were assigned according to the structure shown in Fig. S2 (b) presented in the SI.

Table 2.1. Band positions and assignments of FTIR and Raman spectra for hybrid materials.

FTIR and Raman frequencies (cm^{-1})	Assignment	Ref
3450 (IR)	$\nu(\text{O-H})$ water	[45,46]
2975 (IR), 2930 (R), 2890 (IR)	$\nu(\text{C-H})$	[46,48,49]
1715 (IR), 1725 (R)	$\nu(\text{C=O})$	[47–50]
1634 (IR), 1630 (R)	$\nu(\text{C=C})$	[47–50]
1533 (IR and R)	$\nu(\text{C-C})$ chelating ring	[47]
1455 (IR), 1445 (R), 1410 (R)	$\delta(\text{CH}_2)$ and $\delta(\text{CH}_3)$	[47–49]
1154 (IR)	$\nu(\text{O=})\text{C-O}$	[47,48,50]
1066 (IR)	$\nu(\text{Si-O-Si})$	[51–53]
979 (R), 951 (IR)	$\nu(\text{Si-OH})$	[51–53]
782 (IR)	$\nu(\text{Si-O})$	[51]

The $^{29}\text{Si}\{^1\text{H}\}$ CP-MAS and ^{29}Si MAS spectra of materials with different SiO_2 content are shown in Fig. 2.2 (a) and (b), respectively. The $^{29}\text{Si}\{^1\text{H}\}$ CP-MAS spectra show six resonance signals assigned to T^n and Q^n units, where n represents the number of bridging oxygens in the trifunctional silane $\text{R-Si}(\text{OH})_3$ (R = organic group) species (T^n) and the tetrafunctional silicate $\text{Si}(\text{OH})_4$ species (Q^n). The signals observed at -48, -58 and -65 ppm are assigned to T^1 , T^2 and T^3 units, respectively [58], while the signals at -92, -101 and -110 ppm are characteristic of Q^2 , Q^3 and Q^4 units [59,60], respectively. These species are formed during the hydrolysis and condensation of TEOS and MPTMS.

Furthermore, the ^{29}Si MAS spectra do not show T^n species, reflecting the low concentration of the MPTMS content in all samples.

The ^{29}Si MAS spectra were deconvoluted and the relative areas and the characteristic chemical shifts (δ) of each Q^n unit are summarized in Table 2.2. Only the spectra of the 10 and the 30% SiO_2 samples were not deconvoluted due to the poor signal-to-noise ratio. It can be seen that the chemical shift of the ^{29}Si sites do not change with the SiO_2 content. Furthermore, the fraction of Q^3 units increases with the SiO_2 content up to 90%, suggesting the formation of non-bridging oxygens and Si-OH linkages associated with incomplete dehydration/densification of the network and/or even the heterocondensation between silicate and aluminum species. The 100% SiO_2 hybrid shows a high proportion of Q^4 units, indicating a more connected three-dimensional network of SiO_2 tetrahedrons [59]. The ^{29}Si NMR results are consistent with the observed results for ^{27}Al nuclei which are shown below. Specifically, following thermal treatment at 50°C , the resulting hybrid contains a network formed by Q^4 , $\text{Q}_{1\text{Al}}^3$ and Q^3 units.

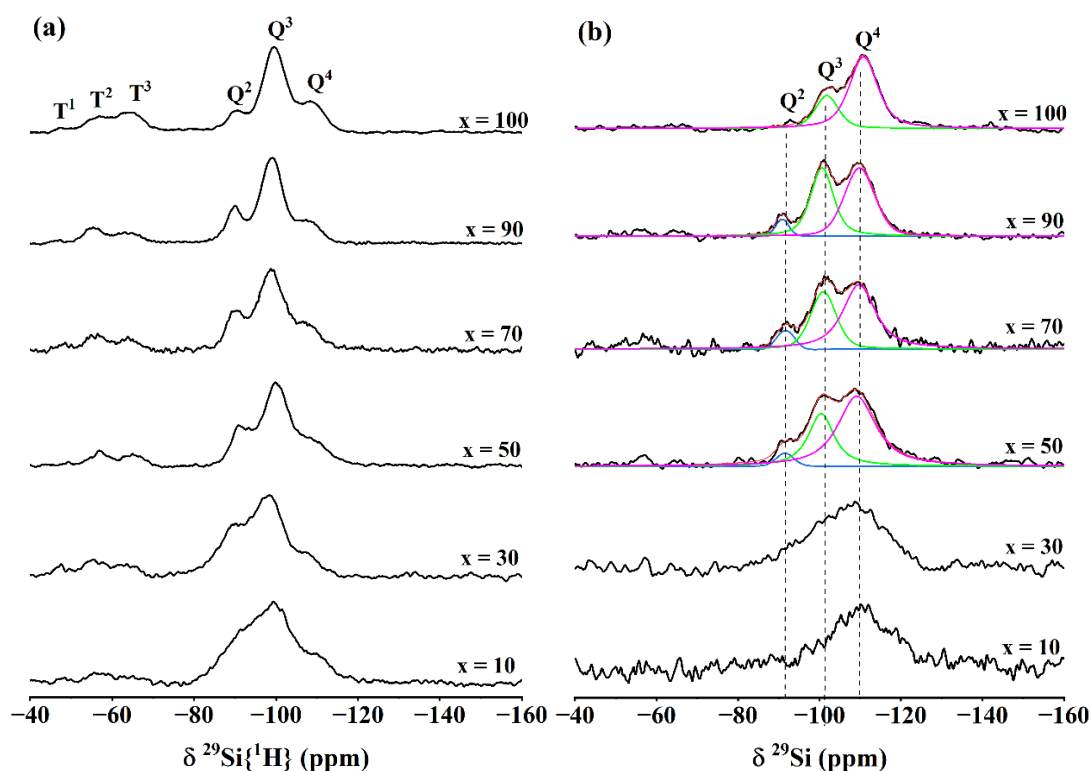


Fig. 2.2. (a) $^{29}\text{Si}\{^1\text{H}\}$ CP-MAS and (b) ^{29}Si MAS deconvolution spectra of hybrid polymers with different SiO_2 content ($x = 10, 30, 50, 70, 90$ and 100 mol.%). The solid black line represents the experimental spectrum and the red line represents the deconvolution envelope.

Table 2.2. Deconvolution results (chemical shift δ_{iso} and fractional areas of the Q^2 , Q^3 and Q^4 units) of the ^{29}Si MAS NMR spectra obtained for the compositions from 50 to 100 mol.% SiO_2 content of the hybrid materials. Estimated errors are ± 0.2 ppm for Chemical Shift and $\pm 2\%$ for Areas.

Sample	Q^2		Q^3		Q^4	
	δ (ppm)	Area (%)	δ (ppm)	Area (%)	δ (ppm)	Area (%)
x = 50	-91	2	-101	44	-110	53
x = 70	-91	4	-101	53	-110	42
x = 90	-91	3	-101	55	-110	43
x = 100	-92	1	-102	37	-111	62

The ^{31}P and ^{27}Al MAS NMR spectra of the hybrid materials are presented in Fig. 2.3 (a) and (b), respectively. All spectra show a broad signal in the range 10 to -40 ppm, corresponding to $\text{P}_{\text{mAl}}^{\text{n}}$ units, where **n** corresponds to the number of phosphate bonded to P units (P-O-P) and **m** is the number of aluminum units bond to P units. The ^{31}P spectra were deconvoluted, and the data from deconvolution are presented in Table 2.3. There are four different environments of orthophosphate species with characteristic ^{31}P chemical shift at 0, -4, -10 and -18 ppm assigned to $\text{P}_{0\text{Al}}^0$, $\text{P}_{1\text{Al}}^0$, $\text{P}_{2\text{Al}}^0$ and $\text{P}_{3\text{Al}}^0$, respectively [38,59]. The different $\text{P}_{\text{mAl}}^{\text{n}}$ unit formations present in the gel were due to incomplete aluminum ligand substitution by phosphate species. The higher amount of Si concentration favors the Al-O-Si bond formation, consequently resulting in PO- unit formation. These observations are in good agreement with reports in the literature showing that the Si-O-P chemical bond is unstable and prone to hydrolysis in solution [61–63]. Furthermore, the data summarized in Table 2.3 show that there is no significant change in area values for the phosphate units up to the 50% SiO_2 sample, however the 70 and 90% SiO_2 samples exhibit a decrease of the $\text{P}_{1\text{Al}}^0$ and $\text{P}_{2\text{Al}}^0$ units while the concentration of species with higher inorganic connectivity ($\text{P}_{3\text{Al}}^0$) increases. During the preparation of Sol-1, 4- and 6-coordinated $\text{Al}(\text{MAEAA})_x(\text{PO}_3)_y$ units are present due to incomplete aluminum ligand substitution by phosphate species. Thus, the higher amount of Si concentration favors the heterocondensation between HEMAP and $\text{Al}(\text{MAEAA})_2$ complex through the increase in the number of linkages of phosphate species with aluminum (Al-O-P) as there is a competition with the formation of Al-O-Si bonds.

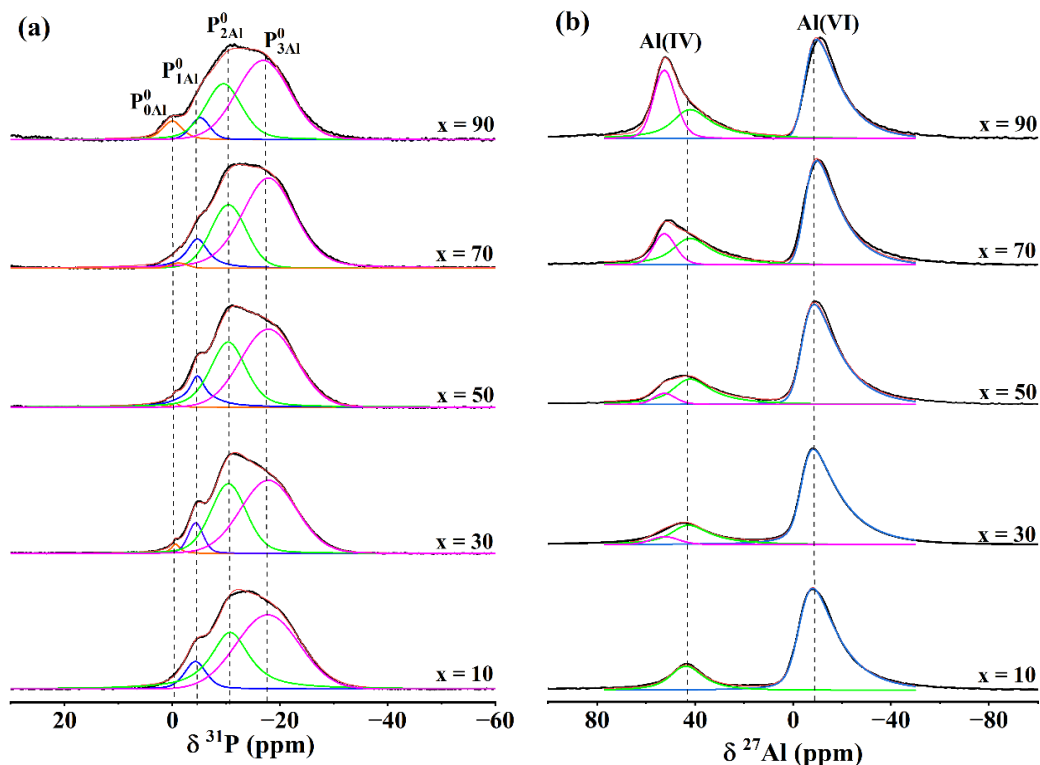


Fig. 2.3. (a) ^{31}P and (b) ^{27}Al MAS NMR spectra of hybrid materials with different SiO_2 content ($x = 10, 30, 50, 70, 90$ and 100 mol.%). The solid black line represents the experimental spectrum and the red line represents the deconvolution envelope.

Table 2.3. Deconvolution results (chemical shift δ_{iso} and fractional areas of the $\text{P}_{0\text{Al}}^0$, $\text{P}_{1\text{Al}}^0$, $\text{P}_{2\text{Al}}^0$ and $\text{P}_{3\text{Al}}^0$ units) of ^{31}P NMR spectra obtained for the compositions from 10 to 90 mol.% SiO_2 content of the hybrid materials. Estimated errors are ± 0.5 ppm for Chemical Shift and $\pm 1\%$ for Areas.

Sample	$\text{P}_{0\text{Al}}^0$		$\text{P}_{1\text{Al}}^0$		$\text{P}_{2\text{Al}}^0$		$\text{P}_{3\text{Al}}^0$	
	δ	Area	δ	Area	δ	Area	δ	Area
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)
x = 10	-	-	-4	8	-11	36	-18	55
x = 30	-0.6	2	-4	7	-10	36	-18	55
x = 50	-0.6	1	-5	12	-10	34	-18	54
x = 70	-0.6	1	-5	11	-10	27	-18	61
x = 90	-0.3	3	-5	11	-10	31	-18	55

The ^{27}Al MAS NMR spectra show a hexacoordinated aluminum site (Al(VI)) between -5 and -2 ppm and two tetraordinated aluminum sites (Al(IV)) between 55 and 45 ppm [21,22]. The isotropic chemical shift (δ_{iso}) and quadrupolar coupling constants (C_Q) for each site were calculated by fitting the spectra using the Czsimple function in the

DMFIT program, and the values are summarized in Table 2.4. The contribution of Al(IV) sites increased, and a downshift was observed with the SiO₂ concentration. This behavior suggests the formation of Al-O-Si bonds from the Al-complex partially hydrolyzed in the AlPO₄ formation. These results agree with the ³¹P MAS NMR spectra, where we could observe different P_{mAl}ⁿ unit formations.

The ²⁷Al TQMAS spectra of the samples presented in Fig. 2.S3 are available in the Supporting Information. The results shown in Fig. 2.S3 confirm the presence of different chemical environments for the Al(IV) and Al(VI) coordination. These different sites are associated with the formation of Al-O-P and Al-O-Si bonds. The Al(OP)₄ and Al(OSi)₄ species are reported to be centered at 45 and 55 ppm, respectively [19,38,59]. Similar materials have been studied by Tayama et al. [22], in which the authors reported that compositions with Al/P =1 showed Al(VI) and Al(IV) sites with characteristic chemical shifts at -6.5 and 51.5/41.9 ppm, respectively. In this work, the ²⁷Al MAS spectra (Fig. 3 (b)) and the data summarized in Table 2.4 indicate the formation of Al(IV) sites and the downshift of the signal with SiO₂ concentration, indicating Al-O-Si formation in the matrix, i.e., the further increase of SiO₂ concentration favors the formation of Al(OSi)₄ species through the conversion of Al(VI) to Al(IV). In addition, in the ³¹P MAS data, the formation of P-O-Al in the species P_{0Al}⁰ and P_{1Al}⁰ is dependent on the hydrolysis equilibrium of HEMAP, but the P_{2Al}⁰ and P_{3Al}⁰ units are directly associated with the competitiveness between the bond formation Al-O-P and Al-O-Si after Si addition. These results suggest the connectivity in the network increase with SiO₂ content, favoring the condensation process of the HEMAP and Al(MAEEA)₂ complex, and the consequent formation of the Al-O-Si and Al-O-P bonds.

The formation of Si-O-Al bonds follows the evolution formation of Q³ units observed in the ²⁹Si MAS data, where the same frequency range can also be assigned to the formation of the Si_{1Al}⁴ [19,64–66] (the nomenclature Si_mⁿ is used, where **n** means the number of Si-O-Si bonds while **m** represents the number of Si-O-Al). This behavior can also be confirmed by the ²⁷Al MAS and ²⁷Al TQMAS data, which shows an increase of the Al(IV) and the presence of the two sites, where the shift at 55 ppm is associated with Al(OSi)₄ species formation [38,59]. As shown in Table 2.3, the phosphate species bond preferentially to Al, resulting in species with typical chemical shift of -4, -10 and -18 ppm. These results indicate that the majority of phosphates species are preferentially bonded to Al-hexacoordinated species.

Table 2.4. ^{27}Al isotropic chemical shift (δ_{iso}) (± 0.2 ppm), fractional areas ($\pm 2\%$) and nuclear electric quadrupolar coupling values (C_Q) (± 0.5 MHz) extracted from the Czsimpl model and second moment ($M_{2(\text{Al-P})}$) ($\pm 10\%$) of the hybrid materials.

Sample	^{27}Al				C_Q (MHz)		$M_{2(\text{Al-P})}$ ($\times 10^6$ rad^2/s^2)	
	Al(OSi) ₄		Al(OP) ₄		Al(IV)		Al(VI)	
	δ_{iso} (ppm)	Area (%)	δ_{iso} (ppm)	Area (%)	Area (%)	δ_{iso} (ppm)	Area (%)	
x = 10	-	-	45	18	18	-2	82	2.0 4.1 - -
x = 30	55	4	45	18	22	-3	78	2.5 4.2 3.4 3.4
x = 50	55	5	45	22	27	-3	73	2.3 4.3 3.1 3.5
x = 70	55	12	45	23	35	-4	65	4.4 4.1 2.6 3.4
x = 90	55	24	45	22	46	-4	54	3.4 4.1 - -
Al(PO ₃) ₃	-	-	-	-	-	-	-	- - 5.8

To further understand the chemical environment of these ^{27}Al sites, double resonance $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR experiments were employed. These experiments recover the heteronuclear magnetic dipole–dipole coupling, which carries information on the distance between the probed nuclei and the number of ^{31}P nuclei surrounding the ^{27}Al site. $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR experiments presented in Fig. 2.4 were carried out for the Al (IV) and Al(VI) species of the hybrid materials with 30, 50 and 70% SiO₂ content, and the $M_{2(\text{Al-P})}$ values are listed in Table 5. Based on the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR data (see Table 5), the Al-P dipolar coupling is less than the Al(PO₃)₃ compound, suggesting a homogeneous distribution of AlPO₄ units and the formation of Al-O-P and Al-O-Si bonds. Additionally, the chemical shift observed for aluminum in an octahedral environment remains constant regardless of the SiO₂ content, suggesting a partial hydrolysis of HEMAP and Al(MAEEA)₂ compounds. These results agree with ^{31}P and ^{27}Al NMR data, where the ^{27}Al TQMAS shows a distribution of the Al(VI) sites shown in Fig. 2.S3 and discussed below.

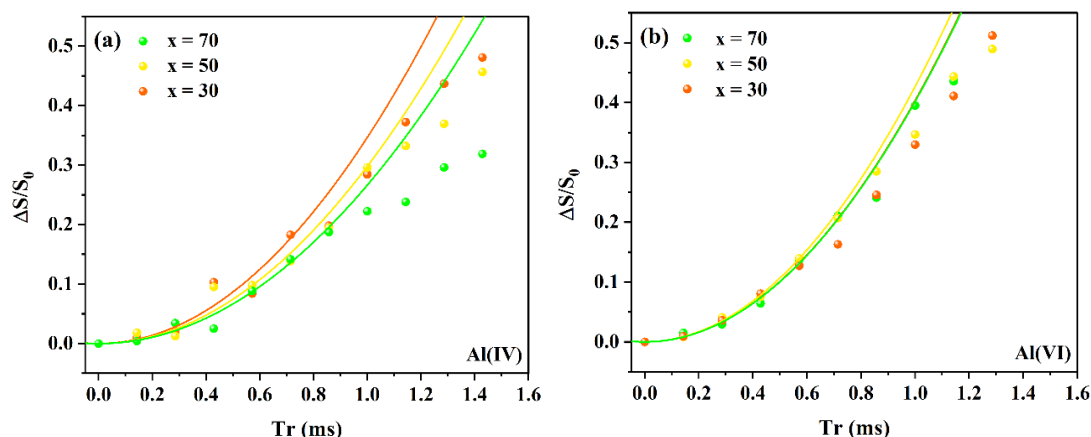


Fig. 2.4. $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR curves for (a) tetracoordinated Al(IV) and (b) hexacoordinated Al(VI) species for $x = 30, 50$ and 70 (mol.%) of SiO_2 content. Solid curves are fits of the data points to eq. (1) within the data range $\Delta S/S_0 \leq 0.2$.

The NMR results clearly show the formation of AlPO_4 units before adding the Si solution. Additionally, there is an interaction between silicate and aluminum species through Si-O-Al bond formation. The partial hydrolysis of the $\text{Al}(\text{MAEEA})_2$ compound also observed in ^{27}Al TQMAS spectra, Fig. 2.S3, as well as the increase of Al(IV) species observed in the ^{27}Al MAS spectra (Fig. 2.3 (b)) are supported by $M_{2(\text{Al-P})}$ values calculated from $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR curves, where a decrease of the Al-P dipolar coupling occurs for Al(IV) species. The AlPO_4 incorporation in SiO_2 preferably occurs with Al in four coordination [21,37]. On the other hand, the phosphate species were initially bonded to partially hydrolyzed Al-hexacoordinated species, as indicated by the $M_{2(\text{Al-P})}$ values obtained from the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR curves presented in Fig. 2.4, which can be attributed to the steric hindrance effect caused by the phosphate-rich coordination of the aluminum site. Based on these results, as the SiO_2 content increases, the hybrid materials form a three-dimensional structure connected by SiO_2 tetrahedra as also showed by FTIR data, which are also connected to the Al-tetracoordinated species. In contrast, the phosphate species are preferentially connected to the Al-hexacoordinated species.

2.3.2. Thermal properties of the hybrid materials

Thermogravimetric analysis was performed to study the evolution of the organic compounds. The TGA and DTG curves of the hybrid materials are shown in Fig. 2.5 (a) and (b), respectively. It can be seen that the residue increases with the SiO_2 concentration, highlighting the high organic content of the aluminum and phosphate precursors.

The experimental inorganic residual values (% mass) obtained by TGA were closed to precursor SiAlP molar composition (see Table 2.S1 in SI). However, a significant difference between the experimental and the calculated values, for both the 90 and 100 mol.% SiO₂ samples, was probably due to the release of the organic sub-product (ethanol) from TEOS and MPTMS during the drying process.

The DTG curves show four thermal events leading to the hybrid materials' thermal degradation. The first thermal event assigned to the evaporation of residual solvent has a maximum weight loss ($T_{\max}$) at 54 °C. The two events with $T_{\max}$ at 300 and 350 °C are assigned to the condensation reactions and the degradation of organic groups. For the sample containing 100% SiO₂, we observed only the event with $T_{\max}$ at 300 °C, therefore this event can be attributed to the degradation of the acrylate groups from the silicon and phosphorous precursors (MPTMS and HEMAP, respectively) as this event also increases as the Al-P proportion is added to the silicate matrix, which can be also supported by the decrease in the percentage weight in TGA curves. On the other hand, the event with $T_{\max}$ at 350 °C can be attributed to the Al(MAEAA)₂ complex because during the synthesis, the Al-complex will not be totally hydrolyzed suggesting the appearance of different Al sites that will be degraded at this temperature. This assignment is in agreement with the ²⁷Al TQMAS NMR results presented within the structural study of the hybrid materials section. Lastly, the thermal event observed between 450 and 600 °C is assigned to the degradation of residual organic groups and/or H₂O. At this temperature range, the degradations of poly-Al(MAEAA)₂ and poly-(HEMAP) are the main thermal events [19,22,67]. The increase in mass residues observed as the SiO₂ content increases is attributed to inorganic heterocondensation through the formation of Si-O-Al, Al-O-P, Si-O-P and Si-O-Si bonds, in agreement with the ²⁹Si, ³¹P and ²⁷Al NMR results presented within the structural study section above.

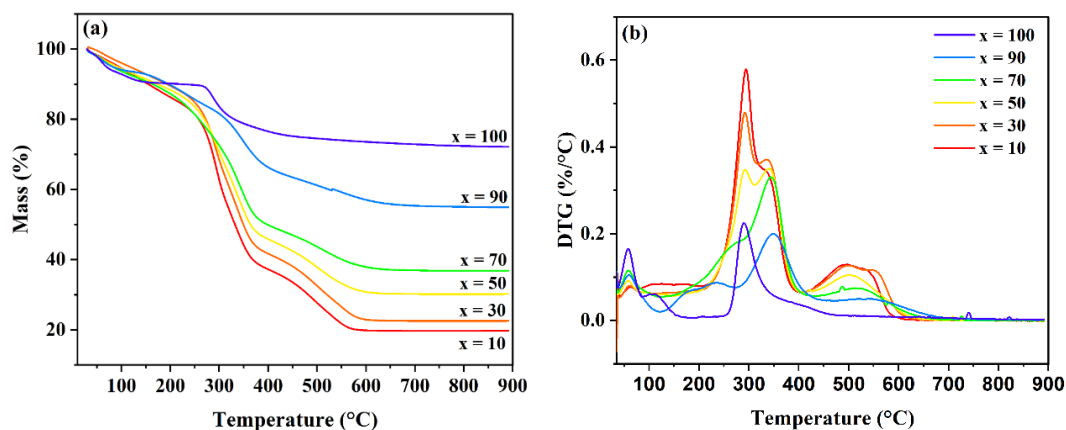


Fig. 2.5. TGA curves of hybrid materials with different SiO₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%).

2.3.3. Characterization of the heat-treated materials

DSC curves and XRD spectra for the materials after heat treatment are presented in Fig. 2.6 and Fig. 2.S4 in the SI, respectively. The glass transition was observed for 90 % and 100% SiO₂ samples, at 1142 and 1184 °C, respectively, while the 10 and 30% SiO₂ samples showed a crystallization peak at 1168 and 1200 °C, which is the range that the crystallization of AlPO₄ is expected [68,69]. The XRD data for all compositions is characteristic of amorphous materials [36]. These results suggest that the heat treatment of the 90 % and 100% SiO₂ samples results in a vitreous material. The remaining samples cannot be confirmed as glasses as the glass transition could not be observed.

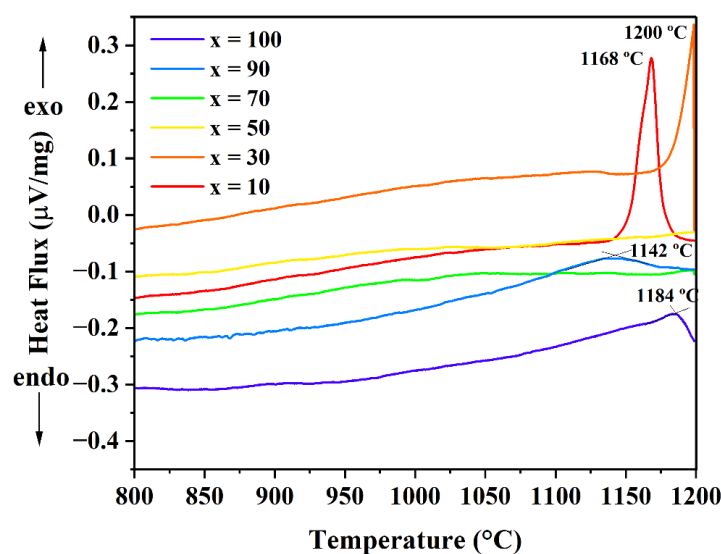


Fig. 2.6. DSC curves for the heat-treated materials with different SiO₂ contents (x = 10, 30, 50, 70, 90 and 100 mol.%).

The FTIR-ATR and Raman spectra of the heat-treated materials are presented in Fig. 2.7 (a) and (b), respectively. FTIR spectra show bands at 1042 and 804 cm^{-1} referring to the stretching of Si-O-Si and Si-O, respectively, which become more defined as the proportion of SiO_2 in the materials increases [51–53]. In Raman spectra the compositions with 100% and 90% of SiO_2 showed three bands at 494, 605 and 975 cm^{-1} , assigned to the planar four-fold ring (D_1), planar three-fold ring (D_2) and the symmetrical stretching of the Si-O-Si bonds (ω_3), respectively. In addition, a broad band was observed between 1000-1200 cm^{-1} , assigned to AlPO_4 -like units, whose intensity increased with the proportion of Al-P in the materials. [7,8,70,71], which corroborate to DSC results above which showed the AlPO_4 crystallization peak for the samples containing 10 and 30% SiO_2 .

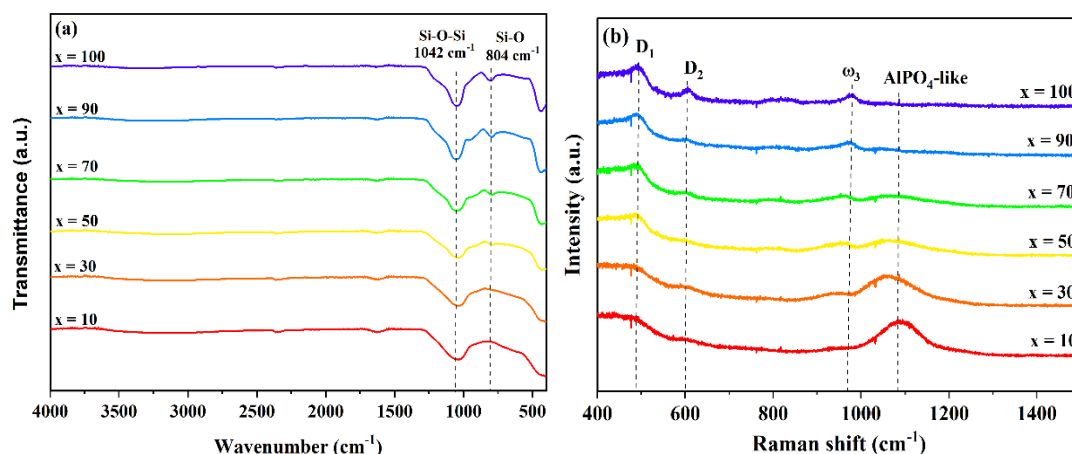
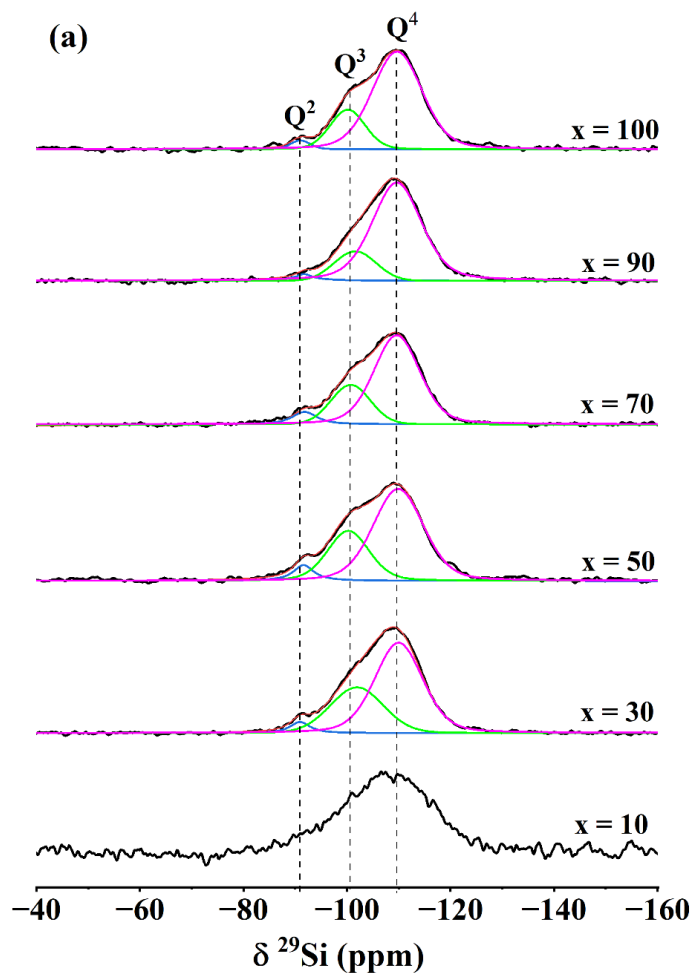


Fig. 2.7. (a) FTIR-ATR and (b) Raman spectra for the heat-treated materials with different SiO_2 contents ($x = 10, 30, 50, 70, 90$ and 100 mol.%).

^{29}Si MAS spectra and the evolution of the integrated area for the ^{29}Si units for the heat-treated materials are presented in Fig. 2.8 (a) and (b), respectively. The ^{29}Si MAS spectra were deconvoluted, and the chemical shift and % relative area values are shown in Table 2.5. The presence of three signals at -92, -101 and -110 ppm can be observed, characteristics of Q^2 , Q^3 and Q^4 units, respectively. As can be seen, the heat treatment results in an increase of homocondensation in all compositions, with the conversion of Q^3 species into Q^4 units, as supported by FTIR data above. The presence of non-bridging oxygens (Si-OH linkages) associated with incomplete dehydration/densification of the network was observed with Q^2 and Q^3 units present in the ^{29}Si spectra shown in Fig. 2.8 (a), which range from 20 to 35%, depending on the composition. On the other hand, we cannot rule out the formation of $\text{Si}_{1\text{Al}}^4$ units in the same chemical shift range, where the %

area of these units' contribution increases with the AIP amount. As can be seen, the heat treatment carried out at 800 °C was not sufficient to eliminate the superficial OH present in the pores generated during the heat treatment. According to the literature, the reduction of OH in such materials can be achieved through heat treatment under a vacuum up to 1100 °C [16,18].



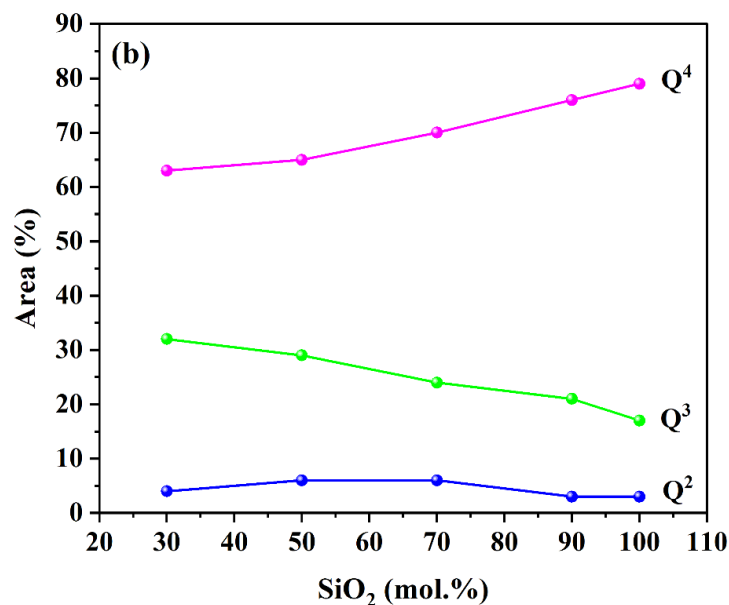


Fig. 2.8. (a) ^{29}Si MAS NMR spectra for the heat-treated materials with different SiO_2 content ($x = 10, 30, 50, 70, 90$ and 100 mol.%). The solid black line represents the experimental spectrum and the dashed red line represents the deconvolution envelope. (b) Q^n units evolution as a function of SiO_2 content.

Table 2.5. Deconvolution results (chemical shift δ_{iso} and fractional areas) of the ^{29}Si MAS NMR spectra obtained for compositions from 30 to 100 mol.% SiO_2 content of the materials heat-treated at 800°C . Estimated errors are ± 0.2 ppm for Chemical Shift and $\pm 2\%$ for Areas.

Sample	Q ²		Q ³ /Si _{1Al} ⁴		Q ⁴	
	δ	Area	δ	Area	δ	Area
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)
x = 30	-91	4	-102	32	-110	63
x = 50	-91	6	-100	29	-110	65
x = 70	-92	6	-101	24	-109	70
x = 90	-92	3	-101	21	-109	76
x = 100	-91	3	-100	17	-110	79

The ^{31}P and ^{27}Al MAS NMR spectra for the heat-treated materials are presented in Fig. 2.9 (a) and (b), respectively. The relative area obtained from deconvoluting each spectrum is summarized in Table 2.6 for ^{31}P nuclei. According to other studies [38,59] the basic structural units in aluminophosphosilicate glasses are formed by orthophosphate (PO_4), and these tetrahedra are identified using the $\text{P}_{\text{mAl}}^{\text{n}}$ notation, where **n** represents the number of bridging oxygen per tetrahedron and **m** is the number of the aluminum unit

bond to P units. The ^{31}P NMR spectra of all compositions for the heat-treated materials are dominated by an asymmetric broad peak centered at -20 ppm, assigned to the orthophosphate linkage to four Al atoms ($\text{P}_{4\text{Al}}^0$), suggesting the AlPO_4 formed in hybrid keep after heat treatment. From deconvolution of the spectra, the formation of three different P environments can be observed, $\text{P}_{3\text{Al}}^0$, $\text{P}_{4\text{Al}}^0$ units at -12 and -20 ppm. We also observed the $\text{P}_{3\text{Al},1\text{Si}}^0$ units (which shows the number of aluminum and silicon unit bonds to P units) at -30 ppm, respectively.

The heat treatment leads to an increase in the condensation reactions, resulting in the formation of Al-O-P and P-O-Si bonds. When comparing with the hybrid material, the formation of the AlPO_4 in the heat-treated samples has a higher contribution of $\text{P}_{3\text{Al}}^0$ units and P-O-Al linkage formation ($\text{P}_{3\text{Al},1\text{Si}}^0$). For compositions above 30% SiO_2 , the resonance line of the $\text{P}_{3\text{Al},1\text{Si}}^0$ units shifts toward high-field and the ratio increases, indicating gradual changes in the second coordination sphere or the formation of P-O-Si bonds. The formation of Si-O-P bonds in the gel is limited due to the competition with the hydrolysis reaction. However, these bonds can be formed during condensation at high temperatures [54,72,73]. The ^{31}P MAS data corroborates with ^{29}Si MAS data shown above, which indicates that homocondensation of silicate species (Si-O-Si) occurs, such as the formation of Si-O-P bonds [59,74].

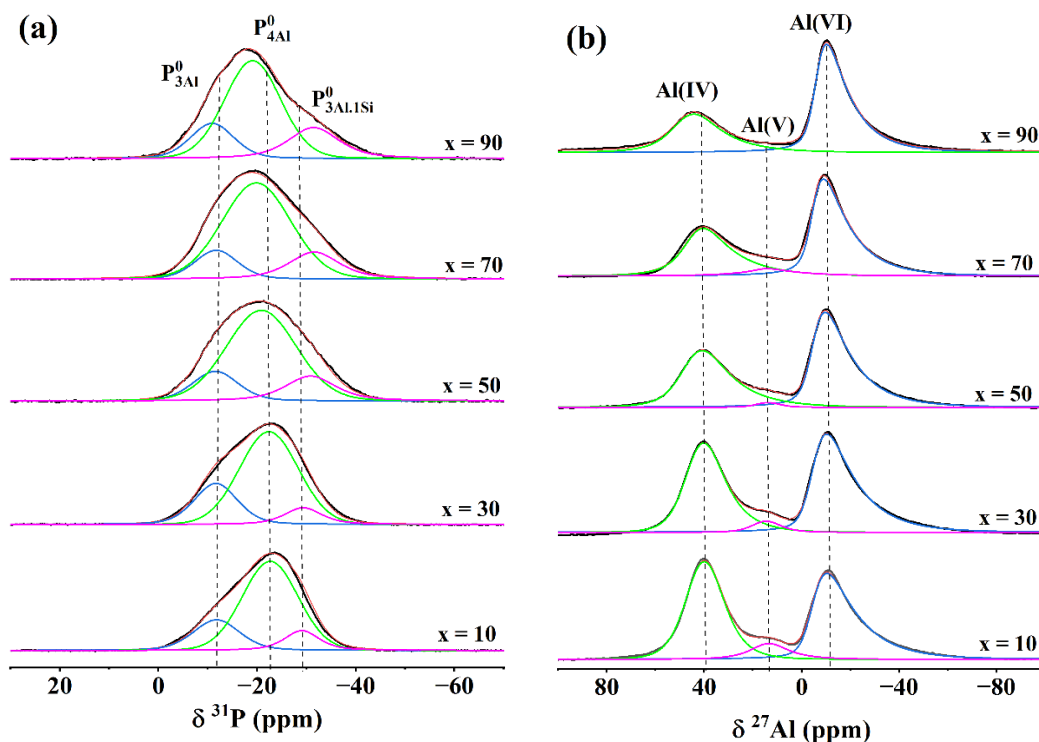


Fig. 2.9. (a) ^{31}P and (b) ^{27}Al MAS NMR spectra for the materials after heat treatment with different SiO_2 content. The solid black line represents the experimental spectrum and the solid red line represents the deconvolution envelope.

Table 2.6. Deconvolution results (chemical shift δ_{iso} and Fractional Areas of the $\text{P}_{3\text{Al}}^0$, $\text{P}_{4\text{Al}}^0$ and $\text{P}_{3\text{Al},1\text{Si}}^0$ units) of the ^{31}P NMR spectra obtained for the compositions from 10 to 90 mol.% SiO_2 content of the materials heat-treated at 800 °C. Estimated errors are ± 0.5 ppm for Chemical Shift and $\pm 1\%$ for Areas.

Sample	$\text{P}_{3\text{Al}}^0$		$\text{P}_{4\text{Al}}^0$		$\text{P}_{3\text{Al},1\text{Si}}^0$	
	δ (ppm)	Area (%)	δ (ppm)	Area (%)	δ (ppm)	Area (%)
x = 10	-12	22	-23	66	-29	12
x = 30	-12	23	-22	67	-29	10
x = 50	-11	16	-21	68	-30	16
x = 70	-11	14	-20	69	-31	17
x = 90	-11	18	-20	61	-31	21
AlPO_4 [76]	-16	31	-25	69	-	-

Fig. 2.9 (b) shows the ^{27}Al MAS NMR results, indicating the presence of the aluminum Al(IV), Al(V) and Al(VI). The resonance lines of the Al(VI) and Al(IV) units can be observed between 0 to -5 ppm and in the range of 55 to 40 ppm, respectively. To analyze the ^{27}Al MAS spectra, the deconvolution was done using the Czsimpl function, and the results obtained from fitting, including the isotropic chemical shift (δ_{iso}) and quadrupolar coupling constants (C_Q) are summarized in Table 2.7. Fig. 2.S5 available in the SI shows the ^{27}Al TQMAS spectra for all compositions. The results indicate only one ^{27}Al chemical environment for the Al(V) and Al(VI) species. However, the signal related to the Al(IV) species has the contribution of two sites (Al-O-Si and Al-O-P), as we have already observed for the hybrid materials. These results confirm the distribution of Al(IV) in two different environments.

After heat treatment, it was observed that a small amount of Al(V) was formed in the network for all compositions. Additionally, there was a higher proportion of Al(IV) species for compositions up to 50% of SiO_2 content. However, for compositions above this concentration, an opposite behavior was observed where the formation of Al(VI) species occurred. As can be seen, an increase in SiO_2 content leads to a decrease in aluminum tetracoordinated species and the formation of $[\text{Al}(\text{OP})_{4-x}(\text{OSi})_x]$ species [38,59]. These results are supported by ^{27}Al - ^{31}P REDOR curves (Fig. 2.10), and the $M_{2(\text{Al-P})}$ values calculated from the parabolic fit are summarized in Table 2.7.

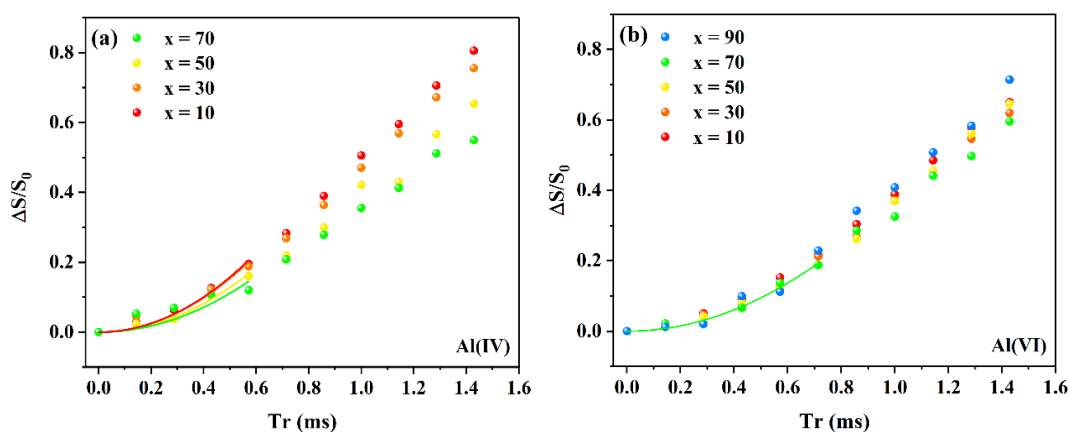


Fig. 2.10. $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR curves for (a) tetracoordinated (Al(IV)) and (b) hexacoordinated (Al(VI)) species for the materials after heat treatment with different SiO_2 contents. Solid curves are fits of the data points to eq. (1) within the data range $\Delta S/S_0 \leq 0.2$.

Table 2.7. ^{27}Al isotropic chemical shift (δ_{iso}) (± 0.2 ppm), fractional areas ($\pm 2\%$) and nuclear electric quadrupolar coupling values (C_Q) (± 0.5 MHz) extracted from the Czsimpl function and Al-P dipolar coupling ($M_{2(\text{Al-P})}$) ($\pm 10\%$) of the materials heat-treated at 800 °C.

Sample	^{27}Al						C_Q (MHz)		$M_{2(\text{Al-P})}$ ($\times 10^6 \text{ rad}^2/\text{s}^2$)	
	Al(IV)		Al(V)		Al(VI)		Al(IV)	Al(VI)	Al(IV)	Al(VI)
	δ_{iso}	Area	δ_{iso}	Area	δ_{iso}	Area				
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)				
x = 10	41	45	15	7	-4	48	1.8	4.5	6.3	4.1
x = 30	41	43	14	4	-4	53	2.8	4.4	6.1	3.4
x = 50	43	42	14	2	-4	56	3.7	4.2	5.1	3.2
x = 70	44	37	15	6	-4	57	3.6	4.0	4.4	3.4
x = 90	47	34	-	-	-5	66	3.2	3.9	-	3.6
$\text{Al}(\text{PO}_3)_3$	-	-	-	-	-	-	-	-	-	5.8

As in the chemical environments of Al(VI) species, the Al-P dipole–dipole coupling also remains the same for all the SiO_2 content. The M_2 values are smaller than those calculated for the Al(IV) species, suggesting the formation of Al-O-Si bonds preferentially. Similar to the hybrid materials, the Al(VI) species behave as a network modifier. Furthermore, M_2 values for Al-tetracoordinated decrease as the SiO_2 content increases in the material, suggesting a decrease in the phosphate species bonded to Al-tetracoordinated.

In accordance with Raman data, the band associated with AlPO_4 -like unit formations observed between $1000\text{--}1200 \text{ cm}^{-1}$ decreases and shifts to a lower frequency as the SiO_2 content increases, which is consistent with the results obtained for ^{29}Si , ^{31}P and ^{27}Al NMR data. Wang et al. [76] have also reported similar behavior, which suggests that the increase of SiO_2 content in the aluminophosphate network promotes the formation of a silicate network and can lead to the segregation of the aluminum-phosphate network. However, in this study, only the composition containing 90 mol.% SiO_2 suggests the segregation formation. In this study, the $[\text{Al}(\text{OP})_{4-x}(\text{OSi})_x]$ species formation occurs by Al-O-Si formation after adding TEOS during gel formation. The same behavior is observed for Al-hexacoordinated, however the Al(VI) species are preferentially linked to the silicon atom.

The chemical shift for AlPO_4 species is around 40 ppm [77], and therefore this shift to more positive values (downfield) from 0 ppm indicates fewer Al-O-P bonds

present in the glass network. This shows that the glass structure is altered as a result of the increase in SiO₂ content, and this result was supported by Raman data in Fig. 2.7 (b) which showed a decrease in the AlPO₄-like units as the SiO₂ content increased. These results were also reported by Deshpande et al. [59], which showed that the elimination of carbonic and hydroxyl ligands from the aluminum site after the heat treatment facilitate the bonding of Al-tetracoordinated with silicate (or phosphate) units. On the other hand, the environment of Al(VI) did not show a significant change in the SiO₂ content, indicating that the Al(VI) site was quite insensitive to the silicate species. The Al-P and Al-Si connectivity supported by the ³¹P MAS data in Fig. 2.9 (a), where we observed the spectra downshift as the SiO₂ content increased indicating a higher contribution of Al-O-P linkages, but the upshift of the P_{3Al,1Si}⁰ units for the samples above 30% SiO₂ led to the formation of phosphate species bond to aluminum and silicate species.

Hybrid materials undergo structural changes when subjected to heat treatment, resulting in increased connectivity of silicon atoms with aluminum and phosphorus atoms, as seen in ²⁹Si NMR data with Q⁴ unit formation. However, the connectivity of Al(VI) with phosphate and silicate species remains unchanged after heat treatment, as indicated by the chemical shift values. This trend is followed by the downshift of the ³¹P sites resonance as the SiO₂ content increases, indicating the higher contribution of P-O-Al linkages and the heterocondensation between silicate and phosphate species occur for the range 30 to 70% of the SiO₂ content.

Based on these results, the heat treatment of the materials increased the connectivity of silicate species. However, the connectivity of the silicate species depended on the SiO₂ content of these materials, as our data showed preferential homocondensation of the silicate species as the SiO₂ content increased.

2.4. Conclusions

Hybrid materials with xSiO₂[(Al₂O₃)₅₀-(P₂O₅)₅₀]_{100-x} composition (10 mol.% < x < 100 mol.%) were produced via sol-gel route, and further heat-treated at 800 °C, yielding non-crystalline materials as confirmed by XRD data. The structural changes from the hybrid materials to the heat-treated samples were investigated by solid-state NMR. The ²⁹Si, ²⁷Al and ³¹P MAS NMR results indicated the AlPO₄ formation in the matrix by the formation of Al-O-P and P-O-Si linkages. After heat treatment, Q⁴ units and Al-tetracoordinated increased, showing that the increase of SiO₂ content resulted in the

formation of a more interconnected SiO₂ tetrahedra network, as well as the formation of Si-O-Al(IV) linkages. However, for 90 mol.% SiO₂ content, network segregation occurred which was supported by ³¹P NMR data. Similar to the hybrid materials, the increase in SiO₂ content induces the replacement of P-O-Al(IV) bonds by Si-O-Al(IV) bonds in the heat-treated materials, as indicated by the downshift of the Al(IV) site, and the decrease of M₂ values for the Al(IV) sites as the SiO₂ content increased in the ²⁷Al{³¹P} REDOR data, which was also confirmed by Raman analysis.

CRedit authorship contribution statement

Beatriz Helena Costa: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gabriel Toshiaki Tayama:** Writing – review & editing, Validation, Conceptualization. **Silvia Helena Santagneli:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to gratefully acknowledge the Brazilian funding agencies FAPESP (process 2018/24735-3) and CAPES. B.C. acknowledges the CAPES fellowship (finance code 001).

References

- [1] S.G. Kosinski, D.M. Krol, T.M. Duncan, D.C. Douglas, J.B. MacChesney, J. R. Simpson, Raman and NMR spectroscopy of SiO₂ glasses CO-doped with Al₂O₃ and P₂O₅, J. Non Cryst. Solids 105 (1988) 45–52, [https://doi.org/10.1016/0022-3093\(88\)90336-5](https://doi.org/10.1016/0022-3093(88)90336-5).

- [2] W. Huang, R.R.A. Syms, Sol-gel silica-on-silicon buried-channel EDWAs, *J. Lightwave Technol.* 21 (2003) 1339–1349, <https://doi.org/10.1109/jlt.2003.812417>.
- [3] Y.M. Tian, L.F. Shen, E.Y.B. Pun, H. Lin, High-aluminum phosphate glasses for single-mode waveguide-typed red light source, *J. Non Cryst. Solids* 426 (2015) 25–31, <https://doi.org/10.1016/j.jnoncrysol.2015.06.015>.
- [4] N. Chanthima, Y. Tariwong, J. Kaewkhao, N.W. Sangwaranatee, N. Sangwaranatee, Effect of alkali oxides on luminescence properties of Eu^{3+} -doped aluminium phosphate glasses, *Mater. Today Proc.* 17 (2019) 1906–1913, <https://doi.org/10.1016/j.matpr.2019.06.229>.
- [5] P. Aryal, H.J. Kim, A. Khan, S. Saha, S.J. Kang, S. Kothan, Y. Yamsuk, J. Kaewkhao, Development of Eu^{3+} -doped phosphate glass for red luminescent solid-state optical devices, *J. Lumin.* 227 (2020) 117564, <https://doi.org/10.1016/j.jlumin.2020.117564>.
- [6] B. Glorieux, T. Salminen, J. Massera, M. Lastusaari, L. Petit, Better understanding of the role of SiO_2 , P_2O_5 and Al_2O_3 on the spectroscopic properties of Yb^{3+} doped silica sol-gel glasses, *J. Non Cryst. Solids* 482 (2018) 46–51, <https://doi.org/10.1016/j.jnoncrysol.2017.12.021>.
- [7] C. Shao, F. Wang, Y. Jiao, S. Wang, X. Wang, C. Yu, L. Hu, Relationship between glass structure and spectroscopic properties in $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Al}^{3+}/\text{P}^{5+}$ -doped silica glasses, *Opt. Mater. Express* 10 (2020) 1169, <https://doi.org/10.1364/ome.389769>.
- [8] F. Wang, C. Shao, C. Yu, S. Wang, L. Zhang, G. Gao, L. Hu, Effect of AlPO_4 join concentration on optical properties and radiation hardening performance of Yb -doped Al_2O_3 - P_2O_5 - SiO_2 glass, *J. Appl. Phys.* (2019) 125, <https://doi.org/10.1063/1.5096469>.
- [9] M. Logrado, H. Eckert, H. Ikeda, S. Nakane, H. Yamazaki, Silica incorporation into sodium aluminum phosphate glasses: structural characterization by Raman spectroscopy and multinuclear solid-state NMR, *J. Non Cryst. Solids* 579 (2022) 121366, <https://doi.org/10.1016/j.jnoncrysol.2021.121366>.
- [10] R.K. Brow, Nature of alumina in phosphate glass: i, properties of sodium aluminophosphate glass, *J. Am. Ceram. Soc.* 76 (1993) 913–918, <https://doi.org/10.1111/j.1151-2916.1993.tb05315.x>.

- [11] S. Liangen, J. Zarzycki, Evolution of the structure of gels of the system $\text{SiO}_2\text{Al}_2\text{O}_3\text{P}_2\text{O}_5$ submitted to thermal treatment, *J. Non Cryst. Solids* 112 (1989) 428–431, [https://doi.org/10.1016/0022-3093\(89\)90567-X](https://doi.org/10.1016/0022-3093(89)90567-X).
- [12] M. Łaczka, M. Ciecierska, Preparation, structure and properties of silicate-phosphate glasses obtained by means of sol-gel method, *J. Sol Gel Sci. Technol.* 3 (1994) 219–227, <https://doi.org/10.1007/BF00486560>.
- [13] J. Livage, P. Barboux, M.T. Vandenborre, C. Schmutz, F. Taulelle, Sol-gel synthesis of phosphates, *J. Non Cryst. Solids* 147–148 (1992) 18–23, [https://doi.org/10.1016/S0022-3093\(05\)80586-1](https://doi.org/10.1016/S0022-3093(05)80586-1).
- [14] F. Lindner, C. Aichele, A. Kriltz, A. Scheffel, H. Bartelt, K. Wondraczek, FTIR multispectral imaging of P/Al-doped silica glass preforms prepared by MCVD in combination with the high temperature evaporation of AlCl_3 , *Opt. Mater. Express* 12 (2022) 184, <https://doi.org/10.1364/ome.444146>.
- [15] H. You, M. Nogami, Three-photon-excited fluorescence of $\text{Al}_2\text{O}_3\text{-SiO}_2$ glass containing Eu^{3+} ions by femtosecond laser irradiation, *Appl. Phys. Lett.* 84 (2004) 2076–2078, <https://doi.org/10.1063/1.1688984>.
- [16] I. Cooperstein, E. Shukrun, O. Press, A. Kamyshny, S. Magdassi, Additive manufacturing of transparent silica glass from solutions, *ACS Appl. Mater. Interfaces* 10 (2018) 18879–18885, <https://doi.org/10.1021/acsami.8b03766>.
- [17] L. Wang, K. Lu, R. Ma, Effects of different polymer precursors on the characteristics of SiOC bulk ceramics, *Appl. Phys. A* 125 (2019) 1–13, <https://doi.org/10.1007/s00339-019-2680-z>. *Mater. Sci. Process.*
- [18] J. Wang, B. Zheng, P. Wang, 3D printed $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped phosphosilicate glass based on sol-gel technology, *J. Non Cryst. Solids* 550 (2020) 120362, <https://doi.org/10.1016/j.jnoncrysol.2020.120362>.
- [19] J. Ren, L. Zhang, H. Eckert, Sol-gel preparation of mesoporous $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses: structural evolution monitored by solid state NMR, *J. Sol Gel Sci. Technol.* 70 (2014) 482–490, <https://doi.org/10.1007/s10971-014-3309-5>.
- [20] C.J. Brinker, G.W. Scherer. *Sol-gel science: the physics and chemistry of sol-gel processing*, Academic Press, New York, 2013.
- [21] G.T. Tayama, S.H. Santagneli, M.D.O. Junior, Y. Messaddeq, Understanding the microstructure connectivity in photopolymerizable aluminum-phosphate-silicate sol □ gel hybrid materials for additive manufacturing, *J. Phys. Chem. C* 127 (2023) 2416–2429, <https://doi.org/10.1021/acs.jpcc.2c08027>.

- [22] G.T. Tayama, S.H. Santagneli, H. Eckert, S. Pawsey, Y. Messaddeq, Preparation and structural characterization of new photopolymerizable transparent aluminum-phosphate hybrid materials as resins for 3D printing, *J. Phys. Chem. C* 124 (2020) 25621–25631, <https://doi.org/10.1021/acs.jpcc.0c08289>.
- [23] P. Judeinstein, C. Sanchez, Hybrid organic–inorganic materials: a land of multidisciplinary, *J. Mater. Chem.* 6 (1996) 511–525, <https://doi.org/10.1039/JM9960600511>.
- [24] L. Nicole, C. Laberty-Robert, L. Rozes, C. Sanchez, Hybrid materials science: a promised land for the integrative design of multifunctional materials, *Nanoscale* 6 (2014) 6267–6292, <https://doi.org/10.1039/c4nr01788a>.
- [25] E. Shukrun Farrell, Y. Schilt, M.Y. Moshkovitz, Y. Levi-Kalisman, U. Raviv, S. Magdassi, 3D printing of ordered mesoporous silica complex structures, *Nano Lett.* 20 (2020) 6598–6605, <https://doi.org/10.1021/acs.nanolett.0c02364>.
- [26] D. Zhang, X. Liu, J. Qiu, 3D printing of glass by additive manufacturing techniques: a review, *Front. Optoelectron.* 14 (2021) 263–277, <https://doi.org/10.1007/s12200-020-1009-z>.
- [27] K. Sasan, A. Lange, T.D. Yee, N. Dudukovic, D.T. Nguyen, M.A. Johnson, O. D. Herrera, J.H. Yoo, A.M. Sawvel, M.E. Ellis, C.M. Mah, R. Ryerson, L.L. Wong, T. Suratwala, J.F. Destino, R. Dylla-Spears, Additive manufacturing of optical quality germania-silica glasses, *ACS Appl. Mater. Interfaces* 12 (2020) 6736–6741, <https://doi.org/10.1021/acsami.9b21136>.
- [28] J.F. Destino, N.A. Dudukovic, M.A. Johnson, D.T. Nguyen, T.D. Yee, G.C. Egan, A. M. Sawvel, W.A. Steele, T.F. Baumann, E.B. Duoss, T. Suratwala, R. Dylla-Spears, 3D printed optical quality silica and silica–titania glasses from sol–gel feedstocks, *Adv. Mater. Technol.* 3 (2018) 1–10, <https://doi.org/10.1002/admt.201700323>.
- [29] S.W. Yung, H.Y. Chiang, Y.S. Lai, F.B. Wu, C. Fu, Y.M. Lee, Thermal, optical and structural properties of Tb doped zinc aluminum phosphate glasses, *Ceram. Int.* 41 (2015) 877–888, <https://doi.org/10.1016/j.ceramint.2014.09.005>.
- [30] H. Nagashima, C. Martineau-Corcoss, G. Tricot, J. Trébosc, F. Pourpoint, J. P. Amoureux, O. Lafon, Recent developments in NMR studies of aluminophosphates, *Annu. Rep. NMR Spectrosc.* 94 (2018) 113–185, <https://doi.org/10.1016/bs.arnmr.2017.12.004>.
- [31] G. Tricot, B. Doumert, B. Revel, M. Bria, J. Trebosc, H. Vezin, Non-homogeneous distribution of Al³⁺ in doped phosphate glasses revealed by ²⁷Al/³¹P solid state

- NMR, *Solid State Nucl. Magn. Reson.* 84 (2017) 137–142, <https://doi.org/10.1016/j.ssnmr.2017.02.003>.
- [32] S. Wegner, L. van Wüllen, G. Tricot, The structure of aluminophosphate glasses revisited: application of modern solid state NMR strategies to determine structural motifs on intermediate length scales, *J. Non Cryst. Solids* 354 (2008) 1703–1714, <https://doi.org/10.1016/j.jnoncrysol.2007.10.034>.
- [33] L. van Wüllen, G. Tricot, S. Wegner, An advanced NMR protocol for the structural characterization of aluminophosphate glasses, *Solid State Nucl. Magn. Reson.* 32 (2007) 44–52, <https://doi.org/10.1016/j.ssnmr.2007.07.004>.
- [34] J. Tsuchida, J. Schneider, M.T. Rinke, H. Eckert, Structure of ternary aluminum metaphosphate glasses, *J. Phys. Chem. C* 115 (2011) 21927–21941, <https://doi.org/10.1021/jp205700j>.
- [35] J.M. Egan, R.M. Wenslow, K.T. Mueller, Mapping aluminum/phosphorus connectivities in aluminophosphate glasses, *J. Non Cryst. Solids* 261 (2000) 115–126, [https://doi.org/10.1016/S0022-3093\(99\)00606-7](https://doi.org/10.1016/S0022-3093(99)00606-7).
- [36] Q. Zhu, G. Zhao, J. Jin, G. Han, The role of phosphate in the glass forming region, structure and mechanical properties for the SiO₂-Al₂O₃-P₂O₅ system contains high-aluminum, *J. Non Cryst. Solids* 583 (2022) 121464, <https://doi.org/10.1016/j.jnoncrysol.2022.121464>.
- [37] D.J. DiGiovanni, J.B. MacChesney, T.Y. Kometani, Structure and properties of silica containing aluminum and phosphorus near the AlPO₄ join, *J. Non Cryst. Solids* 113 (1989) 58–64, [https://doi.org/10.1016/0022-3093\(89\)90318-9](https://doi.org/10.1016/0022-3093(89)90318-9).
- [38] C.C. De Araujo, L. Zhang, H. Eckert, Sol-gel preparation of AlPO₄-SiO₂ glasses with high surface mesoporous structure, *J. Mater. Chem.* 16 (2006) 1323–1331, <https://doi.org/10.1039/b516599g>.
- [39] J.P. Amoureux, C. Fernandez, S. Steuernagel, Z Filtering in MQMAS NMR, *J. Magn. Reson. Ser. A* 123 (1996) 116–118, <https://doi.org/10.1006/jmra.1996.0221>.
- [40] J.S. Terry Gullion, Rotational-echo double-resonance NMR, *J. Magn. Reson.* 81 (1989) 196–200, [https://doi.org/10.1016/0022-2364\(89\)90280-1](https://doi.org/10.1016/0022-2364(89)90280-1).
- [41] M. Bertmer, H. Eckert, Dephasing of spin echoes by multiple heteronuclear dipolar interactions in rotational echo double resonance NMR experiments, *Solid State Nucl. Magn. Reson.* 15 (1999) 139–152, [https://doi.org/10.1016/S0926-2040\(99\)00050-8](https://doi.org/10.1016/S0926-2040(99)00050-8).

- [42] J.C.C. Chan, H. Eckert, Dipolar coupling information in multispin systems: application of a compensated REDOR NMR approach to inorganic phosphates, *J. Magn. Reson.* 147 (2000) 170–178, <https://doi.org/10.1006/jmre.2000.2191>.
- [43] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Modelling one- and two-dimensional solid-state NMR spectra, *Magn. Reson. Chem.* 40 (2002) 70–76, <https://doi.org/10.1002/mrc.984>.
- [44] T.S. Perova, J.K. Vij, H. Xu, Fourier transform infrared study of poly (2-hydroxyethyl methacrylate) PHEMA, *Colloid Polym. Sci.* 275 (1997) 323–332, <https://doi.org/10.1007/s003960050089>.
- [45] A.M. Efimov, V.G. Pogareva, IR absorption spectra of vitreous silica and silicate glasses: the nature of bands in the 1300 to 5000 cm⁻¹ region, *Chem. Geol.* 229 (2006) 198–217, <https://doi.org/10.1016/j.chemgeo.2006.01.022>.
- [46] J. Coates, Encyclopedia of Analytical Chemistry, Interpretation of Infrared Spectra, A Practical Approach, in: John Wiley & Sons, Ltd, Chichester, UK, 2006, pp. 22–31, <https://doi.org/10.1002/9780470027318.a5606>.
- [47] R. Ganesan, S.S. Dinachali, S.H. Lim, M.S.M. Saifullah, W.T. Chong, A.H.H. Lim, J. J. Yong, E.S. Thian, C. He, H.Y. Low, Direct nanoimprint lithography of Al₂O₃ using a chelated monomer-based precursor, *Nanotechnology* (2012) 23, <https://doi.org/10.1088/0957-4484/23/31/315304>.
- [48] R.O.R. Costa, F.S. Lameiras, E.H.M. Nunes, D.C.L. Vasconcelos, W.L. Vasconcelos, Preparation of silica-poly(2-hydroxyethyl methacrylate) hybrids modified with 3-methacryloxypropyltrimethoxysilane, *Ceram. Int.* 42 (2016) 3465–3472, <https://doi.org/10.1016/j.ceramint.2015.10.145>.
- [49] A. Bertoluzza, P. Monti, J.V. Garcia-Ramos, R. Simoni, R. Caramazza, A. Calzavara, Applications of Raman spectroscopy to the ophthalmological field : raman spectra of soft contact lenses made of poly-2-hydroxyethylmethacrylate (PHEMA), *J. Mol. Struct.* 143 (1986) 469–472, [https://doi.org/10.1016/0022-2860\(86\)85302-9](https://doi.org/10.1016/0022-2860(86)85302-9).
- [50] P. Rodič, J. Iskra, I. Milošev, Study of a sol-gel process in the preparation of hybrid coatings for corrosion protection using FTIR and ¹H NMR methods, *J. Non Cryst. Solids* 396–397 (2014) 25–35, <https://doi.org/10.1016/j.jnoncrsol.2014.04.013>.
- [51] R.K. Nariyal, P. Kothari, B. Bisht, FTIR measurements of SiO₂ glass prepared by sol-gel technique, *Chem. Sci. Trans.* 3 (2014) 1064–1066, <https://doi.org/10.7598/cst2014.816>.

- [52] H. Aguiar, J. Serra, P. Gonz'alez, B. Le'on, Structural study of sol–gel silicate glasses by IR and Raman spectroscopies, *J. Non Cryst. Solids* 355 (2009) 475–480, <https://doi.org/10.1016/j.jnoncrysol.2009.01.010>.
- [53] P.J. Launer, B. Arkles. Infrared analysis of organosilicon compounds: spectra-structure correlations, *Silicon Compounds: Silanes & Silicones*, Gelest, Inc Morrisville, 2013.
- [54] J.C. Schrotter, A. Cardenas, M. Smaih, N. Hovnanian, Silicon and phosphorus alkoxide mixture: sol-gel study by spectroscopic technics, *J. Sol Gel Sci. Technol.* 4 (1995) 195–204, <https://doi.org/10.1007/BF00488374>.
- [55] R. Plummer, D.J.T. Hill, A.K. Whittaker, DOSY NMR studies of chemical exchange behavior of poly(2-hydroxyethyl methacrylate), *Macromolecules* 39 (2006) 3878–3889, <https://doi.org/10.1021/ma060355o>.
- [56] E. Ferrari, M. Saladini, F. Pignedoli, F. Spagnolo, R. Benassi, Solvent effect on keto-enol tautomerism in a new β -diketone: a comparison between experimental data and different theoretical approaches, *New J. Chem.* 35 (2011) 2840–2847, <https://doi.org/10.1039/c1nj20576e>.
- [57] X. Ma, H. Wang, S. Jin, Y. Wu, X.J. Liang, Construction of paclitaxel-loaded poly (2-hydroxyethyl methacrylate)-g-poly (lactide)- 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine copolymer nanoparticle delivery system and evaluation of its anticancer activity, *Int. J. Nanomed.* 7 (2012) 1313–1328, <https://doi.org/10.2147/IJN.S29371>.
- [58] L. Delattre, F. Babonneau, Influence of the nature of the R group on the hydrolysis and condensation process of trifunctional silicon alkoxides, $R-Si(OR')_3$, *MRS Proc.* 346 (1994) 365, <https://doi.org/10.1557/PROC-346-365>.
- [59] R.R. Deshpande, L. Zhang, H. Eckert, Sol-gel synthesis of sodium-modified $AlPO_4-SiO_2$ glasses and structural characterization by solid state NMR, *J. Mater. Chem.* 19 (2009) 1151–1159, <https://doi.org/10.1039/b815397c>.
- [60] F. Romero-Gavil'an, S. Barros-Silva, J. Garc'ia-Cañadas, B. Palla, R. Izquierdo, M. Gurruchaga, I. Goñi, J. Suay, Control of the degradation of silica sol-gel hybrid coatings for metal implants prepared by the triple combination of alkoxysilanes, *J. Non Cryst. Solids* 453 (2016) 66–73, <https://doi.org/10.1016/j.jnoncrysol.2016.09.026>.

- [61] C. Fernández-Lorenzo, L. Esquivias, P. Barboux, J. Maquet, F. Taulelle, Sol-gel synthesis of $\text{SiO}_2\text{P}_2\text{O}_5$ glasses, *J. Non Cryst. Solids* 176 (1994) 189–199, [https://doi.org/10.1016/0022-3093\(94\)90077-9](https://doi.org/10.1016/0022-3093(94)90077-9).
- [62] D. Carta, J.C. Knowles, P. Guerry, M.E. Smith, R.J. Newport, Sol-gel synthesis and structural characterisation of $\text{P}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ glasses for biomedical applications, *J. Mater. Chem.* 19 (2009) 150–158, <https://doi.org/10.1039/b813288g>.
- [63] F. Tian, L. Pan, X. Wu, F. Wu, The NMR studies of the $\text{P}_2\text{O}_5\text{SiO}_2$ sol and gel chemistry, *J. Non Cryst. Solids* 104 (1988) 129–134, [https://doi.org/10.1016/0022-3093\(88\)90191-3](https://doi.org/10.1016/0022-3093(88)90191-3).
- [64] T. Gutberlet, H. Hilbig, R.E. Beddoe, Acid attack on hydrated cement - Effect of mineral acids on the degradation process, *Cem. Concr. Res.* 74 (2015) 35–43, <https://doi.org/10.1016/j.cemconres.2015.03.011>.
- [65] M.E. Krüger, A. Heisig, H. Hilbig, H. Eickhoff, D. Heinz, A. Machner, Effect of aluminum on the structure of synthetic alkali-silica gels, *Cem. Concr. Res.* 166 (2023) 107088, <https://doi.org/10.1016/j.cemconres.2022.107088>.
- [66] D.S. Perera, J.V. Hanna, J. Davis, M.G. Blackford, B.A. Latella, Y. Sasaki, E. R. Vance, Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials, *J. Mater. Sci.* 43 (2008) 6562–6566, <https://doi.org/10.1007/s10853-008-2913-6>.
- [67] E. Shukrun, I. Cooperstein, S. Magdassi, 3D-printed organic–ceramic complex hybrid structures with high silica content, *Adv. Sci.* 5 (2018) 1–7, <https://doi.org/10.1002/advs.201800061>.
- [68] M. Ciecińska, P. Goj, A. Stoch, P. Stoch, Thermal properties of $60\text{P}_2\text{O}_5\text{-(}40-x\text{) Al}_2\text{O}_3\text{-}x\text{Na}_2\text{O}$ glasses, *J. Therm. Anal. Calorim.* 139 (2020) 1763–1769, <https://doi.org/10.1007/s10973-019-08606-w>.
- [69] L. Zhang, A. Bögershausen, H. Eckert, Mesoporous AlPO_4 glass from a simple aqueous sol-gel route, *J. Am. Ceram. Soc.* 88 (2005) 897–902, <https://doi.org/10.1111/j.1551-2916.2005.00159.x>.
- [70] L. Todan, E.M. Anghel, P. Osiceanu, R.V.F. Turcu, I. Atkinson, S. Simon, M. Zaharescu, Structural characterization of some sol-gel derived phosphosilicate glasses, *J. Mol. Struct.* 1086 (2015) 161–171, <https://doi.org/10.1016/j.molstruc.2015.01.012>.

- [71] H. Dong, Z. Wang, C. Shao, S. Wang, F. Lou, C. Yu, Y. Chen, L. Hu, Effect of co-dopants on the spectral property of Yb³⁺ doped silica glasses at 1018 nm, *Opt. Mater.* 122 (2021) 111761, <https://doi.org/10.1016/j.optmat.2021.111761> (Amst).
- [72] D. Carta, D.M. Pickup, J.C. Knowles, I. Ahmed, M.E. Smith, R.J. Newport, A structural study of sol-gel and melt-quenched phosphate-based glasses, *J. Non Cryst. Solids* 353 (2007) 1759–1765, <https://doi.org/10.1016/j.jnoncrysol.2007.02.008>.
- [73] C. Coelho, F. Babonneau, T. Azaïs, L. Bonhomm-Courry, J. Maquet, G. Laurent, C. Bonhomme, Chemical bonding in silicophosphate gels: contribution of dipolar and J-derived solid state NMR techniques, *J. Sol Gel Sci. Technol.* 40 (2006) 181–189, <https://doi.org/10.1007/s10971-006-7431-x>.
- [74] G.D. Cody, B. Mysen, G. S'aghi-Szab'o, J.A. Tossell, Silicate-phosphate interactions in silicate glasses and melts : I. A multinuclear (27Al, 29Si, 31P) MAS NMR and ab initio chemical shielding (31P) study of phosphorous speciation in silicate glasses, *Geochim. Cosmochim. Acta* 65 (2001) 2395–2411, [https://doi.org/10.1016/S0016-7037\(01\)00597-X](https://doi.org/10.1016/S0016-7037(01)00597-X).
- [75] L. Zhang, H. Eckert, Short- And medium-range order in sodium aluminophosphate glasses: new insights from high-resolution dipolar solid-state NMR spectroscopy, *J. Phys. Chem. B* 110 (2006) 8946–8958, <https://doi.org/10.1021/jp060501s>.
- [76] X. Wang, F. Munoz, D. He, Y. Ding, J. Ren, W. Chen, H. Li, L. Hu, Effects of SiO₂ on properties and structures of neodymium doped P₂O₅-Al₂O₃-Li₂O-MgO-Sb₂O₃ glasses, *J. Alloys Compd.* 729 (2017) 1038–1045, <https://doi.org/10.1016/j.jallcom.2017.09.093>.
- [77] R. Li, L. Zhang, A.S.S. De Camargo, H. Eckert, Sol-gel prepared AlPO₄ with incorporating rhodamine 6G, *J. Non Cryst. Solids* 356 (2010) 2569–2573, <https://doi.org/10.1016/j.jnoncrysol.2010.05.018>.

Supplementary material

Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials

Beatriz Helena Costa^{1*}, Gabriel Toshiaki Tayama², Silvia Helena Santagneli^{1*}

¹ Institute of Chemistry, São Paulo State University (UNESP), Araraquara, SP, Brazil

² Centre d'optique, photonique et laser (COPL), Université Laval, Québec, G1V 0A6, Canada

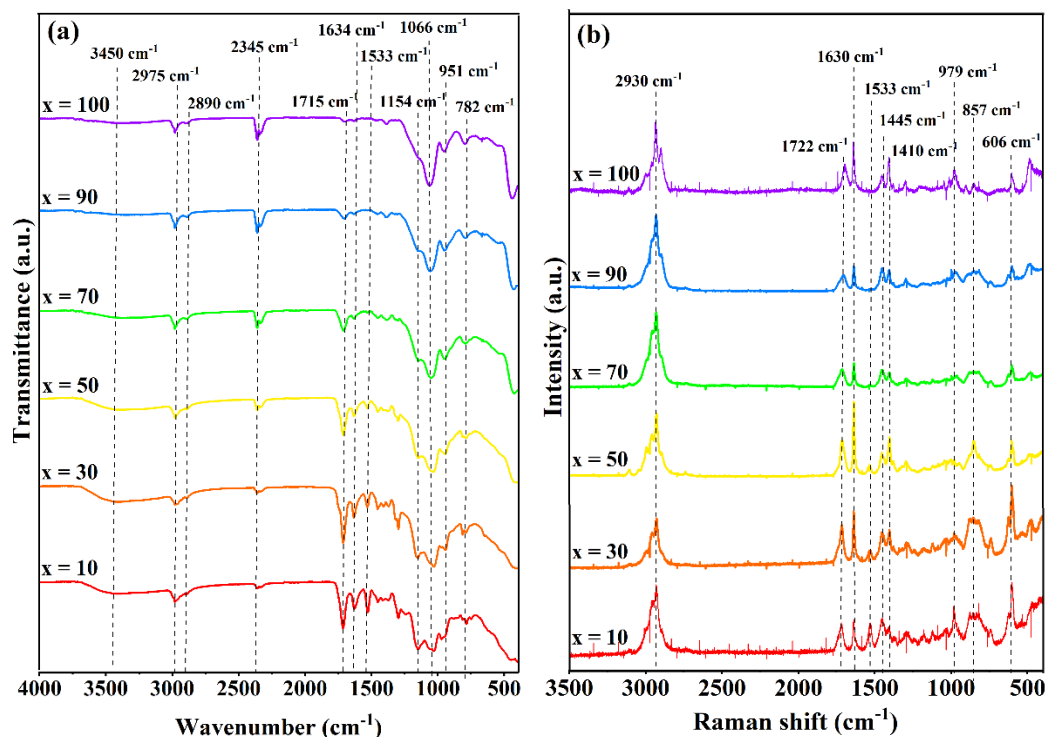


Fig. 2.S1. (a) FTIR-ATR and (b) Raman spectra for the hybrid materials with different SiO₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%).

Table 2.S1. Calculated and experimental residual mass (%) values for the hybrid materials with different SiO₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%).

Sample x	Calculated Residual mass (%)	Experimental Residual mass (%)
10	22	20
30	24	22
50	28	30
70	32	36
90	39	54
100	43	71

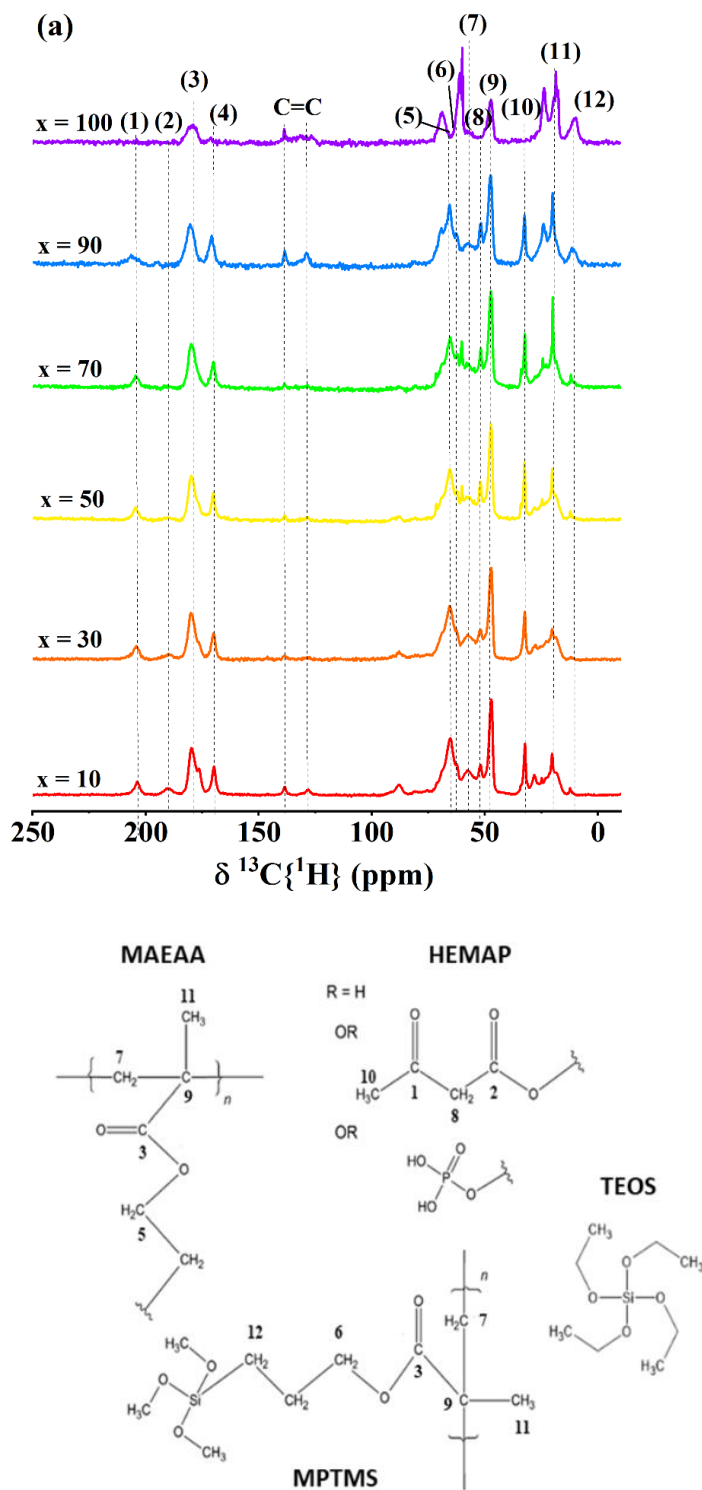


Fig. 2.S2. (a) $^{13}\text{C}\{^1\text{H}\}$ CP-MAS spectra and (b) structural assignment for the hybrid materials with different SiO_2 content ($x = 10, 30, 50, 70, 90$ and 100 in mol%).

The $^{13}\text{C}\{^1\text{H}\}$ CP-MAS spectra of all hybrid materials and each ^{13}C carbon corresponding to the structural assignment are shown in Fig. 2.S2 The carbon signals (3),

(11) and (6) at 179, 19 and 62 ppm were attributed to the carbonyl group (C=O), the CH₃ and the CH₂ closest to the methacrylate group in the MPTMS, respectively. The ¹³C signal (5) at 65 ppm refers to the CH₂ of the ethyl group of HEMAP and MAEAA, which decreases its intensity as a function of the increase of Si content.

The two ¹³C signal (10) and (8) observed at 32 and 52 ppm are attributed to the CH₃ group that is linked to the diketone of the MAEAA, and to the CH₂ group that is located between the diketone carbonyls, respectively. Both increase inversely with the proportion of Si. The ketone groups of the MAEAA were observed at 190 and 204 ppm, corresponding to the ¹³C (2) and (1). The ¹³C signals (9) and (7) observed at 58 and 47 ppm are attributed to the quaternary carbon and the CH₂ group of the polymer chain, respectively. Some unpolymerized groups (C=C) were observed with low intensity at 128 and 138 ppm. These results are in agreement with those observed in the FTIR and Raman spectra. Finally, the ¹³C signal (12) found at 12 ppm was identified as the Si-linked CH₂ present in the MPTMS.

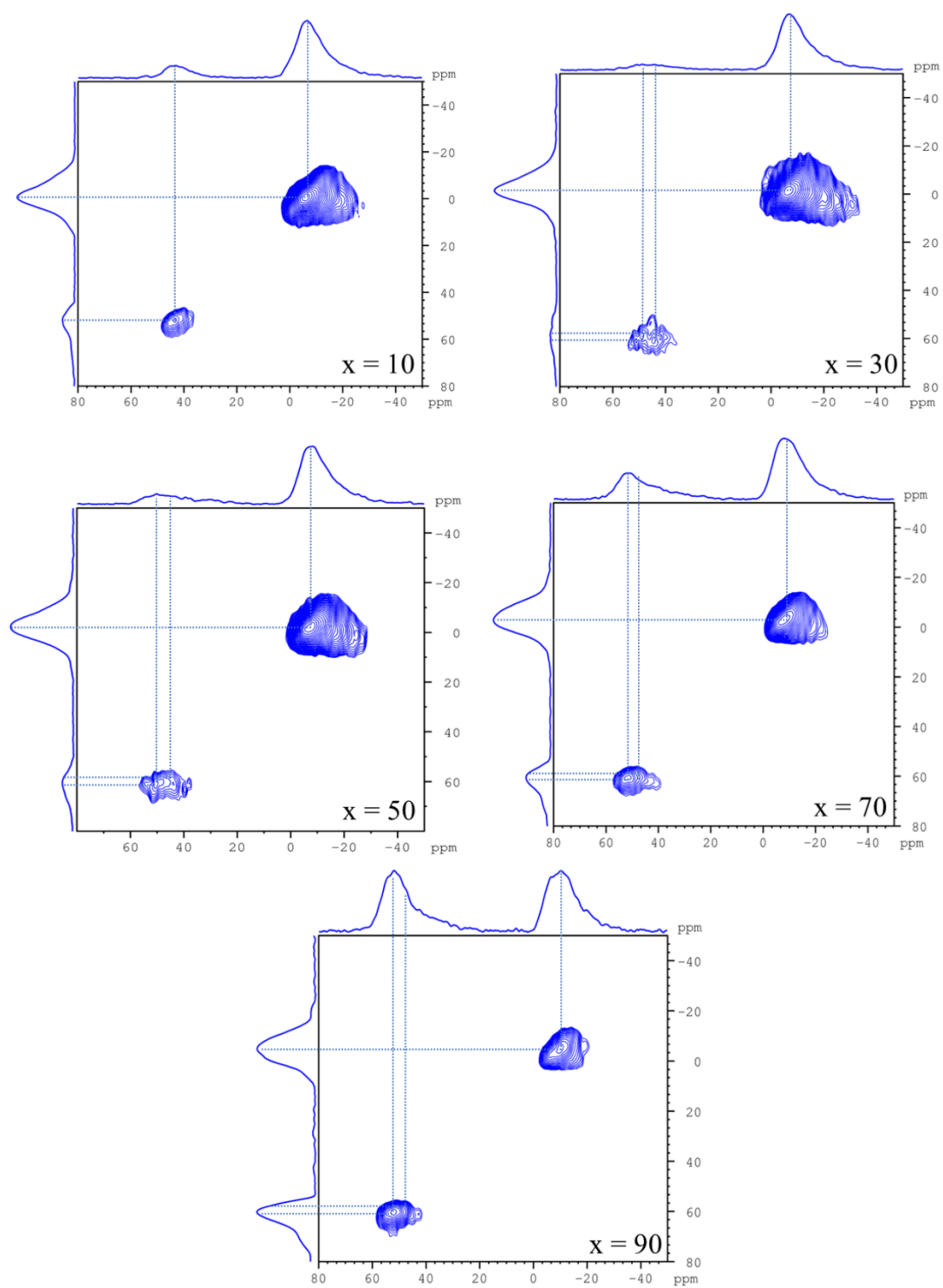


Fig. 2.S3. ^{27}Al TQMAS NMR spectra for the hybrid materials with different SiO_2 concentration ($x = 10, 30, 50, 70$ and 90 mol.%).

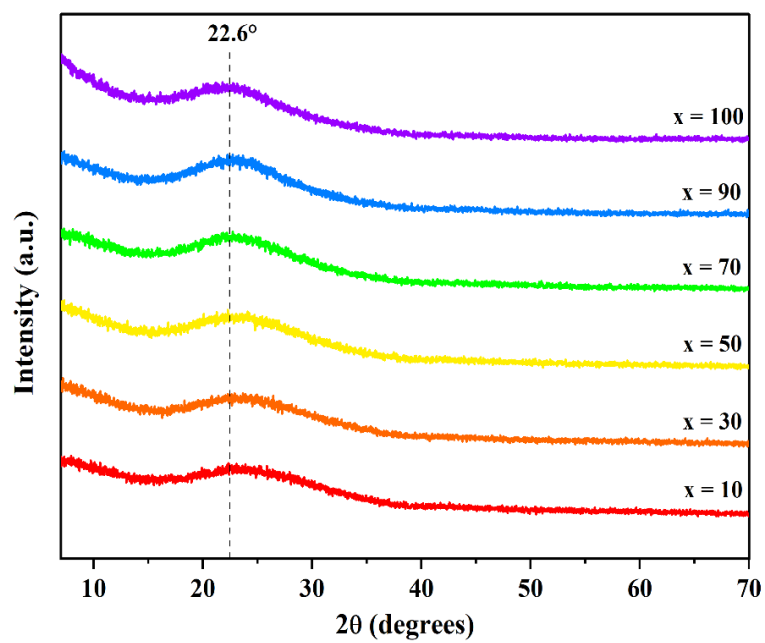


Fig. 2.S4. XRD spectra for the heat-treated materials with different SiO₂ content (x = 10, 30, 50, 70, 90 and 100 mol.%).

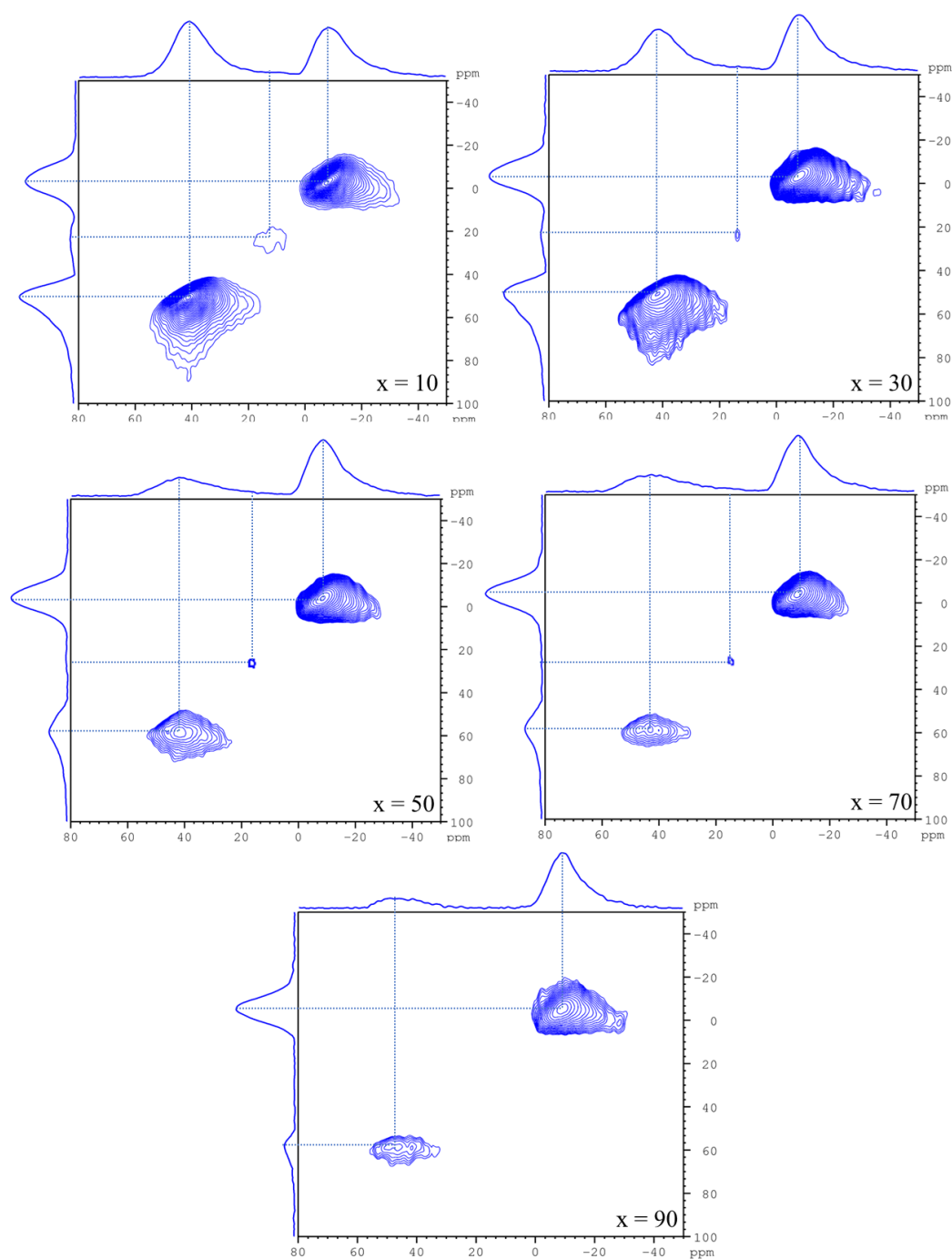
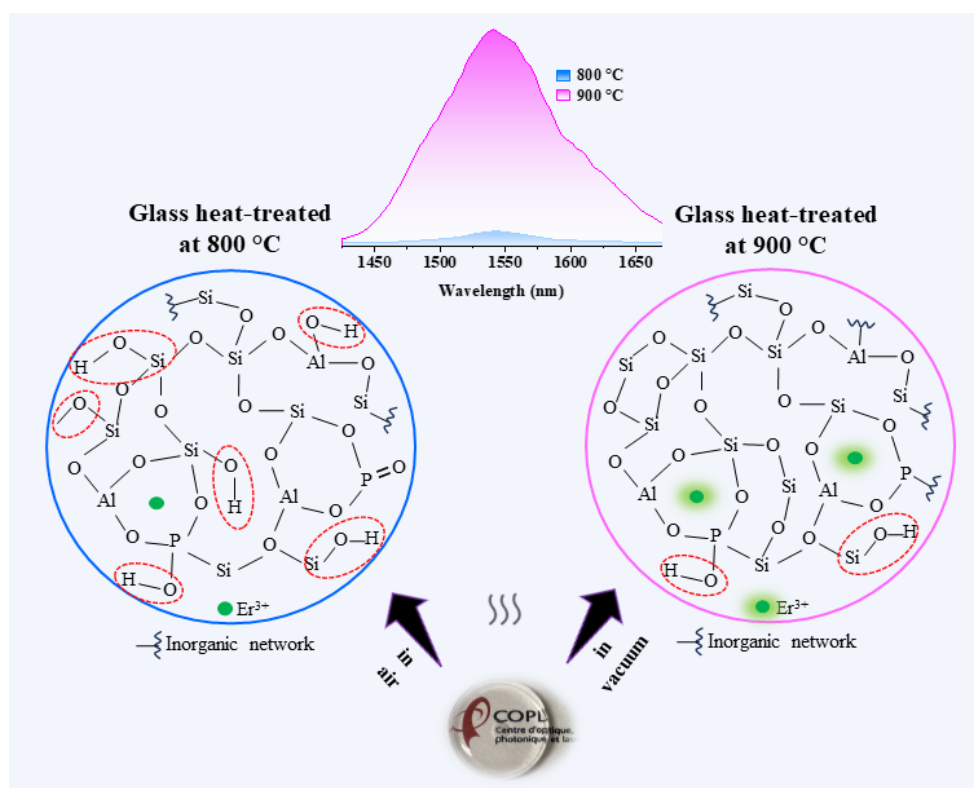


Fig. 2.S5. ^{27}Al TQMAS NMR spectra for the heat-treated materials treatment different SiO_2 concentration ($x = 10, 30, 50, 70$ and 90 mol.%).

CHAPTER 3

Effects of the thermal treatment on structural and luminescence properties of Er^{3+} -doped aluminophosphosilicate glasses obtained by the sol-gel method



3. Effects of the thermal treatment on structural and luminescence properties of Er³⁺-doped aluminophosphosilicate glasses obtained by the sol-gel method

Beatriz H. Costa^{*,a}, Gabriel T. Tayama^b, V. A. G. Rivera^c, Younès Messaddeq^{a,b}, Silvia H. Santagneli^{*,a}

^a Institute of Chemistry, São Paulo State University (UNESP), Araraquara, SP, Brazil

^b Centre d'optique, photonique et laser (COPL), Université Laval, Québec, G1V 0A6, Canada

^c Institute of Physics of São Carlos (IFSC), São Paulo University (USP), São Carlos, SP, Brazil

* Corresponding authors.

E-mail addresses: bh.costa@unesp.br (B.H. Costa), silvia.santagneli@unesp.br (S.H. Santagneli).

<https://doi.org/10.1016/j.jallcom.2024.177112>

Received 2 August 2024; Received in revised form 7 October 2024; Accepted 17 October 2024

Abstract

Transparent glasses were prepared by vacuum heat-treating erbium-doped aluminophosphosilicate gels prepared using the sol-gel method. The evolution of the materials structure with heat-treatment was studied by multinuclear solid-state NMR, Infrared and Raman spectroscopies, X-ray diffraction and SEM microscopy. The optical properties of the resulting materials were assessed by UV-Vis-NIR spectroscopy and luminescence of Er³⁺ ions. Our results showed that the heat treatment under vacuum led to a dense matrix, with an interconnected silicate network through Si-O-Si, Si-O-P and Al-O-P bonds, allowing the formation of different chemical environments for the Er³⁺ ions. Furthermore, heat treatment under vacuum resulted in a remarkable decrease in OH groups, leading to a 180-fold increase in luminescence intensity and FWHM values of around 100 nm for the sample doped with 0.5 mol.% Er³⁺. This new approach offers a novel way for fabricating homogeneous transparent glasses with a wide composition

range, doped with rare earth elements, yielding the development of new optical devices for telecommunications with broadband NIR emission.

Keywords: Erbium-doped; Aluminophosphosilicate glass; Sol-gel method; Optical properties

3.1. Introduction

Rare earth (RE)-doped glasses are key materials for fabricating gain media for laser generation and optical amplification [1,2]. When shaped as optical fibers, these materials are suitable for molecular spectroscopy, medicine, and telecommunications due to their compactness and excellent beam quality [2–5]. In recent years, significant attention has been focused on active glasses and optical fibers covering the C+L band (1530-1625nm) for telecommunications, as the demand for higher data transfer rates has been steadily increasing. Silica (SiO_2)-based optical fibers doped with Er^{3+} ions are widely available due to their transparency in the near-infrared region, along with excellent chemical and mechanical properties [6–8]. However, SiO_2 has low solubility for RE ions, leading to clustering, photoluminescence quenching, and crystallization [9,10]. Furthermore, it is well known that silica glasses doped with Er^{3+} ions exhibit narrow fluorescence emission, covering only the C band. To extend the transmission window into the L-band, several approaches have been explored, including modifications to the silica glass matrix [16,20,21] and the use of alternative glass matrices [22,23]. Therefore, investigating novel glass formers/modifiers and developing new glass processing technologies are promising ways to achieve performance improvements.

In this context, the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ is of great interest in RE-based active optical devices as the presence of Al and P atoms increases RE ion solubility in silicate glasses, thereby reducing clustering, as the strongly polarized Al-O-P bonds help screen the positive charge of RE ions [11–19]. The most common process for producing glass samples is the melt-quenching method. However, the high temperature ($\sim 1700^\circ\text{C}$) required poses challenges in fabricating $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses with high SiO_2 content due to phosphorous evaporation [24–27] and phase separation [28]. In contrast, the sol-gel method [14,29–31] allows the fabrication of SiO_2 glasses at relatively lower temperatures ($\sim 1000^\circ\text{C}$) without significant phosphate loss, as it is immobilized in aluminum-phosphate units [32]. This method enabled the preparation of homogeneous

aluminophosphosilicate (APS) samples, which is unachievable using the melt-quenching method [33–36].

In this work, we report the fabrication of transparent monolithic Er^{3+} -doped aluminophosphosilicate glasses using the sol-gel method which allowed the formation of different chemical environments for the Er^{3+} ions. Hence, a glass composition $95\text{SiO}_2\text{-}5\text{AlPO}_4$ was obtained with varying Er^{3+} concentrations, in which the one doped with 0.5 mol.% Er^{3+} showed the best luminescence results in terms of intensity and broadband NIR emission at $1.5\ \mu\text{m}$ (around 100 nm). The AlPO_4 enhanced the solubility of Er^{3+} in the silica matrix compared to the pure silica glass which allowed a maximum of 1000 ppm. The aluminophosphosilicate gels were prepared from TEOS, aluminum tri-sec-butoxide, hydroxyethyl methacrylate phosphoric acid ester, and 2-(methacryloyloxy)ethyl acetoacetate precursors, then heat-treated to produce glasses with high density and good optical quality.

3.2. Experimental

3.2.1. Synthesis of the Er^{3+} -doped aluminophosphosilicate samples

All reactants were purchased from Sigma-Aldrich and used without further purification. Tetraethyl orthosilicate (TEOS, $\geq 99.0\%$), aluminum tri-sec-butoxide (97.0 %) hydroxyethyl methacrylate phosphoric acid ester (HEMAP, 90.0 %), 2-(methacryloyloxy)ethyl acetoacetate (MAEAA, 95.0 %), methyl alcohol (MeOH, 99.8 %), ethyl alcohol (EtOH, 99.9 %), and distilled water (DIW) were used to synthesize the sol. Nitric acid (HNO_3 65-67 %) and ammonium acetate (NH_4Ac , $\geq 98.0\%$) were used to control the pH. The erbium (III) nitrate pentahydrate ($\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was used as the dopant.

Materials with stoichiometry (mol.%) $95\text{SiO}_2\text{-}5\text{AlPO}_4\text{:}x\text{Er}^{3+}$ were prepared, where $x = 0.05, 0.1, 0.2, 0.5$ and 1.0 mol.%. Initially, the $\text{Al}(\text{MAEAA})_2$ complex was synthesized in a glovebox (argon atmosphere) by adding MAEAA to aluminum tri-sec-butoxide (2:1 ratio) under magnetic stirring. The mixture reacted for approximately 4 h, resulting in a modified aluminum alkoxide that was stable under an ambient atmosphere. The Al-P (1:1) sol was prepared by dissolving the required amount of HEMAP in methanol and adding the $\text{Al}(\text{MAEAA})_2$ complex. The mixture was magnetically stirred for 12 h before methanol was evaporated using a rotary evaporator. The hydrolysis and

condensation of the alkoxysilane were performed using a modified procedure from Cooperstein et al. [30]. TEOS was dissolved in a HNO_3 hydrolysis solution (65 w.t. % EtOH in DIW) under magnetic stirring for 30 min. The NH_4Ac condensation solution was then added, and the mixture was stirred for an additional 10 min. Finally, the required amount of erbium solution was added to the Al-P sol, and the mixture was stirred for 35 min. The erbium solution was prepared by dissolving $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in methanol. The solvent used during the synthesis was then evaporated using a rotary evaporator. Following this, the resulting solutions were stored in plastic vials and aged in an oven at 50°C for 7 days and at 80°C for 5 days, resulting in a dried transparent gel. This synthesis was adapted from the procedure described by Costa et al. [37]. These steps of the synthesis are illustrated in Fig. 3.1. The samples were labeled as APS(T)-x, where T is the heat treatment temperature and x denotes the molar composition of erbium.

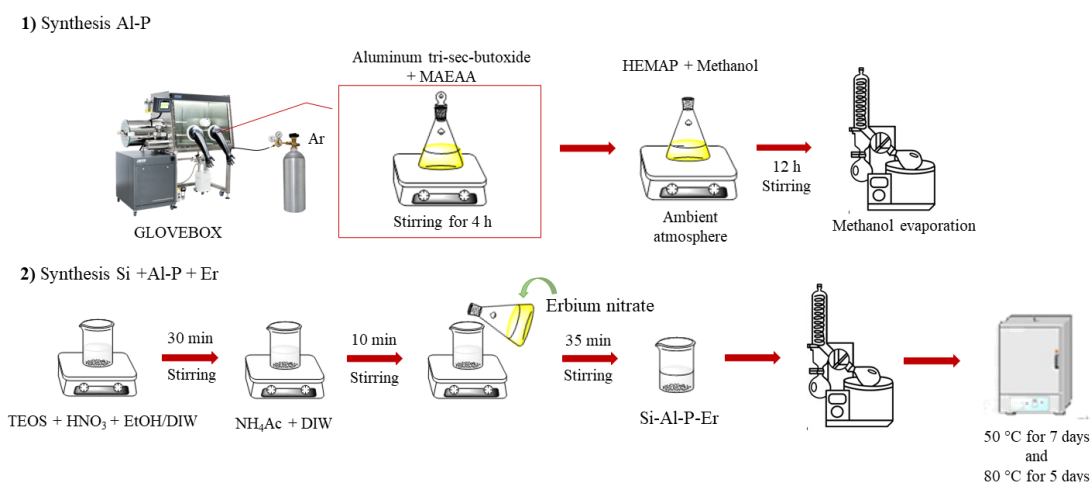


Fig. 3.1. Representative scheme of the sol-gel synthesis route for obtaining the dried aluminophosphosilicate gel.

3.2.2. Heat treatment

The dried gel was heat-treated to remove excess of organic components and achieve densification. The heat treatment was carried out in a furnace (Nabertherm P330) from 80°C up to 800°C , following the heating curve for the debinding process shown in Fig. 3.2. The materials were densified under vacuum at 900°C for 30 min, using a heating rate of 3°C min^{-1} up to 800°C and $0.5^\circ\text{C min}^{-1}$ up to 900°C , with a cooling rate of 3°C min^{-1} . After heat treatment, the final materials had a thickness of 1.2 mm.

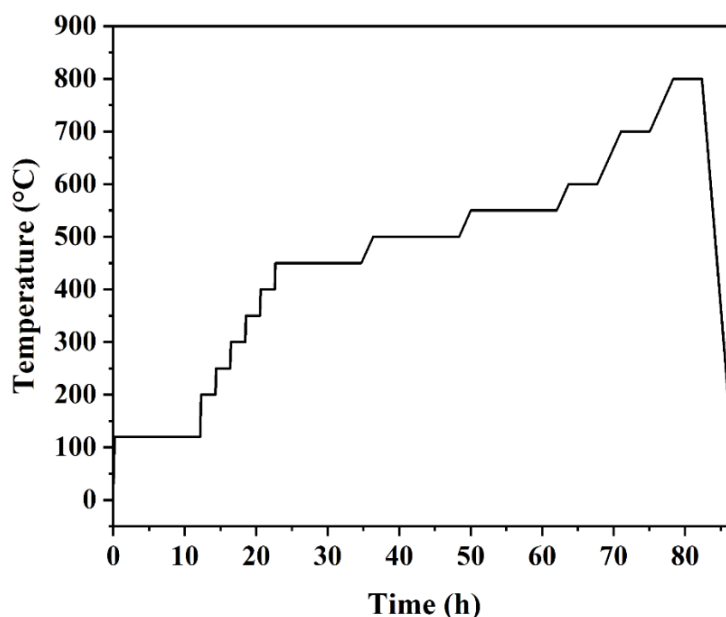


Fig. 3.2. Thermal treatment curve for debinding process of Er^{3+} -doped aluminophosphosilicate gels.

3.2.3. Characterization

The sample densities were measured using an Alfa Mirage MD-300S electronic densimeter based on Archimedes' principle. Anhydrous ethanol was used as an immersion liquid. The concentration of Er^{3+} ions was calculated using the formula: $\text{Er}^{3+} = x \frac{N \cdot \rho}{M}$ where M is the molecular weight of the glass, ρ is the glass density, x is the Er^{3+} mol.%, and N is Avogadro's number ($\sim 6.022 \times 10^{23} \text{ mol}^{-1}$) [38]. The density and concentration of Er^{3+} ions for all samples are presented in Table 1.

FTIR spectra for the materials were collected using a PerkinElmer Frontier FTIR spectrometer. All spectra were recorded in the 1200 - 2700 nm range with 4 nm resolution, and each spectrum was averaged over 16 scans to improve the signal-to-noise ratio.

Raman scattering spectra of the gel and heat-treated materials were collected using a Renishaw inVia spectrometer coupled to a Leica DM2700 microscope. Measurements were performed in the 400-2000 cm^{-1} range using a 785 nm laser.

X-ray diffraction (XRD) measurements were performed using an Aeris Panalytical XRD benchtop diffractometer ($\text{Cu K}\alpha 1/\text{K}\alpha 2$, radiations). XRD patterns were collected in the 5-60° (2θ) range with a step size of 0.02° and a counting time of 1 s per step.

The morphology of the aluminophosphosilicate materials was studied by scanning electron microscopy (SEM) with a FEI Quanta-3D-FEG. The samples were sputter-coated with gold using a Cressington 108 Sputter Coater to minimize surface charging.

Solid-state NMR of ^{29}Si , ^{27}Al , and ^{31}P nuclei in the APS materials was conducted using a Bruker Avance III HD 400WB spectrometer equipped with 4 mm double and triple resonance probes, and for ^1H nuclei using a Bruker Avance Neo spectrometer operating at 14.1 T (600 MHz for ^1H Larmor frequency) equipped with a Bruker HX 1.3 mm probe. The ^{29}Si spectra were measured at a spinning speed of 10 kHz, and the ^{29}Si single pulse NMR spectra were measured using a $\pi/2$ excitation pulse of 3.4 μs and a relaxation time of 600 s. All spectra were externally referenced to Tetramethylsilane (TMS). The ^{31}P and ^{27}Al spectra were recorded at a spinning speed of 14 kHz. The ^{31}P MAS NMR spectra for the APS materials were obtained using a $\pi/2$ excitation pulse of 3.2 μs and a relaxation time of 240 s. The chemical shift was referenced against an external 85% H_3PO_4 standard. The ^{27}Al MAS spectra were collected using a short pulse of 1.4 μs with a relaxation time of 1 s. Chemical shifts are reported relative to a 1 mol L^{-1} $\text{Al}(\text{NO}_3)_3$ aqueous solution. The ^1H single pulse NMR spectra were measured at a spinning speed of 55 kHz, using a $\pi/2$ excitation pulse of 1.2 μs and a relaxation time of 4 s. The chemical shift was referenced using glycine as a secondary reference.

Nitrogen gas physisorption experiments at 77 K were conducted using an ASAP 2020 Plus automatic N_2 adsorption instrument to determine the specific surface area, average pore volume, and pore diameter. Before analyses, the powdered samples were heated under vacuum at 200 $^\circ\text{C}$ for 12 h. Specific surface area values were calculated from adsorption isotherms using the Brunauer-Emmett-Teller (BET) method [39] in the relative pressure (P/P_0) range of 0.003 to 0.90. The average pore volume and diameter were determined from desorption isotherms using the Barrett-Joyner-Halenda (BJH) method [40], assuming cylindrical pores closed at one end.

The refractive index was measured at different wavelengths (532, 632.8, 972.4, 1308 and 1538 nm) using the prism coupling method with an M-Lines (Metricon Model 2010/M Prism Coupler).

The UV-Vis-NIR spectra of the samples were measured using a UV-Vis-NIR spectrophotometer (Cary 5000). The spectra were collected from 300 nm to 2500 nm.

The NIR emission spectra were measured from 1425 nm to 1675 nm, using an OPO excitation source centered at 980 nm, with a frequency of 10 Hz and an average power of 50 mW per pulse. The laser spot had an approximate diameter of 2 mm, and the

signal was collected with an Edinburgh FLS1000 spectrometer coupled to a Tektronix oscilloscope MDO 3022/200 MHz to record the time-dependent decays. Fluoracle software was then used to obtain the NIR emission spectra. All samples were positioned identically during the luminescence measurements to ensure comparability between the different spectra. Each sample was measured three times, and the average was taken to obtain the emission spectrum. The measurement resolution was 4 nm, with a 2 min acquisition time, and 50 nm spectral slit width.

The absorption and emission cross-sections were calculated using the McCumber theory [41], which uses the linear absorption coefficients of Er^{3+} ions for the emission cross-section approximation. The absorption cross-section ($\sigma_{\text{abs}}(\lambda)$) was calculated using the Lambert-Beer equation [33], and the emission cross-section ($\sigma_{\text{ems}}(\lambda)$) was calculated using the McCumber relation [42], which is a good approximation in this case [23].

3.3. Results and discussion

The dried gel at 80 °C and the glass samples after different thermal treatment temperatures are presented in Fig. 3.3. As can be seen, the dried gel samples are yellow (Fig. 3 (a)) and became colorless after heat treatment. The heat treatment is a critical step as the gas release directly affects the final material's integrity and optical properties [43]. At low temperatures, gaseous products are released at low pressure from the volume by capillarity, without causing cracks. At higher temperatures, CO_2 is released from the oxidation of residual carbon components, requiring control of the CO_2 release rate to prevent cracking [43].



Fig. 3.3. Aluminophosphosilicate samples heat-treated at different temperatures (a) gel dried at 80 °C, (b) 550 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C and (f) 900 °C (under vacuum).

The density evolution with heat treatment temperature shows a 26.6% volumetric shrinkage after treating the samples at 800 °C. As the heat treatment temperature increases, pores formed from the evaporation of residual solvents collapse as the matrix densifies, and the glass network becomes more compact due to an increase in Si-O, Al-O

and P-O bonds [44], especially after heat treatment under vacuum (see Table 3.1). This behavior has already been reported by Cooperstein et al. [30].

Table 3.1. Density (ρ) and Er^{3+} concentration values for APS(T)-0.2 samples, where T is the heat treatment temperature and x corresponds to the molar composition of erbium.

Sample	Density (g/cm^3)	Er^{3+} calculated concentration ($\times 10^{18}$ ions/ cm^3)
APS80	1.46	8.01
APS550	1.47	8.08
APS600	1.48	8.11
APS700	1.50	8.27
APS800	1.53	8.44
APS900	1.96	10.77

FTIR and Raman spectra are presented in Fig. 3.S1 (a) and (b), respectively, in the Supporting Information (SI). The FTIR spectra show transmission windows for the APS(T)-0.2 samples in the IR range (1200 – 2700 nm) similar to pure silica glass [45]. The vibrational bands at 1403 and 1900 nm are assigned to the overtones of hydroxyl (OH) bonds stretching, while the band at 2210 nm is assigned to the stretching of water and silanol groups (Si-OH) [46,47]. This clearly indicates incomplete dehydration/densification of the network, because EtOH/DIW are used as solvents to promote the hydrolysis and the formation of Si-OH species. Nonetheless, the heat treatment at 900 °C under vacuum substantially reduces OH groups, leading to condensation reactions between Si with Al and/or P species.

Raman spectra for the APS80-0.2 samples showed vibrational bands at 1725 and 1533 cm^{-1} assigned to the stretching of the carbonyl group (C=O) present in the methacrylate and the C-C stretching of the ring in the $\text{Al}(\text{MAEAA})_2$ complex, respectively. Bands in the range of 1445 to 1410 cm^{-1} were assigned to the symmetrical and asymmetrical deformations of CH_2 and CH_3 groups [32,48], which disappeared after heat treatment. Vibrational bands related to the silica network at 440, 492, 604, and 815 cm^{-1} , corresponding to symmetric bending (ω_1), the planar four-fold ring (D_1), the planar three-fold ring (D_2), and symmetric stretching (ω_3) of the Si-O-Si bonds, respectively, appear as the heat treatment temperature increased. The band at 975 cm^{-1} , assigned to Si-

OH stretching, decreased in intensity at higher temperatures due to condensation reactions [12,14,16,17,49,50]. Additionally, the band assigned to the stretching of the P=O bond [51,52] at 1373 cm^{-1} decreased in intensity with increasing heat treatment temperature, as condensation reactions between phosphate species and silicon and/or aluminum continued at high temperatures [53–55]. The final samples were non-crystalline, as shown by X-ray diffractograms, with a single halo at 23° , indicating amorphous silica [56] (Fig. 3.S2 in SI).

The SEM images, shown in Fig. 3.4, illustrate the samples heat-treated at different temperatures. The images reveal that the samples have a smooth surface, with pore formation due to the burn-off of residual DIW, EtOH, and organic components as the heat treatment temperature increases. At 800°C , the porosity is significantly reduced and completely disappears after heat treatment at 900°C under vacuum, when the matrix densifies. This same behavior was also observed by Wang et al. [33].

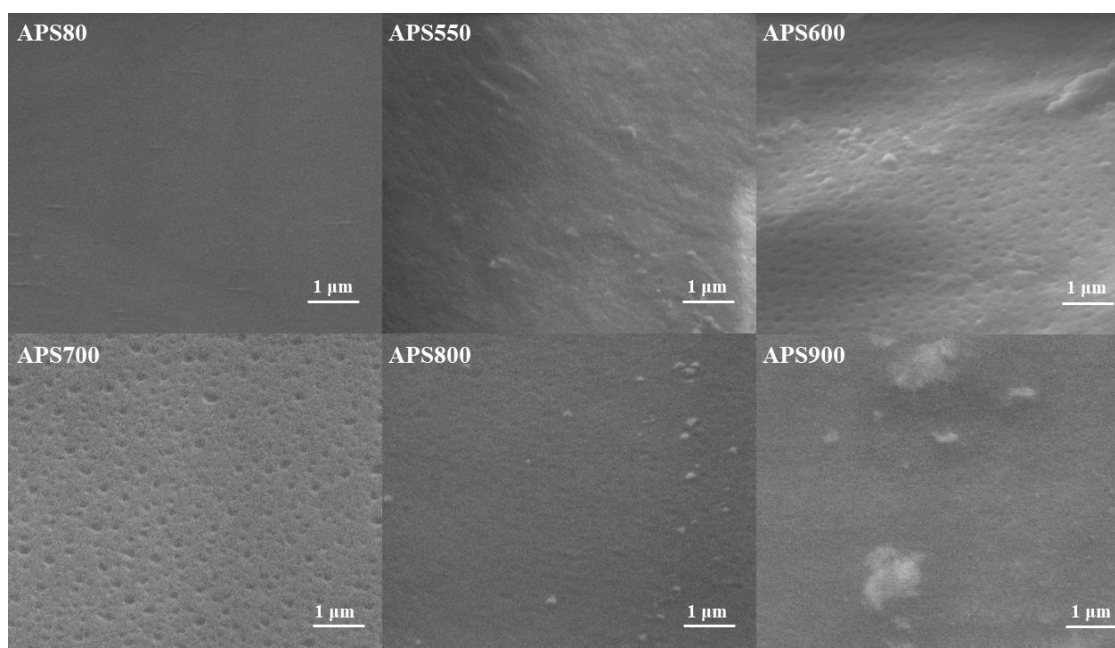


Fig. 3.4. SEM images for the APS(T)-0.2 samples, where T is the heat treatment temperature.

The ^{29}Si MAS spectra for the samples heat-treated at different temperatures show three resonance signals assigned to the Q^n unit, where n represents the number of bridging oxygens (Si-O-Si bonds). The deconvoluted spectra and the evolution of the integrated area for each Q^n unit are presented in Fig. 3.5 and Fig. 3.7 (a), respectively. The relative area and chemical shift obtained for each Q^n unit are summarized in Table 3.S1 in the

Supporting Information section. Three signals at -92, -101, and -110 ppm can be observed, corresponding to Q^2 , Q^3 , and Q^4 units, respectively [57,58]. Q^2 and Q^3 units are associated with the presence of two and one non-bridging oxygens (Si-OH linkages), respectively, while in Q^4 , the silicon atom is linked with four Si atoms through Si-O-Si bonds. As seen, the structural evolution from the gel to the glass shows an increase in homocondensation reactions through the conversion of Q^3 species into Q^4 units. However, the heat treatment up to 800 °C was insufficient to eliminate the superficial OH found in the pores formed during the evaporation of residual solvents and/or degradation of organic compounds. The heat treatment under vacuum at 900 °C led to a decrease in Q^2 and Q^3 species and a further increase in Q^4 units, which was expected since heat treatment under vacuum can reduce OH groups in these materials [30,33].

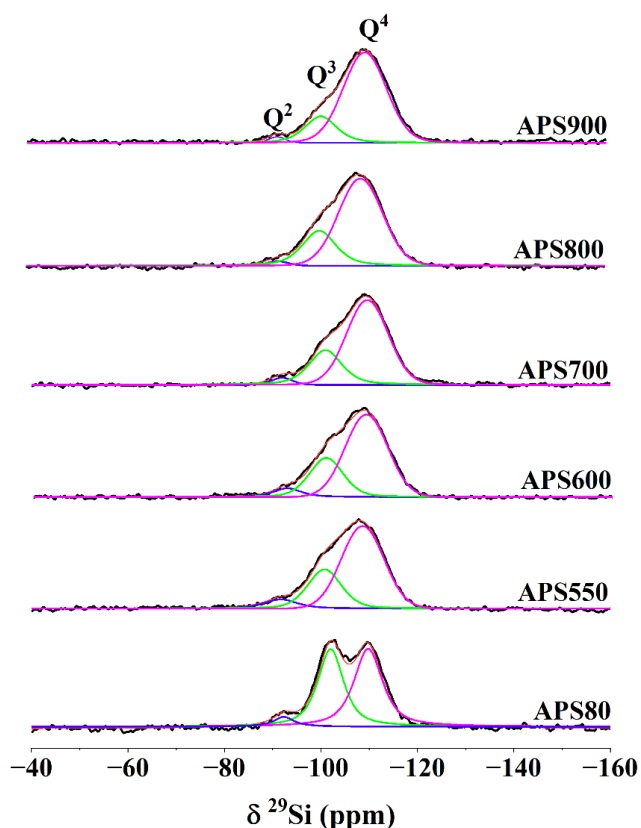


Fig. 3.5. ^{29}Si MAS NMR spectra for the APS(T) samples heat-treated at different temperatures. The solid black line represents the experimental spectrum, and the solid red line represents the deconvolution envelope.

The ^{31}P and ^{27}Al MAS NMR spectra for the heat-treated samples are presented in Fig. 6 (a) and (b), respectively, and the evolution of the integrated area for each $\text{P}_{\text{mAl}}^{\text{n}}$ and Al unit is shown in Fig. 3.7 (b) and (c). The relative area and chemical shift obtained from

deconvoluting each ^{31}P spectrum are summarized in Table 3.S2 in the Support Information. According to the literature [57,59], aluminophosphosilicate glasses are formed by orthophosphate (PO_4) species, which are identified using the $\text{P}_{\text{mAl}}^{\text{n}}$ notation, where **n** represents the number of bridging oxygen per tetrahedron, and **m** represents the number of aluminum units bonded to P units. The ^{31}P NMR spectra showed a broad and asymmetric line, suggesting the formation of four different P chemical environments $\text{P}_{2\text{Al}}^0$, $\text{P}_{3\text{Al}}^0$, $\text{P}_{4\text{Al}}^0$, and $\text{P}_{3\text{Al},1\text{Si}}^0$ at -12, -21, -30, and -37 ppm, respectively, as well as an increase in $\text{P}_{4\text{Al}}^0$ and $\text{P}_{3\text{Al},1\text{Si}}^0$ with the formation and densification of the glass.

The increase in the heat treatment temperature resulted in a higher degree of condensation, observed by the formation of Al-O-P and P-O-Si bonds. Compared to the gel, the heat-treated materials predominantly comprise $\text{P}_{4\text{Al}}^0$ and $\text{P}_{3\text{Al},1\text{Si}}^0$ species. During synthesis, the Si-O-P bond is sensitive to water and can be easily hydrolyzed, but condensation between silicate and phosphate species can occur at high temperatures [53–55]. As shown, heat treatment under vacuum at 900 °C led to the formation of $\text{P}_{4\text{Al}}^0$ and $\text{P}_{3\text{Al},1\text{Si}}^0$ species. The $\text{P}_{3\text{Al},1\text{Si}}^0$ unit shifts toward high-field, indicating gradual changes in the second coordination sphere and the formation of P-O-Si bonds. These results are consistent with the reduction of OH groups observed in the FTIR data, indicating the formation of homo- and heterocondensation bonds between silicate and phosphate species, as observed by the ^{29}Si MAS data presented above, which indicated the homocondensation of silicate species (Si-O-Si) and the formation of Si-O-P linkages.

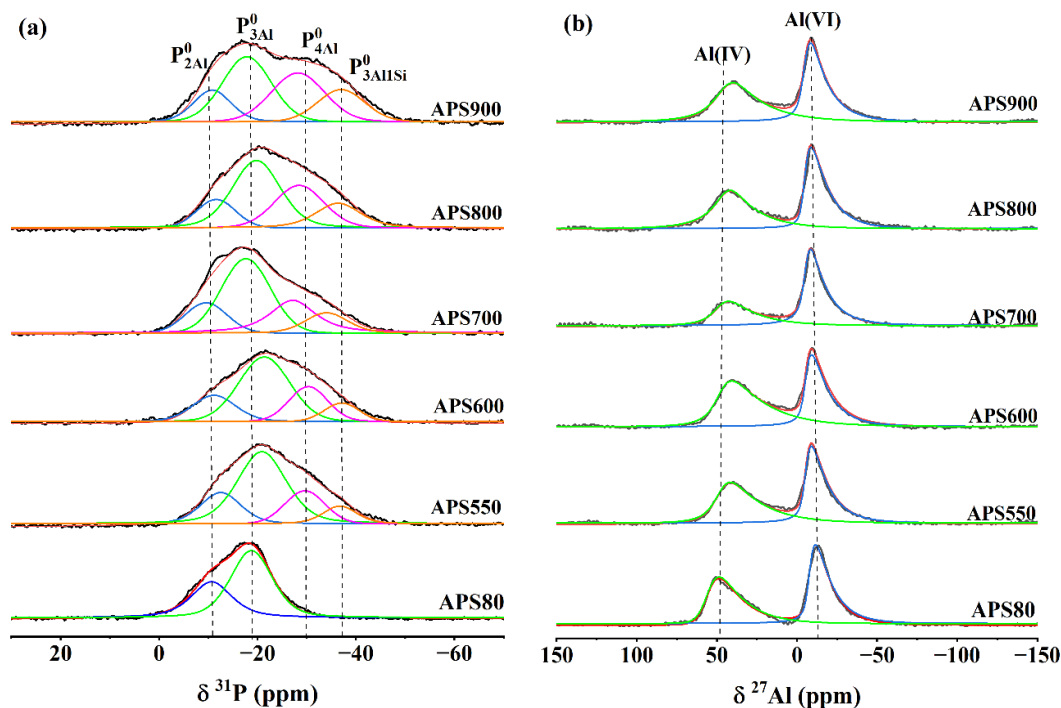


Fig. 3.6. (a) ^{31}P and (b) ^{27}Al MAS NMR for the APS(T) samples heat-treated at different temperatures. The solid black line represents the experimental spectrum, and the solid red line represents the deconvolution envelope.

The ^{27}Al MAS NMR spectra show the presence of aluminum in Al(IV), Al(V) and Al(VI) coordination sites (see Fig. 3.6 (b)). The resonance lines of the Al(VI) and Al(IV) units are observed in the ranges of -4 to -7 ppm and 56 to 46 ppm, respectively. Deconvolution was performed using the Czsimple function in the DMFit program [60], and the fitting results, including the percentage of integrated area, isotropic chemical shift (δ_{iso}), and quadrupolar coupling constant (C_Q), are summarized in Table 3.S3 in the Supporting Information. The formation of Al(IV) and Al(VI) species occurs during gel formation, without significant changes in aluminum coordination sites after heat treatment. During heat treatment, the partially hydrolyzed Al(IV) sites were preferentially bonded to phosphorus, as $\text{Al}(\text{OP})_4$ species are reported to be centered at 45 ppm [57,59]. These results indicate that most phosphate species are bonded to aluminum atoms, which is consistent with the ^{31}P NMR data. Above 600 °C, we observed a lower proportion of Al(IV) units and a shift to higher chemical shift values, indicating the formation of Al-O-Si bonds. However, at 800 and 900 °C, there is a higher proportion of Al(IV) units, with a low contribution of Al(V) units. The chemical shift values of Al(IV) units shift to lower values, confirming that the Al(IV) units are preferentially bonded to phosphate species. Indeed, the heat treatment favors the formation of AlPO_4 in the matrix, and condensation

reactions between phosphate and silicate species are promoted, while aluminum bonds preferentially to phosphate species. However, we cannot rule out the formation of Si-O-Al bonds, which have the same frequency range as Si_{1Al}^4 units (the nomenclature Si_m^n is used, where **n** refers to the number of Si-O-Si bonds and **m** represents the number of Si-O-Al bonds) as the Q^3 units in the ^{29}Si NMR spectrum [34,61–63]. During synthesis, the high Si content favors heterocondensation between aluminum and phosphate species (Al-O-P), with a minor occurrence of Al-O-Si bonds.

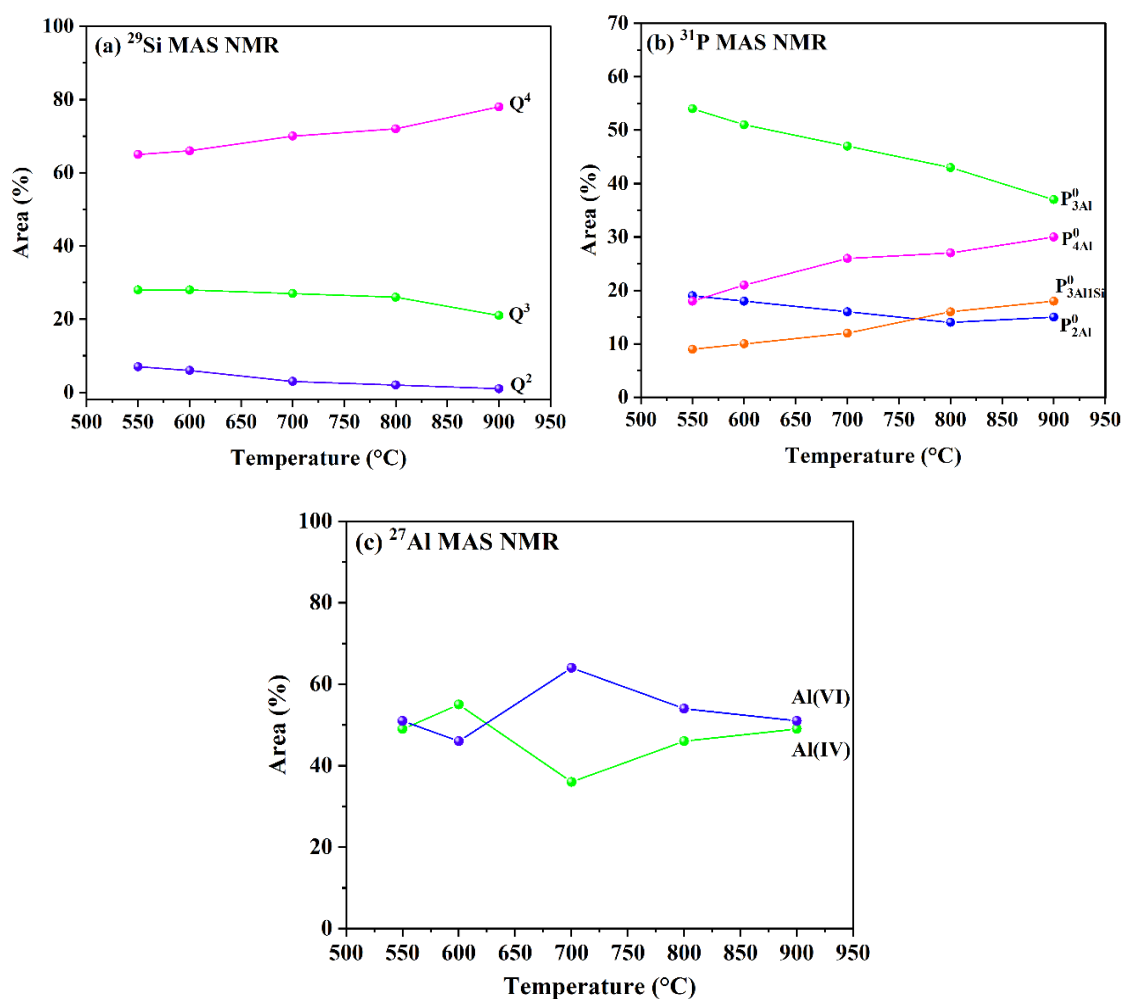
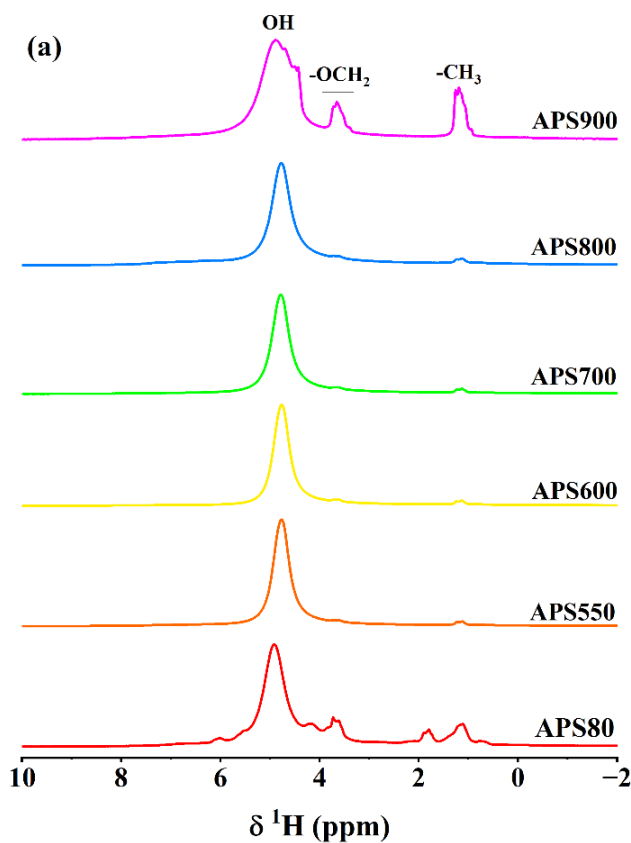


Fig. 3.7. Area's evolution as a function of the heat treatment temperature of (a) Q^n units in ^{29}Si MAS NMR, (b) P_{mAl}^n units in ^{31}P MAS NMR and (c) Al units in ^{27}Al MAS NMR.

The 1H MAS NMR normalized spectra for the heat-treated samples are presented in Fig. 3.8 (a). Similar SiAlP materials have been studied by Tayama et al. [32,64], and the APS80 material showed signals between 0 and 2 ppm, corresponding to $-CH_2$ and $-CH_3$ groups, which mostly disappeared after the debinding process when the organic

compounds were released. After heat treatment at high temperatures (above 550 °C), the APS(T) materials showed only signals referred to OH groups (from water) at 4.8 ppm, and signals referred to -OCH₂ and -CH₃ from ethanol at 3.6 and 1.2 ppm, respectively [64–67].

In the ¹H NMR data shown in Fig. 3.8 (b), a decrease in the OH signal is observed as the heat treatment temperature increases. After heat treatment under vacuum at 900 °C, there was a significant reduction in the intensity of this signal, which is consistent with the FTIR results shown in Fig. 3.S1 in the Supporting Information section. However, the signal associated with ethanol at 1.2 ppm remains unchanged regardless of the heat treatment temperature, even after vacuum treatment, suggesting the entrapment of solvent inside the pores formed during the debinding process.



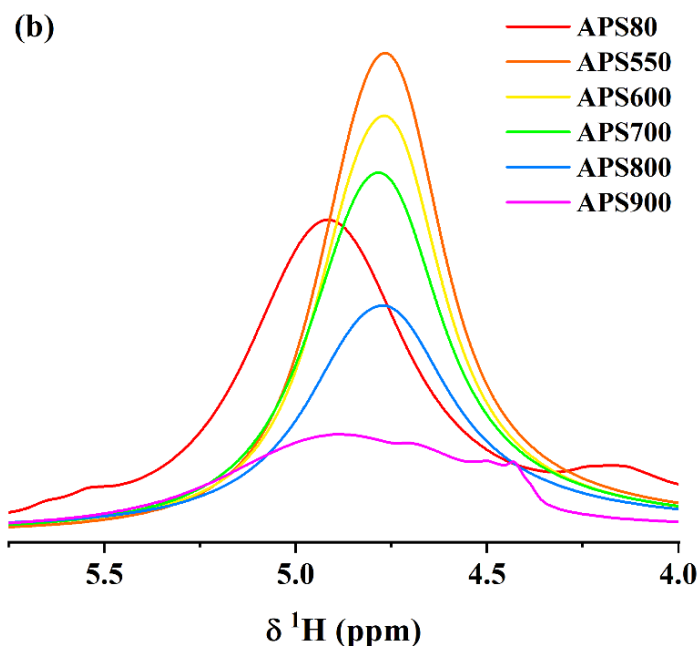


Fig. 3.8. (a) ^1H MAS NMR spectra and (b) OH signal in ^1H MAS NMR spectra for the APS(T) samples heat-treated at different temperatures.

Nitrogen gas adsorption and desorption isotherms for the APS samples obtained at 800 °C in air and 900 °C in vacuum are shown in Fig. 3.S3 (in the Supporting Information), and the values of the surface area, average pore volume, and pore diameter are compiled in Table 3.2. The APS800 sample exhibits a Type I(b) isotherm profile, typical of materials with a broad range of pore size distributions, including wider micropores and possibly narrow mesopores ($< \sim 2.5$ nm) [68,69]. Additionally, this material exhibited high adsorbed gas volumes without hysteresis. In contrast, the APS900 sample shows a Type V isotherm without hysteresis, revealing low adsorbed gas volumes, characteristic of mesoporous materials [68,69]. As can be seen, the values of surface area, average pore volume, and pore diameter decreased after heat treatment under vacuum, likely due to the reduction of OH groups and densification of the matrix, as confirmed by FTIR and NMR data. This same behavior was also observed by Araujo et al. [59] for glasses obtained by the sol-gel method, as this synthesis route can generate surface pores during heat treatment due to the evaporation of residual solvent and the degradation of organic components.

Table 3.2. BET surface area (S_{BET}), the average pore volume (V_p), and the average pore diameter (r_p) for the APS800 and APS900 samples heat-treated in air and under vacuum, respectively.

	S_{BET} (m^2/g)	V_p (cm^3/g)	r_p (nm)
APS800	317.14 ± 5.39	0.13	1.65
APS900	72.91 ± 1.57	0.03	1.56

The refractive indices for the APS800-0.2 and APS900-0.2 glasses at different wavelengths are shown in Fig. 3.9, compared with the refractive indices of pure fused SiO_2 glass. It can be observed that the refractive index values for both glasses are close to those of pure fused SiO_2 glass [70]. However, the difference is related to the proportion of Al_2O_3 - P_2O_5 present in these materials, as the equimolar concentration can decrease the refractive index due to the formation of AlPO_4 [16,18,71]. Additionally, the difference in refractive indices between the two samples is related to the presence of non-bridging oxygen (NBO) bond in the glass matrix, which decreases the refractive index [72,73]. As we observed, the APS900-0.2 glass heat-treated under vacuum showed slightly higher refractive index values than the APS800-0.2 glass heat-treated in air, due to the presence of fewer NBO bond in its matrix, as confirmed by NMR data, which indicated a higher condensation degree between silicate, phosphate or/and aluminum species.

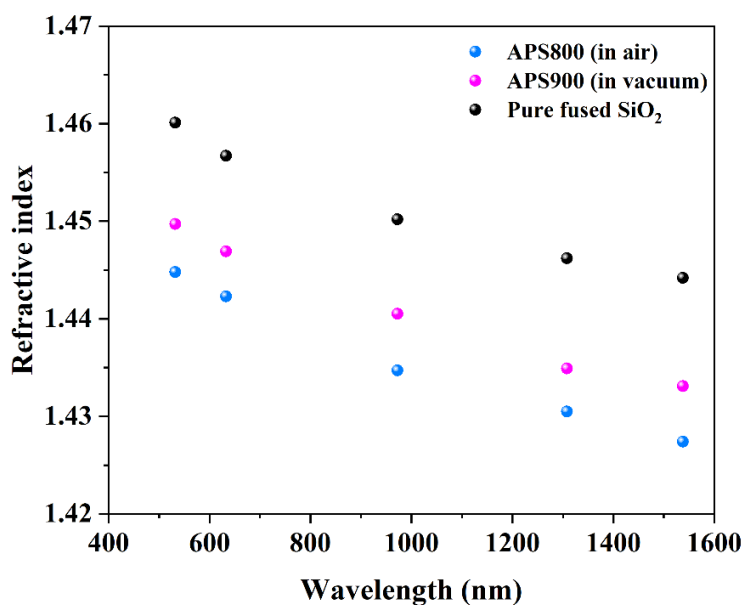


Fig. 3.9. Refractive index (± 0.0001) values for the APS800-0.2 and APS900-0.2 samples heat-treated at 800 and 900 °C in air and under vacuum, respectively, and for pure fused SiO_2 glass.

The absorption spectrum of the heat-treated materials at different temperatures in the UV-Vis-NIR region is shown in Fig. 3.10. As observed, the APS80-0.2 sample does not exhibit absorption bands in the visible range, but bands referring to organic groups are still visible in the UV and NIR ranges. These bands decrease as the temperature increases, due to the burning off of organic groups. However, bands associated with OH groups from water and silanol groups can still be observed at 1403, 1903, and 2264 nm [30,33]. After heat treatment, particularly at high temperatures (700 and 800 °C), the samples show absorption bands at 379, 520, 650, and 975 nm, corresponding to the $^4I_{15/2} \rightarrow \{^4G_{11/2}, ^2H_{11/2}, ^4F_{9/2}, \text{ and } ^4I_{11/2}\}$ transitions of Er^{3+} ions, respectively [74]. However, the band at 1535 nm, assigned to the transition of $^4I_{15/2} \rightarrow ^4I_{13/2}$ of Er^{3+} ions, could not be observed due to the overlapping with the O-H stretching broadband at 1403 nm (originated from both Si-OH groups and H_2O molecules), which is responsible for luminescence quenching in Er^{3+} -doped glasses through non-radiative relaxation from the $^4I_{13/2}$ energy level [75].

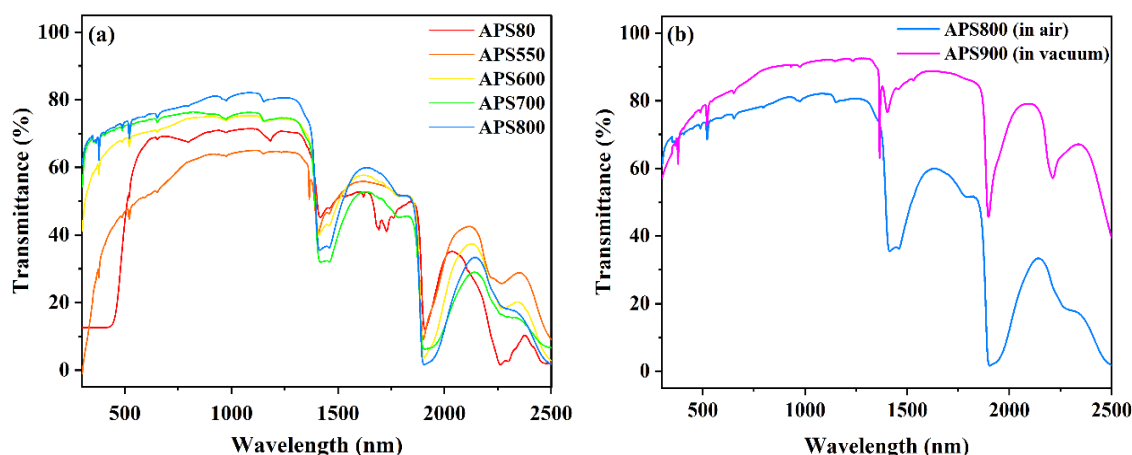


Fig. 3.10. UV-Vis-NIR absorption spectra for the (a) APS(T)-0.2 samples and (b) APS800-0.2 and APS900-0.2 glasses heat-treated at 800 °C in air and 900 °C in vacuum, respectively.

As shown in Fig. 3.10 (b), the UV-Vis-NIR absorption spectrum for the APS800-0.2 glass still exhibits the band referring to OH stretching at 1403 and 1903 nm from water, which overlaps with the 1535 nm absorption band of Er^{3+} ions, as well as the band attributed to OH from silanol groups at 2264 nm [30,33,76]. In the APS900-0.2 glass, after heat treatment under vacuum, there was a decrease in all bands referring to OH groups, mainly the band at 1403 nm, allowing the Er^{3+} band at 1535 nm to be observed.

The Er^{3+} emission spectra for the APS(T)-x samples with different Er^{3+} contents (0.05 to 1.0 mol.%) heat-treated at 800 °C in air and 900 °C under vacuum are shown in Fig. 3.11 (a) and (b), respectively. All samples heat-treated at both temperatures exhibited a luminescence signal at 1540 nm. However, the APS800-x glasses showed much lower luminescence - approximately 180 times less - compared to the APS900-x glasses heat-treated under vacuum. This reduced luminescence is attributed to the higher amount of water, as shown in Fig. 3.10 (b), which contributes to non-radiative relaxation of the Er^{3+} ions [75]. In contrast, the APS900-x glasses exhibited a broad emission band in the range of 1450 to 1650 nm. Additionally, luminescence intensity increases with the amount of Er^{3+} added to the matrix, reaching a maximum of 0.5 (mol.%) (Fig. 11). Beyond this concentration, the luminescence intensity decreases due to the formation of erbium clusters. It is important to note that the lineshape spectrum obtained in our measurements differs from the traditional silica lineshape, which can be assigned to the addition of Al and P and the new sol-gel process used.

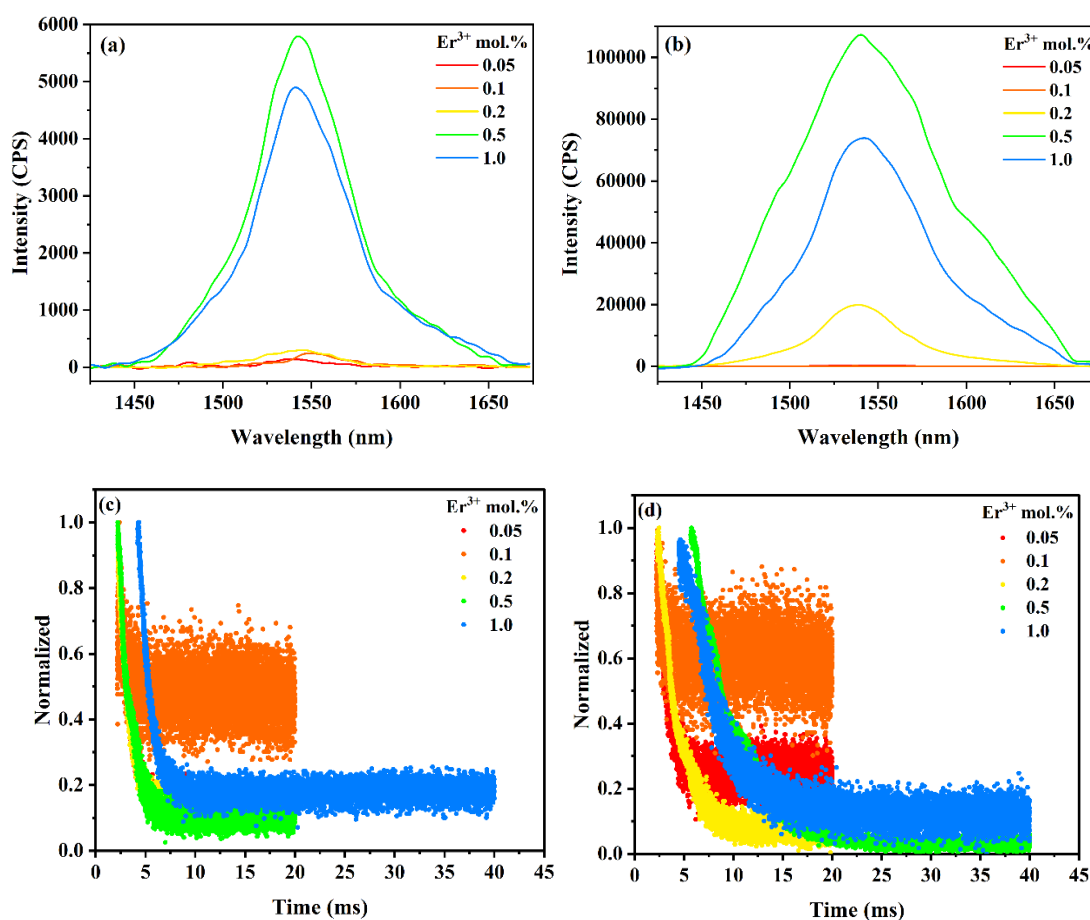


Fig. 3.11. Non-normalized intensity emission spectra heat-treated (a) in air at 800 °C and (b) under vacuum at 900 °C. Normalized lifetime decay curves heat-treated (c) in air at

800 °C and (d) under vacuum at 900 °C for APS materials containing different Er^{3+} content (0.05 to 1.0 mol.%).

The broadband (~ 101 nm) observed in the Al/P = 1 APS900-0.5 sample makes it a promising candidate for optical amplifiers in the C+L bands (1530 $\sim$ 1625 nm), as it may improve gain flatness in these bands. The lifetime decay curves of all samples shown in Fig. 3.11 (c) and (d) exhibits a bi-exponential behavior, described by the equation $y = y_0 + A_1 e^{-(x-x_0/t_1)} + A_2 e^{-(x-x_0/t_2)}$. The R^2 values obtained from the decay exponential fit are greater than 0.99, indicating a good approximation of the lifetime values. The lifetime and FWHM values are shown in Table 3.3. It can be observed that the lifetime values for the materials heat-treated at 800 °C in air are lower compared to those heat-treated under vacuum.

Table 3.3. Lifetime (ms) and FWHM (nm) values for the APS(T)-x (x is the molar composition of erbium) samples heat-treated at 800 °C in air and 900 °C under vacuum.

Er^{3+} content (mol.%)	at 800 °C (in air)		at 900 °C (in vacuum)	
	Lifetime (ms)	FWHM (nm)	Lifetime (ms)	FWHM (nm)
0.05	0.98	39.6	1.00	44.1
0.1	0.99	30.1	0.98	52.8
0.2	1.00	44.9	2.00	56.8
0.5	1.15	65.3	4.45	101.7
1.0	1.06	62.9	3.00	79.4

For the sake of comparison, the lifetime and FWHM values for the sample containing 0.5 mol.% of Er^{3+} in this work, along with those from other studies in the literature based on Er^{3+} -doped silicate glasses containing Al and/or P synthesized by the sol-gel method, are compiled in Table 3.4.

Table 3.4. Lifetime and FWHM values for Er^{3+} -doped silicate glasses containing Al and/or P obtained by the sol-gel method reported in this research and in the literature.

Glass	Method	Lifetime (ms)	FWHM (nm)	Reference
Er^{3+} -doped Aluminophosphosilicate	Sol-gel	4.45	101.7	This work
$\text{Er}^{3+}/\text{Yb}^{3+}$ -doped Phosphosilicate	Sol-gel	1.29	32.8	[33]
$\text{Er}^{3+}/\text{Yb}^{3+}$ -doped Aluminophosphosilicate	Sol-gel + Melt-quenching	11.9	45.6	[16]
$\text{Er}^{3+}/\text{Yb}^{3+}$ -doped Phosphosilicate	Sol-gel + Melt-quenching	8.99	-	[21]

Table 3.4 shows that the lifetime and FWHM values obtained in this work are higher than those reported by Wang et al. [33], who used the sol-gel method and appropriate heat treatment to obtain transparent monolithic samples. In contrast, Shao et al. [16] and Cheng et al. [21] obtained higher values, as they combined sol-gel and melt-quenching methods. This combination results in a transparent glass with a fully densified matrix and no OH groups, which is responsible for luminescence quenching. However, in the present work, a transparent monolithic glass was achieved through heat treatment maintaining the material's structure. The FWHM value was higher than in all the studies presented in Table 3.4, indicating its potential for use in multiple telecommunication channels as this broadband covers the C + L windows (1530-1625 nm). Additionally, the glass obtained in this work was not doped with Yb^{3+} , which typically enhances the luminescence intensity and lifetime values of Er^{3+} through energy transfer between the two ions. Our approach provides homogeneous transparent glass doped with Er^{3+} ions produced at a lower temperature. Furthermore, the luminescence properties can be improved by densifying the matrix at a higher temperature and using Yb^{3+} as a co-dopant.

Our results are comparable to Er^{3+} -doped fibers obtained by Modified Chemical Vapor Deposition (MCVD) methods [11], in which the authors reported obtaining a single-mode erbium-doped aluminophosphosilicate fiber doped with 0.06 mol.% of Er_2O_3 , 1.77 mol.% of Al_2O_3 and 1.04 mol.% of P_2O_5 with NIR emission at 1584 nm and lifetime value of 11 ms. However, using the method described here to obtain fibers based on SiAlP also results in some issues such as phase separation, crystallization, and

compositional deviations similar to those observed with the melt-quenching method. Since P_2O_5 is well-known for its low melting temperature ($\sim 340^\circ\text{C}$) and sublimation point ($\sim 360^\circ\text{C}$), it is challenging to avoid its evaporation at high temperatures (around $1600\text{--}2300^\circ\text{C}$) during the MCVD process. Furthermore, the sublimation process of P_2O_5 leads to the loss of most of the doped REs and Al from the fiber preform core [77]. Therefore, the sol-gel method can be combined with the MCVD method for producing erbium-doped aluminophosphosilicate glass preforms. Indeed, this strategy is still underexplored in the literature, with only one study reported by Yang et al. [78]. In this study, the authors combined the sol-gel method with the MCVD method and achieved an optical fiber with a composition of $96.7\text{SiO}_2\text{--}3\text{Al}_2\text{O}_3\text{--}0.3\text{Er}_2\text{O}_3$ (in mol.%) with high optical properties and good doping homogeneity due to the sol-gel method.

The absorption and emission cross-section spectra for the APS900-x were calculated using the McCumber theory, as only these materials exhibited the erbium absorption band at 1535 nm in the UV-Vis-NIR spectra (Fig. 3.S4 in the Supporting Information). Fig. 3.12 (a) shows the absorption and emission cross-sections for Er^{3+} ions spectra in the APS900-0.5 sample. The absorption and emission cross-sections for the materials doped with 0.2 and 1.0 mol.% of Er^{3+} are shown in Fig. 3.S5 in the Supporting Information section. The $\sigma_{\text{abs}}(\lambda)$ and $\sigma_{\text{ems}}(\lambda)$ values for these materials are compiled in Table 5, which can be compared with the 7.9×10^{-21} and $7.3 \times 10^{-21} \text{ cm}^2$ values reported by Mandal et al. [79] for $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped silica glass obtained via the sol-gel method. To achieve a high gain for fabricating fiber amplifiers, the emission cross-section should be as high as possible. Therefore, the gain spectra for the APS900-x samples were calculated using the formula $\text{Gain} = [p \times \sigma_{\text{ems}}(\lambda) - (1 - p) \times \sigma_{\text{abs}}(\lambda)]$, where p represents the percentage of Er^{3+} ions in the excited state (the population inversion ratio between the $^4I_{13/2}$ and $^4I_{15/2}$ energy levels). For the APS900-0.5 sample, this is shown in Fig. 3.12 (b), while the gain spectra for the materials doped with 0.2 and 1.0 mol.% of Er^{3+} are shown in Fig. 3.S5 in the SI. It has been observed that the gain becomes positive if the population inversion exceeds $p = 0.6$. This suggests that a flat amplification bandwidth between 1510 and 1550 nm can be achieved with a common population inversion greater than 60% via optical pumping. This amplification cross-section covers the 1530–1565 nm (C) channel in the optical telecommunication window. In the studies presented in Table 3.4, the authors did not calculate the absorption and emission cross-sections or gain for Er^{3+} ions in the glasses, primarily for erbium-doped silicate glasses obtained by the sol-gel method. Additionally, the literature does not report data for these parameters for comparison.

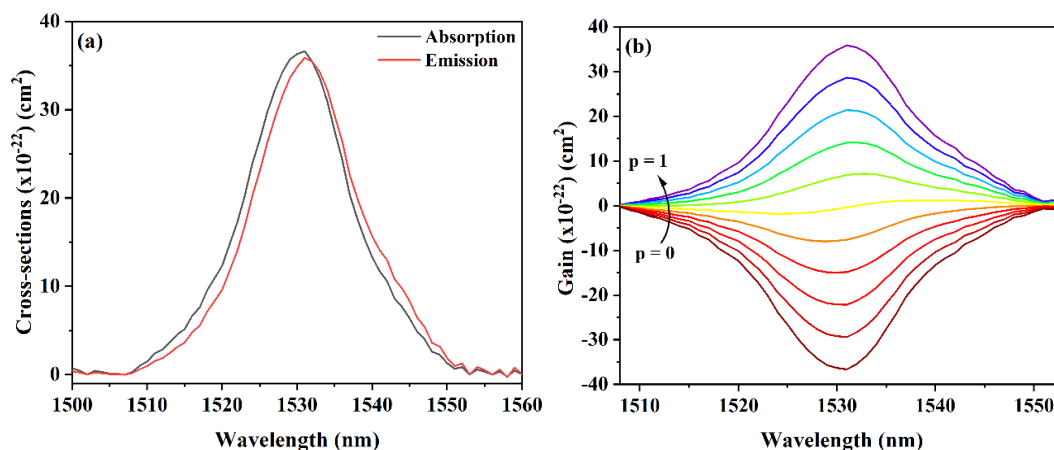


Fig. 3.12. (a) Absorption and emission cross-sections of APS900-0.5 and (b) Gain spectra of the APS900-0.5 sample determined from Fig. (a).

Table 3.5. Absorption ($\sigma_{\text{abs}}(\lambda)$) and emission ($\sigma_{\text{ems}}(\lambda)$) cross-sections of the Er^{3+} ions for the APS900-x materials (x is the molar composition of erbium).

Er^{3+} content (mol.%)	σ_{abs} (cm^2)	σ_{ems} (cm^2)
0.2	7.55×10^{-23}	7.25×10^{-23}
0.5	3.63×10^{-22}	3.48×10^{-22}
1.0	3.91×10^{-22}	3.76×10^{-22}

Based on these results, the structural evolution from the gel to the material heat-treated at 800 °C in air led to an increase in Q^4 units in the ^{29}Si NMR data due to the homocondensation of silicate species and increased connectivity of silicon atoms with aluminum and phosphate. However, this material still presented OH groups from water and silanol groups, as confirmed by UV-Vis-NIR data, which is characteristic of the sol-gel process. The heat treatment under vacuum at 900 °C led to the densification of the matrix, as shown by N_2 gas physisorption analysis, and increased the formation of Si-O-Si, Si-O-P, and Al-O-P linkages, as observed by ^{29}Si , ^{31}P , and ^{27}Al NMR data. This heat treatment also resulted in a decrease in OH groups, as supported by absorption spectra and ^1H NMR data. The structural changes induced by heat treatment under vacuum increased the luminescence intensity, lifetime, and FWHM values. The luminescence study showed that Al and P species enhanced the solubility of rare earth elements compared to pure silica glass (with a maximum erbium content of 1000 ppm) [8]. However, above 0.5 mol.% of Er^{3+} content, luminescence quenching is observed, probably due to the formation of erbium clusters, which leads to non-radiative relaxation.

3.4. Conclusion

The Er^{3+} -doped aluminophosphosilicate glasses with high optical quality were synthesized using the sol-gel method. FTIR and ^1H NMR results indicated a small amount of hydroxyl and silanol groups, which are typical of sol-gel glass materials. The heat treatment under vacuum improved matrix densification and promoted the formation of Si-O-Si, Si-O-P, and Al-O-P bonds. These results were supported by FTIR, UV-Vis-NIR, and ^1H MAS NMR data, which showed a decrease in OH groups after heat treatment under vacuum. This led to an increase in luminescence intensity by approximately 180 times and a FWHM value of around 100 nm, especially for the sample doped with 0.5 mol.% Er^{3+} . However, luminescence quenching was observed for compositions containing more than 0.5 mol.% Er^{3+} , likely due to cluster formation. The heat treatment under vacuum also increased the bridging oxygen (BO) bond in the silica matrix, resulting in a higher refractive index value. Finally, absorption and emission cross-sections were calculated, and the gain became positive when the population inversion was greater than 60% via optical pumping. The sol-gel method allowed the fabrication of SiPAl glasses doped with Er^{3+} ions at a lower temperature compared to the conventional high-temperature melt-quenching method ($\sim 1700^\circ\text{C}$). Therefore, this new synthetic route can be applied across a wide composition range, leading to the development of new optical devices for telecommunications with broadband emission.

CRedit authorship contribution statement

Silvia H. Santagneli: Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition. **Beatriz H. Costa:** Writing – original draft, methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gabriel T. Tayama:** Writing – review & editing, Validation, Conceptualization. **V.A.G. Rivera:** Writing – review & editing, Validation, Methodology, Conceptualization. **Younès Messaddeq:** Writing – review & editing, Validation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to gratefully acknowledge the Brazilian funding agencies FAPESP (process 2018/24735–3) and CAPES. B.C. acknowledges the CAPES and CAPES PrInt fellowship (finance code 001). Y. Messaddeq acknowledges the Sentinelle Nord.

Data Availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2024.177112.

References

- [1] M.J. Weber, Lawrence Livermore National Laboratory University of California, Livermore, CA 94550, USA, *J. Non. Cryst. Solids*. 123 (1990) 208–222.
- [2] J. Ballato, H. Ebendorff-Heidepriem, J. Zhao, L. Petit, J. Troles, Glass and process development for the next generation of optical fibers: A review, *Fibers*. 5 (2017) 1–25. <https://doi.org/10.3390/fib5010011>.
- [3] P. Peterka, I. Kašík, V. Matějec, W. Blanc, B. Faure, B. Dussardier, G. Monnom, V. Kubeček, Thulium-doped silica-based optical fibers for cladding-pumped fiber amplifiers, *Opt. Mater. (Amst)*. 30 (2007) 174–176. <https://doi.org/10.1016/j.optmat.2006.11.039>.

- [4] H. Inaba, Y. Akimoto, K. Tamura, E. Yoshida, T. Komukai, M. Nakazawa, Experimental observation of mode behavior in erbium-doped optical fiber ring laser, *Opt. Commun.* 180 (2000) 121–125. [https://doi.org/10.1016/S0030-4018\(00\)00669-6](https://doi.org/10.1016/S0030-4018(00)00669-6).
- [5] H. El Hamzaoui, M. Bouazaoui, B. Capoen, Sol-Gel Derived Optical and Photonic Materials, *Sol-Gel Deriv. Opt. Photonic Mater.* (2020) 315–346. <https://doi.org/10.1016/c2018-0-02962-x>.
- [6] J.F. Destino, N.A. Dudukovic, M.A. Johnson, D.T. Nguyen, T.D. Yee, G.C. Egan, A.M. Sawvel, W.A. Steele, T.F. Baumann, E.B. Duoss, T. Suratwala, R. Dylla-Spears, 3D Printed Optical Quality Silica and Silica–Titania Glasses from Sol–Gel Feedstocks, *Adv. Mater. Technol.* 3 (2018) 1–10. <https://doi.org/10.1002/admt.201700323>.
- [7] F. Kotz, P. Risch, D. Helmer, B.E. Rapp, High-Performance Materials for 3D Printing in Chemical Synthesis Applications, *Adv. Mater.* 31 (2019). <https://doi.org/10.1002/adma.201805982>.
- [8] L.D. Iskhakova, F.O. Milovich, M.E. Likhachev, D.S. Lipatov, M. V. Yashkov, A.S. Lobanov, A.N. Guryanov, Analysis of elemental distributions and phase separation in rare-earth-doped silica-based fiber preforms and optical fibers, *J. Non. Cryst. Solids.* 554 (2021) 120616. <https://doi.org/10.1016/j.jnoncrysol.2020.120616>.
- [9] K. Kajihara, S. Kuwatani, K. Kanamura, Sol-Gel synthesis of rare-earth and phosphorus codoped monolithic silica glasses from a cosolvent-free phase-separating system, *Appl. Phys. Express.* 5 (2012) 0–3. <https://doi.org/10.1143/APEX.5.012601>.
- [10] K. Kaneko, K. Kajihara, K. Kanamura, Cosolvent-free sol-gel synthesis of rare-earth and aluminum codoped monolithic silica glasses, *J. Ceram. Soc. Japan.* 121 (2013) 299–302. <https://doi.org/10.2109/jcersj2.121.299>.
- [11] M.-P. Lord, L. Talbot, O. Boily, T. Boilard, G. Gariépy, S. Grelet, P. Paradis, V. Boulanger, N. Grégoire, S. Morency, Y. Messaddeq, M. Bernier, Erbium-doped aluminophosphosilicate all-fiber laser operating at 1584 nm, *Opt. Express.* 28 (2020) 3378. <https://doi.org/10.1364/oe.379574>.
- [12] S.G. Kosinski, D.M. Krol, T.M. Duncan, D.C. Douglas, J.B. MacChesney, J.R. Simpson, Raman and NMR spectroscopy of SiO₂ glasses CO-doped with Al₂O₃

- and P₂O₅, *J. Non. Cryst. Solids*. 105 (1988) 45–52. [https://doi.org/10.1016/0022-3093\(88\)90336-5](https://doi.org/10.1016/0022-3093(88)90336-5).
- [13] W. Huang, R.R.A. Syms, S. Member, Sol-Gel Silica-on-Silicon Buried-Channel EDWAs, 21 (2003) 1339–1349.
- [14] B. Glorieux, T. Salminen, J. Massera, M. Lastusaari, L. Petit, Better understanding of the role of SiO₂, P₂O₅ and Al₂O₃ on the spectroscopic properties of Yb³⁺ + doped silica sol-gel glasses, *J. Non. Cryst. Solids*. 482 (2018) 46–51. <https://doi.org/10.1016/j.jnoncrysol.2017.12.021>.
- [15] M.M. Bubnov, V.N. Vechkanov, A.N. Gur'Yanov, K. V. Zotov, D.S. Lipatov, M.E. Likhachev, M. V. Yashkov, Fabrication and optical properties of fibers with an Al₂O₃-P₂O₅-SiO₂ glass core, *Inorg. Mater.* 45 (2009) 444–449. <https://doi.org/10.1134/S0020168509040220>.
- [16] C. Shao, F. Wang, Y. Jiao, S. Wang, X. Wang, C. Yu, L. Hu, Relationship between glass structure and spectroscopic properties in Er³⁺/Yb³⁺/Al³⁺/P⁵⁺-doped silica glasses, *Opt. Mater. Express*. 10 (2020) 1169. <https://doi.org/10.1364/ome.389769>.
- [17] F. Wang, C. Shao, C. Yu, S. Wang, L. Zhang, G. Gao, L. Hu, Effect of AlPO₄ join concentration on optical properties and radiation hardening performance of Yb-doped Al₂O₃-P₂O₅-SiO₂ glass, *J. Appl. Phys.* 125 (2019). <https://doi.org/10.1063/1.5096469>.
- [18] S. Kuhn, S. Hein, C. Hupel, J. Nold, N. Haarlammert, T. Schreiber, R. Eberhardt, A. Tünnermann, Modelling the refractive index behavior of Al,P-doped SiO₂, fabricated by means of all-solution doping, in the vicinity of Al:P = 1:1, *Opt. Mater. Express*. 8 (2018) 1328. <https://doi.org/10.1364/ome.8.001328>.
- [19] A. El Sayed, S. Pilz, H. Najafi, D.T.L. Alexander, M. Hochstrasser, V. Romano, Fabrication and characteristics of Yb-doped silica fibers produced by the sol-gel based granulated silica method, *Fibers*. 6 (2018). <https://doi.org/10.3390/fib6040082>.
- [20] M.E. Likhachev, M.M. Bubnov, K. V Zotov, O.I. Medvedkov, D.S. Lipatov, M. V Yashkov, A.N. Gur'yanov, Erbium-doped aluminophosphosilicate optical fibres, *Quantum Electron.* 40 (2010) 633–638. <https://doi.org/10.1070/qe2010v040n07abeh014326>.
- [21] Y. Cheng, H. Dong, C. Yu, Q. Yang, Y. Jiao, S. Wang, C. Shao, L. Hu, Y. Dai, Temperature Dependence of Absorption and Energy Transfer Efficiency of

- Er³⁺/Yb³⁺/P⁵⁺ Co-Doped Silica Fiber Core Glasses, *Materials* (Basel). 15 (2022) 1–11. <https://doi.org/10.3390/ma15030996>.
- [22] I.C. Pinto, V.A.G. Rivera, R. Falci, V. Fuertes, S. LaRochelle, Y. Messaddeq, Tailoring near-infrared luminescence with Er³⁺/Tm³⁺/Yb³⁺ tri-doped tellurite glasses for applications in the C, L and U bands, *J. Lumin.* 265 (2024) 120206. <https://doi.org/10.1016/j.jlumin.2023.120206>.
- [23] V.A.G. Rivera, I.C. Pinto, R. Falci, V. Fuertes, Y. Messaddeq, Novel insights into the electronic and optical properties of the 1.53- μ m emission in Er³⁺-doped oxide- and oxyfluoride- tellurite glasses for optical communications, *J. Alloys Compd.* 976 (2024) 173182. <https://doi.org/10.1016/j.jallcom.2023.173182>.
- [24] S. Liangen, J. Zarzycki, Evolution of the structure of gels of the system SiO₂Al₂O₃P₂O₅ submitted to thermal treatment, *J. Non. Cryst. Solids.* 112 (1989) 428–431. [https://doi.org/10.1016/0022-3093\(89\)90567-X](https://doi.org/10.1016/0022-3093(89)90567-X).
- [25] M. Łaczka, M. Ciecńska, Preparation, structure and properties of silicate-phosphate glasses obtained by means of sol-gel method, *J. Sol-Gel Sci. Technol.* 3 (1994) 219–227. <https://doi.org/10.1007/BF00486560>.
- [26] J. Livage, P. Barboux, M.T. Vandenborre, C. Schmutz, F. Taulelle, Sol-gel synthesis of phosphates, *J. Non. Cryst. Solids.* 147–148 (1992) 18–23. [https://doi.org/10.1016/S0022-3093\(05\)80586-1](https://doi.org/10.1016/S0022-3093(05)80586-1).
- [27] F. Lindner, C. Aichele, A. Kriltz, A. Scheffel, H. Bartelt, K. Wondraczek, FTIR multispectral imaging of P/Al-doped silica glass preforms prepared by MCVD in combination with the high temperature evaporation of AlCl₃, *Opt. Mater. Express.* 12 (2022) 184. <https://doi.org/10.1364/ome.444146>.
- [28] B. Roy, H. Jain, Phase Separation and Structural Differences between Alkali Silicate Glasses Prepared by the Sol-Gel and Melt-Quench Methods, *J. Am. Ceram. Soc.* 81 (2005) 2360–2370. <https://doi.org/10.1111/j.1151-2916.1998.tb02632.x>.
- [29] H. You, M. Nogami, Three-photon-excited fluorescence of Al₂O₃-SiO₂ glass containing Eu³⁺ ions by femtosecond laser irradiation, *Appl. Phys. Lett.* 84 (2004) 2076–2078. <https://doi.org/10.1063/1.1688984>.
- [30] I. Cooperstein, E. Shukrun, O. Press, A. Kamyshny, S. Magdassi, Additive Manufacturing of Transparent Silica Glass from Solutions, *ACS Appl. Mater. Interfaces.* 10 (2018) 18879–18885. <https://doi.org/10.1021/acsami.8b03766>.

- [31] G.C. Righini, C. Armellini, M. Ferrari, A. Carlotto, A. Carpentiero, A. Chiappini, A. Chiasera, A. Lukowiak, T.N.L. Tran, S. Varas, Sol–Gel Photonic Glasses: From Material to Application †, *Materials* (Basel). 16 (2023). <https://doi.org/10.3390/ma16072724>.
- [32] G.T. Tayama, S.H. Santagneli, H. Eckert, S. Pawsey, Y. Messaddeq, Preparation and Structural Characterization of New Photopolymerizable Transparent Aluminum-Phosphate Hybrid Materials as Resins for 3D Printing, *J. Phys. Chem. C*. 124 (2020) 25621–25631. <https://doi.org/10.1021/acs.jpcc.0c08289>.
- [33] J. Wang, B. Zheng, P. Wang, 3D printed Er³⁺/Yb³⁺ co-doped phosphosilicate glass based on sol-gel technology, *J. Non. Cryst. Solids*. 550 (2020) 120362. <https://doi.org/10.1016/j.jnoncrsol.2020.120362>.
- [34] J. Ren, L. Zhang, H. Eckert, Sol-gel preparation of mesoporous Al₂O₃-SiO₂ glasses: Structural evolution monitored by solid state NMR, *J. Sol-Gel Sci. Technol.* 70 (2014) 482–490. <https://doi.org/10.1007/s10971-014-3309-5>.
- [35] C.J. Brinker, G.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, *Sol-Gel Sci. Phys. Chem. Sol-Gel Process.* (2013) 1–908. <https://doi.org/10.1016/C2009-0-22386-5>.
- [36] T. Woignier, J. Phalippou, *Glasses: Sol–Gel Methods*, *Ref. Modul. Mater. Sci. Mater. Eng.* (2016) 1–6. <https://doi.org/10.1016/b978-0-12-803581-8.02341-9>.
- [37] B.H. Costa, G.T. Tayama, S.H. Santagneli, Structural evolution study by solid-state NMR of photopolymerizable aluminophosphosilicate hybrid materials, *J. Non. Cryst. Solids*. 639 (2024) 123105. <https://doi.org/10.1016/j.jnoncrsol.2024.123105>.
- [38] O.B. Silva, V.A.G. Rivera, Y. Ledemi, Y. Messaddeq, E. Marega, Germanium concentration effects on the visible emission properties of Er³⁺ in tellurite glasses, *J. Lumin.* 232 (2021) 117808. <https://doi.org/10.1016/j.jlumin.2020.117808>.
- [39] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.* 60 (1938) 309–319. <https://doi.org/10.1021/ja01269a023>.
- [40] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, *J. Am. Chem. Soc.* 73 (1951) 373–380. <https://doi.org/10.1021/ja01145a126>.

- [41] D.E. McCumber, Einstein relations connecting broadband emission and absorption spectra, *Phys. Rev.* 136 (1964) 16–19. <https://doi.org/10.1103/PhysRev.136.A954>.
- [42] V.A.G. Rivera, L.C. Barbosa, Spectroscopic properties of Er³⁺-doped sodium-modified tellurite glasses for use as optical amplifiers at 1540 nm, *J. Lumin.* 156 (2014) 116–123. <https://doi.org/10.1016/j.jlumin.2014.07.023>.
- [43] K. Wang, M. Qiu, C. Jiao, J. Gu, D. Xie, C. Wang, X. Tang, Z. Wei, L. Shen, Study on defect-free debinding green body of ceramic formed by DLP technology, *Ceram. Int.* 46 (2020) 2438–2446. <https://doi.org/10.1016/j.ceramint.2019.09.237>.
- [44] A. Mehaboob, V. Fuertes, V.A.G. Rivera, Y. Messaddeq, Tailoring ultrabroadband near-infrared luminescence in Bi-doped germanosilicate glasses, *Sci. Rep.* 13 (2023) 1–14. <https://doi.org/10.1038/s41598-023-49898-1>.
- [45] J. Lucas, J. Troles, X.H. Zhang, C. Boussard-Pledel, M. Poulain, B. Bureau, Glasses to see beyond visible, *Comptes Rendus Chim.* 21 (2018) 916–922. <https://doi.org/10.1016/j.crci.2018.02.010>.
- [46] J. Muncan, R. Tsenkova, Aquaphotomics-From Innovative Knowledge to Integrative Platform in Science and Technology, *Molecules.* 24 (2019). <https://doi.org/10.3390/molecules24152742>.
- [47] E. Stolper, Water in silicate glasses: An infrared spectroscopic study, *Contrib. to Mineral. Petrol.* 81 (1982) 1–17. <https://doi.org/10.1007/BF00371154>.
- [48] A. Bertoluzza, P. Monti, J. V. Garcia-Ramos, R. Simoni, R. Caramazza, A. Calzavara, Applications of Raman spectroscopy to the ophthalmological field: Raman spectra of soft contact lenses made of poly-2-hydroxyethylmethacrylate (PHEMA)., *J. Mol. Struct.* 143 (1986) 469–472. [https://doi.org/10.1016/0022-2860\(86\)85302-9](https://doi.org/10.1016/0022-2860(86)85302-9).
- [49] L. Todan, E.M. Anghel, P. Osiceanu, R.V.F. Turcu, I. Atkinson, S. Simon, M. Zaharescu, Structural characterization of some sol-gel derived phosphosilicate glasses, *J. Mol. Struct.* 1086 (2015) 161–171. <https://doi.org/10.1016/j.molstruc.2015.01.012>.
- [50] H. Dong, Z. Wang, C. Shao, S. Wang, F. Lou, C. Yu, Y. Chen, L. Hu, Effect of co-dopants on the spectral property of Yb³⁺ doped silica glasses at 1018 nm, *Opt. Mater. (Amst).* 122 (2021) 111761. <https://doi.org/10.1016/j.optmat.2021.111761>.

- [51] X. Wang, F. Munoz, D. He, Y. Ding, J. Ren, W. Chen, H. Li, L. Hu, Effects of SiO₂ on properties and structures of neodymium doped P₂O₅-Al₂O₃-Li₂O-MgO-Sb₂O₃ glasses, *J. Alloys Compd.* 729 (2017) 1038–1045. <https://doi.org/10.1016/j.jallcom.2017.09.093>.
- [52] M. Guo, C. Shao, F. Shi, F. Wang, S. Wang, C. Yu, L. Zhang, J. Ren, L. Hu, Effect of thermal annealing on structures and properties of Yb³⁺/Al³⁺/P⁵⁺ co-doped silica glasses, *J. Non. Cryst. Solids.* 522 (2019) 119563. <https://doi.org/10.1016/j.jnoncrysol.2019.119563>.
- [53] D. Carta, D.M. Pickup, J.C. Knowles, I. Ahmed, M.E. Smith, R.J. Newport, A structural study of sol-gel and melt-quenched phosphate-based glasses, *J. Non. Cryst. Solids.* 353 (2007) 1759–1765. <https://doi.org/10.1016/j.jnoncrysol.2007.02.008>.
- [54] C. Coelho, F. Babonneau, T. Azais, L. Bonhomm-Courry, J. Maquet, G. Laurent, C. Bonhomme, Chemical bonding in silicophosphate gels: Contribution of dipolar and J-derived solid state NMR techniques, *J. Sol-Gel Sci. Technol.* 40 (2006) 181–189. <https://doi.org/10.1007/s10971-006-7431-x>.
- [55] J.C. Schrotter, A. Cardenas, M. Smaih, N. Hovnanian, Silicon and phosphorus alkoxide mixture: Sol-gel study by spectroscopic technics, *J. Sol-Gel Sci. Technol.* 4 (1995) 195–204. <https://doi.org/10.1007/BF00488374>.
- [56] D. Zhang, X. Liu, J. Qiu, 3D printing of glass by additive manufacturing techniques: a review, *Front. Optoelectron.* 14 (2021) 263–277. <https://doi.org/10.1007/s12200-020-1009-z>.
- [57] R.R. Deshpande, L. Zhang, H. Eckert, Sol-gel synthesis of sodium-modified AlPO₄-SiO₂ glasses and structural characterization by solid state NMR, *J. Mater. Chem.* 19 (2009) 1151–1159. <https://doi.org/10.1039/b815397c>.
- [58] F. Romero-Gavilán, S. Barros-Silva, J. García-Cañadas, B. Palla, R. Izquierdo, M. Gurruchaga, I. Goñi, J. Suay, Control of the degradation of silica sol-gel hybrid coatings for metal implants prepared by the triple combination of alkoxysilanes, *J. Non. Cryst. Solids.* 453 (2016) 66–73. <https://doi.org/10.1016/j.jnoncrysol.2016.09.026>.
- [59] C.C. De Araujo, L. Zhang, H. Eckert, Sol-gel preparation of AlPO₄-SiO₂ glasses with high surface mesoporous structure, *J. Mater. Chem.* 16 (2006) 1323–1331. <https://doi.org/10.1039/b516599g>.

- [60] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.O. Durand, B. Bujoli, Z. Gan, G. Hoatson, Modelling one- and two-dimensional solid-state NMR spectra, *Magn. Reson. Chem.* 40 (2002) 70–76. <https://doi.org/10.1002/mrc.984>.
- [61] T. Gutberlet, H. Hilbig, R.E. Beddoe, Acid attack on hydrated cement - Effect of mineral acids on the degradation process, *Cem. Concr. Res.* 74 (2015) 35–43. <https://doi.org/10.1016/j.cemconres.2015.03.011>.
- [62] M.E. Krüger, A. Heisig, H. Hilbig, H. Eickhoff, D. Heinz, A. Machner, Effect of aluminum on the structure of synthetic alkali-silica gels, *Cem. Concr. Res.* 166 (2023) 107088. <https://doi.org/10.1016/j.cemconres.2022.107088>.
- [63] D.S. Perera, J. V. Hanna, J. Davis, M.G. Blackford, B.A. Latella, Y. Sasaki, E.R. Vance, Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials, *J. Mater. Sci.* 43 (2008) 6562–6566. <https://doi.org/10.1007/s10853-008-2913-6>.
- [64] G.T. Tayama, S.H. Santagneli, M.D.O. Junior, Y. Messaddeq, Understanding the Microstructure Connectivity in Photopolymerizable Aluminum-Phosphate-Silicate Sol – Gel Hybrid Materials for Additive Manufacturing, (2023). <https://doi.org/10.1021/acs.jpcc.2c08027>.
- [65] L. Camus, V. Goletto, J. Maquet, C. Gervais, C. Bonhomme, F. Babonneau, D. Massiot, 1H MAS-NMR at high spinning rate: An interesting characterization tool for hybrid materials, *J. Sol-Gel Sci. Technol.* 26 (2003) 311–314. <https://doi.org/10.1023/A:1020732022863>.
- [66] F. Babonneau, C. Bonhomme, Solid-State NMR Characterization of Sol–Gel Materials: Recent Advances, in: *Sol-Gel Handb.*, Wiley, 2015: pp. 651–672. <https://doi.org/10.1002/9783527670819.ch20>.
- [67] C. Bonhomme, C. Coelho, N. Baccile, C. Gervais, T. Azaïs, F. Babonneau, Advanced solid state NMR techniques for the characterization of sol-gel-derived materials, *Acc. Chem. Res.* 40 (2007) 738–746. <https://doi.org/10.1021/ar600030j>.
- [68] K.S.W. Sing, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, *Pure Appl. Chem.* 57 (1985) 603–619. <https://doi.org/10.1351/pac198557040603>.
- [69] M. Thommes, K. Kaneko, A. V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the

- evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.* 87 (2015) 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.
- [70] I.H. Malitson, Interspecimen Comparison of the Refractive Index of Fused Silica*,†, *J. Opt. Soc. Am.* 55 (1965) 1205. <https://doi.org/10.1364/josa.55.001205>.
- [71] W. Xu, J. Ren, C. Shao, X. Wang, M. Wang, L. Zhang, D. Chen, S. Wang, C. Yu, L. Hu, Effect of P5+ on spectroscopy and structure of Yb3+/Al3+/P5+ co-doped silica glass, *J. Lumin.* 167 (2015) 8–15. <https://doi.org/10.1016/j.jlumin.2015.05.061>.
- [72] H.C. Çamiçi, T. Guérineau, V.A.G. Rivera, R.F. Falci, S. LaRochelle, Y. Messaddeq, The role of tungsten oxide in Er3+-doped bismuth-germanate glasses for optical amplification in L-band, *Sci. Rep.* 13 (2023) 1–10. <https://doi.org/10.1038/s41598-023-35995-8>.
- [73] M.T. Lanagan, L. Cai, L.A. Lamberson, J. Wu, E. Streltsova, N.J. Smith, Dielectric polarizability of alkali and alkaline-earth modified silicate glasses at microwave frequency, *Appl. Phys. Lett.* 116 (2020). <https://doi.org/10.1063/5.0008646>.
- [74] W.T. Carnall, P.R. Fields, B.G. Wybourne, Spectral intensities of the trivalent lanthanides and actinides in solution. I. Pr3+, Nd3+, Er3+, Tm3+, and Yb3+, *J. Chem. Phys.* 42 (1965) 3797–3806. <https://doi.org/10.1063/1.1695840>.
- [75] H. Hayashi, N. Sugimoto, S. Tanabe, S. Ohara, Effect of hydroxyl groups on erbium-doped bismuth-oxide-based glasses for fiber amplifiers, *J. Appl. Phys.* 99 (2006). <https://doi.org/10.1063/1.2192267>.
- [76] W. Stręk, P.J. Dereń, K. Maruszewski, E. Pawlik, W. Wojcik, G.E. Malashkevich, V.I. Gaishun, Spectroscopic properties of erbium doped silica glasses obtained by sol-gel method, *J. Alloys Compd.* 275–277 (1998) 420–423. [https://doi.org/10.1016/s0925-8388\(98\)00360-0](https://doi.org/10.1016/s0925-8388(98)00360-0).
- [77] C. Gao, Z. Huang, Y. Wang, H. Zhan, L. Ni, K. Peng, Y. Li, Z. Jia, X. Wang, A. You, X. Xiang, J. Wang, F. Jing, H. Lin, A. Lin, Yb-doped Aluminophosphosilicate Laser Fiber, 8724 (2016). <https://doi.org/10.1109/JLT.2016.2602372>.
- [78] Q. Yang, Y. Jiao, C. Yu, C. Shao, F. Lou, S. Wang, L. Zhang, Q. Yang, L. Hu, Gain and laser performance of heavily Er-doped silica fiber fabricated by MCVD

combined with the sol-gel method, *Chinese Opt. Lett.* 19 (2021) 110603.
<https://doi.org/10.3788/col202119.110603>.

- [79] D. Mandal, H.D. Banerjee, M.L.N. Goswami, H.N. Acharya, Synthesis of Er^{3+} and $\text{Er}^{3+} : \text{Yb}^{3+}$ doped sol-gel derived silica glass and studies on their optical properties, *Bull. Mater. Sci.* 27 (2004) 367–372.
<https://doi.org/10.1007/BF02704774>.

Supplementary material

Effects of the thermal treatment on structural and luminescence properties of Er³⁺-doped aluminophosphosilicate glasses obtained by the sol-gel method

Beatriz H. Costa^{*,a}, Gabriel T. Tayama^b, V. A. G. Rivera^c, Younès Messaddeq^{a,b}, Silvia H. Santagneli^{*,a}

^a Institute of Chemistry, São Paulo State University (UNESP), Araraquara, SP, Brazil

^b Centre d'optique, photonique et laser (COPL), Université Laval, Québec, G1V 0A6, Canada

^c Institute of Physics of São Carlos (IFSC), São Paulo University (USP), São Carlos, SP, Brazil

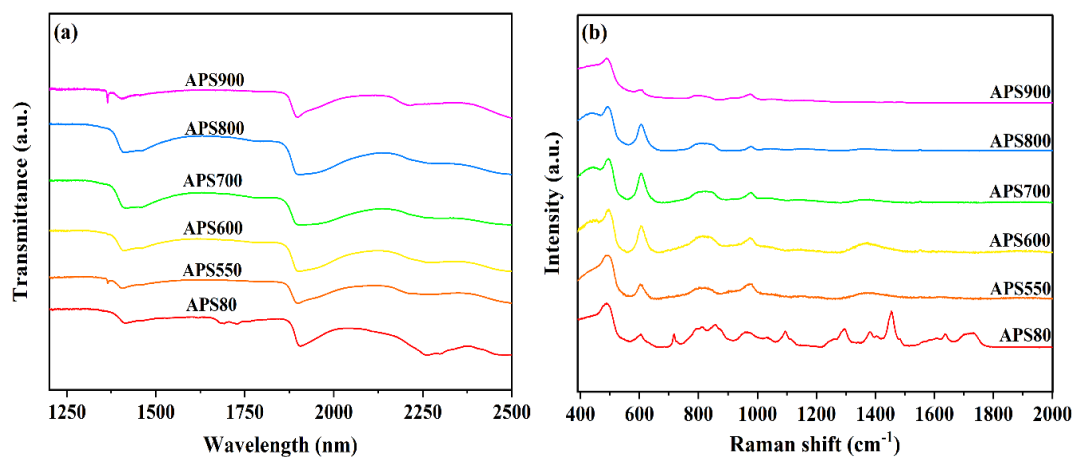


Fig. 3.S1. (a) FTIR and (b) Raman spectra for the APS(T)-0.2 samples, where T is the heat treatment temperature.

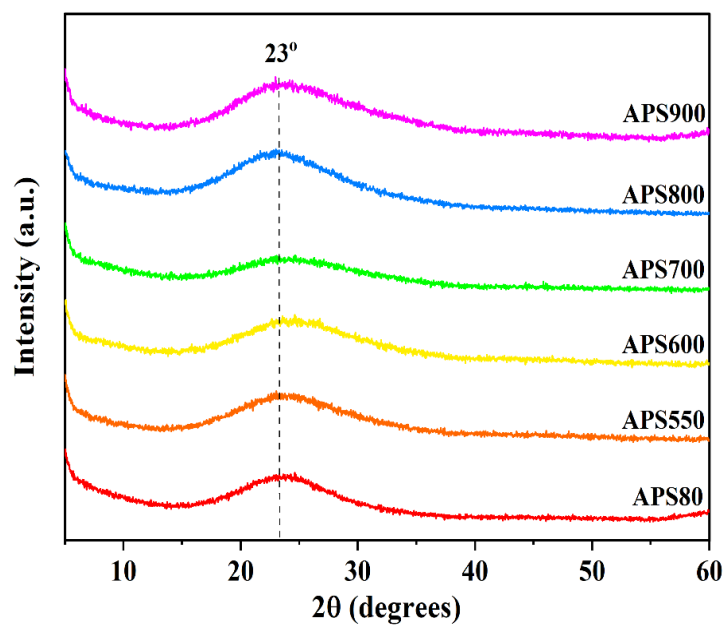


Fig. 3.S2. XRD patterns for the APS(T)-0.2 samples, where T is the heat treatment temperature.

Table 3.S1. Deconvolution results (chemical shift δ_{iso} and fractional areas) of the ^{29}Si MAS NMR spectra obtained for the APS(T) samples.

Sample	Q^2		Q^3		Q^4	
	δ	Area	δ	Area	δ	Area
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)
APS80	-92	5	-102	50	-110	45
APS550	-92	7	-101	28	-109	65
APS600	-92	6	-101	28	-109	66
APS700	-92	3	-101	27	-110	70
APS800	-92	2	-101	26	-110	72
APS900	-92	1	-101	21	-110	78

Table 3.S2. Deconvolution results (chemical shift δ_{iso} and fractional areas of the $P_{2\text{Al}}^0$, $P_{3\text{Al}}^0$, $P_{4\text{Al}}^0$ and $P_{3\text{Al},1\text{Si}}^0$ units) of the ^{31}P NMR spectra obtained for the APS(T) samples.

Sample	$P_{2\text{Al}}^0$		$P_{3\text{Al}}^0$		$P_{4\text{Al}}^0$		$P_{3\text{Al},1\text{Si}}^0$	
	δ	Area	δ	Area	δ	Area	δ	Area
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)
APS80	-12	37	-19	63	-	-	-	-
APS550	-12	19	-21	54	-30	18	-37	9
APS600	-11	18	-21	51	-30	21	-37	10
APS700	-10	16	-18	47	-27	26	-34	12
APS800	-12	14	-20	43	-28	27	-36	16
APS900	-11	15	-18	37	-28	30	-37	18

Table 3.S3. ^{27}Al isotropic chemical shift (δ_{iso}) and nuclear electric quadrupolar coupling values (C_Q) extracted from the Czsimpler function for the APS samples heat-treated at different temperatures (80, 550, 600, 700, 800 in air and 900 °C in vacuum).

Sample	^{27}Al				C_Q (MHz)	
	Al(IV)		Al(VI)		Al(IV)	Al(VI)
	δ_{iso} (ppm)	Area (%)	δ_{iso} (ppm)	Area (%)		
APS80	56	47	-7	53	4.9	4.0
APS550	47	49	-5	51	4.9	3.9
APS600	47	54	-5	46	5.3	4.0
APS700	53	36	-5	64	5.7	3.8
APS800	49	46	-4	54	4.8	4.2
APS900	47	49	-4	51	5.0	4.0

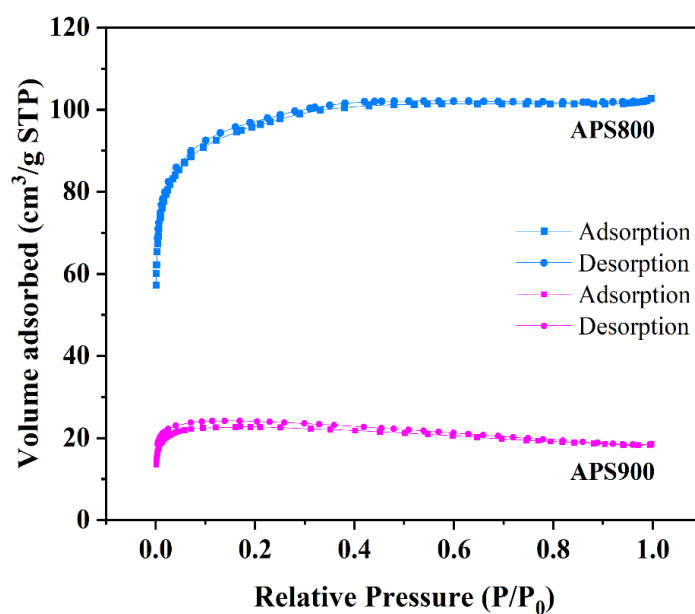


Fig. 3.S3. Adsorption and desorption nitrogen gas isotherms obtained by N_2 physisorption analysis for the APS800 and APS900 samples heat-treated at 800 °C in air and 900 °C in vacuum.

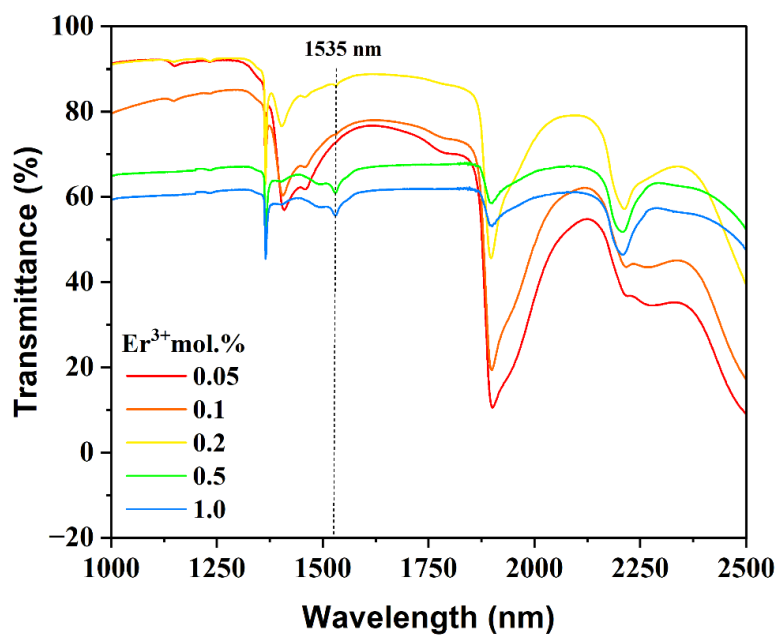


Fig. 3.S4. UV-Vis-NIR spectra for the APS900 samples doped with different Er^{3+} content (0.05 to 1.0 mol.%) heat-treated at 900 °C under vacuum.

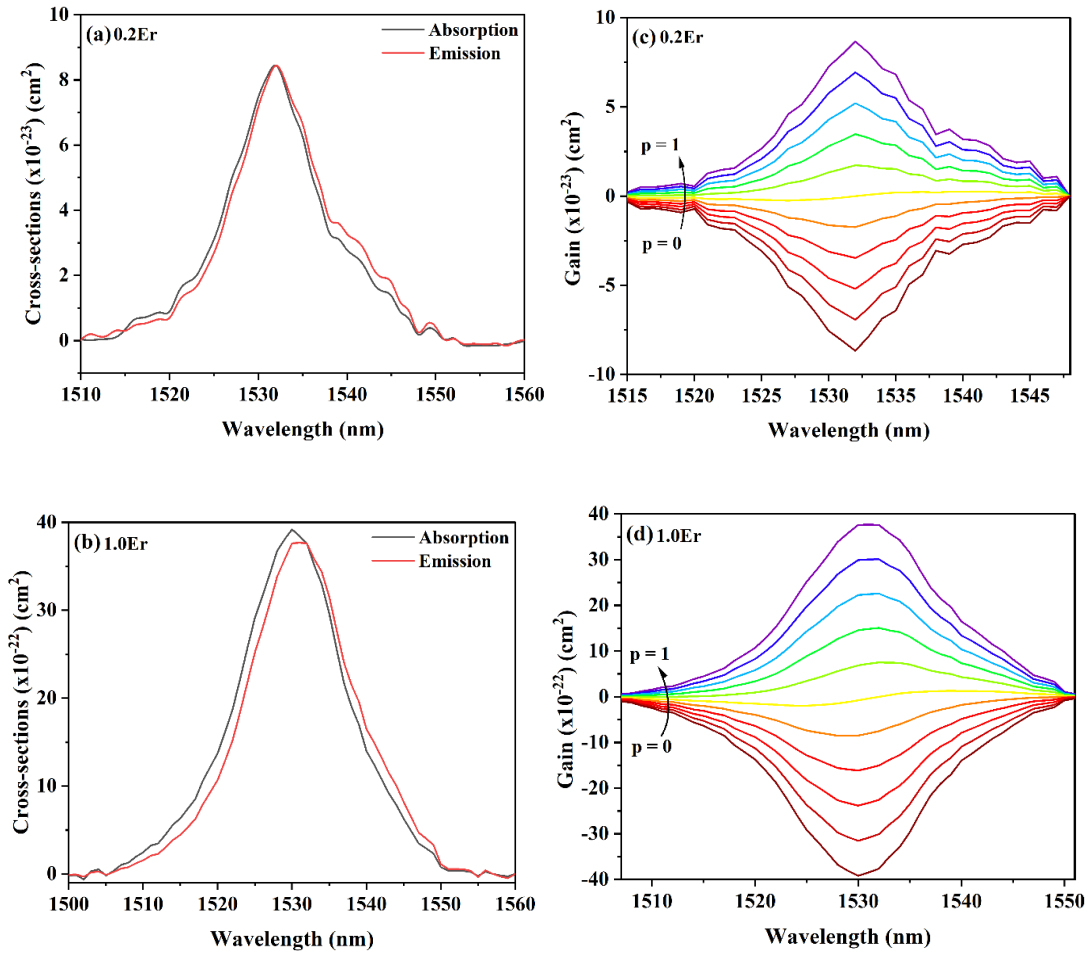


Fig. 3.S5. (a-b) Absorption and emission cross-sections of the Er^{3+} ions and (c-d) Gain spectra by the McCumber theory of the APS900 samples doped with 0.2 and 1.0 mol.% of Er^{3+} .

CHAPTER 4

General conclusions and perspectives

4. General conclusions and perspectives

This section provides a general conclusion of the chapters and addresses the work's perspectives.

According to the developed Ph.D research, the sol-gel method proved to be an effective route for the synthesis of aluminophosphosilicate-based materials, both undoped and Er^{3+} -doped, with controlled compositions and desirable optical properties. For the undoped hybrid materials with the composition $x\text{SiO}_2[(\text{Al}_2\text{O}_3)_{50}-(\text{P}_2\text{O}_5)_{50}]_{100-x}$, structural evolution was confirmed through solid-state NMR and XRD analyses, showing the formation of AlPO_4 , Al-O-P, and P-O-Si linkages after heat treatment at 800 °C. The increase in SiO_2 content led to a more interconnected SiO_2 tetrahedral network and a higher degree of heterocondensation. This structural transformation was also evidenced by a shift in the NMR and Raman data, suggesting the replacement of P-O-Al(IV) by Si-O-Al(IV) bonds.

In the case of Er^{3+} -doped aluminophosphosilicate glasses, the sol-gel method combined with vacuum heat treatment enhanced matrix densification and significantly reduced hydroxyl (OH) groups, which are known for causing quenching of luminescence. The controlled removal of these groups led to a remarkable increase in luminescence intensity, especially for the glass doped with 0.5 mol.% Er^{3+} , where a 180-fold increase in intensity and a Full Width at Half Maximum (FWHM) of 100 nm were observed. Nonetheless, luminescence quenching was noted for Er^{3+} concentrations above 0.5 mol.%, due to the formation of Er^{3+} clusters, which promoted non-radiative losses. The vacuum heat treatment also resulted in a higher refractive index, attributed to the increased formation of bridging oxygen (BO) bond within the silica matrix.

Overall, this study highlights the versatility of this new sol-gel approach in fabricating aluminophosphosilicate glasses with tailored structural and optical properties. The method not only allows the development of non-crystalline materials with complex bonding environments but also offers a low-temperature alternative to traditional high-temperature melting processes. These findings demonstrate the potential for using such materials in the development of new optical devices, particularly for telecommunications systems, where broadband near-infrared (NIR) emission in the C+L bands is crucial. The combination of high optical quality, tunable structural features, and enhanced luminescence makes these materials promising candidates for future applications in optical amplifiers and other photonic devices.

For future perspectives, the idea is to investigate the effects of AlPO_4 -join on the luminescence of $(95-100)\text{SiO}_2:x\text{AlPO}_4$ doped with 0.5 mol.% Er^{3+} glass and further combine both methods (MCVD + sol-gel) to obtain a preform. This approach is still not common in the literature, but it could be a way to avoid problems such as crystallization, phase separation, or composition deviation that usually appear when the MCVD is employed to obtain preforms based on aluminophosphosilicate glass doped with RE ions.

In conclusion, the knowledge acquired through this thesis includes:

- Synthesis of hybrid materials and glasses by sol-gel method;
- Hybrid and glasses characterization techniques;
- Solid-state NMR (data treatment and interpretation);
- Importance of drying process and controlled heat treatment;
- Photoluminescence properties.