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Silver (Ag) nanoclusters and lanthanides (Er^{3+} , Pr^{3+} , Yb^{3+}) ions
functionalized glassy materials for light sources, luminescent
layers for silicon solar cell and waveguide application

TARCIO DE CASTRO SILVA

PhD Thesis
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TÍTULO DA TESE: "Silver (Ag) nanoclusters and lanthanides (Er^{3+} , Pr^{3+} , Yb^{3+}) ions functionalized glassy materials for light sources, luminescent layers for silicon solar cell and waveguide application"

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Araraquara, 28 de junho de 2018

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DEDICATION

I would like to express my eternal thoughts and love for those who passed away and made part in my life. Your faces are carved in my memories father "Alcebiades", uncle "Deilane" and grandmother "Caroline". There is no one single day that you are not remembered.

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RESUMO

Materiais vítreos se tornaram um dos mais atrativos materiais devido a fácil e rápida preparação. Durante as últimas décadas, várias aplicações têm sido exploradas e a viabilidade para mudança de frequência, conversão ascendente (upconversion) e descendente de energia (downconversion), geração de radiação visível com similaridade das emissões cromáticas azul, verde e vermelho; guia de onda, camadas luminescentes para células solares, geração de segundo harmônico e outros, estão publicadas. Propriedades estruturais como baixa energia de vibração estrutural (fônon), estabilidade química e ampla transparência óptica, tem sido o principal alvo para explorar uma excelente matriz para a dopagem com terras-raras. Por exemplo, íons Er^{3+} é um dos candidatos mais adequados para a propriedade de “upconversion” devido a absorção na região do infravermelho em 0,9 e 1,5 μm e consequente emissão na região do visível e infravermelho. Devido às suas propriedades espectroscópicas, os lantanídeos, geralmente, exibem emissões com linhas estreitas devido à fraca interação com o campo cristalino da matriz. Por outro lado, íons metálicos como a prata (Ag), exibem uma ampla banda de emissão e excitação. A propriedade mais interessante dos íons prata é que a emissão visível pode ser ajustada de acordo com a forma e tamanho das espécies de pratas presentes em uma amostra. Esta propriedade abre um largo espectro de aplicações nas quais a radiação visível pode ser explorada. Neste sentido, um dos principais objetivos dessa tese é mostrar a preparação de materiais vítreos contendo íons lantanídeos como Er^{3+} e $\text{Pr}^{3+}/\text{Yb}^{3+}$ e /ou íons prata e nanoclusters de prata para aplicação em camadas luminescentes para células solares, geração de luz branca, guia de onda e investigação dos processos de “upconversion” e “downconversion”. Para este propósito, materiais vítreos com composição molar $40\text{InF}_3\text{-}20\text{ZnF}_2\text{-}20\text{Sr-}20\text{BaF}_2$ (vidros fluoroindatos) e $50\text{NaPO}_3\text{-}25\text{ZnF}_2\text{-}15\text{CdF}_2\text{-}10\text{YF}_3$ (vidros fluorofosfatos) foram selecionados. Os vidros fluoroindatos foram dopados com íons Er^{3+} com diferentes concentrações e os vidros fluorofosfatos com diferentes concentrações de pratas. Composições com diferentes concentrações de prata e os lantanídeos $\text{Pr}^{3+}/\text{Yb}^{3+}$ também foram preparadas. As amostras vítreas foram preparadas pelo método de fusão-choque térmico. Os materiais de partida foram homogeneizados em almofariz. A fusão dos compostos para os vidros fluoroindatos foram realizadas em tubo de platina a 850 °C durante 20

minutos e vertidos em um molde metálico pré-aquecido em 260 °C, enquanto que a obtenção dos vidros fluorofosfatos se deu com fusão a 1000 °C durante 30 minutos e vertidos em molde pré-aquecido a 300 °C. A primeira parte desta tese mostra a preparação e avaliação das propriedades estruturais e espectroscópicas dos materiais vítreos. Absorção, excitação e espectros de emissão, o tamanho e morfologia dos nanoclusters de prata (para os vidros fluorofosfatos) bem como as propriedades térmicas foram analisadas. A segunda parte desta tese está relacionada com a aplicação dos vidros fluoroindatos como camadas luminescentes para o aumento da fotocorrente em uma célula solar de silício monocristalino e monofacial. Os vidros obtidos foram cortados e opticamente polidos de modo a obter amostras com as dimensões de 5.4 x 4.3 x 3.2 mm. As amostras foram colocadas na superfície de uma célula solar. Neste ponto, as diferentes concentrações de íons Er^{3+} , que estão associadas à diferentes intensidades de emissão, foram analisadas nas medidas de fotocorrente.

A terceira parte desta tese traz uma breve introdução aos nanoclusters de prata, que será a base para a compreensão dos resultados obtidos dos vidros fluorofosfatos. A maior parte dos resultados foram obtidos em colaboração com o “Institut de Chimie de la Matière Condensée de Bordeaux”, exceto os resultados das amostras preparadas para obtenção de radiação branca, capítulo 4. As amostras previamente preparadas com composição molar $45\text{NaPO}_3\text{-}25\text{MgF}_2\text{-}15\text{CdF}_2\text{-}15\text{YF}_3\text{-}5\text{AgNO}_3$, foram cortadas e polidas de modo a obter amostras com dimensão 7 x 4 x 2 mm. A estabilização dos nanoclusters de prata se deu através da técnica “Direct Laser Writing (DLW)”, utilizando laser de femtosegundo (fs) KGW:Yb, operando com linha espectral em 1030 nm e bombardeando a amostra com diferentes pulsos de energia. A irradiância laser foi controlada um modulador acústico-óptico permitindo a acumulação de $N=10^5\text{-}10^6$ com energia variando entre 20 e 150 nJ. As microestruturas de prata gravadas nas amostras foram avaliadas de acordo com suas propriedades de absorção e emissão. Em adição, neste amostra foi avaliada a viabilidade como guia de onda. Por último, na amostra com composição molar $(30\text{-}x)\text{NaPO}_3\text{-}30\text{MgF}_2\text{-}30\text{BaF}_2\text{-}10\text{YF}_3\text{-}0.5\text{Pr}\text{-}0.5\text{Yb} - x\text{Ag}$ ($x = 0, 2, 4$ and 10) foi analisada a transferência de energia dos nanoclusters de prata e os terras-raras Pr^{3+} e Yb^{3+} . Os resultados apresentados nesta tese representam uma direção promissora para explorar materiais emissores com ampla emissão espectral com potencial uso em

conversão descendente de energia “downconversion”, camadas para aplicações fotovoltaicas, fósforos e guias de ondas.

Palavras-chave: Vidros fluoroindatos; vidros fluorofosfatos, “upconversion”, “downconversion”, transferência de energia, célula solar, nanoclusters de prata, “direct laser writing” e guias de onda.

ABSTRACT

Glassy materials have become one of the most attractive materials owing their easy and fast preparation. During the last decades, several applications have been explored and the feasibility for frequency change, upconversion and downconversion, white light generation, waveguide, luminescent layers for solar cell, second harmonic generation and other, are reported. Structural properties like low energy phonon, chemical stability, broad transparency optical window have been the main target to explore a good host materials for lanthanides dopage. For example, Er^{3+} is one of the most suitable candidate for upconversion since it has 1,5 μm and 0,9 μm absorption. Owing to their spectroscopic properties, lanthanides, generally, show visible emissions with narrow lines due to the poor interaction with the crystalline field of the host material. On the other hand, metal ions such as silver; generally, shows a broadband emission and absorption. The most interesting spectroscopic properties of silver is that the visible emission may be tunable according to the size and shape of the silver species in the host materials. This property opens a large spectrum of application in which the visible light can be explored. In this sense, the main goal of this thesis is to show the preparation of glassy materials containing lanthanides such as Er^{3+} , $\text{Pr}^{3+}/\text{Yb}^{3+}$ and/or silver ions and nanoclusters for luminescent layers for solar cell and photonic applications. The glassy materials selected for such purposes were fluoroindate glasses and fluorophosphate glasses. The samples were prepared by the conventional melting-quenching method. The raw materials with high purity were weighted and mixed according to the following molar composition: $40\text{InF}_3\text{-}20\text{ZnF}_2\text{-}20\text{Sr-}20\text{BaF}_2$ (fluoroindate glass) and $50\text{NaPO}_3\text{-}25\text{ZnF}_2\text{-}15\text{CdF}_2\text{-}10\text{YF}_3$ (fluorophosphate glass). Besides, other compositions of fluorophosphate glasses were also synthesized. Fluoroindate glasses were doped with different Er^{3+} amount and the fluorophosphate glasses with different silver amounts. The raw materials of the fluoroindate glasses were melted in a platinum tube at 850 °C during 20 minutes and poured out in a mold pre-heated at 260 °C. On the other hand, the raw materials of the fluorophosphate glasses were melted in a platinum crucible at 1000 °C during 30 min and poured out in a mol pre-heated at 300 °C. The first part of this thesis was the preparation and the evaluation of the structural and spectroscopic properties of these glasses. Absorption, excitation and emission spectra, size and morphology of the silver nanoclusters (for

the fluorophosphate glasses) as well as thermal properties were analyzed. The second part of this thesis is related to the application of the fluorindate samples as luminescent layers for enhance photocurrent in a monocrystalline and monofacial silicon solar cell. The glasses obtained were cut and polished in order to obtain samples with dimensions 5.4 x 4.3 x 3.2 mm. The functional glass pieces were placed on the surface of the solar cell. At this point, the different Er^{3+} amount, which is associated with different upconversion intensity responses were evaluated in the photocurrent measures.

The third part of this thesis brings a brief introduction to the silver nanoclusters that will be the bases to understand the results obtained from the fluorophosphate glasses. Majority of these results was obtained in collaboration with "Institut de Chimie de la Matière Condensée de Bordeaux", except the results of the samples for white light generation, shown in the chapter 4. The samples previously prepared with molar composition $45\text{NaPO}_3\text{-}25\text{MgF}_2\text{-}15\text{CdF}_2\text{-}15\text{YF}_3\text{-}5\text{AgNO}_3$, were cut and polished in order to obtain samples with dimension 7 x 4 x 2 mm. The stabilization of silver nanoclusters was carried out by direct laser writing (DLW technique), using a femtosecond laser (KGW:Yb) operating at 1030 nm and delivering different energy pulses. The laser irradiance were controlled with an acousto-optic modulator enabling the accumulation of $N=10^5\text{-}10^6$ pulses with energy pulses going from 20 nJ up to 150 nJ. The microstructures of silver nanoclusters were evaluated according their absorption and emission properties. Still, for this sample we also analyzed the feasibility as waveguiding material. For last but no least, the sample with molar composition $(30\text{-}x)\text{NaPO}_3\text{-}30\text{MgF}_2\text{-}30\text{BaF}_2\text{-}10\text{YF}_3\text{-}0.5\text{Pr}\text{-}0.5\text{Yb}\text{-}x\text{Ag}$ ($x = 0, 2, 4$ and 10) was prepared in order to evaluate the energy transfer among the silver species and the rare earths Pr^{3+} and Yb^{3+} . The results presented in this thesis represent a promising direction to explore broadband emitter's with potential use in down-conversion, layers for photovoltaic application, phosphors and waveguide. .

Keywords: Fluorindate glasses, fluorophosphate glasses, upconversion, downconversion, energy transfer, solar cell, silver nanoclusters, direct laser writing and waveguide.

“Next time someone complains that you have made a mistake, tell him that may be a good thing. Because without imperfection, neither you nor I would exist.”

(Stephen Hawking, 2010)

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LIST OF ABBREVIATIONS

Ag – Silver	HRTEM – High Resolution Transmission Electron Microscopy
Ag NC's – Silver Nanoclusters	kV – Kilovolt
Ag NP's – Silver Nanoparticles	LED – Light Emitting Diode
a-Si - Amorphous silicon	LLSC – Luminescent Layer for Solar Cell
CB – Conduction Band	Ln ³⁺ - Lanthanides
CET – Cooperative Energy Transfer	mc-Si - Multicrystalline silicon
CIE - Commission Internationale d'Eclairage	PA – Photon Avalanche
CR – Cross Relaxation	PV – Photovoltaic
CTB – Charge Transfer Band	SAED – Selected Area Electron Diffraction
DC – Downconversion	SC – Solar Cell
DLW – Direct Laser Writing	Si SC – Silicon Solar Cell
E _g – Bandgap	Single-crystalline silicon – sc-Si
EMU – Energy Migration Upconversion	SPR – Surface Plasmon Resonance
ESA – Excited State Absorption	TEM – Transmission Electron Microscopy
ET – Energy Transfer	T _g – Transition Temperature
ETE – Energy Transfer Efficiency	UC – Upconversion
ETU – Energy Transfer Upconversion	UV – Ultraviolet
FWHM – Full Width of Half-Maximum	Vis – Visible
GSA – Ground State Absorption	WG – Waveguide

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Luminescent layers for solar cell application

During the past 30 years there has been a remarkable growth in the use of luminescent materials for solar cell application. A huge variety of amorphous and crystalline materials has been employed in order to increase the photocurrent of different photovoltaic systems. In this sense, lanthanides ions have been employed as good candidates for luminescent layers, which may be used in the rear and the top face of certain solar cells. In this chapter, we present an overview of the solar cells landscape, the drawbacks associated with the solar spectrum mismatch and the pathways to overcome such issues. A greater emphasis is given to the solar cell from the first generation that are silicon-based solar cells. Along this chapter, it may be note that this kind of cell is taken as example to explain an increment of efficiency using luminescent layers. However, it is far beyond of this chapter to deal with efficiency using an AM 1.5G conditions as well as the measure of short-circuit current, fill factor and other parameters related. For this purpose, whenever necessary, the reader is direct to some references throughout the chapter. Besides, rare-earth spectroscopy is also mentioned as well as one of the most explored properties, the “upconversion” phenomenon.

1 Introduction

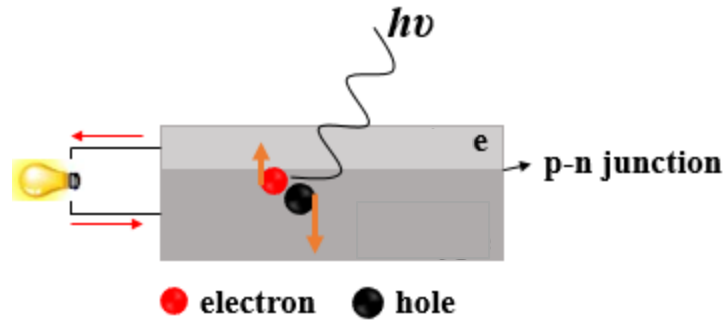
The large-scale use of fossil fuels has brought serious issues of global warming and environmental pollution due to the nonrenewable energy consumption [KANG et al, 2010; LUNT; BULOVIC, 2011]. Since the introduction of first commercial solar cell (SC) in the 70ths years, research efforts in SC scaled up the knowledge to sustainable sources. Presently, solar energy is an emerging and alternate source of energy that can direct the usage to the clean and abundant form of energy [AHMED; HABIB; JAVAID, 2015]. Moreover, solar energy is one of the few renewable, low-carbon resource with maturity to meet ever-growing global demand for electricity [JEAN et al., 2015].

Daily, the sun delivers about 174 000 TW of energy to the upper level of the atmosphere, meaning 10 000 times more energy than our global energy consumption [RUHLE; SHALOM; ZABAN, 2011]. This energy corresponds to an average energy power 1366 TW.m^{-2} . Taking into account atmosphere absorption and scattering, this value is reduced to 1000 W.m^{-2} . Moreover, with further losses due to seasonal

variation, oblique incident radiation, weather attenuation and cloud cover, leads to a global daily average of 183 W.m^{-2} [JACOBSON; DELUCCHI, 2011].

The most direct way to convert solar radiation into electricity is the use of photovoltaic (PV) cells, also commonly named as solar cells (SC). In such device, a semiconductor composed by a positive and negative (p-n) junction develops photovoltage. The detailed process to generate current is ascribed as following: when solar radiation (photons) is absorbed, electrons raise to a higher energy state, and then they flow to an external circuit, since electron-hole recombination pair is avoided. Electron and holes move to opposite electrodes and their recombination generate electric current. Such photovoltaic effect happens when few conditions are observed: (i) photons absorbed by the solar cell must to have energy equal or higher than the bandgap (E_g) of the cell; (ii) the absorption of photons must to guarantee the formation of electron-hole pair, also called charge carriers; (iii) spatial separation of the charge carriers is observed by a p-n junction, so that any recombination is prevented; (iv) after electron flowing in the external circuit, electron-hole must to be regenerated again on the positive layer. For the sake of brevity, only main factors to generate photocurrent are mentioned above, however, the electric current density is affected by factors like shading, cell temperature, cable thickness, solar radiation intensity, climate conditions, cell lifetime and other [CHOPRA; PAULSON; DUTTA, 2004; GOETZBERGER; HEBLING; SCHOCK, 2002]. Moreover, Figure 1.1 represents the simplest configuration in which the SC is based in a double-layer (p-n junction) diode. Along this chapter, we are going to show complexes system, like those shown in Figure 1.2, in which several layer may be present in a PV device.

Figure 1.1. Schematic of a single-junction solar cell.



Along the last 5 decades, solar cell technology has grown dramatically owing the evolution of new materials that found their specific niche through different SC generation. In 2015, Jean et al. has presented a review paper regarding solar cell technology where the classification follows a trend in which the primary light-absorbing material was taken into account. According to them, two categories are defined: wafer-based cells and thin-film cells, respectively. Still, the generations are also referred as first, second and third generation, where the first one refers to the wafer-based SC, the second one refers to thin-film SC and the third one refers to the commercial thin-film SC. Here, we adopted the same definition described by Jean et al. [JEAN et al, 2015].

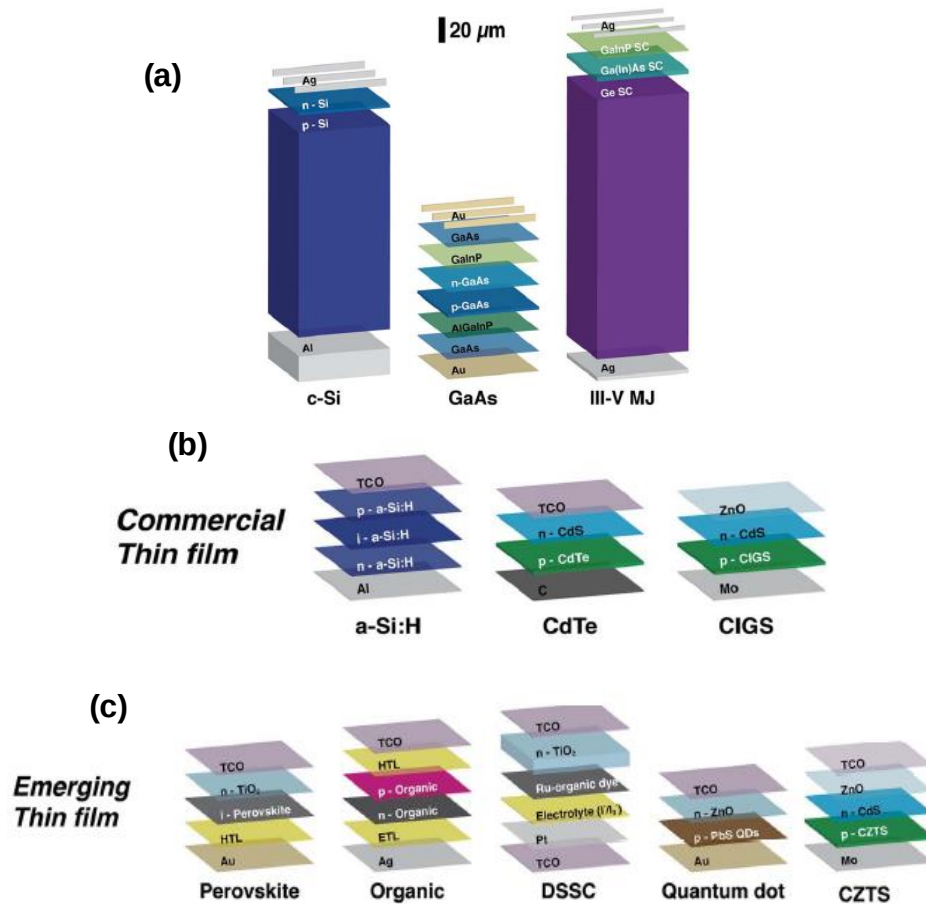
Figure 1.2 a-c shows the SC technology according wafer-based and thin-film classification. Wafer-based SC, or also called first generation, comprises the most mature of all photovoltaic technology and commercially speaking, that is silicon SC (Figure 1.2a). Silicon SC are classified as single-crystalline (sc-Si), multicrystalline (mc-Si) and amorphous (a-Si). Record cell efficiency for sc-Si, mc-Si and a-Si stand at 25.6%, 20.8% and 10.2% [GREEN, 2015], respectively. Nowadays, the global production counts with 90% of c-Si. In a general view, Si SC is composed by a positive (p-Si) and negative layer (n-Si) in which the thickness of the negative is smaller than the positive one. Back and frontal contacts are constituted of aluminum (Al) layer and thin strips of deposited silver (Ag). Other two SC compose the first generation, they are GaAs (Gallium arsenide) and III-IV MJ (Multijunction), Figure 1.2a. The major feature of III-IV MJ is the multiphoton absorption. In other words, this SC is able to absorb in different bandgaps across the solar spectrum. Two or more single-junction

layer composes this cell, in which each layer is stacked by decreasing the energy gap of the semiconductor. The main advantage of this configuration is the reduction of thermalization losses and the efficiency for two, three and four junctions can reach 46%, 44.4% and 34.1%, respectively. However, high cost materials and complex manufacturing limit a high-scale production.

Figure 1.2b shows the second SC generation, which is composed by commercial thin-film like a:Si-H (Hydrogenated amorphous silicon), CdTe (Cadmium telluride) and CIGS (Copper indium gallium diselenide). Cell efficiency for these SC are 12.2% for a:Si-H, 21% for CdTe and 21.7% for CIGS. A higher absorption efficiency is the key advantage compared to Si SC, and this allows the use of thin films of few microns of thickness. Besides, low material application may reduce the final cost; also, transport and installation may become easy task for this technology. However, limiting factor like high toxicity of cadmium, telluride; low abundance of indium and light-induced degradation for a:Si-H can hinder the large-scale application of these cells [JEAN et al, 2015].

Third generation extends the concept of thin film for nanostructured materials such as organic, perovskite, quantum dots, dye-sensitized solar cell (DSSC) and copper zinc tin sulfide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS), Figure 1.2c. Key advantages for this generation is the ability to form flexible, light and thin SC, simple process manufacturing, low-temperature processing compared to those SC from the first generation and second [HAMAN et al, 2008; GREEN et al, 2002]. Solar efficiency for these SC are 20,1% (Perovskite), 11,1% (Organic), 12,3% (DSSC), 9,2% (Quantum dots) and 12,6% (CZTS). Despite the high plenty of organic elements that is advantageous for large-scale deployment, these SC, naturally face constraints issues like low durability and toxicity in Perovskite cells, low lifetime for all SC compared to the Si SC, in which each module has medium lifetime of 25 years [QIAO et al, 2018]. Still, unlike Si, cells from the second and third generation suffer with scarce elements and photodegradation under long time ultraviolet dose.

Figure 1.2. Solar cell generation according to wafer-based and thin-film classification. (a) First generation: wafer-based; (b) second generation: commercial thin film; and (c) second generation: thin-film.

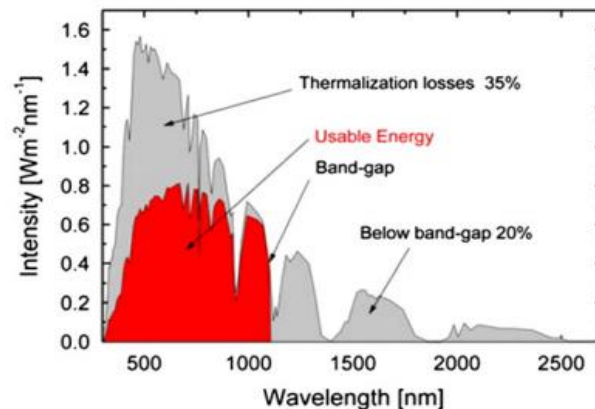


SC technology landscape still drives attention and efforts to cells from the first generation, especially, Si SC. Silicon counts with high abundance in earth crust, non-toxicity and higher cell efficiency. However, one major drawback hinder the enhancement of the efficiency that is solar spectrum mismatch. The maximum theoretic efficiency demonstrated for a single junction SC is 32%, this limit was first theoretically established by Shockley-Queisser [SHOCKLEY; QUEISSER, 1960]. Indeed, SC efficiency is limited also by the fact that sunlight reaches the surface cell in a non-concentrated and diffuse form, so that external devices (mirrors) are required to focus the radiation direct to the cell [CORREIA et al., 2014].

Solar spectrum mismatch brings two consequences to SC with a specific bandgap (E_g), that is the thermalization of charge carriers and sub-bandgap loss, or also called loss by transmitted photons. Thermalization process is generated by absorption of high-energy photons, photons with energy higher than SC E_g . Meanwhile, sub-bandgap losses is generated by transmission of lower energy-photons, photons with lower energy than SC E_g . Both kind of photons, higher and lower energy than SC E_g , cannot be efficiently converted in electric energy. Taking as example Si SC with a bandgap of 1.1 eV (1100 nm), a broad part of the solar spectrum will be lost by thermalization and transmission. Solar spectrum on the surface earth widely ranges from 300 to 2500 nm with maximum intensity around at 500 to 600 nm [RODRÍGUEZ-RODRÍGUEZ, 2016] as it is shown in Figure 1.3. Grey color depicts the solar radiation incident in the earth's surface and the red region depicts the Si sensibility on the solar spectrum. Part of the incident energy (35%) is lost by thermalization and 20% by transmission (sub-bandgap photons) [ASIM et al., 2012].

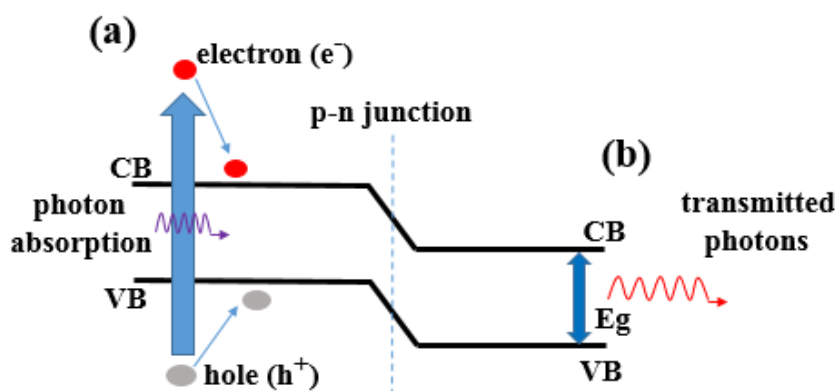
Losses process by thermalized photons and transmitted photons can be represented by the scheme in the Figure 1.4. Thermalization process are generated when charges arise straightforward to the edges of the conduction band (CB) and valence band (VB), process (a). Such excess of energy is readily dissipated as heat and its loss is substantial for SC with small bandgap. Contrarily, the SC cannot absorb transmitted photons, since its energy is not suitable to generate an electron-hole pair. The process (b) represents loss process by transmitted photons [RICHARDS, 2006].

Figure 1.3. Solar spectrum at earth's surface. The red region emphasizes the portion of the terrestrial sunlight that is absorbed by a silicon SC with bandgap of 1.12 eV, and spectral regions that are lost by thermalization and below bandgap or transmitted photons [ASIM et al, 2012].



Spectral mismatch in solar cell motivated many efforts to develop new materials with specific features to overcome such limitation [SARK et al, 2014]. The optimism in SC science inflates with the discover of the enhancement of efficiency conversion by modifying the input spectrum. Such conversion would be possible using lanthanide-based materials in which exhibit upconversion and downconversion phenomenon [CORREIA et al, 2014; ENDE; AARTS; MEIJERINK, 2009]. The next topic, we present a brief physics and chemistry introduction concerning lanthanides elements as well as their application in solar cell. For the sake of brevity, only the most employed lanthanide elements will be treat. Still, we are going to restrict the application of lanthanides elements in amorphous materials as well as their use as luminescent layers.

Figure 1.4. Losses in a single-junction SC. Process (a), thermalization photons and (b), transmitted photons. Adapted from reference [RICHARDS, 2006].



1.2 Lanthanides

Lanthanides ions (Ln^{3+}) are commonly formed by ionization of an outer electron of atoms located at the bottom of the periodic table after lanthanum: from Cerium (atomic number 58) to Ytterbium (atomic number 70), which possess the electronic configuration $5s^2 5p^6 5d^1 4f^1 6s^2$ and $5s^2 5p^6 4f^{14} 6s^2$, respectively [SOLÉ; BAUSÁ; JAQUE, 2005]. Lanthanides ions have general configuration $[\text{Xe}]4f^{n-1} 5d 6s^2$, where [Xe] stands for the Xenon electronic structure and n is the number of electrons in the unfilled $4f$ shell, that varies from 1 (Ce^{3+}) to 13 (Yb^{3+}). Although some ions may assume divalent (Sm^{2+} , Eu^{2+} , Yb^{2+}) and tetravalent state of oxidation (Ce^{4+} , Tb^{4+} , Pr^{4+}), the trivalent state is the most stable. To reach such ionization, the Ln^{3+} may lose a $5d$, $6s$

and one of the $4f$ electrons, leaving a partially filled $4f$ orbital that is shielded by the $5s$ and $5p$ orbitals [DWIVEDI; ZILIO, 2013]. Table 1 summarizes the lanthanide atoms in a trivalent configuration, the number of electrons valence on the $4f$ orbital of each atom and the electronic configuration as well.

Table 1.1: Number (n) of electrons distributed in the unfilled $4f$ orbital of Ln^{3+} ions and the electronic configuration. Adapted from the reference [SOLÉ; BAUSA; JAQUE, 2005].

Atomic Number	(Ln^{3+}) ion	n	Electronic configuration (Ln^{3+})
58	Ce^{3+}	1	$4f^1 5s^2 5p^6$
59	Pr^{3+}	2	$4f^2 5s^2 5p^6$
60	Nd^{3+}	3	$4f^3 5s^2 5p^6$
61	Pm^{3+}	4	$4f^4 5s^2 5p^6$
62	Sm^{3+}	5	$4f^5 5s^2 5p^6$
63	Eu^{3+}	6	$4f^6 5s^2 5p^6$
64	Gd^{3+}	7	$4f^7 5s^2 5p^6$
65	Tb^{3+}	8	$4f^8 5s^2 5p^6$
66	Dy^{3+}	9	$4f^9 5s^2 5p^6$
67	Ho^{3+}	10	$4f^{10} 5s^2 5p^6$
68	Er^{3+}	11	$4f^{11} 5s^2 5p^6$
69	Tm^{3+}	12	$4f^{12} 5s^2 5p^6$
70	Yb^{3+}	13	$4f^{13} 5s^2 5p^6$

Since the orbitals $5s^2$ and $5p^6$ are totally filled electronically, optical and magnetic properties are ruled by the unfilled $4f$ shell and in some ions like Ce^{4+} and Eu^{2+} , by the $5d$ vacant orbital [REID, 2016]. However, yttrium (Y) also has +3 oxidation state and does not show optical transitions. In addition, Lanthanum (La^{3+}) and Lutetium ions (Lu^{3+}) have a completely empty and a completely filled $4f$ shell, therefore they are not optically active. Moreover, the $4f$ - $4f$ direct interaction between neighboring rare-earth

ions may be considered as negligible and the behavior of the 4f electrons seems to be different from that s, p and d electrons [WYBOURNE, 2004].

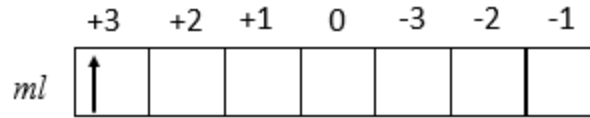
The shielded effect of the 4f orbital results in a poor interaction with the closest neighbor in a crystalline medium, by consequence, these inner electrons do not participate directly in chemical bonds. Such case, leads to the well-known situation “*weak crystalline field*”, which an ion is slightly perturbed by the crystalline field. The effect of the crystal field is to produce a slight shift in the energy levels and to cause additional level splitting within the *f* shell.

The electrons confined within the 4f orbital experiment a rearrange that is parity-forbidden. However, owing to a forced dipole electric transitions, most of the radiative transition become partially allowed by mixing the 4f orbitals with other orbitals that have different parity. In this sense, a promotion of a 4f electron into the 5d orbital are allowed by parity rule. In addition, a charge transfer band (CTB) can also implies an electronic transition in a trivalent lanthanide. This transition is allowed by the Laporte’s selection rule [BUNZLI, 2007].

Taking into account the low perturbation of the 4f electrons by a electric field, the *f-f* transitions become quite narrow and sharp compared to metal ion environment that directly affects the electrons involved on the optical properties. Consequently, a RE^{3+} ion may have similar optical spectra among several different crystalline or amorphous medium [JORGENSEN; REISFELD, 2005; TANABE, 2015].

1.3 Energy levels of the RE^{3+}

When a RE^{3+} ion is dispersed in a crystalline host, it will experiment an electric field that will slightly perturb the $^{2S+1}L_J$ states, where S and L are the total spin and total orbital quantum number, J is the total angular quantum number, which can assume the values $J = (L+S); (L+S) - 1; (L+S) - 2; \dots; (L-S)$ [SOLÉ; BAUSÁ; JAQUE, 2005]. In spectroscopic notation, *L* may assume different symbols that are derived from the spectroscopic lines corresponding to s, p, d, f (sharp, principal, diffuse and fundamental) orbitals. For example, we may predict the ground state to the Ce^{3+} ion, which has an electronic configuration $4f^1 5s^2 5p^6$. According to the Pauli Exclusion Principle, this only one electron 4f may be distributed in the following diagram box:

Figure 1.5. Electronic distribution of the Ce^{3+} ion in a box diagram.

Since $ml = +3$ and $L = \sum ml$, the orbital quantum number (L) will be 3. Each L is associated to a symbol that is characteristic of the spectroscopic lines corresponding to the orbitals sharp, principal, diffuse and fundamental (s , p , d , f).

$$\begin{array}{ccccccccc} L = & 0 & 1 & 2 & 3 & 4 & 5 & & \\ & S & P & D & F & G & H & & \end{array} \quad (1)$$

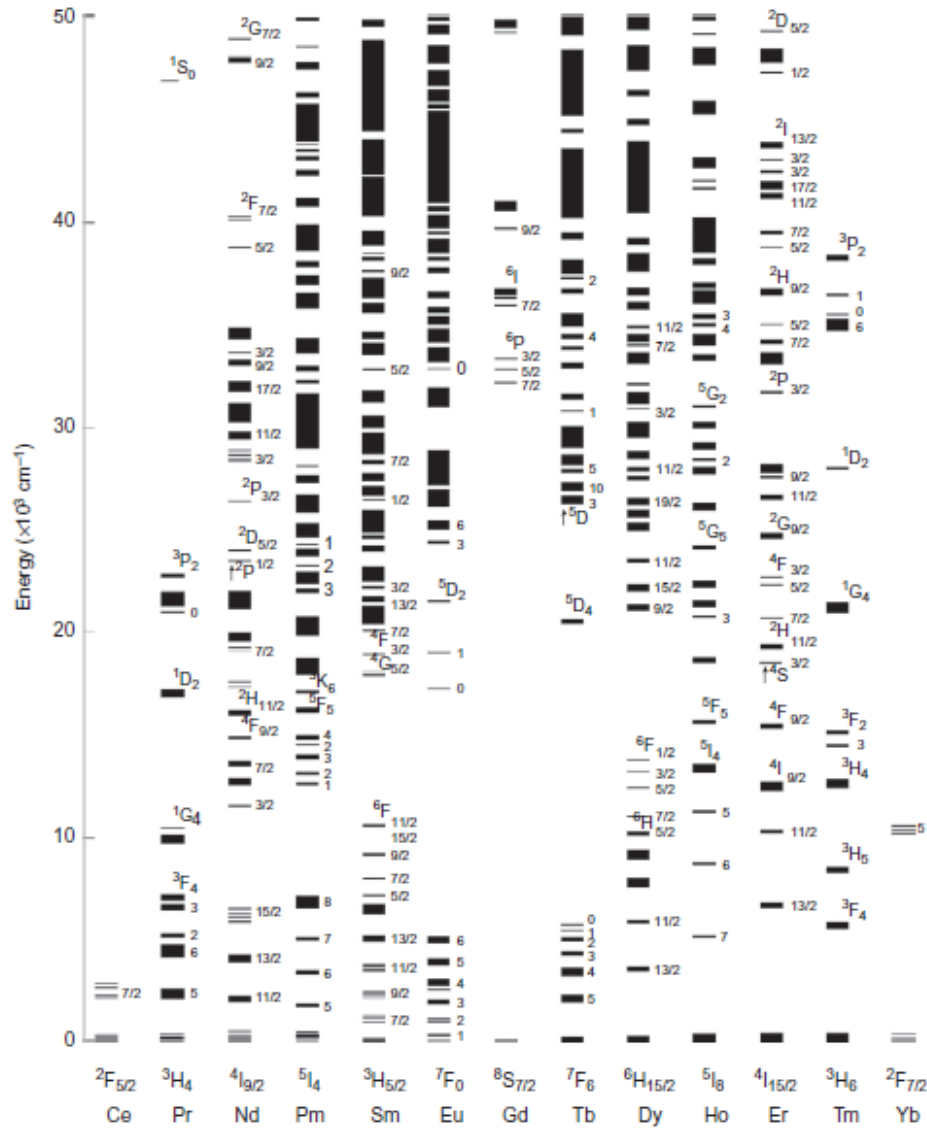
Assuming that $L = 3$, the electron from the Ce^{3+} will be in an orbital associated to a quantum number F . Another quantum number to determine is spin total (m_s) that is associated to the electronic orientation and can have positive and negative values. Assuming a positive configuration to the spin electronic ($+1/2$), the m_s will be equal to $+1/2$, and considering that $S = \sum m_s$, the total spin is $S = +1/2$ and $2S+1$ is equal to 2. As $J = (L+S); (L+S) - 1; (L+S) - 2; \dots; (L-S)$ and S is $+1/2$, the state with the lowest J value ($L-S$) is $5/2$. Therefore, spectroscopic term for the ground state of the Ce^{3+} ions is $^2F_{5/2}$.

The barycenter of energy of each $^{2S+1}L_J$ states may change according to the electric field surround the Ln^{3+} , since the electric field depend on the site symmetry and the nature of the ions in the crystal [YUHUA, 2015]. However, since the Re^{3+} ions assume a free-ion behavior, the position of the multiplets are almost independent of the crystal. Therefore, the gross feature of the energy level diagram remain unchanged [SOLÉ; BAUSÁ; JAQUE, 2005]. The maximum number of sublevels components for each $^{2S+1}L_J$ level is given by $2J+1$ when J is an integer and $2J+1/2$, when J is half-integer.

The absorption spectra of the Re^{3+} ions in lanthanum chloride crystal were target of extensive research by Dieke's group [BUNZLI, 2007]. The entire $^{2S+1}L_J$ levels of energy of all the trivalent ions are shown in the Figure 1.6. The distribution varies from Ce^{3+} ($4f^1$) to Yb^{3+} ($4f^{13}$). The short horizontal lines indicates the energies of the $^{2S+1}L_J$ multiplets and the width of the lines representing the crystal-field splittings of the multiplets. The largest split among the states by the order of 10^4 cm^{-1} are caused by

Coulomb interaction. The spin-orbit (S-L) interaction splits the terms in multiples separated by the order of 10^3 cm^{-1} . For the last, the crystal-field interaction split the multiplets by order of 10^2 cm^{-1} [WHEG et al, 2000].

Figure 1.6. Energy level for trivalent rare-earth ions (RE^{3+}) in LaF_3 crystal [ELISEEVA; BUNZLI, 2010].



1.4 Upconversion

One of the most explored spectroscopic properties of the RE^{3+} is the upconversion (UC). The origin of the first research in UC can be date in 1959 by Bloembergen, who proposed lanthanide-doped materials as infrared quantum counters [BLOEMBERGEN, 1959]. Nowadays, the interest in this phenomenon is far beyond

and covers a wide research field. A huge variety of potential applications is explored, for example, bio-imaging [LIU; HOU; GAO, 2014], white light modulation [KARATAIRI; HOPPE, 2016; ELISEEVA; BUNZLI, 2011], thermal sensors [LALLA et al, 2015], photocatalysis [ULLAH et al, 2017], spectral converters for sola cell [GOLDSCHMIDT; FISCHER, 2015; SHPAISMAN, 2008], solid-state lasers and others [LIAN et al., 2013; -19; DONG, 2017; VASILIEV, 2016].

The term UC refers to a non-linear process in which the continuous absorption of two or more low-energy photons leads to the emission of high-energy photons (anti-Stokes emission) [REID, 2016]. Figure 1.7 summarizes the simplified mechanisms of UC emissions, which may be described as following: the first step corresponds in an excitation through a near-infrared source, indicated by the orange arrow in the Figure 1.7 (a)-(e). In this step, one electron that is in its ground state (E_0) is excited and occupies the first metastable state (E_1). This first step is fundamental and common to all the mechanisms; excited state absorption (ESA), energy transfer upconversion (ETU), photon avalanche (PA), cooperative energy transfer (CET) and energy migration upconversion (EMU). The second step differs from each mechanism. For example, the first mechanism (Figure 1.7a), the UC occurs in a single ion. After absorption of one photon, the same excited electron (now in E_1 state) absorbs another photon of the same energy and goes to a further higher excited state (named as E_2). From this state, radiative transition is observed with emission of a higher-energy radiation.

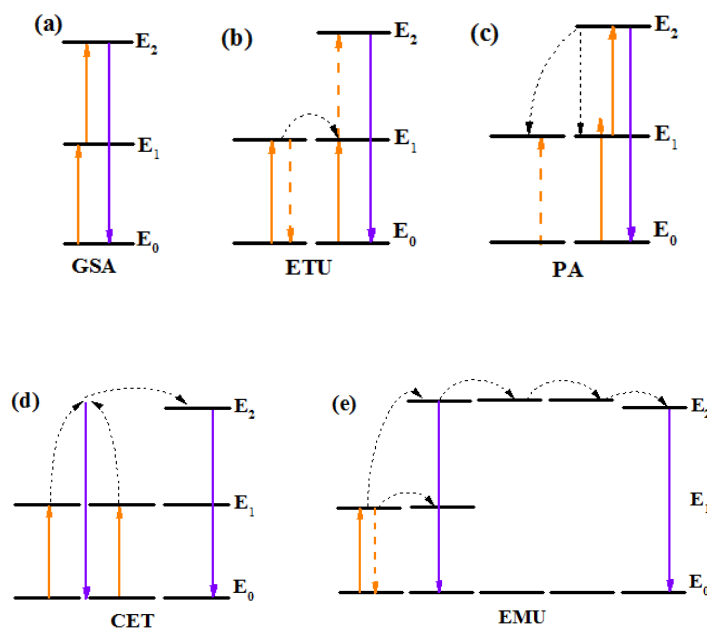
In an ETU mechanism (Figure 1.7b), two ions are involved and they are commonly named as sensitizer and activator, in which the sensitizer, generally, has a higher cross section than the activator. Since the first intermediated state from the sensitizer and activator are spaced in a close distance (resonant), the sensitizer transfer energy to adjacent ion that is excited to the E_2 state. Commonly, the mechanism that happens between two ions is called “*upconversion cooperative system*” and can be observed between two similar ions or different ions [SUN, 2015]. However, for different ions the primordial condition is that the metastable state of the two ions must to be energetically close.

When the energy gap between an intermediated state and the ground state is non-resonant with the pump power, the PA can produce population in an excited state whose energy exceeds that the pump photon [JOUBERT et al, 1999; STRUMPEL et

al, 2007], as it is shown in the Figure 1.7c. This electron will be excited to a higher state energy (E_2) by an ESA. Then, a cross relaxation (CR) excites an adjacent ion and the level of the same ion. It is peculiar to mention that a UC photon can be generated without a GSA step. In this case, the consumption of superexcited ions must be less than the ground state ions [SUN, 2015].

Another mechanism that takes place in a cooperative sense is the CET, shown in the Figure 1.7d. In this process, two sensitizer ions are needed to sensitize the activator. This is due to an absence of a long-lived metastable state of the sensitizer. The last mechanism is the EMU, shown in the Figure 1.7e. In 2011, Liu and coworkers introduced this new UC mechanism based in core-shell structured nanoparticles. In the EMU, the energy transfer from the core to the shell follows a cascade-type sensitization in which the sensitizer is located on the core and the activator on the last shell [WANG, 2011].

Figure 1.7. Simplified energy levels for different two photons mechanisms in UC process. The excitation of the sensitizers ions are represented by orange arrows, non-radiative transition are represented by black dotted arrows and the purple arrows represent visible emission from the excited state E_2 to the ground state E_0 , respectively.

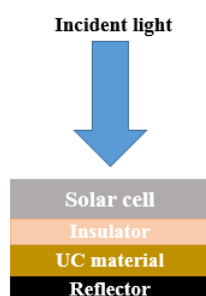


Despite the benefits resulting from the UC emissions (see applications in the beginning of this section), the main limitation of the RE^{3+} is the narrow and weak absorption associated with the nature of the $4f-4f$ transitions [BUNZLI; PIGUET, 2005], which is shielded by the orbitals $6s$ and $6p$. For comparison, the Yb^{3+} that is the most efficient sensitizer used for generation of UC emission, has approximately a cross section of 10^{-20} cm^2 , that is 1000 to 10000 lower than a dye molecule ($10^{-17} - 10^{-16} \text{ cm}^2$). Still, the narrow spectral absorption, over 10 times narrower than an organic dye, compromises their utility for several applications. For example, the excitation using natural sources, like the sun, is not feasible to generate UC emission. Indeed, this phenomenon happens by using commercial sources, like diode laser operating at 808, 980 and 1500 nm [RODRÍGUEZ-RODRÍGUEZ, 2013]. Last but not the least, the total efficiency of an UC system can reach a maximum 50% since two photons is necessary to provide one photon.

1.5 Upconversion for photovoltaic application

Bringing back the concept of solar mismatch in solar cell, here considering the transmitted photons, first mentioned on the introduction of this chapter, we are able to scale-up one of the most interesting application of the upconversion phenomenon. Trupke et al. [TRUPKE; GREEN, WURFEL, 2002] performed the first theoretical approach investigating UC in photovoltaic devices. The authors report a theoretical system in which an upconverter layer is located in the rear level of a bifacial solar cell and the harvesting of sub-band-gap photons allowed them to find 63,2% of quantum efficiency for concentrated sunlight and 47,6% for nonconcentrated sunlight. Figure 1.8 summarizes the system used by Trupke et al.

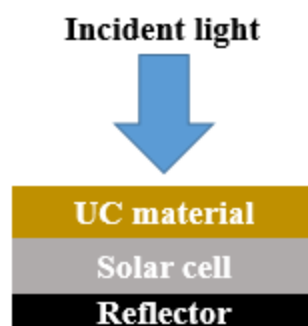
Figure 1.8. Scheme of an ideal system for UC in a bifacial solar cell proposed by Trupke et al. Adapted from the reference [TRUPKE; GREEN, WURFEL, 2002].



The packed system is composed by a bifacial solar cell, an insulator to isolate electronically the solar cell and the UC layer. Beneath the UC material, a reflector is located to reflect back the light emitted by the UC layer. Trupke et al. assumed that a photon selectivity would be applied to generate extra electron-hole pairs on the solar cell. In other words, the UC material would absorb the radiation transmitted by the first layer, here considered as solar cell. Then, the transmitted radiation absorbed by the UC material is delivered with a higher energy photon. The rear reflector located below the UC layer, reflects the light back to the solar cell. In this way, all the radiation converted by the UC layer is used to generate an electron-hole pair on the photovoltaic device.

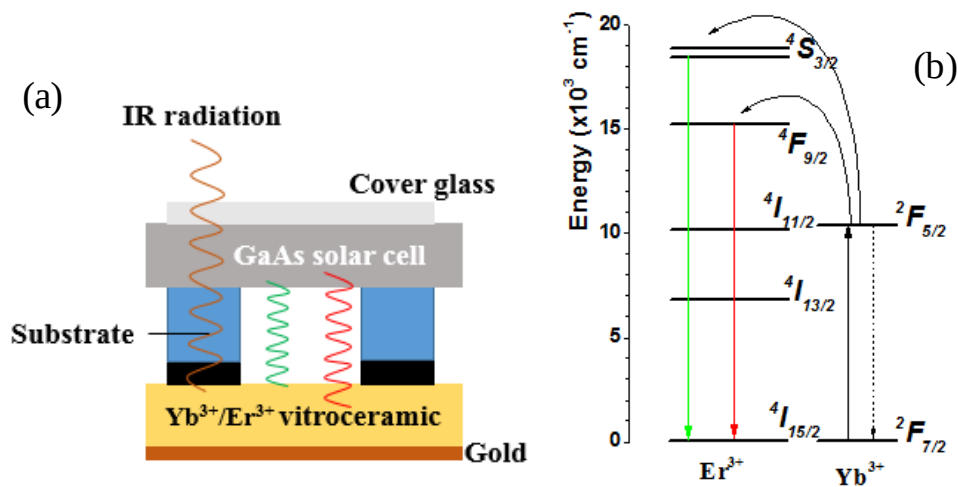
Viorel Badescu [BADESCU, 2008], in 2008, presented an extended study of the seminal work of Trupke et al. Badescu compared two different approaches: (i) a system composed by a solar cell and Upconversion layer (SC-UC) and (ii) upconversion layer and solar cell (UC-SC). In other words, the system (ii) presents the upconversion layer on the top level of the solar cell. Indeed, in this new approach, it is totally predictable that part of the radiation emitted by the UC layer, would be lost on the top surface (emission in all spatial directions). Moreover, part of the incident radiation would be lost by scattering on the UC layer. Therefore, no benefit can be expected when a UC layer is placed at the front of the solar cell.

Figure 1.9. Experimental scheme of an UC material and a solar cell proposed by Badescu. Adapted from the reference [BADESCU, 2008].



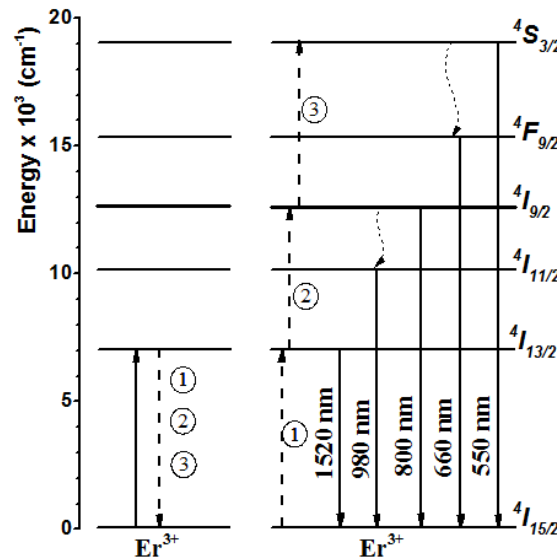
Few years earlier, in the 90th years, experimental insight has shown promising results by using the rare earth Er^{3+} and Yb^{3+} as upconverter materials in GaAs solar cell. In 1996, Gibart et al. [GILBART, 1996] developed a device based in a vitroceramic co-doped with $\text{Yb}^{3+}/\text{Er}^{3+}$ to use part of the infrared radiation otherwise lost by transmission in a GaAs solar cell. Figure 1.10a shows the setup used and 1.10b shows the energy levels of the $\text{Yb}^{3+}/\text{Er}^{3+}$ pair according to the mechanism proposed by the authors. An infrared laser (980 nm) irradiates the front face of a GaAs solar cell. The radiation pumping is called “*bellow bandgap IR irradiation*” because the radiation energy is lower than the bandgap of the solar cell, so that the incident radiation is transmitted to the upconverter material. By two-photon UC mechanism, the vitroceramic emits green and red radiations, according to the mechanism from the Figure 1.10b in which the Yb^{3+} ion absorbs two photons and after energy transfer to the closest Er^{3+} , then useful radiation is emitted to generates electron-hole pairs in a GaAs solar cell. In this experiment, a Ti-Sapphire IR laser at 1.39 eV lighted the GaAs solar cell, which has bandgap of 1.42 eV. For an input excitation of 1 W, the authors found an efficiency of 2.5% illuminating a substrate of 0.039 cm² of sensitive area

Figure 1.10. (a) Experimental setup of a GaAs solar cell coupled with $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped vitroceramic, and (b) energy levels showing red and green emissions after energy transfer from Yb^{3+} to Er^{3+} . Figure (a) was adapted from the reference [GILBART, 1996].



Regarding to the most commercial deployed solar cell, silicon was first applied in a proof-of-principle in 2003, when Shalav et al. [SHALAV, 2007] reported a bifacial solar cell with the upconverter $\text{NaYF}_4:\text{Er}^{3+}$ in the rear side of the device. Indeed, the rare earth Er^{3+} is one of the most useful ion for upconversion applications. The first excited state is the $^4I_{13/2}$ and the energetic different between this state and the ground state ($^4I_{15/2}$) is 0,827 eV that is equivalent to 1500 nm [CHEN, 2015]. Still, the states $^4I_{9/2}$ and $^4S_{3/2}$ are multiples of the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition, so that an excitation at 1500 nm is ideally suited to populates the excited states and then releases visible and near-infrared photons due to its upconversion. Figure 1.11 shows UC between two ions Er^{3+} in which one is the sensitizer and the second one is the activator. Upon excitation around 1500 nm, the excited levels of the activator can be populated after subsequent energy transfer (ET) from the sensitizer, and then, radiative transitions can be observed through the emission of light at 980, 810, 660, 550 and 410 nm.

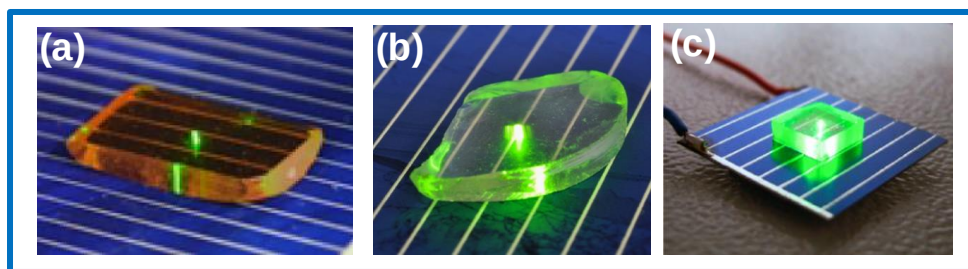
Figure 1.11. Energy levels of two Er^{3+} ions showing UC process upon excitation at 1500 nm. Three subsequent ET from the sensitizer to the activator guarantee the population of the excited states in which UC emission is observed.



Another proof-of-principle is that when a luminescent layer is placed on the top level of a solar cell. Despite proved by Badescu, that first mentioned no benefits can be achieved by placing a UC material in front of a solar cell, studies have shown an

increase in the photocurrent when the samples are excited between 1480 and 1550 nm [RODRÍGUEZ-RODRÍGUEZ et al, 2016; KRISHNAIAH et al, 2017; HENKE et al, 2009]. Indeed, in a commercial point of view, a device in which a layer present deleterious effect to the global efficiency is not desired, otherwise merely for research and developing new luminescent materials. Moreover, since the layer do not modify the solar cell features but only the incident radiation by spectral modification, applications of layers on the top level of solar cell are still attractive to stud photocurrent enhancement by UC properties. Figure 1.12 shows three experimental setup to measure photocurrent response when a UC layer is placed on the top level of a silicon solar cell. In Figure 1.12a, a tellurite glass doped with Er^{3+} and excited at 1500 nm; in 1.12b, a fluoroindate glass co-doped with Yb^{3+} - Er^{3+} and is excited at 1480 nm and in 1.12c, Er^{3+} containing fluorozirconate glass is excited at 1540 nm. All the glasses are perpendicularly excited by a near-infrared source and the green color is due to the Er^{3+} transition ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$). In both cases, the samples are not use as encapsulated glass. In other words, samples are smaller than the active are of the solar cells, as we can see from the digital pictures (a), (b) and (c).

Figure 1.12. Working principle of a luminescent layer placed at the top level of a silicon solar cell. Adapted from the references [RODRÍGUEZ-RODRÍGUEZ et al, 2016; KRISHNAIAH et al, 2017; HENKE et al, 2009].

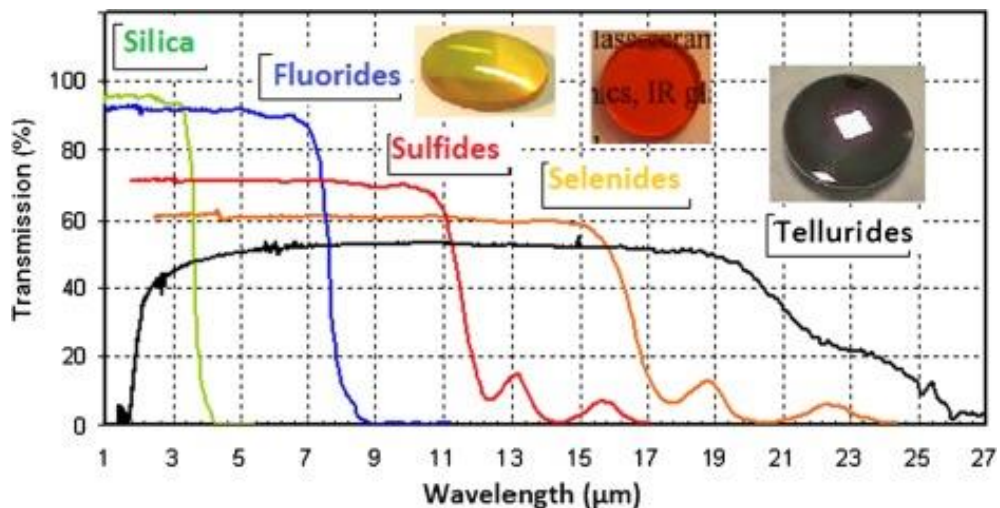


1.6 Materials for upconversion

There is a vast literature concerning monocrystalline and polycrystalline upconverter materials as luminescent layer for solar cell, in this section we introduced an overview regarding materials for potential upconversion application. Still, we restrict throughout the text to the use of the Er^{3+} -doped materials for UC in luminescent layers, as introduced in the last topics. As scribed before, lanthanide as Er^{3+} , for example, exhibit absorption in the near infrared. The main interest in materials for upconversion is that the window transparency extend to the visible and infrared domain [CALVEZ, 2017]. Visible transparency is defined by electronic transition from the valence band to the conduction band [NALIN et al, 2016]. In other words, the bandgap (E_g), that is the energy gap between the valence and conduction band, which is associated to short wavelengths, defines the transparency in the visible range. On the other hand, vibrational modes defines the transparency in longer wavelength (infrared). Generally, massive atoms such as selenium (Se), sulfur (S) and tellurium extend the transmission band to longer wavelengths [CALVEZ, 2017].

Figure 1.13 presents the window transparency for some Chalcogenide glasses. The global transparency is governed by the electronic transition (short wavelength) and vibrational modes (longer wavelength). Silica and fluoride glasses have high transparency in the visible range (not shown), meanwhile sulfides, selenides and tellurides glasses have lower transparency in the visible range.

Figure 1.13. Window transparency for Chalcogenide glasses [CALVEZ, 2017].



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UC mechanisms under 1550 nm excitation in Er^{3+} -doped fluoroindate glasses

In this chapter, we report the preparation of fluoroindate glasses by the melting-quenching method. A series of samples bearing different Er^{3+} concentrations were studied and characterized according to their luminescent properties. Upon excitation at 1550 nm, the Er^{3+} -doped fluoroindate glasses show green, red and near-infrared emissions. Energy transfer upconversion (ETU) of the closest Er^{3+} neighbour ions is the mechanism responsible for the upconversion (UC) emissions and its probability increases to higher Er^{3+} amount. Enhanced near-infrared emission at 1000 nm, is observed when the glass contains 7 mol% of Er^{3+} , which increases the photovoltaic response of a monocrystalline and monofacial silicon solar cell. For the photovoltaic applications, all samples were prepared to use as encapsulated glasses with same solar cell dimensions.

2.1 Introduction

Luminescent layers for solar cell (LLSC) have been studied in the last decades to increase the solar photons harvesting and thereby enhancing the solar cell (SC) efficiency [LAHOZ, 2011; RICHARDS, 2006; SHALAV, 2004]. It has been demonstrated that the integration of bulk inorganic glasses in different SC display some advantages comparing to the powder materials [SONG; ZHANG; ZHU, 2016; CHANDER, 2016]. Such layers offer less steps preparation methods, allow a fast assembly and no interference in the electric current flow on the semiconductor is observed due to the absence of contact with the photoanode. Moreover, optical properties such as absorption and emission of the active center may be optimized separately from the SC.

Most of these layers comprises near infrared absorption and provide visible and near infrared emission by the addition of certain types of trivalent lanthanides Ln^{3+} [FEENSTRA, 2015; RODRÍGUEZ-RODRÍGUEZ, 2016]. Er^{3+} has become one of the most deployed candidate for SC application due to its energy levels that are multiples of the transition $^4I_{15/2} \rightarrow ^4I_{13/2}$, which may be activated when excited at wavelengths between 1400 and 1580 nm [QIAN, 2004; GIBART, 1996]. In a resonant manner, the transitions that raise the green ($^4S_{3/2} \rightarrow ^4I_{15/2}$), red ($^4I_{9/2} \rightarrow ^4I_{15/2}$) and near infrared

emissions ($^4I_{11/2} \rightarrow ^4I_{15/2}$) may occur by sequential absorption of lower energy photons of the same through the energy state absorption (ESA) and energy transfer up-conversion (ETU) mechanisms [DONG; SUN; YAN, 2015; MARTIN 1999]. Indeed, previous papers have been reported the energy transfer interaction between Er^{3+} - Yb^{3+} co-doped glasses [YANG, 2014; LI, 2011; SHAN, 2011].

Considering the most traditional and employed SC, the crystalline silicon (c-Si) absorbs radiation more effectively closed to his bandgap (1.12 eV) [MAALEJ et al, 2016]. In other words, photons with higher wavelength than 1100 nm are lost by transmission and, therefore, may not be used to generate photocurrent. These are called sub band-gap photons [GOLDSCHMIDT; FISHER, 2015]. An alternative to overcome this drawback is to use lanthanide-based materials, which convert infrared radiation into visible light and, in some cases, near infrared radiation through up-conversion (UC) mechanisms. This phenomenon consists of a sequential absorption of two or more photons by a RE^{3+} ion, followed by the emission of one photon with higher energy [SHALAV; RICHARDS; GREEN, 2007; AUZEL, 2004]. Thus, these materials can increase SC photocurrent by converting absorbed low energy photons in high-energy photons useful for the silicon cells [CORREIA et al, 2014].

Many efforts have been devoted to the study of luminescent properties of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped glass systems in order to increase the efficiency of SC through UC emissions [WILD, 2010; YAO, 2016; SHAN; DEMOPOULOS, 2010]. Among the glass systems, fluoroindate glasses are promising candidates due to their low phonon energy ($\sim 500 \text{ cm}^{-1}$) and large transparency window from 250 to 8000 nm, depending the chemical composition [BORRERO-GONZÁLEZ et al, 2013]. M. Rodríguez *et al.* reported visible and near infrared UC emissions of an $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped fluoroindate glasses upon 1480 nm excitation. Furthermore, they showed that visible and infrared emissions improved the response in the short-circuit current of a monofacial and monocrystalline silicon plate. Recently, Balaji *et al.* reported the influence of 980 nm emission in an $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped fluorotellurite glass in the photocurrent of a multi-crystalline silicon SC. In fact, the majority of the works are aiming to an enhancement of 980 nm emission through the energy transfer due to the $\text{Er}^{3+} \rightarrow \text{Yb}^{3+}$ interaction.

Although the $\text{Er}^{3+}/\text{Yb}^{3+}$ pair is vastly used for enhancing silicon SC efficiency, this work aims to study that the strictly control of Er^{3+} concentration containing in a low

phonon energy glass host, can provide an enhancement of SC current through UC emissions under near infrared excitation. The benefits of Er^{3+} single doped materials concerning SC applications have already been demonstrated [SHALAV, 2005; WANG, 2012; PELLÉ; IVANOVA; GUILLEMOLES, 2011]. In this context, we present the preparation and UC mechanism in fluoroindate glasses by addition of different Er^{3+} amounts. Taking into account photoluminescence analysis, a detailed investigation was done to understand the role of Er^{3+} in the energy transfer according to their Vis-NIR emission and decay time dynamics. Furthermore, we analyzed the dependence of UC emission in the enhancement of short circuit-current of a commercial silicon when excitation at 1550 nm is used.

2.2 Experimental Section

The glass samples with different Er^{3+} amounts were prepared according to the molar composition $(100-x)[40\text{-InF}_3\text{-}20\text{ZnF}_2\text{-}20\text{SrF}_2\text{-}20\text{BaF}_2]\text{:xErF}_3$ varying x from 0.1 to 7 mol%. The samples were prepared by the standard melting quenching method. The raw materials were In_2O_3 (Metaleurop-99.999%), ZnF_2 (Fluka-97%), SrF_2 (Alfa Aesar-99%), BaF_2 (Acros Organics-99%) and Er_2O_3 (Sigma-Aldrich-99.99%). The reagents were stoichiometrically weighted and well-mixed with an excess of ammonium bifluoride, NH_4HF_2 , and heated at 330 °C during 2 h for fluorination reaction of the oxides precursors. The melting was carried out at 850 °C during 20 min in a platinum tube placed into a vertical electric furnace. Then, the melt was poured out onto a pre-heated mold at 240 °C, annealed for 2 hours and slowly cooled at room temperature to minimize residual internal stress during the quenching process. This preparation method is presented elsewhere [MANZANI et al, 2013]. For the sake of a better understanding, the samples were named as IZSB-E01, IZSB-E05, IZSB-E1, IZSB-E2, IZSB-E4, IZSB-E5 and IZSB-E7.

The absorption spectra were carried out at room temperature on the polished samples by using a Carry 500 Spectrophotometer (Varian) from 200 to 2000 nm with a resolution of 1 nm. The UC luminescence measurements were performed under excitation at 1550 nm with maximum power of 22 mW (The Rock – NP Photonics). The visible and near infrared emissions were recorded with a portable Ocean Optics (USB 2000+) detector, sensitive from 200 to 1100 nm. The luminescence decay curves were

obtained by using a Horiba Jobin Yvon fluorimeter (Fluorolog 3) equipped with a two-photomultiplier tube (PMT) for visible and near-infrared detections (Hamamatsu model H10330A) and a pulsed Xe lamp of 450 W. All measurements have been performed at room temperature.

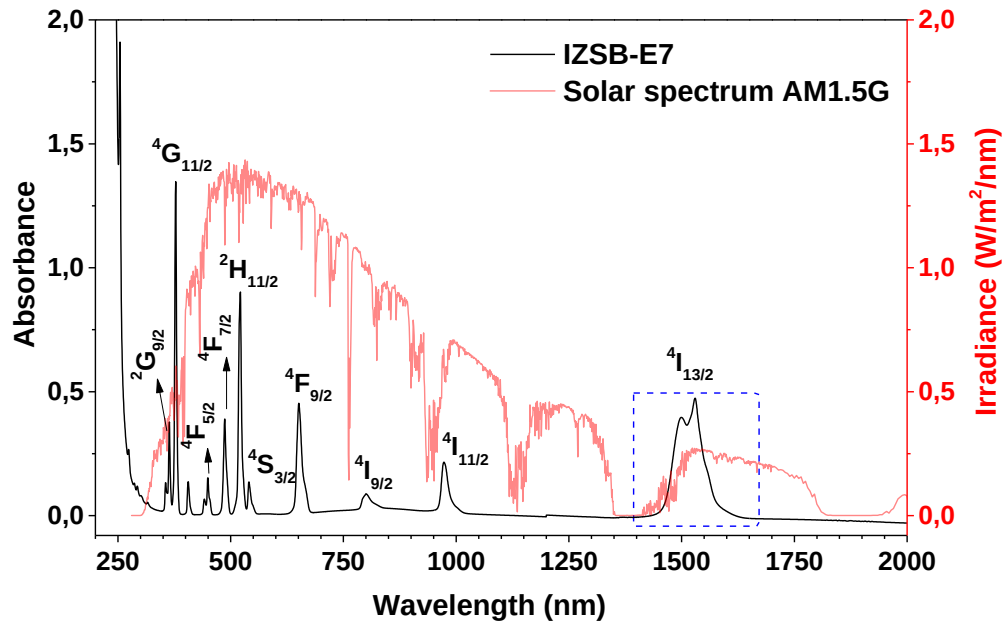
As a proof of concept, the efficiency of luminescent layers was analyzed by performing photocurrent measurements in a monofacial and monocrystalline silicon solar cell (BPW-32 diode) with dimensions of 5.4 x 4.3 x 3.2 mm and sensitive area of 7.5 mm². For such purpose, the functional glass pieces were placed on the surface of the SC. For the photocurrent measurements, the samples were cut and polished in order to obtain similar dimensions of the SC, acting as encapsulating glass with 7.5 mm², same area of the diode. Sample thickness of all samples was 1 mm. The sides of the samples were covered using aluminum foil in order to minimize the loss of the emitted radiation. The samples were placed on the top of the silicon diode and perpendicularly excited with a focused broadband source operating with maximum at 1550 nm. The microampere short-circuit current was recorded for all samples by using a Keithley multimeter model 2700.

2.3 Results and discussions

2.3.1 Photoluminescence properties

The absorption spectrum of the sample IZSB-E7 is depicted in Figure 2.1. Erbium (Er^{3+}) ions absorption bands comprise the visible region from 380 nm to the infrared at 1700 nm. Absorption bands are assigned to the electronic transitions from ground state level $^4\text{I}_{15/2}$, to the $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{9/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$, $^2\text{H}_{11/2}$, $^4\text{F}_{7/2}$, $^4\text{F}_{5/2}$, $^4\text{G}_{11/2}$ and $^2\text{G}_{9/2}$ excited states [PUJOL et al, 2013]. The absorption edge at UV part (below 300 nm) corresponds to the transparency of the host glasses.

Figure 2.1. Absorption spectrum of the sample IZSB-E7 (black line) and partial solar radiation spectrum AM1.5G (pink line). The dashed blue square emphasize the overlapping between Er^{3+} absorption and solar spectrum emission over 1550 nm.

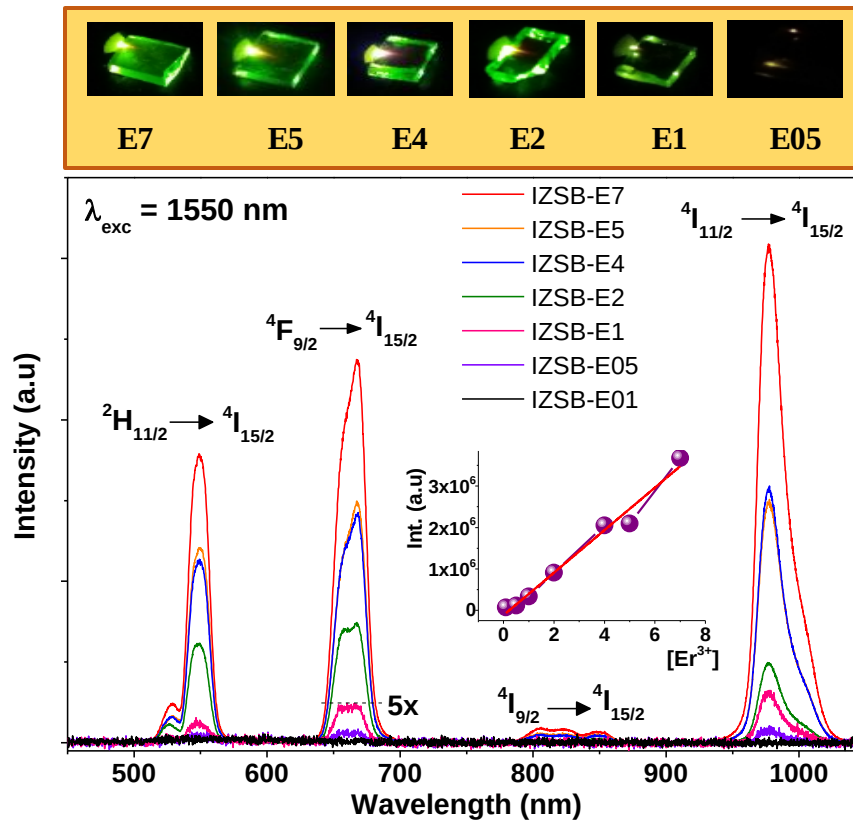


At first comparison, the largest Er^{3+} absorption (around 1500 nm) matches with a spectral portion of the solar spectrum whose is partially shown in Figure 2.1. In addition, it is important to emphasize that wavelengths above 1100 nm are not absorbed by a silicon SC. In this way, the use of Er^{3+} is feasible and promising for PV applications and it is possible to increase the efficiency of a traditional SC by the absorption of sub-bandgap photons and convert them into useful energy inside the silicon band-gap energy [VAN DER ENDE; AARTSA; MEIJERINK, 2009]. Indeed, in Figure 2.1, the dashed blue square represents the region of Er^{3+} absorption; however the intensity of their bands does not represent a real area comparison with the solar spectrum which is out of range scale.

Figure 2.2 shows the emission spectra of IZSB samples with the characteristic Er^{3+} emissions around 525, 550, 660, 820, 850 and 979 nm, assigned to the transitions $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$, $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ and $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$, respectively. All the spectra were obtained under excitation at 1550 nm and 20 mW. As it is shown, the infrared emission is stronger than the green and red one for the sample E7. For the IZSB-E01 sample, no emission is seen with the naked eye and

only a very weak signal was detected in the PL measurements. The emissions show a great dependence on the Er^{3+} concentration, the intensity increases and reaches a maximum in 7 mol%. Still, the Figure 2.2 shows digital pictures of the samples, whose present a remarkable green emission for the samples IZSB-E7, IZSB-E5, IZSB-E4 and IZSB-E2, a weak emission for IZSB-E1 and a very weak green spot for the sample IZSB-E01 (not shown). All the samples have the same dimensions and the laser beam was sideward incident.

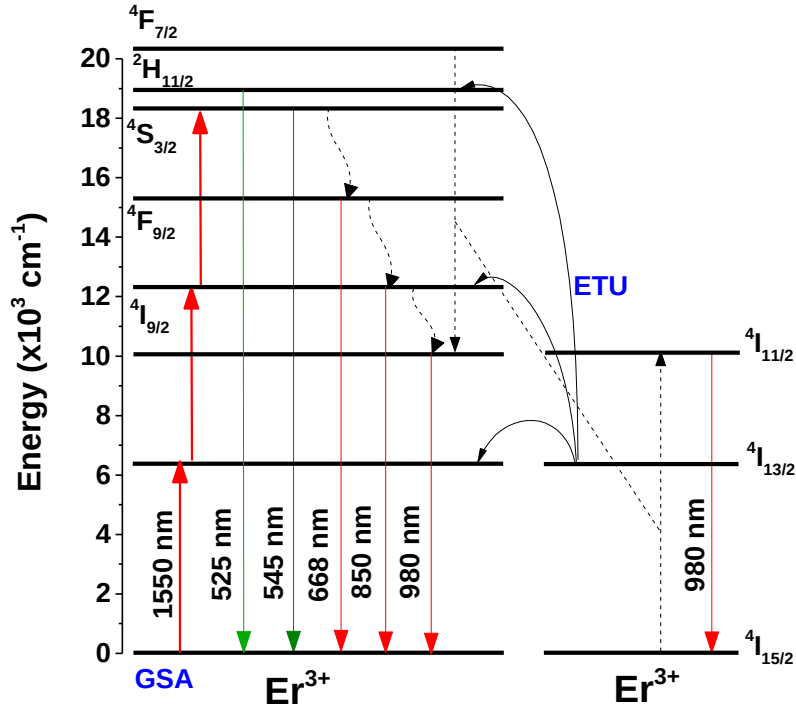
Figure 2.2. Visible and near-infrared UC emission upon 1550 nm excitation and digital pictures of the samples (top level). The sample IZSB-E01 does not exhibit emission in the visible region and the UC emission is negligible. The intensity of the samples IZSB-E1, IZSB-E05 and IZSB-E01 was multiplied by a factor of 5.



It is noteworthy to mention that the emission at 979 nm is one of the most desirable emissions for SC applications. This emission is equivalent to Si bandgap (1.1

eV); therefore, it is more able to generate photocurrent comparing to the green and red emission, which present a higher thermalization losses [RICHARDS, 2006]. From the Figure 2.2 we can see a broadband emission at 979 nm comparing to the visible emissions. The intensity dependency with the Er^{3+} concentration follows the same trend to the visible emissions. The highest intensity emission is observed for the sample with 7 mol%. The mechanisms which lead to the visible and near infrared emissions of the Er^{3+} , involve two well-known established mechanisms: (i) ground state absorption (GSA), and (ii) energy transfer upconversion (ETU) [CATUNDA et al, 1996; KRISHNAIAH, 2016]. Upon excitation at 1500 nm, electrons from the ground state level $^4\text{I}_{15/2}$ are excited to the first energy level $^4\text{I}_{13/2}$ through the ground state absorption (GSA). After subsequent ETU and non-radioactive transitions, the levels $^4\text{I}_{11/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$ and $^4\text{H}_{11/2}$ are populated. Since the energy difference between the states $^4\text{I}_{9/2}$ and $^4\text{I}_{11/2}$ is $2,300\text{ cm}^{-1}$, it requires more than 4 phonons in a fluoroindate host (energy phonon 500 cm^{-1}) to relax non-radiatively, therefore, a three-sequential ETU is favored. From the populated states mentioned above, radiative transitions take place due to the relaxation of excited electrons to the ground state, through the transitions $^4\text{I}_{11/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$, $^4\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$. The infrared UC emission is higher compared to the green and red one for the sample IZSB-E7, this indicates a higher rate of population of the state $^4\text{I}_{11/2}$. In fact, the Er^{3+} emissions rate are highly dependent with ion concentration, wavelength and excitation power [VETRONE, 2003; LU; GILLIN; HERNÁNDEZ, 2014; KUMAR; POKHREL; SARDAR, 2012]. Still, for the sample IZSB-E7 we believe that an ETU increases the NIR emission, meanwhile for lower amount (2, 1 and 0.5 mol%) the red and infrared, the intensity is quite similar. A third and not disposable mechanisms that may takes place, is the cross relaxation (CR). The energy difference between the transitions $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ is very close, thus the population of the state $^4\text{I}_{11/2}$ may occurs by the CR mechanisms and increase the NIR emission. The Figure 2.3 represents the partial diagram levels of energy of Er^{3+} ions in fluoroindate glasses.

Figure 2.3. Schematic energy level diagram for Er^{3+} -doped fluoroindate glass under excitation at 1550 nm.



Decay curves of the samples regarding the green, red and NIR emissions are depicted in the Figure 2.4 and the values of the experimental decay curves are depicted on the table 1. The samples were excited at 521 nm and emissions were fixed at 550, 668 and 980 nm. The curves were fitted by a mono-exponential function and the life times are shown in the table 2.1. The interaction $\text{Er}^{3+}\text{-Er}^{3+}$ plays an important role since its length is ruled by the Er^{3+} concentration, and the smaller distance is straight responsible by the decreasing in lifetime for all the radiative emissions. The longer decay time for the states $^4\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ comparing to the state $^4\text{I}_{11/2}$, indicates that these first two state are associated with more non-radiative transition process, meanwhile, the population of the state $^4\text{I}_{11/2}$ is favored, leading to a higher intensity in the PI measure.

Figure 2.4. Decay time for green, red and near-infrared emission under excitation at 521 nm, figure (a), (b) and (c), respectively.

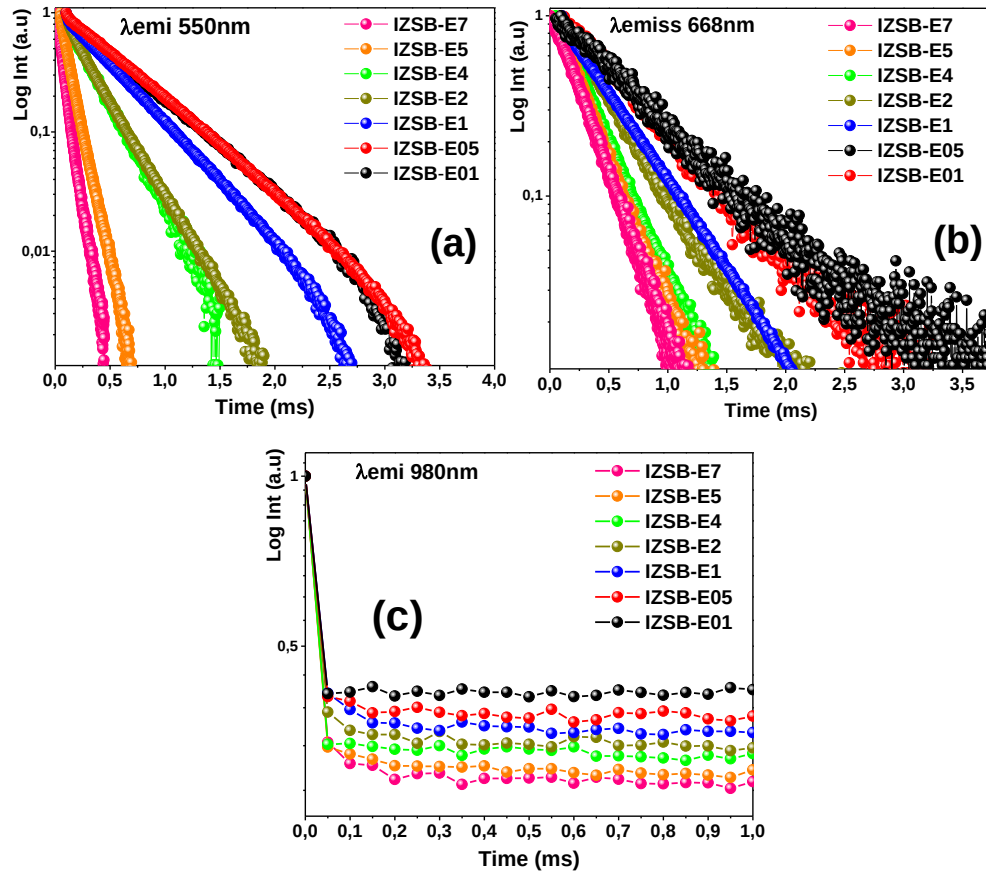


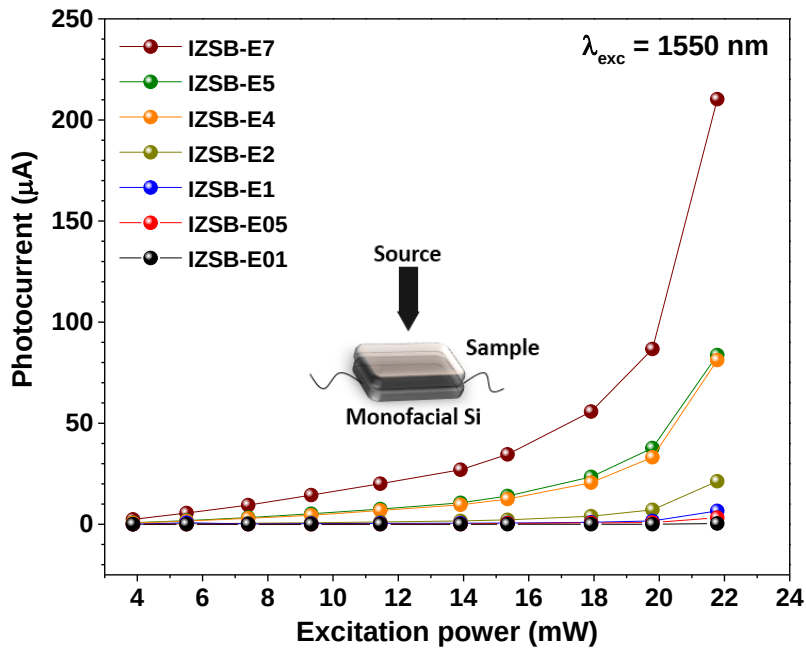
Table 2.1. Experimental decay time values for the samples under excitation at 521 nm.

Sample	Time (ms)		
	Green (550 nm)	Red (668 nm)	NIR (980 nm)
IZSB-E01	0.563	0.678	0.503
IZSB-E05	0.579	0.580	0.461
IZSB-E1	0.447	0.449	0.304
IZSB-E2	0.238	0.384	0.296
IZSB-E4	0.090	0.302	0.275
IZSB-E5	0.067	0.295	0.125
IZSB-E7	0.060	0.270	0.103

2.3.2 Photocurrent analysis

For the better understanding the viability to use up converter materials coupled in solar cells, we performed photocurrent measurements by placing the samples under a commercial and monofacial silicon SC. The samples were perpendicularly excited at 1550 nm with a laser source. To minimize the loss of the UC radiation, we covered the four edges of the samples with aluminum foil. The experimental setup is shown in Figure 2.5.

Figure 2.5. Photocurrent analysis of the samples as a function of the power source excitation. Experimental setup for the photocurrent analysis (inset figure). The samples were placed on the top of a Si solar cell and excited with a perpendicular beam at 1550 nm. All the measurements were performed in a dark room.



In agreement with the UC intensities, for the sample with 7 mol%, the Si SC exhibits the highest short-circuit current value, meanwhile a very weak signal is observed to the samples with 0.5 and 0.1 mol%. The maximum values for all samples are observed under excitation at 22 mW. Under direct illumination or using an undoped sample, the short-circuit current was negligible.

It is important to emphasize that, when the samples are placed on the top of the SC, a substantial fraction of the emitted radiation is lost through the top of the uncovered surface (surface where the laser beam is focused). In the last two decades, several studies have presented the concept of UC materials using a luminescent layer located at the rear face of a bifacial solar cell, instead of at the top. Besides, a mirror located beneath the luminescent layer, would help to collect the UC emission at the rear surface. Indeed, a plenty publication has demonstrated the feasibility of UC phenomenon to enhance the efficiency of SC even when the samples are placed on the top. However, this method is acceptable as a proof of concept, but not for commercial purposes.

Unfortunately, it is a hard task to compare the presented results with those already related in the literature. Most of them reports short-circuit current in small pieces of glass comparing to the active SC area. Moreover, take into account some parameters like glass thickness, refractive index, impurities, mono and/or polycrystalline diode and monochromatic excitation; we may expect different photocurrent values. In fact, a figure of merit for this kind of analysis is needed and would be necessary to compare the SC performance among different glass systems.

2.4 Conclusions

In conclusion, we have prepared fluoroindate glasses with different Er³⁺ concentration for the enhancement of a monocrystalline solar cell photocurrent. All the Er³⁺ compositions allowed us to obtain green, red and near infrared emissions by UC mechanisms. The near-infrared emission at 980 nm, which is close to the Si bandgap, increases when the concentration is up to 7 mol% of Er³⁺ and decreases above this percentage. According to the short circuit-current measurements, we have verified the influence of UC emissions in the generation of extra current by placing the samples under a monocrystalline Si solar cell. The excitation at 1550 nm with 22 mW provided a maximum of 200 μ A to the SC showing the highest UC emission.

2.5 References

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A brief introduction to the silver nanoclusters

The outstanding properties of the rare earth presented in the previous chapters whose portray electron migration in shielded orbital, find an opposite landscape from the metallic elements of the periodic table. It is known that emission and excitation barely change in amorphous and crystalline media in rare earths, thus light tunability often depends on the combination of two or more elements. This chapter describes electronic interaction in silver nanoclusters that underlie their use as emitter for white light obtention, waveguide and other. From now on, for the sake of brevity, silver nanoclusters will be referred as “Ag NC’s”. Silver nanoclusters can also be expressed as Ag_m^{n+} where m is the number of Ag entities and $n+$ is the oxidation state. The use of Ag NC’s offers a distinct path, and sometimes easier, to achieve desirable emission in the visible range since concentration and the thermal history are strictly defined. The next three chapters highlight experimental methodology to obtain fluorophosphate glasses doped with Ag NC’s as well as the spectroscopic investigation and applications as photonic materials. More specifically, a major emphasis will be given to the size distribution, absorption, emission and lifetime of different size nanoclusters in fluorophosphate glasses. Still, some selected results resulted from the partnership UNESP/ICMCB will be shown.

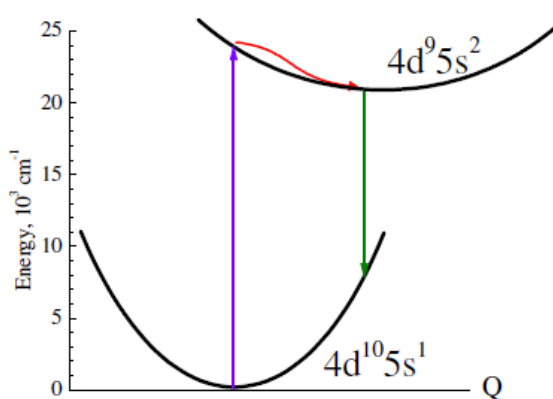
3.1 Silver nanoclusters

Silver nanoclusters “Ag NC’s” are the combination of several to tens of metal atoms and size below 2 nm [PATEL; SAHOO; MOHANTY, 2016]. However, there still a scientific conflict concerning the specific quantity of atoms and the size of the nanoclusters. Thus, slightly distinct values may be found in the literature [BROWN et al., 2017; FARES et al, 2017].

In an opposite path to the lanthanide spectroscopy where emission and absorption are result of electron interaction in shielded orbital (4f), Ag NC’s offer a broad spectroscopy due to the moving of delocalized electrons in the conduction band d and s . Since the size of Ag NC’s is further reduced to about 1 nm, the band structure shows a discontinuous character and assumes discrete energy levels, similar to the energy levels of organic molecules. Although the high number of publications of silver nanoclusters and nanoparticles in spectroscopy studies, there is still a lack of

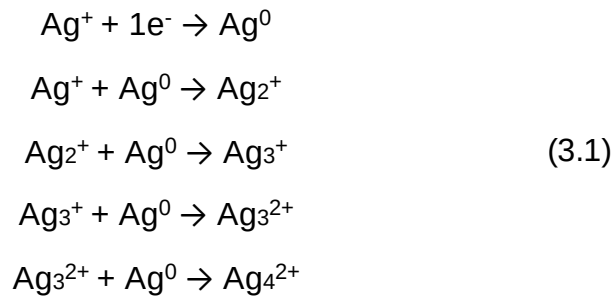
investigation concerning silver diagram levels of energy. Up until now, the most cited work was carried out by Tikhomirov et al., where they suggest a mechanism shown in the Figure below.

Figure 3.1. Diagram energy levels of the Ag NC's proposed by Tikhomirov et al., [TIKHOMIROV et al, 2010]. The ground state ($4d^{10}5s^1$) and the first excited state ($4d^95s^2$) may find another configuration in the literature according to the dominant nanocluster in a specific material.



Indeed, this approach used by Tikhomirov and the co-authors comes from the assessment of Ag^+ ions in strontium fluoride crystals, investigated by P. Boutinaud and co-authors [BOUTINAUD; MONNIER; BILL, 1994]. As the number of atoms varies in Ag NC's, the number of excited states varies as well, so an accurate diagram levels is precisely a hard task to define. Still, the exact number of atoms in Ag NC's, most probably, may find an acceptable value in theoretical calculations. In practice, many research groups uses transmission electron microscopy (TEM) to predict the size of Ag NC's, however, it is know that the electron beam can interacts with silver by reducing the nanoclusters. In this sense, in mostly cases a large size distribution is find, so the number of excited states of the clusters change considerably. Therefore, the specie Ag_m^{n+} (another notation for Ag NC's) is a combination of several kind of species with different excited states and, therefore, a generic diagram level is plausible.

In terms of spectroscopy studies, the transition electronic behavior depends on the stabilization of the clusters in the host matrix. Viscosity, solubility, pH in liquid solution, thermal treatment, concentration and cooling treatment play crucial role for the successful synthesis of Ag NC's. A slight variation in one of these parameters can favor the formation of one specific specie, several species concomitantly or also the presence of silver nanoparticles. For instance, we are going to emphasize the most cited species that are Ag^0 , Ag^+ , Ag_2^{2+} and Ag_4^{2+} . These species are formed by the mechanism (3.1):



The mechanism above takes into account only the interaction Ag-Ag and free electrons originating from a host matrix, and it was first proposed by Tikhomirov et al. 2010, to explain Ag NC's formation in oxyfluoride glasses. According to the seminal work of Tikhomirov, electrons are extracted from intrinsic defects, called F^- , then the reduction of Ag^+ into Ag^0 and aggregation with other charged ions leads to the formation of dimers (Ag_2^+), trimers (Ag_3^{2+}) and tetramers (Ag_4^{2+}). It is noteworthy to mention that F^- ions in glasses originates from the fluoride compounds such as PbF_2 , CdF_2 and other [TIKHOMIROV et al., 2010]. In this case, two Ag^+ may substitutes one Pb^{2+} and one Cd^{2+} to maintain charge compensation. From here, it is good to emphasize that, in fact, the reduction of Ag^+ by F^- represents merely a hypothesis since the donation of one electron of F^- to Ag^+ is still not confirmed. Most probable, the ionic migration of F^- at the melting temperature favor the formation of negative clusters that attracts positive charge species such as Ag^+ , then the negative charge compensates the positive charges of the silver ions.

It is believed that in high amount of silver, the thermal history of the glass can lead to agglomeration of Ag^+ to form silver nanoparticles (Ag NP's). For instance, this is the last scenario of the silver mechanism (not shown in the mechanism 3.1) and

yellowish brown glass is obtained. Silver nanoparticles are nominated as Ag NP's and they present "surface plasmon resonance" (SPR) effect. The SPR effect describes the interaction of the light with the electronic cloud in the metallic surface. Still, it is recognized that Ag NP's are non-luminescent even though they show absorption. Despite the non-emission behavior of the Ag NP's, the SPR effect can enhance the luminescence of the closest ions. For example, it is proved the enhancement of rare-earth emission efficiency by the Ag NP's presence [WU et al, 2011; DOUSTI et al, 2013; DOUSTI, 2013] and references therein. However, it is out of scope of this thesis the stud of SPR effect, more details may be seen in the following references MATHPAL, et al. 2015 and SHESTAKOV, et al. 2013.

It is commonly emphasized that Ag NC's bridge the gap between Ag NP's and bulk metals. Meanwhile Ag NC's show radiative emission due the electronic transition in several excited state, Ag NP's only exhibit electronic oscillation when interaction with light takes place. For the last, the freely moving delocalized electrons in the conduction band of the bulk metals are only responsible for the reflection of light [DÍEZ and RAS, 2011]. Figure 3.2 shows the effect of size on the electronic structure of single atom, Ag NC's, Ag NP's and bulk metal. With further increment on the size structure, discrete levels of energy give rise to a continuous electronic band, in bulk metals. The free electrons in this electronic band no longer exhibit radiative transition and emission of light is not observed.

The variety of Ag NC's offers the possibility to obtain broadband luminescence, which covers completely the visible range of the spectrum [SHESTAKOV et al., 2013]. Figure 3.3 shows excitation and emission spectrum of oxyfluoride glass doped with 5% of AgNO₃. Excitation spectra are collected with emissions fixed at 450, 500, 550 and 700 nm, and the emission are observed with excitation at 320, 355, 380 and 457 nm.

Figure 3.2. Electronic structure according to the different size of the silver metal. The electronic structure is broken down when the number of atoms increase in the metal (Adapted from DÍEZ and RAS, 2011).

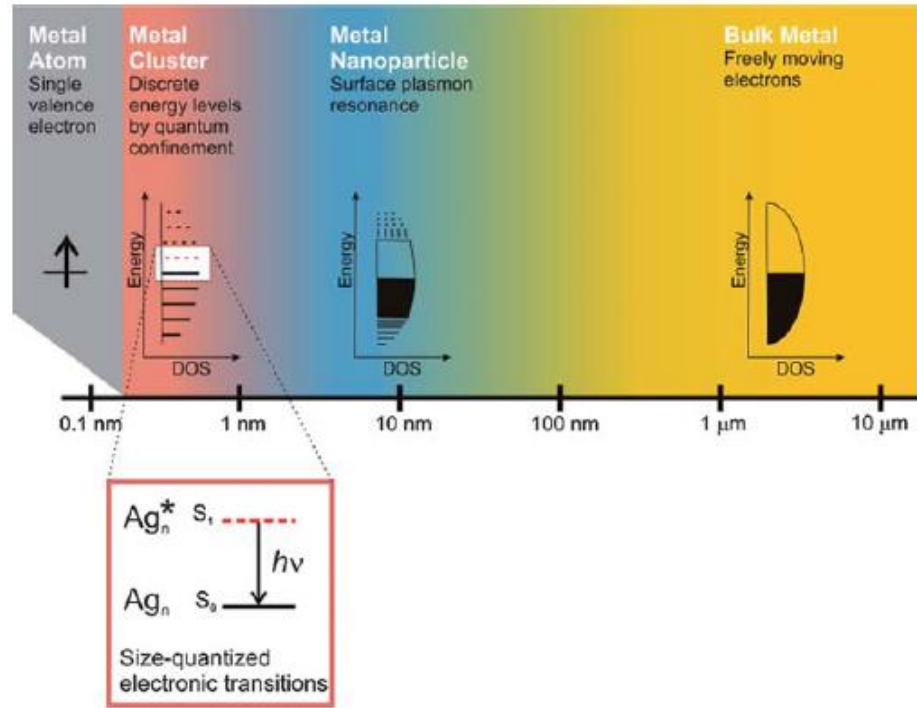
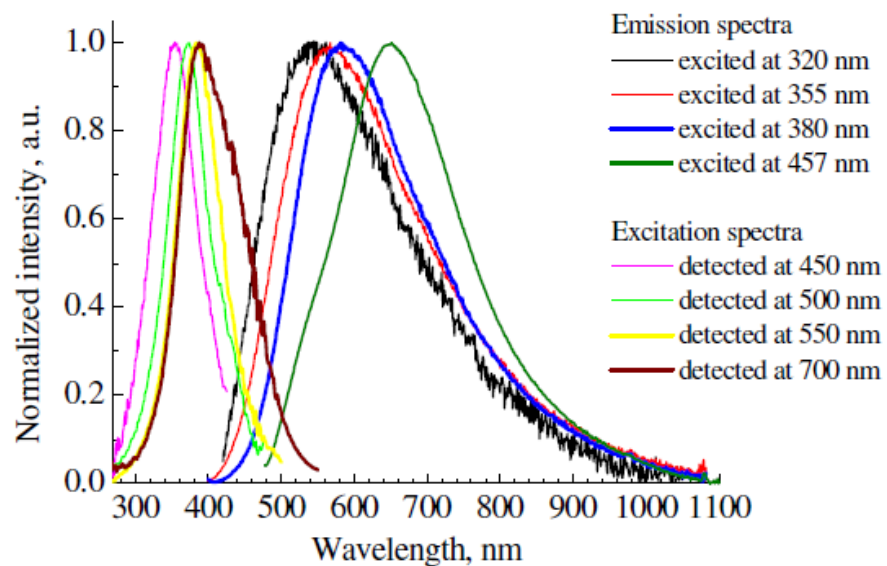


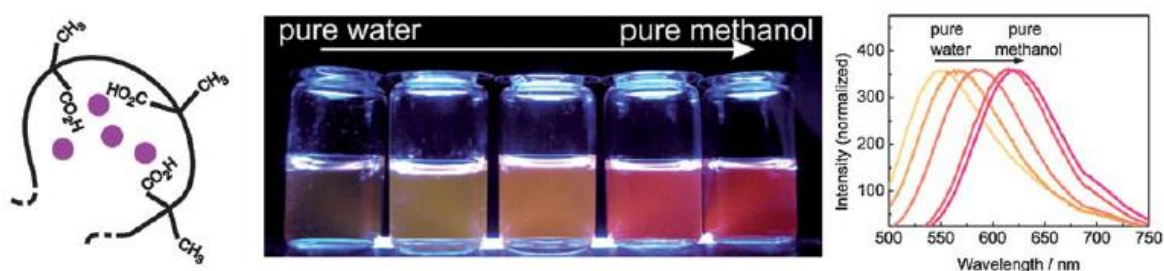
Figure 3.3. Excitation and emission spectra of oxyfluoride glass doped with 5% of $AgNO_3$. Excitation are represented on the left side and emission on the right side as well.



3.2. Materials for Ag NC's stabilization

The stabilization of Ag NC's is still a huge challenge since several parameters might to be optimized. As mentioned before, thermal treatment, pH, silver concentration and viscosity of the host material can lead to the obtention of several silver species. For instance, these are the parameters will be discussed in the next section, however, it is know that rare earths such europium can interact with Ag^+ ions changing the oxidation state of silver [LI et al, 2013; DOUSTI et al, 2013]. Ag NC's have been prepared and stabilized in a gamma of organic and inorganic matrix. For example, Figure 3.4 shows Ag NC's prepared in poly(methacrylic)acid and using water and methanol for stabilization, digital photograph under UV light and the respective emission spectra of the solution.

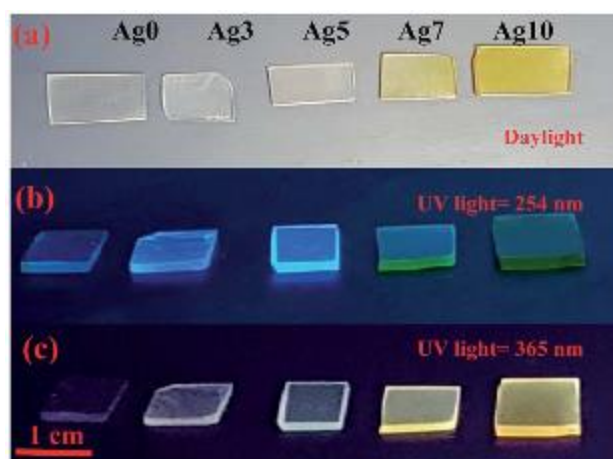
Figure 3.4. Ag NC's stabilized in poly(methacrylic)acid. Ag NC's are protected by the carboxyl groups. Photograph and emission spectra of the solutions [DÍEZ et al, 2010].



On the other hand, glassy materials have an appealing set of advantages compared to nanocrystals, polymers and organic fluorophores for Ag NC's stabilization. They have less step preparation, non-tedious step of synthesis, do not require purification of reagents and so on. Oxyfluoride glasses are one of the most reported glassy materials for nanoclusters obtention. For what it is worth, Kuznetsov and colleagues have published several articles, which cover since preparation, photoluminescent properties, white light generation and related topics, some references may be checked [KUZNETSOV et al, 2013; KUZNETSOV; TIKHOMIROV; MOSHCHALKOV, 2013; KUZNETSOV et al, 2012]. Recently, Fares et al., demonstrated the feasibility of fluorophosphate glasses for dispersion of high amount of AgNO_3 , up to 10 mol%. However, besides the stabilization of Ag NC's, for 7 and 10

mol% the authors reported the presence of Ag NP's, as we can see in the Figure 3.5(a) for the samples Ag7 and Ag10, where we can see a yellowish color. The glasses show a remarkable luminescence under UV excitation, 254 and 365 nm.

Figure 3.5. Fluorophosphate glasses containing different silver amounts. (a) Daylight photography of the samples and under UV irradiation, (b) and (c) [FARES et al, 2017].



3.3 Effect of temperature, concentration and femtosecond laser radiation on the Ag NC's stabilization

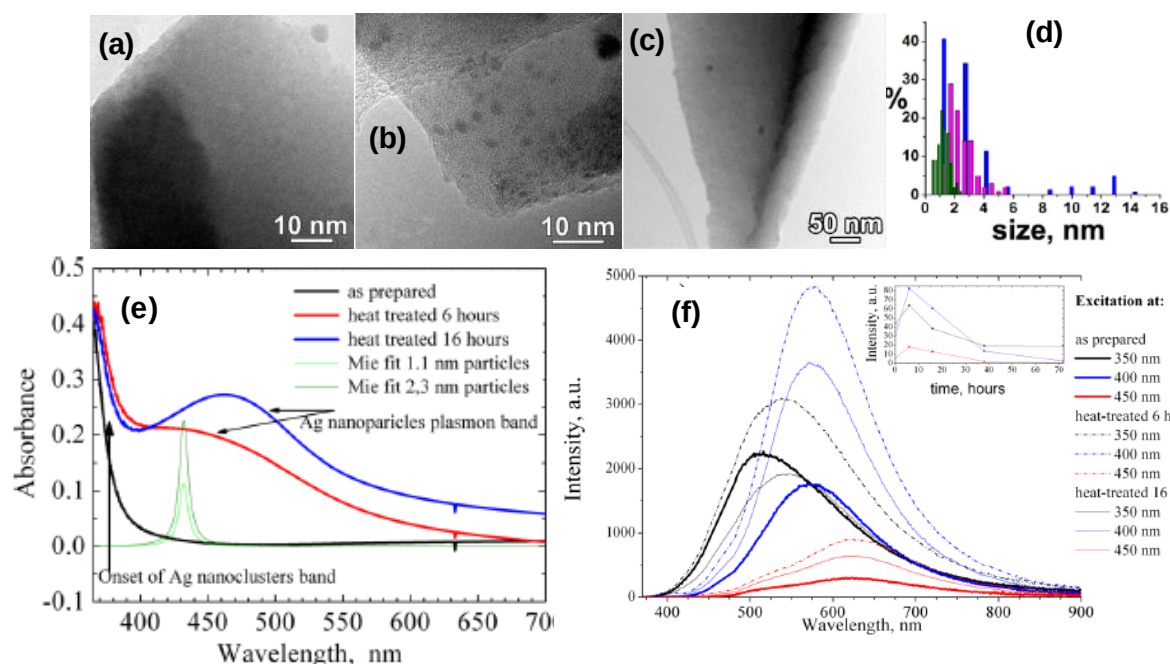
3.3.1 Temperature dependence

Recently, systematic experimental studies have been reported in glassy materials in order to understand the silver behavior face to temperature, concentration, and laser radiation [KUSNETSOV et al, 2012; SHESTAKOV et al, 2013; BELLEC et al, 2010]. Indeed, temperature and concentration are related and they must to be adjusted during the material preparation. The main difficulty is preventing the agglomeration of Ag^+ ions, which may be lead, in a non-desirable case, to the formation of Ag NP's. Most of the cases, temperature dependence shows a tendency in agglomeration due to the Ag^+ ions mobility. In such cases, the final stage is the Ag NP's obtention and the SPR effect is present. It is good to emphasize here that the temperature dependence is indeed related to the thermal treatment after the melting quenching and, in some cases, a thermal treatment below vitreous temperature applied after glass obtention.

Generally, heat treatments are performed to minimize mechanical stress and the growth of Ag NC's and Ag NC's is observed concomitantly.

Shestakov et al., studied temperature dependence of Ag NC's and Ag NP's in oxyfluoride glass. Figure 4.7a shows high-resolution transmission electron microscopy (HRTEM) images of the as-prepared oxyfluoride glass doped with 0.15 atom% of Ag. The sample is composed only by Ag NC's and the average size is 1.1 nm, after heat treatment of 6 hours, the nanoclusters increase and reach particle size of 2.3 nm (Figure 3.6b). With further increment on the time, 16 hours, the average particle size is defined by two subsets, one 2.3 nm and another by 10 to 15 nm (Figure 3.6c). The average particle size is better shown in the Figure 3.6d. Interestingly, the Figures 3.6a and b show a higher number of black spots randomly distributed in the glassy volume, after 16 hours of heat treatment only few spots are shown in Figure 3.6c. This indicates that small nanoclusters migrate to form bigger nanoparticles. Indeed, the authors realized that after 6 hours of heat treatment is sufficient to convert nanoclusters in nanoparticles, and the amount of nanoparticles increase when the heat treatment is carry out in 16 hours. The effect of the Ag NC's and Ag NP's on the spectroscopic properties is show in the Figure 3.6 e and f. The absorption spectra (Figure 3.6e) of the sample after heat treatment show broad absorptions in the visible range with tail that extend up to 650 nm. These band are ascribed as plasmon absorption and have FWHM of approximately 150 nm (red and blue line). Contrarily, the as-prepared glass does not exhibit absorption in the visible range (black line). Unfortunately, the authors have minimized the absorption of the Ag NC's that extend until 200 nm. Indeed, a higher emphasis was given to the plasmon absorption and the absorption of the nanoclusters was omitted. The emission spectrum of the sample shows a red shift when the excitation is carried out at different wavelengths 350, 400 and 450 nm. This phenomenon indicates the presence of different size nanoclusters that emits at blue, green and red region. More emphasis on the luminescence dependence with silver concentration is given in the next chapter.

Figure 3.6. (a) HRTEM of as-prepared oxyfluoride glass, (b) 6 hours and (c) 16 hours of heat treatment. (d) Size distribution of the Ag NC's. (e) Absorption spectra and (f) emission spectra excited at different wavelengths. Adapted from [SHESTAKOV et al, 2013].

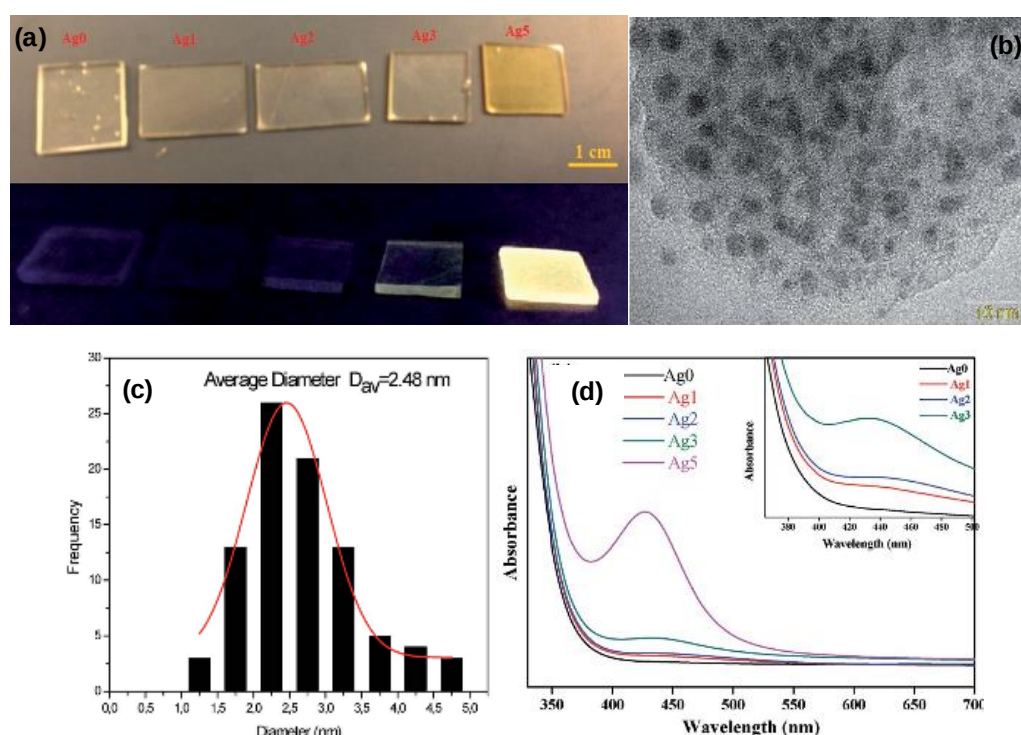


3.3.2 Concentration dependence

Another aspect to be considered here is the dependence of the Ag NC's with the concentration. Perhaps, concentration is the key factor that leads to the stabilization of nanoclusters and nanoparticles. The maximum solubility of silver in glass is reached when only Ag^+ species are present. In other words, a homogeneous solid solution is formed and there is no phase separation. The increment on silver amount leads to agglomeration and several species may be present, counting with Ag NP's. The formation of the silver species was discussed in the mechanism (1). To better examine the consequences of Ag concentration in glasses, Figure 3.7 shows fluorophosphate glasses doped with different silver amounts. One can see that in high concentration as 5% of AgNO_3 , the glass presents a yellowish color and the Ag NC's are homogeneously distributed, as we can see in Figure 3.7b. The average particle size is 2.48 nm for this sample. Indeed, despite the obtention of Ag NC's, this average

also includes nanoparticles according to the absorption spectra shown in 3.7d, where we can see a plasmon band between 360 and 550 nm. The absorption of the Ag NC's is not shown in this figure.

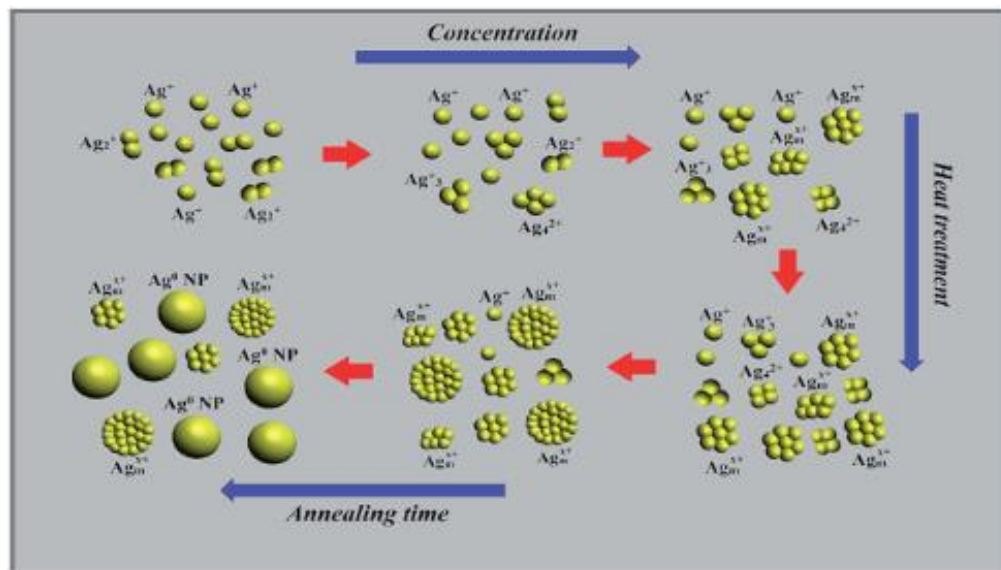
Figure 3.7. Ag NC's and Ag NP's obtained in fluorophosphate glasses. (a) Photography of the samples in daylight and under ultraviolet radiation. (b) Transmission electron microscopy with 10 nm of resolution, (c) size distribution of the Ag NC's and (d) absorption spectra of the samples. Adapted from Fares et al. 2017.



In fact, nucleation and growth of silver species rely on the strict optimization of temperature and concentration and it was mentioned that is a hard task to control the concomitant obtention of reduced and non-reduced species. Still, chemical compounds play an important role on the reduction of ions and clusters as mentioned in case of F^- ions in fluoride host glasses. In this thesis, we dealt with fluorophosphate glasses, covering preparation, nanoclusters stabilization by concentration and infrared radiation, spectroscopy properties and applications, therefore a more detailed emphasis is given for this family of glass. However, more example of the role of chemical compounds in glasses can be found in [MA et al, 2017]. An overview of

temperature and silver concentration is given by Fares et al., where the authors portrayed the entire stage of silver species. Initially, concentration is responsible for the solubility of Ag^+ , nucleation and growth of Ag NC's. Thereafter, heat treatment and annealing time are responsible for the obtention of big nanoclusters such as Ag_m^{x+} (last stage before Ag NP's) and nanoparticles. In this overview the authors defined a hypothetical situation in fluorophosphate glass, and Ag NP's is not drawn in this scheme in the concentration adjust and after heat treatment. However, this overview does not represent a tendency and might not be extrapolated for all situation since Ag NP's can be formed after heat treatment.

Figure 3.8. Schematic of the Ag NC's and Ag NP's obtention proposed by Fares et al. 2017. Size-dependence of Ag species in fluorophosphate glasses are driven by concentration, heat treatment and annealing time (FARES et al, 2017).



3.3.3 Ag NC's induced by femtosecond laser radiation

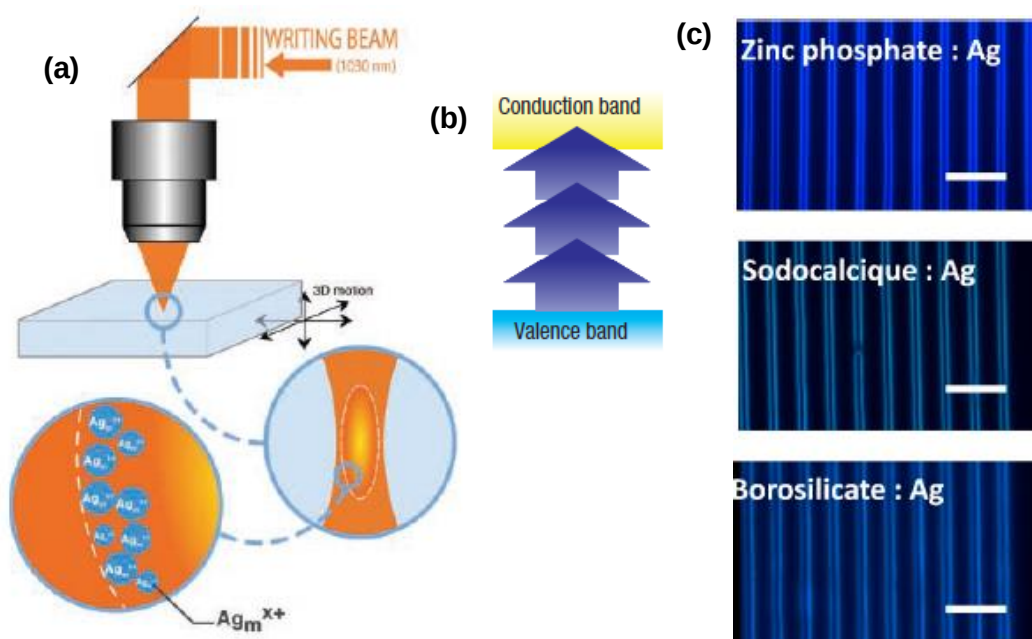
During the last two decades, direct laser writing (DLW) technique has demonstrated to be an efficient alternative for silver reduction [PETIT et al, 2015]. The reduction takes place when a femtosecond laser, generally with energy of a few hundreds of nanojoules, induces a nonlinear ionization in a large number of electrons that, in turn, transfer energy to the lattice [ROYON et al, 2011; GATASS; MAZUR, 2008]. The high

energy density localized in a small area and the nonlinear nature of the absorption modifies the local chemistry and significantly changes the optical properties of the affected region [LIU et al, 2008; GATASS; MAZUR, 2008]. The irradiation can also induce a phase modification, such as crystallization in an amorphous matrix, leaving behind a permanent change in the refractive index. Besides, when the energy of excitation exceeds a certain threshold, the femtosecond laser can induce cracking, voids and localized melting. Figure 3.9a shows an uncompleted setup for femtosecond laser machining process. The femtosecond laser passes leading behind Ag NC's, or also named Ag_m^{X+} .

During the DLW technique, the clusterization process can be optimized to occur at surface or in-deep the host matrix, such conditions are achieved by controlling the laser parameters (fluency, number of pulses and repetition rate) [ROYON et al, 2011; BELLEC et al, 2010]. Moreover, a spatial size distribution of the Ag NC's can be obtained when the sample is submitted to different laser pulses. There is a few models dealing with size and shape formation of Ag NC's [SMETANINA et al, 2016] in glass. The model presented by SMETANINA et al. involves photoionization, laser heating of the samples, diffusion, kinetic reactions and dissociation of metallic species. However, it is far beyond the scope of this thesis investigate mathematics models to explain Ag NC's formation in glass. For instance, the Ag NC's formation after interaction femtosecond laser-sample can be perceived by the large absorption and emission spectrum throughout the chapter 6.

Laser-induced microstructures has been reported in many homogeneous glassy materials such as zinc phosphate, boro-germanate, borate and other systems [BOURHIS, et al, 2013; SMETANINA et al, 2016; VANGHELUWE et al, 2016; LIU et al, 2008]. An ideal host glass for patterning of Ag NC's microstructures would exhibit chemical and physical resistance, high glass temperature transition (T_g), present a high transparence at the wavelength of operation and a smooth refractive index increase when irradiated by femtosecond pulses [BÉRUBÉ, et al, 2017]. Figure 3.9b shows microscope fluorescence images of laser-induced Ag NC's in three distinct glasses: phosphate, sodocalcique and borosilicate.

Figure 3.9. (a) Schematic illustration of femtosecond laser writing in a transparent host matrix. When a high enough energy pulses is focused into a material, optical breakdown is observed. In this case, silver ions (Ag^+) is reduced into silver nanoclusters (Ag_m^{x+}); (b) Multiphoton absorption promotes electrons from the valence band to the conduction band; (c) optical microscope images (excitation at 375 nm) of linear Ag NC's formed after femtosecond laser irradiation. Adapted from the references [GATASS; MAZUR, 2008; SMETANINA, 2016].



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White light generation in fluorophosphate glasses doped Ag nanoclusters

The emission properties of Ag nanoclusters (Ag NC's) dispersed in a transparent fluorophosphate glass host is presented in this chapter. The as-prepared glasses show that the Ag NC's emit in a broad white emission band covering the visible region. Changing the excitation wavelength is possible to tuning the emission from blue to yellow. The spectral width of the white light is most likely due to the presence of a variety of Ag NC's with different sizes, particularly emitting in the blue, green and red regions. The possible interaction mechanism between the different Ag species was elucidated. The observed results provide a new platform to acquire a broadband tunable light source.

4.1 Introduction

Luminescence of silver by quantum confinement have attracted interest owing to a variety of potential novel applications, such as biomedical applications, nano-sensors, white light generation, luminescent lamps, flexible monitors and down-shifting of the solar spectrum for enhanced efficiency in solar cells [DÍEZ; RAS, 2011; DÍEZ et al, 2009; TIKHOMIROV et al, 2010; KUZNETSOV et al, 2012; RODRÍGUEZ et al, 2010; ROY; BARNAL; BANERJEE, 2014; ROY et al, 2015; BARAL et al., 2017; ROY; BANERJEE, 2011; RAO; PRADEEP, 2010]. In general, the optical responses of metals depend on their sizes. In the case of metallic nanoparticles (NPs), the luminescent properties are very poor but they absorb light strongly due to surface plasmon resonance effects arising from the collective oscillation of conduction electrons upon interaction with light. [DÍEZ; RAS, 2011; BOYD; YU; SHEN, 1986; GEDDES et al, 2013]. However, the reduction of the particle size down to few nanometers, approaching the Fermi wavelength, leads to break up the continuous band structure of the metal into discrete energy levels [DÍEZ; RAS, 2011]. In this case, the metal is called a NC's in which the collective oscillation of electrons is obstructed otherwise the particle is not plasmonic [DÍEZ; RAS, 2011]. In contrast, interaction with light is still possible though, via electronic transitions between the energy levels and thus NC's are capable of intense light absorption as well as for

tunable visible emission both in the linear and non-linear optical regime [DÍEZ; RAS, 2011, RUSSIER-ANTOINE et al, 2016].

Recently, special attention is paid to oxide glassy materials doped with luminescent Ag NC's owing their superior mechanical, structural and optical properties, which may give more benefits for photonic applications [KUZNETSOV et al, 2013; ZHOU et al, 2016]. In fact, oxide glass are exceptionally attractive due to their high metal solubility [YAMANE; ASAHARA, 2000], which allows tuning the material optical properties based on the dopants concentration. Most recently, Tikhomirov et al. demonstrated that the introduction of $\text{CdF}_2/\text{PbF}_2$ into silicate glass network favors the dispersion of Ag NC's across the whole bulk glass [KUZNETSOV et al, 2010; VELAZQUEZ et al, 2012; CUONG et al, 2012]. It was demonstrated that the emission of Ag NC's depends on the size and can be tuned from UV, VIS and near-IR by selective excitation. However, the luminescent properties of the Ag NC's depend not only on their size but also on the choice of the host material [KUZNETSOV et al, 2013]. Since the average size distribution decreases in the medium with high viscosity due to slow diffusion of silver atoms towards nuclei [PARK; PARK; PARK, 2011], oxyfluoride glasses based on silica, which present a very low viscosity, diminished their potential in photonic applications based in the size distribution of small NC's. Particular properties of fluorophosphate glass such as high viscosity, low glass transition temperature, low melting point, and low optical dispersion, allow this host matrix to be an advantageous over oxyfluoride glass based silica [GALLEANI et al, 2017; ASEEV et al, 2012].

In this direction, Ag doped fluorophosphate glasses were prepared by simple single-step melt-quenching route. To the best of our knowledge, rare earth free white light was generated from Ag NC's dispersed in fluorophosphates glass.

4.2 Experimental section

The Ag NC's doped fluorophosphate glasses were prepared by conventional melt-quenching method using high-purity compounds (99.9%, Sigma-Aldrich). The chemical formula of the glass host, $(50-x)\text{NaPO}_3-25\text{ZnF}_2-15\text{CdF}_2-10\text{YF}_3$, was adjusted to ensure its glassy stability against devitrification. AgNO_3 (purity 99.9%) was added, in different mol%, ($x = 0, 3, 5, 7$ and 10 mol %, labeled as Ag0, Ag3, Ag5, Ag7 and Ag10, respectively) as a resource of silver NCs. Approximately 7 g batches

were mixed and then melted in an alumina crucible at 900 °C for 1 h under ambient atmosphere. The melt was casted into a pre-heated stainless steel mold at 320 °C (value obtained from differential scanning calorimetric-DSC measurements) to remove any residual internal stress induced by the rapid cooling of the glass melt. The glass was left at such temperature during 1 h before to be cooled down to room temperature. Finally, the obtained glasses were cut and polished with thickness of 2 mm for optical measurements.

Transmission electron microscopy (TEM) investigations were carried out using a Philips CM200 equipment operating at 200 kV and equipped with X-ray energy dispersive spectroscopy (EDS) Bruker model XFlash 6Ti30. Samples were put in an agate mortar and grinded thoroughly. Then, approximately 0.1 mg of powder and 10 mL of isopropyl alcohol were placed in a glass vial that was placed in an ultrasonic bath for 15 min to disperse the nanopowder. Some drops of this suspension were applied on a copper grid coated with carbon film. Afterward, the deposited sample on the copper grid was dried in air before TEM analysis.

UV-Vis absorption spectra as well as transmission spectra were recorded using a Varian Cary 500 double beam spectrophotometer on the polished samples of 2 mm thickness. Excitation and emission spectra were obtained using Fluorolog (Horiba Jobin Yvon) equipment. Both measurements were obtained from glass pieces. For excitation measurements the emission wavelength was set at 550 nm. Slits were adjusted to lead a resolution of 1 nm for both excitation and emission. All measurements were performed at room temperature and corrected by the instrument response.

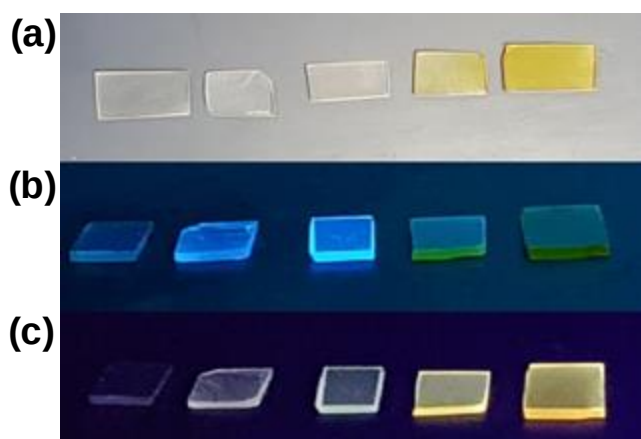
4.3 Results and discussion

4.3.1 Optical properties and nanostructure analysis

Figure 4.1a shows the pictures of the fluorophosphate glasses under daylight and UV light for 254 and 365 nm excitation wavelengths, Figure 4.1b and c, respectively. As we can see from Figure 4.1a, the glasses are homogeneous, transparent and colorless for the samples containing low Ag content and pass to yellow color for samples containing higher concentration of AgNO₃. The change in color is induced by the formation of Ag NC's and/or Ag NP's within the glass network with large

amounts of AgNO_3 and will be discussed below. Under excitation with UV lamp at 254 nm (Figure 1b, a strong blue emission has been detected, which increases with the Ag doping level (samples Ag3 and Ag5), and becomes green in the glasses with higher concentration of silver (samples Ag7 and Ag10). On the other hand, luminescence image of the same glass samples, excited with a UV lamp at 365 nm indicates a different color rendering of the emission from white (Ag3 and Ag5 glass samples) to yellow (Ag7 and Ag 10 glass samples) according to their AgNO_3 content, as depicted in the Figure 4.1c. Such behavior point out that the emission of Ag particles doped fluorophosphate glasses depend strongly on the excitation wavelength and structure of the Ag particles dispersed into the glass network.

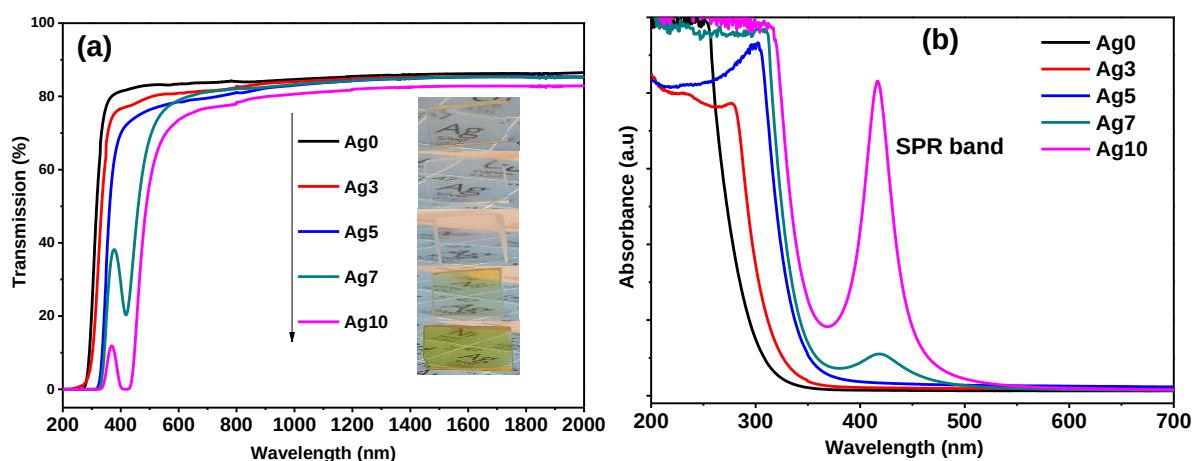
Figure 4.1. Daylight pictures (a), luminescence images excited by a UV lamp at 254 nm (b) and 365 nm (c) for all the glasses.



The transmission spectra from ultraviolet to near-infrared range of the prepared glasses are presented in Figure 4.2a. As observed, the transparency of Agx glass samples is altered with increasing of Ag doping level. Firstly, the ultraviolet cut-off wavelength is red-shifted from 280 to 345 nm and it is also accompanied by a curvature of the top of transmission edge. Secondly, the maximum transmission in near-infrared range slightly decreases from 87% to 82% with increasing of AgNO_3 concentration. The evolution of transmission under different doping condition can also be evident from the pictures in Figure 4.2a. Both effects can be explained by the presence of scattering centers within the glass network, whose concentration,

dimensions and/or shape evolve with increasing AgNO_3 concentration. This observation is strongly proved from the absorption spectra of the corresponding glasses presented in Figure 4.2b. In fact, a weak absorption peak located at about 415 nm is detected in the Ag7 glass sample with a full width at half maximum of approximately 50 nm, which is typically attributed to the presence of SPR of Ag NPs [TIKHOMIROV et al, 2012]. In addition, the plasmon absorption band becomes more intense with increasing of AgNO_3 concentration. These effects are related to an increase of size of the Ag NCs and/or in the amount of Ag NPs within the glass network. For samples with low (3 mol%) and intermediate (5 mol%) AgNO_3 doping, it can be clearly seen that the absorbance spectra do not show any absorption bands in the violet part of the spectra. Similar absorption features were observed in other previous works, where the authors assigned this behavior to the reduced particle size, which is too small (1-2 nm) to generate a SPR absorption band [BAISHYA et al, 2008; PEREIRO; BALDOMIR, 2017; ZHENG, 2017].

Figure 4.2. (a) UV-visible and near infrared transmission spectra of glass samples as a function of AgNO_3 concentration with their corresponding photograph presented in inset. (b) Absorption spectra of Ag NCs doped prepared glasses.

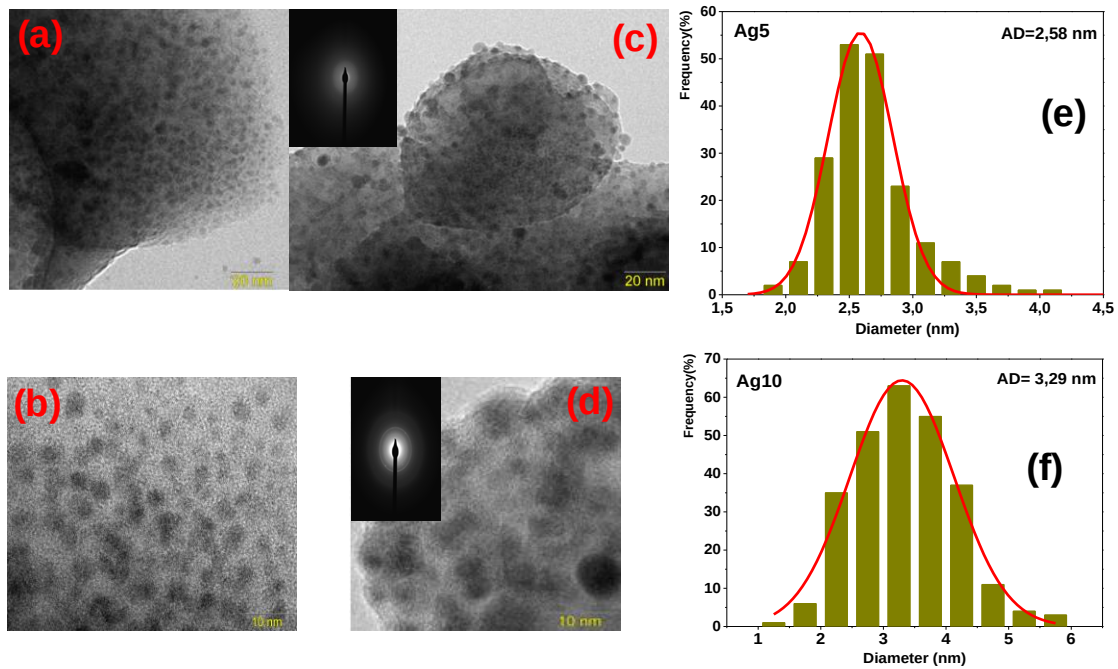


The nanostructure properties of the glasses were analyzed by the means of transmission electron microscopy (TEM) and selected area electron diffraction pattern (SAED). TEM, SAED analysis and diameter distribution of prepared samples were carried out for two different concentrations of AgNO_3 (5 and 10 mol %). The

size distributions of the silver NC's of the samples were obtained by the analysis of ~250 particles. Figure 4.3c and 4.3d shows the TEM micrographs for the sample Ag10. The micrographs for Ag doped glasses shows that spherical particles, visible as dark contrast spots, are homogeneously dispersed in the glassy matrix with average diameter (AD) of 2.58 and 3.29 nm for Ag5 and Ag10 samples, respectively (see the histogram in Figure 4.3e and 4.3f). One can see that the Ag particles remain amorphous in the prepared glass samples. In fact, the amorphous character of Ag clusters is evidenced by SAED pattern, which contains only diffuse diffraction rings typical for an amorphous phase.

It should be noted that these tiny particles are spontaneously formed without heat treatment. In this sense, a reduction mechanism must be considered which is responsible for the particle formation of the tiny Ag particles during melting step. Perhaps the silver reduction could occur due to the electrons ejected directly from defects that are intrinsic to the glass, namely F^- vacancies residing within fluorophosphate glasses. In fact, the mechanisms for the formation of Ag NC's within oxyfluoride glass host have been suggested recently. According to Tikhomirov et al. [TIKHOMIROV et al, 2010] the F^- centers residing in glass network, where an electron substitutes onto the place of an F^- , favors the formation, stabilization and homogeneous dispersion of Ag NC's. In such condition, the electrons released diffuse to occupy the vacant sites such as Ag^+ ions. The reduction mechanism resulting in the formation of Ag NC's is described through the following reactions from the scheme 3.1, where neutral Ag NC's and Ag^+ ions intrinsically condense and resulting the formation of other Ag NC's, consisting of a few Ag atoms defined as Ag_m^{x+} clusters, such as Ag dimers (Ag_2^+), Ag trimers (Ag_3^{2+}) and tetramers (Ag_4^{2+}) [LIU et al, 2015].

Figure 4.3. TEM images of Ag5 (a and b) and Ag10 (c and d) samples as well as corresponding diameter distribution (e) and (f), respectively. Selected area electron diffraction pattern (SAED) taken from Ag5 and Ag10 samples.

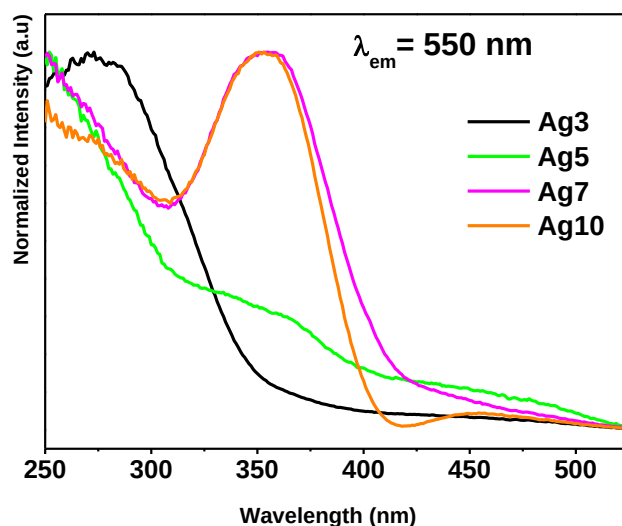


It should be noted here that the average diameter of the large particles appears to be around 5 (± 1) nm. Note that the annealing time was carried out at 320 °C, which is below the glass transition temperature (385 °C), to remove any residual internal stress induced by the rapid cooling of the glass melt. Thus, the larger particles observed in TEM micrographs (>5 nm) are most likely generated during the sample preparation and also the annealing time. In fact, the Ag particles within fluoride network present very high mobility already at 300 °C [TIKHOMIROV et al, 2010]. Thus, the large Ag particles observed are formed during the annealing process due to the high mobility of the Ag particles in the fluorophosphate matrix.

4.3.2 Excitation and emission spectra dependences on Ag nanoclusters concentrations

Excitation spectra for the samples were recorded at several wavelengths in the range between 250–550 nm. Results obtained at 550 nm are reported in Figure 4.4. One can see that excitation of Ag NC's doped fluorophosphate glasses depend strongly on the silver concentration, and the local environment around the Ag particles. The excitation bands spanning the range from 270 to 400 nm are related to different types of Ag NC's with different size, while the band centered at 458 nm for the Ag10 glass samples can be ascribed to the presence of a new emitting center, presumably Ag NC's with large average diameter. A similar broad excitation at around 270 nm which is related to Ag NCs (Ag_4^{2+}) was also reported for other glasses [KULESZA et al, 2011; LIN et al, 2013].

Figure 4.4. Normalized excitation spectra (PLE). The emission was fixed at 550 nm.

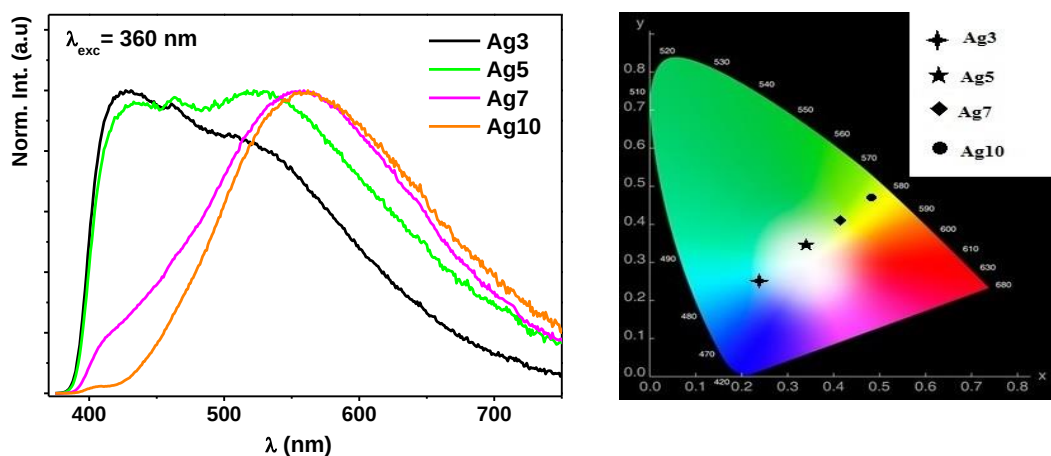


Obviously, a difference in the relative intensity of the two bands is observed (centered at 270 and 360 nm) with the increases of AgNO_3 concentration. The band at higher wavelength (360 nm) being more prominent in Ag10 glass samples and shifts to longer wavelength with increases of the AgNO_3 concentration. These unique concentration-dependent PLE properties could not be related to glass defect centers,

but are strongly pointed to the multiplicity of size/site distribution of Ag NCs because of the perturbation induced by the rearrangement of the Ag species [BORSELLA et al, 1998].

The normalized emission spectra of the Ag_x glass samples upon excitation of 360 nm are shown in Figure 4.5a. It is shown that the Ag NC's emit a broad luminescence band almost covering the visible light region (from 400 to 800 nm). Note that the un-doped glass sample (Ag₀) did not show any appreciable emission. Therefore, the luminescence in the prepared glasses is due to Ag NC's. A strict concentration dependence luminescent performance is observed. In fact, increasing the Ag amount level, the emission spectra are shifted to the red at the same excitation wavelength indicating that the average Ag NC's size increases with the Ag doping. The histograms of the prepared glasses support this point of view (Figure 4.3e and 4.3f). Additionally, the CIE chromaticity diagram for the prepared glasses reported in Figure 4.5ab indicates a different color rendering of the emission from blue (Ag₃) to yellow (Ag₇ and Ag₁₀ samples) while Ag₅ glass sample indicates a white emission. These results point out an inhomogeneous broadening due to a number of factors, including number of Ag atoms comprising the NC's, different surroundings in the fluorophosphate network, shape and size/site distribution.

Figure 4.5. (a) Normalized emission spectra of the samples excited at 360 nm; (b) chromaticity diagram.



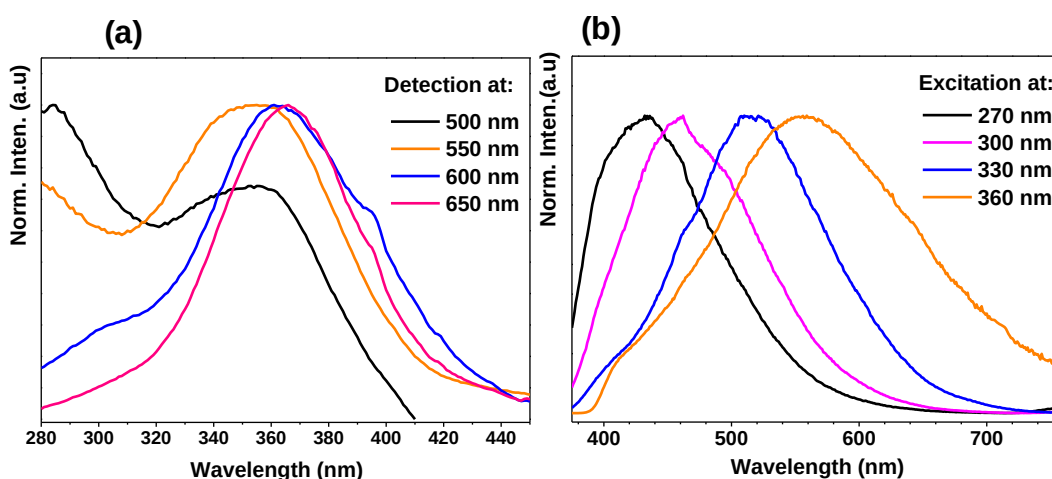
An analysis of these spectra highlights on the mechanism governing the emission of Ag NC's within prepared fluorophosphate glasses. One can see that the green and the red bands become more prominent with increasing Ag concentration at the expense of the blue band that decreases with the increases of Ag doping level, this effect being stronger in Ag10 glass sample. Two mechanisms can explain this effect: variations size/site distribution of Ag NC's and/or an energy transfer occurs between Ag NC's close to each other.

It was previously demonstrated that the radiative transitions originated from outer d-orbitals, which means that the luminescence is sensitive to local crystal fields [KUZNETSOV et al, 2013]. As the silver concentration increases, the number of silver atoms in NC's rises up and then increasing the size of the NC's. Consequently, the crystal field environment of Ag NC's is affected which leads to the change in the intensity as well as the shape of the emission band. According to Tikhomirov et al. [TIKHOMIROV et al, 2013], the short wavelength part of the Ag emission spectra corresponds to the emission by smaller size Ag NC's (called "Blue" NC's); while the long wavelength part corresponds to emission by larger size NC's (called "Green" and "Red" Ag NC's). Hence, the decreases in the blue emission as the silver concentration increases can be explained by the decrease of the amount of smaller size Ag NC's. On the other hand, the increases of green and red emissions are related mostly to the evolution of the amount of larger NC's called here "Red" and "Green" Ag NC's. As described before, the evolution of the different silver species with the increase in the AgNO_3 concentration can be described by a two-step mechanism. The first step consists in the formation of color centers (Ag^0 and Ag^{2+}) [LIU et al, 2015]. Then, when the concentration of silver is high enough, the amount of color centers is sufficient to allow their clustering in Ag_m^{x+} species. As the concentration of silver increases, the reduction rate also increases and results in the enlargement of size and concentration of Ag NC's. This is maybe explaining the increases of "Green"/"Red" NC's at the expense of the "Blue" NC's. Our TEM images support this point of view since the volume fraction of large NC's (>3nm) increases, while the volume fraction of small NC's (<2 nm) decreases with the increases of Ag doping level.

Additionally, Figure 4.6 (a and b) depicts the normalized excitation and emission spectra respectively of the fluorophosphate glass doped with 7 mol% AgNO_3

monitored at different wavelengths. As we can see, a shift of the detection and excitation wavelength from blue to the red results in red shift of the respective excitation and emission spectra in addition to the evolution in the relative intensity of the broad band related to Ag NC's spanning the range from 270 to 400 nm. A similar behavior has been detected in previous work and as explained by M. V. Shestakov et al [SHESTAKOV et al, 2014], this unique wavelength-dependent emission and excitation properties is related to the dispersion of Ag NC's with varying surroundings, i.e. with varying an Ag NC's site, and to the presence of a variety of Ag NC's with different sizes.

Figure 4.6. Normalized (a) excitation and (b) emission spectra of the fluorophosphate glass doped with 7mol% AgNO₃ monitored at different wavelengths, respectively.



The second possible factor responsible for this effect is the energy transfer between neighboring Ag NC's. Recently, a model has been achieved by A. S. Kuznetsov et al. in which they demonstrate that energy transfer occurs from the smaller Ag NC's emitting in the blue to either more larger Ag NC's emitting in the green and further in the red, or directly to Ag NC's emitting in the red [VELAZQUEZ et al, 2012].

Combining the TEM results and emission spectra of prepared fluorophosphate glasses, we can conclude that, when the size of blue Ag NC's reaches a critical value, they apparently cease to emit and/or they transfer energy to green and red

NC's. Hence, the luminescence properties of Ag NC's are mostly defined by the size as well as by the number of Ag NC's within glass network. The relationship between an Ag NC's size and its fluorescence properties will be discussed more in the next section.

4.3.3 Emission spectra dependence on excitation wavelengths

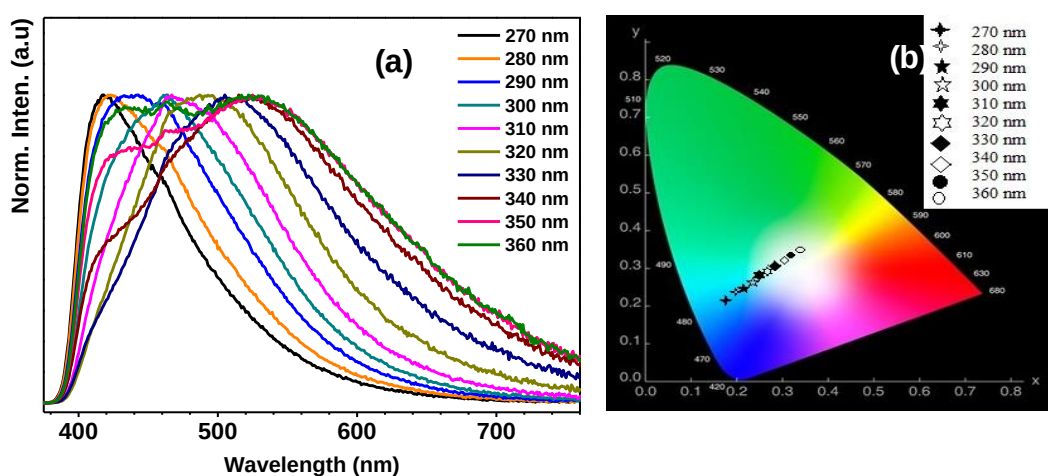
It is important to evaluate the excitation dependence on the emission properties of Ag NC's doped glasses for practical applications. Since a white color emission is generated from Ag5 glass sample with excitation wavelength near to 360 nm, we turn our attention into improving this result, which maybe provides useful information for applications in the field of white LEDs. Previously, the excitation spectrum of Ag5 glass sample indicates that the most intense excitation wavelengths for Ag NC's were located at 270 and 360 nm, respectively. In the following section, these wavelengths were used as optimal excitation wavelengths to record emission spectra of Ag5 glass sample.

The normalized emission spectra of the Ag5 sample upon excitation of different wavelengths according to the absorption band in the range of 270-360 nm are shown in Figure 4.7a. As we can see, the position and shape of the emission depend strongly on the excitation wavelength. When the excitation wavelength is shorter than 310 nm, the emission spectra merely exhibits a single band with the maximum shifting from the violet to the blue region, i.e., from 420 to 470 nm. On the other hand, dual mode emission bands in the range of 400-620 nm covering blue and green region gradually emerge with excitation wavelength in the range of 310-330 nm. Excitation at longer wavelength (>340 nm) resulting in a broad luminescence band almost covering the visible light region (from 400 to 800 nm). In fact, there is a strong relationship between an Ag NC's size and its fluorescence excitation wavelengths [XU; SUSLICK, 2015]. As we can see, the emission maximum was found to shift to longer wavelengths with increasing excitation wavelengths from 270 nm to 360 nm, which confirms a distribution of Ag NC's with different size and this match well with the earlier reported respective spectra of Ag NC's doped oxyfluoride glasses [TIKHOMIROV et al, 2002; LIU et al, 2015]. A similar shifting with excitation wavelength has been detected in semiconductor quantum dots, and it has been

related to the size-selective excitation of the quantum dots [KUZNETSOV et al, 2015; CHOI; DICKSON; YU, 2012]. Thus, this unique wavelength-dependent emission and excitation properties are strongly related to Ag NC's comprising different numbers of Ag atoms, otherwise, related to the presence of a variety of Ag NC's with different sizes and geometry, particularly emitting in the blue, green and red region [TIKHOMIROV et al, 2010; KUSNETSOV et al, 2013].

As described before on previous works [TIKHOMIROV et al, 2010], the blue part of the Ag emission spectrum corresponds to the emission of the small size Ag NC's (KUSNETSOV et al, 2013 as blue NC's), while the green and red parts correspond to emission of large size NC's (KUSNETSOV et al, 2013 as green and red NC's). The chromaticity diagram presented in Figure 4.7b resumes the color rendering tuning obtained from the glass samples for different excitation wavelengths. As it is shown in the Figure 4.7b, white color emission with varying tint can be generated under UV excitation (> 330 nm). The obtained emission results suggest that sample Ag5 is useful for white light generation in fluorescent lamps and UV LEDs.

Figure 4.7. Normalized emission spectra (a) the CIE chromaticity diagram (b).



To obtain a deeper insight about the mechanism governing the emission of Ag NCs, the microsecond decay curves of Ag5 glass sample at different wavelengths upon 360 nm excitation were recorded. The emission was detected at 420, 550 and 620 nm; the results are presented in Figure 4.8. The decay curves are fitted by a double exponential function given by [LIN et al, 2013]:

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_{fast}}\right) + A_2 \exp\left(\frac{-t}{\tau_{slow}}\right) \quad (4.2)$$

Where I is the luminescent intensity, A_1 and A_2 constants, t the time, τ_{fast} and τ_{slow} the fast and long lifetimes, respectively. The calculated lifetimes, as shown in Table 4.I, indicates that the luminescent dynamics of Ag NC's dispersed in glass host are in the microsecond regime. The fast and slow regimes evident in the lifetime data. In addition, the results show that the lifetimes are shorter for blue emission wavelengths relative to the green and red emission wavelengths. We believe that the multiplicity of size/site distribution of Ag NC's could be responsible for the obtained lifetimes. The obtained experimental curves are consistent with those reported for emitting Ag NC's dispersed in other glasses [VELAZQUEZ et al, 2012; LIN et al, 2013].

As we can see, the slow PL lifetimes of the multi-exponential decay are shorter at blue emission (68 μ s) wavelengths than for green and red emissions (114 and 131 μ s, respectively). Analogous lifetime dependence was observed for the luminescence decay of Ag NC's doped Y-zeolites [CHEN et al, 2002] interpreted using a model involving four-level system: two singlet states and two close thermalized metastable triplet levels. The short lifetime (68 μ s) is due to the allowed singlet-singlet transition while the longer lifetimes (114 and 131 μ s) are due to the forbidden triplet-singlet transition, as it was explain in previous works [SHESTAKOV et al, 2013]. Moreover, Lin et al. [LIN et al, 2013] explain the observed distinct lifetimes to the multiplicity of size/site distribution of Ag NC's.

It is far beyond the scope of this contribution to perform a computational methods of quantum chemistry for a more comprehensive mechanism governing the luminescence of Ag NC's, as well as, the reduction mechanism of Ag NC's within the

new glass system, however, the results reported herein are still interesting and some general considerations can be drawn from the experimental results, particularly TEM microscopy, luminescence decay curves and the obtained excitation and emission spectra of prepared glasses. Combining all, we can conclude that, emission of blue NC's occurs by fast singlet-singlet transition while the green and red NC's occur by slow triplet-singlet.

Figure 4.8. Luminescence decay curves for different detected wavelengths upon excitation at 360 nm.

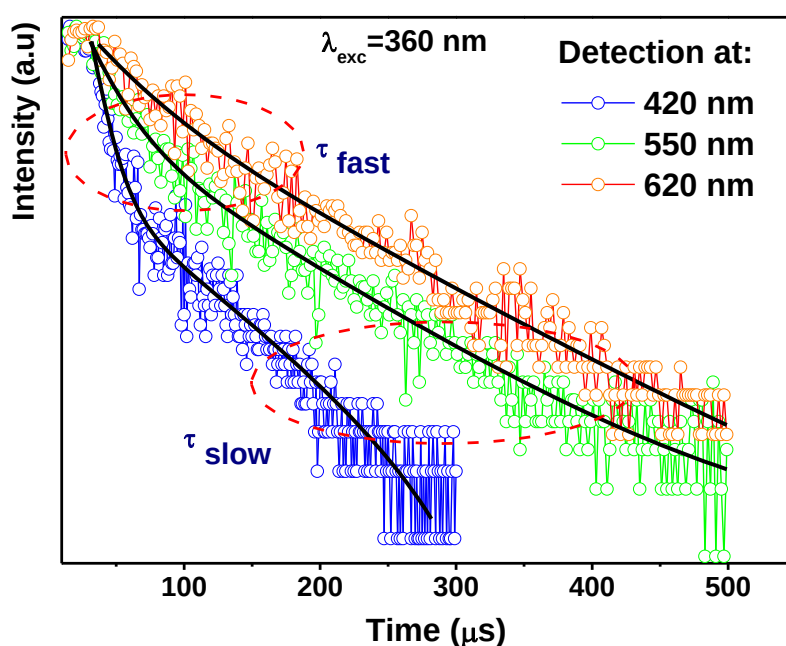


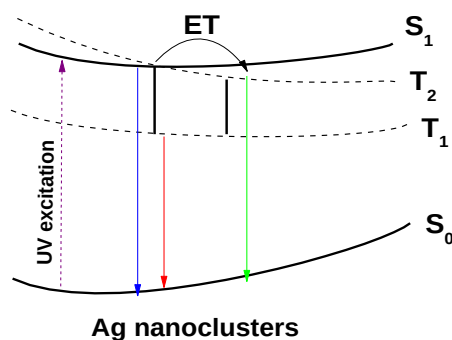
Table 4.1: Experimental decay time values of 5 mol% AgNO₃ doped sample at different detected wavelengths.

Emission at:	T _{fast} (μs)	T _{slow} (μs)
420 nm	11	68
550 nm	24	114
620 nm	39	131

The simplified energy level diagram suggested in Figure 4.9 illustrates the excitation and emission mechanism in Ag_m^{x+} NC's resulting the white light. We follow here the notations proposed by Velázquez et al [VELAZQUEZ et al, 2012]. According to the authors, only the lowest electronic states contribute on the process of luminescence related to Ag NC's. Here, S_0 represent the ground state, S_1 is the excited singlet state, while T_1 and T_2 are the excited triplet states, respectively [VELAZQUEZ et al, 2012].

When an excitation occurs with UV light, an electron undergoes a transition from the ground state S_0 to the excited singlet state S_1 . As we can see from model involving the four-level, five possible emission transitions can occur around the blue, green, red, infrared and far infrared ranges of the spectrum originated from $S_1 \rightarrow S_0$, $T_2 \rightarrow S_0$, $T_1 \rightarrow S_0$, $S_1 \rightarrow T_1$ and $T_2 \rightarrow T_1$ transitions, respectively. First, the excitation at shorter-wavelength (between 270 and 330 nm) will transfer the electron to S_1 state giving rise to a blue [VELAZQUEZ et al, 2012]. On the other hand, an excitation wavelength near to 360 nm will excite the electron in a low-lying single state of S_1 , which will rapidly relaxes to triplets excited states via slow triplet-singlet transitions $T_2 \rightarrow S_0$ (green-yellow emission) and $T_1 \rightarrow S_0$ (red emission) [VELAZQUEZ et al, 2012], in addition to the shorter singlet-singlet transition $S_1 \rightarrow S_0$ and then giving rise to a broad emission band almost covering the visible light region (from 400 to 800 nm). The last two transitions $S_1 \rightarrow T_1$ and $T_2 \rightarrow T_1$ are quenched non-radiatively by cross-relaxation energy transfer due to their relatively small energy / quantum resulting in increasing of yellow-red emission band $T_1 \rightarrow S_0$ [VELAZQUEZ et al, 2012].

In summary, three basic groups of Ag NC's are responsible for the blue, green and red luminescence. The blue emitting NC's have the smallest size and the size of NC's increases from the blue to the green and further to the red with the increases of AgNO_3 concentration. This follows from the dependence of emission wavelength versus Ag doping level and from direct structural measurements by transmission electron microscopy. The results of emission spectra dependence on Ag NC's concentrations indicates that the green and the red emissions bands becomes more prominent at the expense of the blue emission band which decrease with the increases of Ag doping level. Therefore, we conclude that when the "blue" Ag NCs reach a critical size, they apparently cease to emit and/or they transfer energy to "green" and "red" NC's.

Figure 4.9. Schematic configuration coordinate diagram of Ag_m^{x+} NC's.

4.4 Conclusions

In this contribution, emission properties of silver NC's within fluorophosphate glassy matrices were studied. The findings show that the formation and the growth of NC's with different size are determined by glass-intrinsic reduction mechanisms. When excited under UV, Ag NC's dispersed in the glass matrix exhibit single broad-band emission, covering the VIS range of the spectrum, giving rise to a white emission. It implies a broad range of applications such as light emitting diodes. Our present systematic study provides useful information for further development of nano-photonics devices.

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Photoluminescence of silver species and Pr^{3+} , Yb^{3+} co-doped fluorophosphate glasses

Spectroscopy interaction among different silver species in co-doped $\text{Pr}^{3+}/\text{Yb}^{3+}$ fluorophosphate glasses is shown in this chapter. Through the solubility of Ag into fluorophosphate glasses, different charged species characterized as Ag^+ and Ag_m^{n+} were formed and identified according to their broadband absorption and excitation in the UV-Vis region. By means of transmission electron microscopy, we observed an increase in size with the increment of Ag amount, leading to the formation of Ag nanoparticles. Photoluminescence measurements showed the Ag_m^{n+} species present broadband emission in the visible region upon excitation at different wavelengths due to the different sizes of nanoclusters. Energy transfer process were observed for glasses doped with Yb^{3+} and co-doped with $\text{Pr}^{3+}/\text{Yb}^{3+}$. Thus, time resolved spectra results, for the most concentrated sample, demonstrated the size-dependent behavior due to a redshift in the visible emission. This approach represents a promising direction to explore broadband emitters materials with potential use in down-conversion layers for photovoltaic application, phosphors and beyond.

5.1 Introduction

Materials containing metal ions, such as silver have paved new advances in modern spectroscopy. Counting with the rich optical properties of silver nanoclusters and nanoparticles, new materials have been developed for numerous applications like solar cell efficiency enhancement [ENRICH, 2013], light frequency converter [MA, 2014], white light generation [MA et al, 2016; JING et al, 2012] and others [DESMOULIN et al, 2015; KHALIL et al, 2017; KUZNETSOV, 2013]. The large UV-Vis absorption and emission is ascribed to the evolution of certain charged and uncharged silver species like, for example, Ag^+ , Ag^0 , Ag_4^{2+} and Ag_m^{n+} [YE et al, 2016; CHOI; DICKSON; YU, 2012]. These species result from the agglomeration of few atoms forming nanoclusters (NC's) up to few nanometers [DÍEZ; RAS, 2011]. Moreover, taking into account the energy levels of the NC's, the absorption and emission of light as well as its tunability is allowed since exist a size-dependent spectroscopy [HALPERIN, 1986].

This contrasting size-dependent behavior makes silver NC's suitable for rare earth (RE) coupling, aiming a modulation and enhancement of luminescence in both visible and near-infrared ranges [RAJESH et al, 2017; JIMÉNEZ et al, 2017]. In one of the first publication regarding NC's-RE interaction, Tikhomirov *et al.*, reported an energy transfer (ET) between Ag NC's and Yb^{3+} in oxyfluoride glasses. In that case, the Yb^{3+} emission at 1000 nm was achieved by resonant and non-resonant excitation in Ag NC's. Huiyun Wang *et al.*, studied a broadening excitation by co-doping oxyfluoride glass with $\text{Eu}^{3+}/\text{Yb}^{3+}$ and by controlling the growth and stabilization of Ag NC's. Recently, Zhuang Guo *et al.*, proved that Ag NC's is an efficient broadband sensitizer for Sm^{3+} ions in the visible range. In fact, by controlling the Ag solubility in glass, several NC's species may be tailored to provide a broadband absorption and emission in the UV-Vis region [DUBROVIN et al, 2014].

Size-dependent Ag NC's has been investigated in different glass hosts. Previous publications indicate that many factors might affect the size distribution of Ag species, such as heat treatment, Ag concentration, glass network changes and RE doping [KUZNETSOV et al, 2012; MA et al, 2017; JIAO et al, 2014; LI et al, 2013]. Concomitantly, in a system that presents rare earth ions, Ag NC's and NP's may benefit of certain interactions like surface plasmon resonance (SPR) and energy transfer (ET) in such a way that visible and near-infrared emissions of RE^{3+} ions may be modulated [WU et al, 2011; WEI et al, 2012]. Indeed, the forbidden character of $4f - 4f$ transition make the UV-Vis cross-section of the RE^{3+} small. On the other hand, the presence of Ag entities can boost the absorption efficiency, in this sense an efficient interaction among RE, Ag NC's and NP's can globally enhance the luminescence by plasmonic and ET mechanisms [MATHPAL et al, 2015].

In this work, fluorophosphate glasses with molar composition $30\text{NaPO}_3\text{-}30\text{MnF}_2\text{-}30\text{BaF}_2\text{-}10\text{YF}_3$ were prepared via melting quenching method by co-doping with $\text{Pr}^{3+}/\text{Yb}^{3+}$ and different Ag contents. We investigate the spectroscopy properties of the $\text{Pr}^{3+}/\text{Yb}^{3+}$ pair as a function of Ag concentration by combining the down-conversion and the broadband absorption and emission properties of Ag nanoclusters and single ions. To verify the effect of Ag in the emission and excitation spectrum, a sample without Ag was prepared. Still, for comparison, a sample without Pr^{3+} was prepared to show the energy transfer from the Ag NC's and Ag^+ to the Yb^{3+} ions.

5.2 Experimental section

5.2.1 Glass preparation

The glass samples were prepared by the melting-quenching technique with the following chemical composition (mol %): $(30-x)\text{NaPO}_3-30\text{MgF}_2-30\text{BaF}_2-10\text{YF}_3-0.5\text{Pr}-0.5\text{Yb}-x\text{Ag}$ ($x = 0, 2, 4$ and 10) with, approximately, 5 g to each batch with the molar percentage of rare earths and silver replacing a certain amount of NaPO_3 . All compounds used were 99,9% purity (Sigma Aldrich). The raw materials were thoroughly mixed in a speed mixer with 1000 rpm, transferred to an alumina crucible and melted at 1000 °C for 30 min in ambient atmosphere. The melt was poured onto a stainless-steel mold, preheated at 340 °C and kept at this temperature for 2 h to reduce mechanical stress due to the fast cooling. Table 1 summarizes the sample compositions, the amount of Pr^{3+} and Yb^{3+} was fixed in 0,5 mol% and Ag ranging from 0 to 10 mol%. For comparison purpose, a pure host and a sample without silver were prepared and the results of these two samples are inserted in the spectroscopy results.

Table 5.1: Molar composition of the raw materials and sample nomenclature.

Compounds (mol%)							Label
NaPO_3	MgF_2	BaF_2	YF_3	Pr_2O_3	YbF_3	AgNO_3	
30	30	30	10	0	0	0	Pure host
29	30	30	10	0.5	0.5	0	PYAg0
27	30	30	10	0.5	0.5	2	PYAg2
25	30	30	10	0.5	0.5	4	PYAg4
19	30	30	10	0.5	0.5	10	PYAg10
19.5	30	30	10	0	0.5	10	YAg10

5.2.2 Characterizations

Absorption spectra were recorded using a Carry 5000 Spectrometer (Varian) double-beam coupled with resolution of 1 nm. All samples were polished to optical quality in order to obtain 2 mm of thickness. The excitation, emission and time resolved spectra were collected in a Horiba Jobin Yvon Fluorolog 3 equipped with Xenon lamp (450 W), photomultiplier tube (PMT - Hamamatsu R298) for the infrared detection and visible

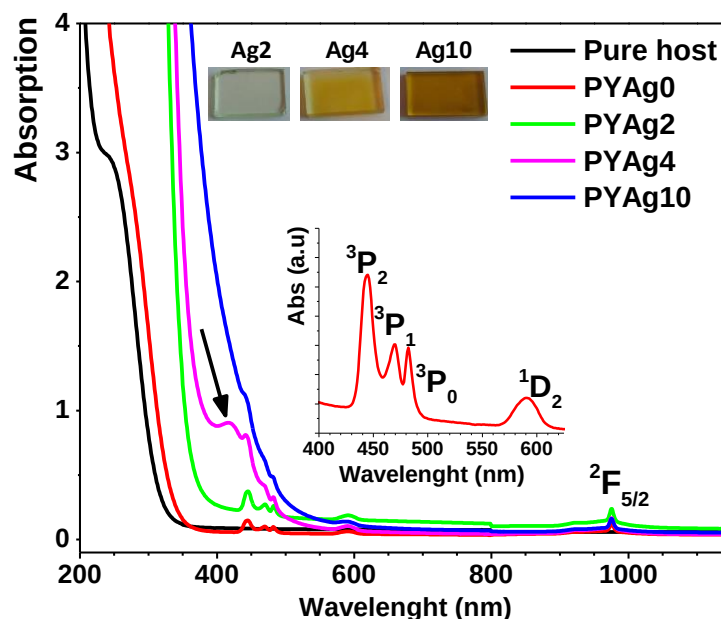
signal. All measurements were performed at room temperature and the samples were grinded in order to avoid re-absorption process. The presence of Ag nanoparticles and nanoclusters were confirmed by a 200 kV Transmission Electron Microscopy (Philips CM200 – 200 kV).

5.3 Results and discussions

5.3.1 Absorption Spectra

Absorption spectra of the fluorophosphate glasses are depicted in Figure 5.1. The expected $4f-4f$ absorption lines of rare earth doped samples are detected. Pr^{3+} doped glass shows four lines ranging from 400 to 650 nm, which are emphasized on the inset graph. These peaks correspond to the $^3H_4 \rightarrow ^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ excited states transitions and are located at 445, 469, 482 and 591 nm respectively. The Yb^{3+} ($^2F_{7/2} \rightarrow ^2F_{5/2}$) absorption lines are visible at around 1000 nm. No real influence of the rare earth doping is evidenced as the charge transfer band between Yb^{3+} and the ligands or the $4f-5d$ absorption band of Pr^{3+} are both expected at higher energy in fluorine hosts. The cut-off from the pure host (black line) starts in 350 nm, and this limit is shifted for higher wavelengths when the concentration of Ag amounts increases. For the 4 and 10 mol% of Ag content, a strong absorption increases between 400 nm and 550 nm. This band overlaps the Pr^{3+} ions absorption. Their contribution appears as shoulder and/or modulation of the curves. In addition, a higher Ag amount reduces the transparency in the visible due to the brown color of the samples PYAg4 and PYAg10 (see inset digital pictures). This color is attributed to the growth of Ag NC's and NP's, which increases during the annealing time [FARES et al, 2017].

Figure 5.1. Absorption spectra of the pure (black line), and co-doped with $\text{Pr}^{3+}/\text{Yb}^{3+}$ and different Ag amount. Increasing the Ag amount, the Ag NC's absorption increases and overlaps the Pr^{3+} absorption between 400 and 500 nm. The inset shows Pr^{3+} absorption lines in the visible range for the sample PYAg0 and the digital pictures show the change in color as a function of the Ag content.



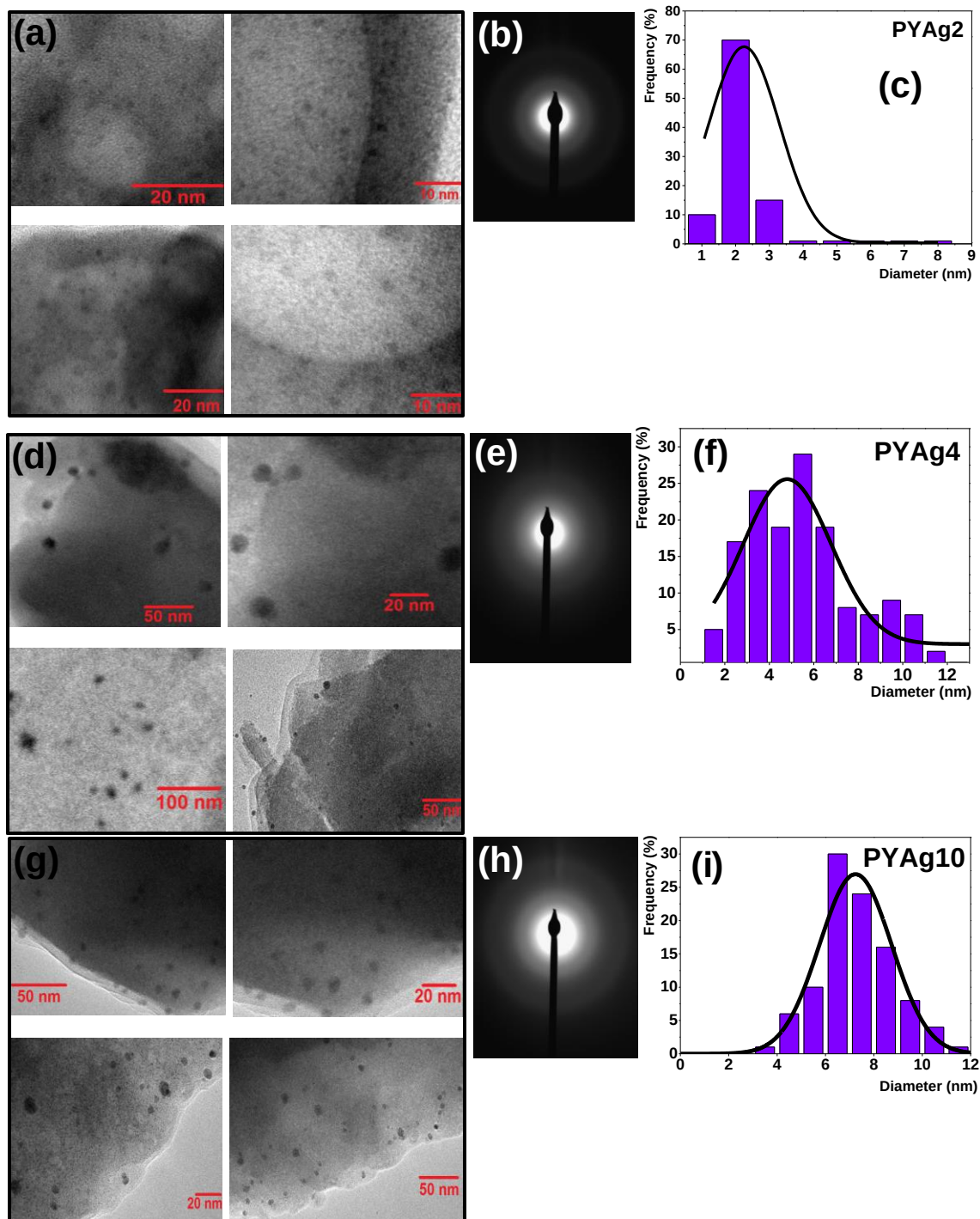
5.3.2 Transmission Electron Microscopy

To obtain a deeper insight concerning the formation of Ag NC's, transmission electron microscopy (TEM) has been performed (Figure 5.2 a, d and g). The results indicate a growth in the NC's size with further increment in Ag amount. Shape of NP's and NC's are quite regular and the size distribution increases, as shown on the histogram, Figure 5.2 (c), (f) and (i). This observation, could lead to two plausible mechanisms to obtain Ag as NP's and NC's. First, the solubility of Ag^+ takes place up to less than 2 mol%. In other words, an homogeneous network of phosphate groups $[\text{PO}_3]^-$ and fluoride ions (F^-), being counterbalanced by positive ions, is formed in this condition and several NC's are already observed. At this concentration, majority of the introduced Ag exists as Ag^+ ions and Ag_m^{n+} (molecular silver species, also called in this paper as NC's). This NC's are characterized by the absence of diffraction planes, as we can see in the Figure 5.2 (b) (Selected Area Electron Diffraction - SAED). Second, in concentration

higher than 2%, the Ag^+ rich system leads to an increment in Ag_m^{n+} size due to agglomeration and mobility of Ag^+ on the glass network. In this case, an ideal system is reached by the presence of Ag^+ and constant increment on the size NC's. The different Ag_m^{n+} size remains amorphous in all the samples, as we can see by the diffraction rings on the Figure 5.2(b), (e) and (h). Interestingly, it should be expected that all the Ag^+ would be in a homogeneous dispersion since this glass system is rich in F^- centers. Moreover, the meta-phosphate groups $[PO_3^-]$, as well as F^- ions, should ensure a better Ag^+ ions dispensability since the interaction between positive and negative charges is guaranteed. However, not even these negative centers were capable to avoid Ag agglomeration, due to Ag NC's presence. In a previous publication, Hssen *et al.*, prepared a similar glass system but, with higher percentage of meta-phosphate groups (up to 40%). In this publication, the authors were able to dissolve up to 5 mol% of Ag and it was observed for this concentration, all the Ag was presented in Ag^+ ions and NC's, homogeneously distributed. In this sense, we may infer that Ag ions must have a higher dispensability when the $[PO_3^-]$ groups are in a larger amount compared to fluoride ions. Therefore, a higher viscosity (introduced by the phosphate groups) may be the driven force to the Ag dispersion.

For the last step, the F^- rich fluorophosphate glass may favor the reduction of the charged specie Ag_m^{n+} to form Ag NP's due to its ionic mobility and intrinsic ability to form F^- centers [TIKHOMIROV *et al*, 2010]. Although the SAED analysis show a lack of crystallinity on the samples, the sample with 10 mol% of Ag shows a weak absorption band at 420 nm (see Figure 5.1 – pink line). This band is related to the absorption of crystalline nanoparticles that present surface plasmon resonance (SPR) effect. In fact, taking into account the stoichiometric quantities of 30 mol% MgF_2 , 20% BaF_2 and 10 mol% of YF_3 , we predict that discrete F^- may migrate along the glass volume during the annealing time and reduce the charged Ag_m^{n+} clusters into NP's by trapping this NC's in F^- reservoir. In addition, another mechanism of crystallization to emphasize is that the interaction between small nanoclusters (less than 5 nm) and the electron beam might favor nano crystallization under high voltage as 200 kV. Therefore, NP's may be formed by the reduction of charged species during the synthesis and in a small quantity, during the interaction between electron beam and the tiny pieces of the grinded glass samples.

Figure 5.2. TEM images of the samples PYAg2 (a), PYAg4 (d), PYAg10 (g) and selected area electron diffraction (b), (e) and (h) for the respective samples (right side). Figures (c), (f) and (i) represent the size distribution of the NC's and NP's.



5.3.3 Spectroscopy Results

In order to evaluate the spectroscopic properties of Ag species, we dedicated a deep attention to the photoluminescent properties. From the point of view of emission and excitation, each Ag entity has its own behavior and this may give us an extra information to better elucidate the Ag evolution in our glass system. Figure 5.3 (a) shows the excitation spectrum of all samples with emission fixed at 564 nm (this wavelength makes possible the discrimination between Ag and Pr^{3+} contribution, by selectively exciting the silver clusters). Figure 5.3 (b) shows the excitation spectrum for the sample PYAg10 with the emission fixed at 606 nm (Pr^{3+} emission peaks) and the Figure 5.3 (c) shows the excitation spectrum with emission fixed at 980 nm (Yb^{3+} emission lines). Figure (a) displays an ensemble of different Ag species, which are well defined and labeled on the deconvolutions spectra, as shown in Figures 5.3 (d)-(f). As discussed above, the noticeable number of species indicates a poor dispersion of Ag in this glass composition leading to a quenching of solubility even at 2 mol%. In this concentration, two main excitation bands are observed around 250 and 280 nm, whose are assigned to the $^3D_1 \rightarrow ^1S_0$ Ag^+ transition [CUONG et al, 2013]. A weak absorption is observed at 370 nm, which is due to Ag_m^{n+} species. With the continuous increment of Ag amount, the intensity of the Ag^+ excitation decreases partially at 4 and 10 mol%, whereas the species Ag_m^{n+} is favored. The excitation positions of these bands have a slightly shift for higher wavelengths, which is related to the growth of the Ag_m^{n+} . The Figures 5.3 (b) and (c), which correspond to excitation graph performed at 606 nm (Pr^{3+} levels) and 980 nm (Yb^{3+} levels), show the three absorption lines of Pr^{3+} already mentioned. These bands are overlapped by the Ag_m^{n+} excitation and absorption, correlative to Figure 5.1. In these two cases, the results suggest an energy transfer between silver species and rare earth ions as well as between rare earth elements.

Figure 5.3. Excitation spectra with emission wavelength fixed at 564 nm (a); excitation with emission fixed at 606 nm (Pr^{3+} lines) and 980 nm (Yb^{3+} lines), (b) and (c), respectively. Deconvolutions of the excitation bands for the samples PYAg2 (d), PYAg4 (e) and PYAg10 (f).

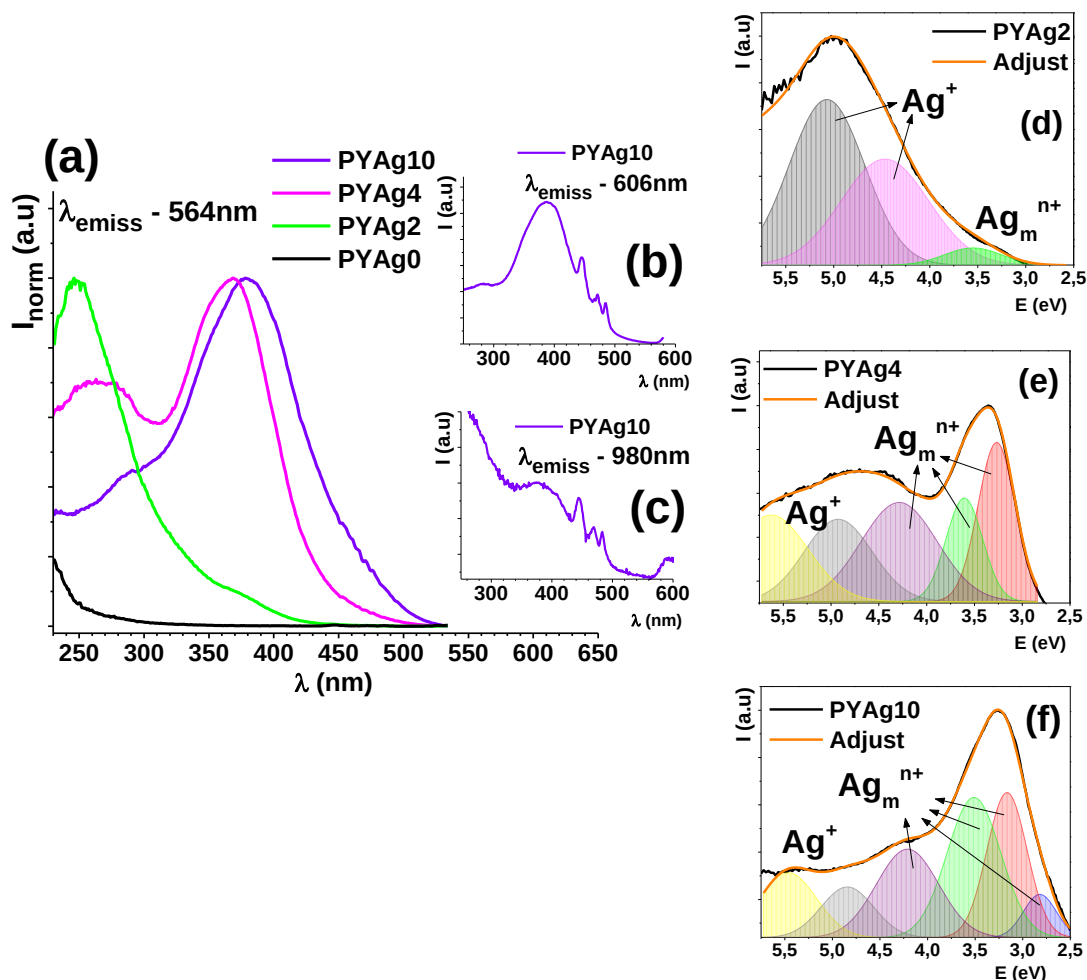
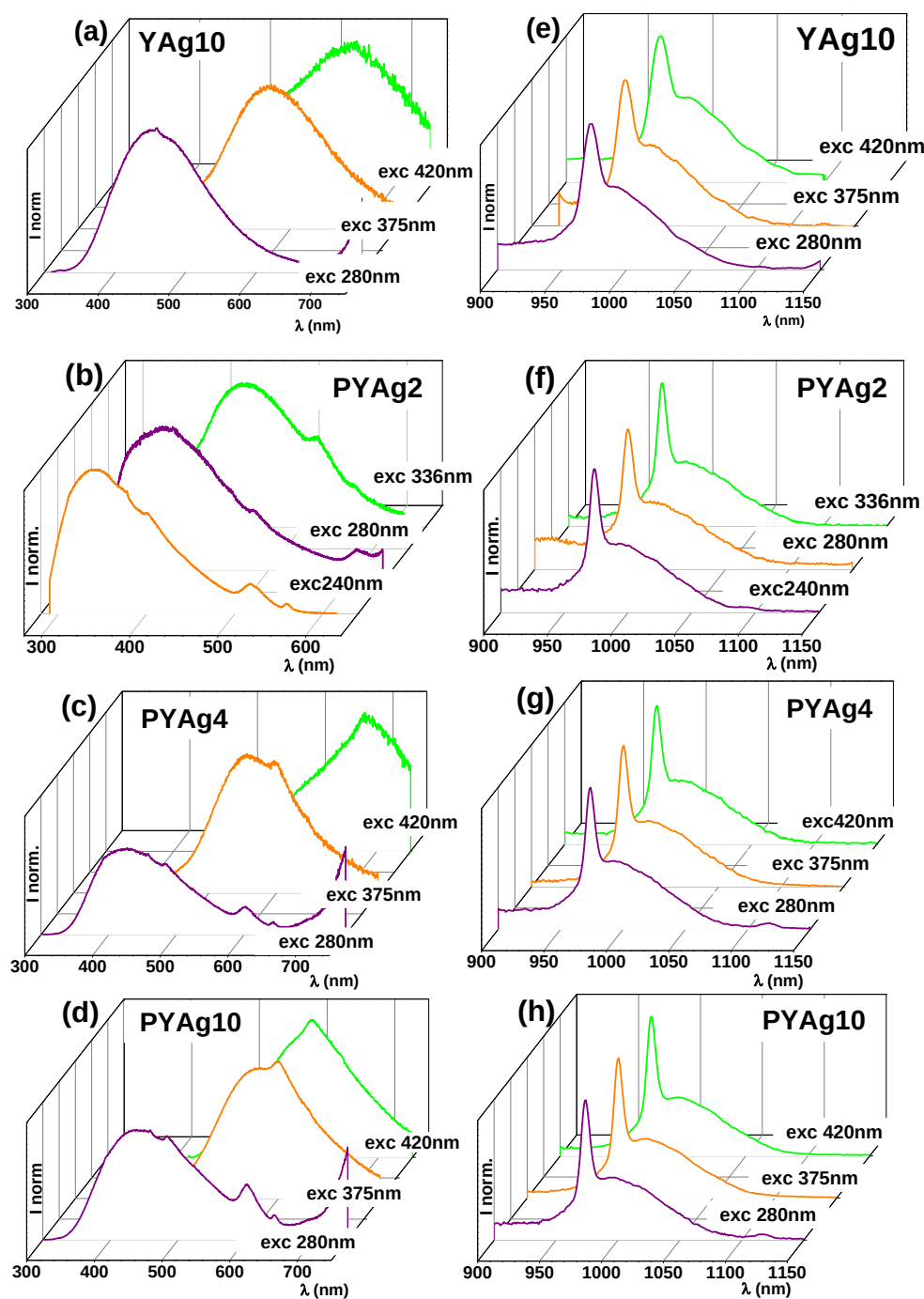


Figure 5.4 shows the emission spectra of the samples with different excitation wavelengths in agreement with the deconvolution proposed in Figure 5.3. A non Pr^{3+} content sample is also described (Figure 5.4a and 5.4e). Visible emissions are shown in the left side (a-d) and the near-infrared on the right side (e-h) as well. The main emission is due to silver species contribution. Besides, for the excitation between 270 and 420 nm (Ag_m^{n+}), we observed a redshift due to an increasing in the NC's size in relation with the increased silver content. This is in accordance with previous publications concerning luminescence dependence NC's properties [KUZNETSOV et al, 2013; TIKHOMIROV et al, 2012]. Since the main Pr^{3+} absorptions are in the range

from 425 to 500 nm, we might mention that an energy transfer (ET) occurs when the excitation is carried out in the Ag NC's (270 to 420 nm). Meanwhile the Pr³⁺ emission appears as sharp and weak peak, the Yb³⁺ emission is totally evident between 900 and 1150 nm, which correspond to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition. The ytterbium emission is also visible in the Pr³⁺ free sample. The Ag $\rightarrow$ Yb³⁺ ET was also reported for the oxyfluoride system [TIKHOMIROV et al, 2012]. For the sake of brevity, only 3 different excitation is shown for the samples, Figure (e)-(h). However, the Yb³⁺ emission may be achieve exciting from 250 up to 450 nm.

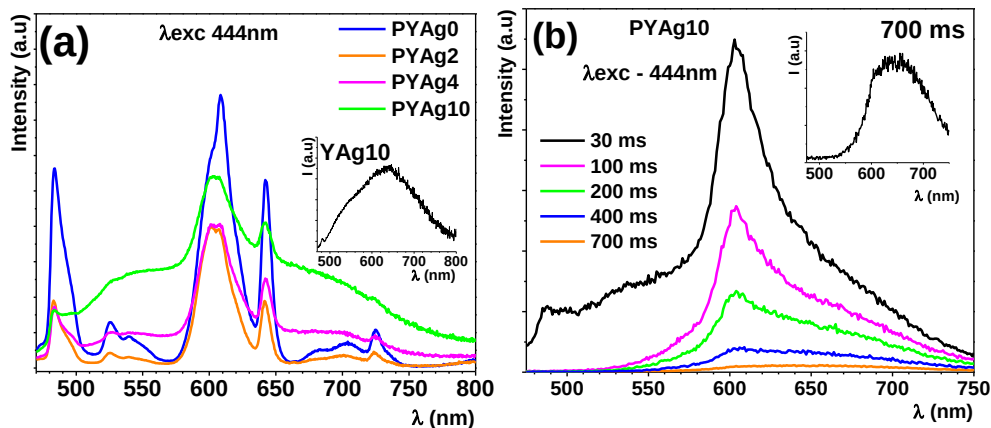
It is worth to note that the sample PYAg4 exhibits a very weak relative absorption at 425 nm in its absorption spectrum (Figure 4.1 – black arrow). This absorption is due to surface plasmon resonance (SPR) that rises from the small crystalline nanoparticles that have no luminescence themselves [TIKHOMIROV et al, 2010]. Still, compared to the nanoclusters absorption, we may presume a lack of substantial amount of Ag NP's with size and shape proper to generate a comparable SPR effect. Therefore, the gross features from the emission spectra in the visible part (Figure 5.4 a-d) lead us to believe that overall emission is due to the NC's and Ag⁺ ions. Besides, it is out of scope of this work to achieve the investigation of Ag NP's.

Figure 5.4. Emission spectra in visible range (a–d) and near-infrared (e–h) performed for excitation in silver species absorption. The broadband emissions in the visible range characterize the emissions of Ag and $\text{Ag}_m^{\text{n+}}$ species and an ET is observed by the Pr^{3+} emission at 500 and 606 nm (figure 5b-d). Yb^{3+} emission resulting from ET, observed at different Ag NC's excitation (e-h).



For the excitation at 444 nm (Pr^{3+} : $^3\text{H}_4 \rightarrow ^3\text{P}_2$), we can see the characteristic green and orange emission of Pr^{3+} ions, blue line from Figure 5.5 (a). The main emissions are centered at around 486, 606 and 700 nm, which correspond to the radiative transitions $^3\text{P}_0 \rightarrow ^3\text{H}_4$, $^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{F}_2$, respectively. With the addition of Ag, the Pr^{3+} emissions is reduced and a broadband rises, covering the region between 480 and 800 nm. The quenching of the green emission is more accentuated compared to the red one. For the sample with 10 mol%, the green almost disappeared. For comparison, the inset of the Figure 5.5 (a) shows the emission of the sample without Pr^{3+} under the same excitation (444 nm); in this case, we can see a wide emission that is similar to the samples co-doped with $\text{Pr}^{3+}/\text{Yb}^{3+}$ and containing different Ag contents. At this point, we need to emphasize that the wavelength 444 nm, excites the Ag_m^{n+} species and Pr^{3+} ions, according to the above-mentioned excitation spectrum (Figure 5.3b). The high Ag amount favors the Ag_m^{n+} absorption in contrast to Pr^{3+} 4f-4f lines, leading to a partial quenching on the electronic population of the state $^3\text{P}_0$, responsible for the green emission. This is enhanced for the highest silver content samples. In parallel, this competitive absorption also affects the $^1\text{D}_2$ level population from which the red luminescence is emitted.

Considering that 444 nm is an effective excitation for the Pr^{3+} ions and Ag_m^{n+} species, time resolved spectra were collected under this excitation for different delay time, as showed in the Figure 5.5 (b). After 30 ms from the source-pulsed, the states $^3\text{F}_2$ (642 nm) and $^3\text{F}_4$ (722 nm) are totally quenched. With further delay, up to 100 ms, the state $^3\text{H}_4$ no longer emits and the transition associated to the $^1\text{D}_2$ level at 606 nm decreases the intensity. At this point, the visible emission is influenced by long decay time species, the biggest NC's from the specie Ag_m^{n+} and the emission is broader and shifted to higher wavelengths. In 700 ms, the intensity is relatively weak and the maximum is around 650 nm. Interestingly, the emission that persists at 700 ms is quite similar to the emission of the sample YAg10 (inset graph of the Figure 5.5a and 5.5b). In this case, only the long living Ag_m^{n+} NC's, responsible for the red emission are activated.

Figure 5.5. (a) Visible emission of co-doped ($\text{Pr}^{3+}/\text{Yb}^{3+}$) and different Ag amount in fluorophosphate glasses; (b) time resolved spectra for the sample PYAg10.

In agreement with the photoluminescence quenching for the green and red emission, the Figures 5.6 (a) and (b) show the decay times for the Pr^{3+} transitions $^3P_0 \rightarrow ^3H_4$ (486 nm) and $^1D_2 \rightarrow ^3H_4$ (606 nm), respectively. The values were calculated by using a double-exponential equation (5.1):

$$I(t) = A_1 \cdot e^{(-x/\tau_1)} + A_2 \cdot e^{(-x/\tau_2)} \quad (5.1)$$

where $I(t)$ is the intensity, A_1 and A_2 are constants, x is the time, τ_1 and τ_2 are the fast and slow decay time, respectively. The obtained values are summarize on the table 5.2.

Table 5.2: Experimental decay times of the samples under excitation at 444 nm and emission at 486 nm and 606 nm. The average time of the fast (τ_1) and slow (τ_2) decay is given by τ_M . Decay time values is given in ms (milliseconds).

Sample	$^3P_0 \rightarrow ^3H_4$ (486 nm)			$^1D_2 \rightarrow ^3H_4$ (606 nm)		
	τ_1	τ_2	τ_M	τ_1	τ_2	τ_M
PYAg0	0,336	1,949	1,063	0,202	0,215	0,208
PYAg2	1,352	1,372	1,353	0,245	0,632	0,295
PYAg4	0,670	2,764	1,640	0,187	0,437	0,207
PYAg10	1,327	2,459	1,358	0,191	1,541	0,207

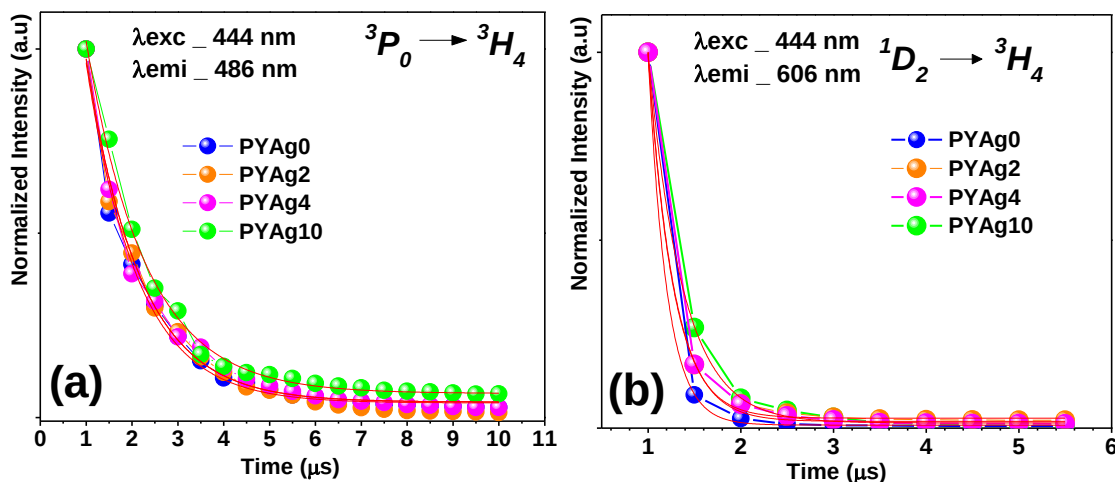
Concentration quenching observed from the Pr^{3+} emissions affected the decay times, leading to an increase of the average values. The results obtained here indicates a depopulation of the levels $^3P_1$ and $^1D_2$ with the increase in the Ag content. The energy transfer efficiency (ETE) from the state $^3P_0$ level of Pr^{3+} to closest ions could be calculated using the following equation [LIU et al, 2012]: Here, we are considering Yb^{3+} and Ag_m^{n+} as closest neighbors from the Pr^{3+} ions.

$$\eta = 1 - \tau_M / \tau_{M0} \quad (5.2)$$

Where, τ_M is the average decay time of the samples with Ag and τ_{M0} is the average decay time without Ag (PYAg0). Assuming the transition $^3P_0 \rightarrow ^3H_4$ (484 nm) and the experimental values on the table 2, the ETE estimated is approximately 27% for the sample with 2 mol%, 54% for 4 mol% and 28 % for 10 mol% of Ag. However, it is important to mention that these values represent not only an ET from the Pr^{3+} to Yb^{3+} , but also, an ET from the Pr^{3+} to the Ag_m^{n+} , since these two species have resonant energy levels (see Figure 5.8). Obviously, as the concentration of Pr^{3+} and Yb^{3+} is fixed, the Ag amount plays an important role on the ET values. Moreover, as we can see from the Figure 7 (a), the increment of Ag amount does not enhance the Yb^{3+} emission, since a broad emission rises in the green, red and extend with a weak tail to the near-infrared region. Therefore, we may conclude that the values observed here, most probable, are due to an ET between Pr^{3+} and Ag_m^{n+} .

In the same sense, the ETE for the transition $^1D_2 \rightarrow ^3H_4$ (606 nm) are given by the values of ~ 42% for 2 mol%, 0.4% for 4 mol% and 0.4% for 10 mol% of Ag. These results indicate a significant ET on the sample with 2 mol%. On the other hand, the samples with 4 and 10 mol%, this indicates that when the excitation is fixed at 444 nm, the transition $^1D_2 \rightarrow ^3H_4$ (Pr^{3+} : 606 nm) is not affected by the presence of Ag. In fact, comparing the intensity of the emissions at 483 and 606 nm, the first one is more affected by the Ag, since the intensity decrease considerably. Indeed, these values of ETE might be considerate as rough results since Pr^{3+} and Ag NC's show emissions at the same region and the components cannot be separated.

Figure 5.6. Decay curves of Pr^{3+} ions with emission fixed at 486 nm ($^3P_0 \rightarrow ^3H_4$) and 606 nm ($^1D_2 \rightarrow ^3H_4$) under excitation at 444 nm, figures (c) and (d), respectively. The red lines are double exponential fit.



The result of Ag increment also had a detrimental effect to the near-infrared emission from the Yb^{3+} ions, as we can see in the Figure 5.7a. Most probably, the electronic population from the emitting states of the Ag occurs more efficiently compared to the rare earth ions. Herein, we need to emphasize either Yb^{3+} and Ag NC's do not possess intermediate resonant levels of energy (see Figure 5.8). In this sense, it is not expect an ET from Yb^{3+} to Ag NC's. Therefore, the excitation at 444 nm favors an electronic population from the excited states of the NC's instead the Pr^{3+} and Yb^{3+} . Still, it is noteworthy to remember that we were able to observe an ET from the Ag NC's to the Yb^{3+} for the sample without Pr^{3+} , (see Figure 5.4e). This is another mechanism for Yb^{3+} activation, but it does not increase the Yb^{3+} emission itself when the Ag concentration is increased. In agreement with the PL intensities from the Yb^{3+} emission, the decay curve show a faster decay from the sample without Ag. On the other hand, the samples with Ag show similar values.

Figure 5.7. (a) Near-infrared emission obtained for the sample without Ag (PYAg0) and with different Ag amount upon excitation at 444 nm; (b) experimental decay curves of the samples upon excitation at 444 nm and emission at 980 nm. The red line are double exponential fit.

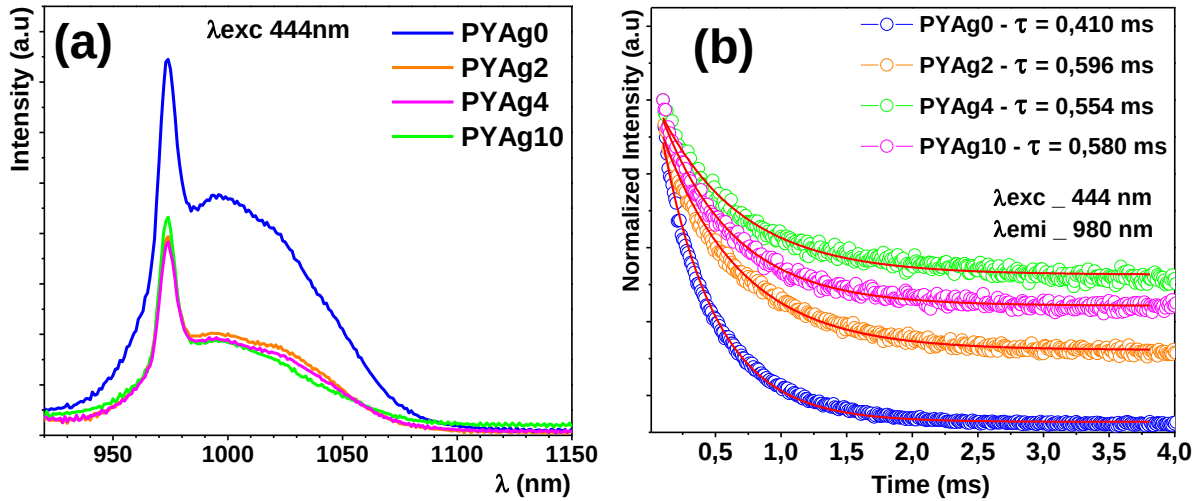
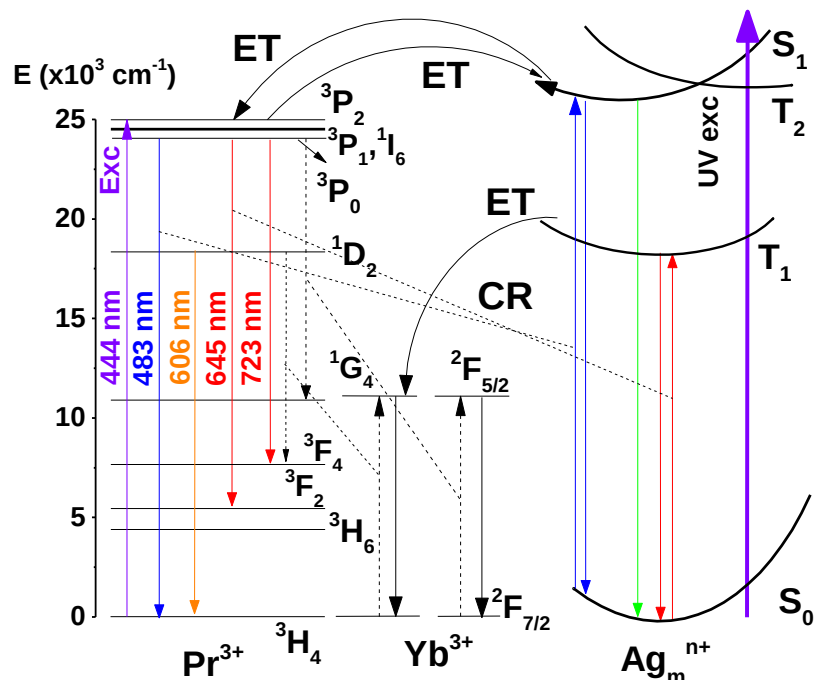


Figure 5.8 shows the partial diagram of energy levels of the $\text{Pr}^{3+}/\text{Yb}^{3+}$ co-doped samples and containing Ag NC's. Previous publications have addressed the issue according the presence of Ag_m^{n+} and rare earth [MA et al, 2014; VELÁZQUEZ et al, 2012]. The broadband visible emission rises from the radiative transitions of the excited states T_1 , T_2 and S_1 to the ground state S_0 to the Ag NC's [TIKHOMIROV et al, 2010]. Upon 444 nm excitation, Pr^{3+} may excite electrons from the ground state $^3H_4$ to the excited states $^3P_2$, $^3P_1$, $^1I_6$, $^3P_0$ and $^1D_2$. From these states, we observe radiative transitions whose give visible emissions.

Figure 5.8. Partial diagram of energy levels of co-doped $\text{Pr}^{3+}/\text{Yb}^{3+}$ and Ag nanoclusters in fluorophosphate glass.



5.4 Conclusions

In summary, fluorophosphate glasses co-doped with $\text{Pr}^{3+}/\text{Yb}^{3+}$ and containing different Ag contents were prepared by the melting quenching method. The nano structured Ag NC's were formed with different sizes according to an increment in the Ag amount. These NC's have showed is a potential advantage comparing to co-doped system $\text{Pr}^{3+}/\text{Yb}^{3+}$ due to a variety of Ag excitation in the UV-Vis and with a rich tunability in the visible range. Besides, a NIR emission could be verified by ET from the Ag NC's to the Yb^{3+} ions. In addition, the time decay kinetics and time resolved spectra proved a quenching in the Pr^{3+} ions and a redshift on the visible emission at longer delay time.

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Microstructures tailored by direct laser writing (DLW) technique in Ag containing fluorophosphate glass: application in 3D waveguide

Materials containing silver nanoclusters (Ag NC's) are promising candidates in the modern spectroscopy owing their tunable optical properties. Combined with direct laser writing (DLW) technique, Ag NC's may be tailored in 3D fluorescent microstructures, such as waveguides. Herein, we investigate the spectroscopy properties of Ag NC's dispersed in a fluorophosphate glass, as well as the dependence of the luminescent properties with the size distribution. Three-dimensional microstructures were tailored by back-and-forth displacements of a high-power femtosecond (fs) laser operating at 1030 nm and depositing different energy doses. Spectroscopic properties of each tailored microstructure was investigated by micro-absorption and microfluorescence. In addition, thanks to the high photosensitive of glasses, the microstructured Ag NC's allowed us the photo-inscription of waveguide as well as the study of its mode profile. Herein, this study offers a new class of glassy materials with high potential for photonic and nonlinear optical applications.

6.1 Introduction

Direct laser writing (DLW) has become for the two last decades a suitable technique to 3D micro-structuring [GATTASS; MAZUR, 2008]. Micro patterned structures may be obtained by interaction of a pulsed femtosecond laser, with transparent materials containing metallic ions, such as silver (Ag) [ROYON, 2011; SIIMAN; LUMEAU; GLEBOV, 2008]. Nowadays, a diversity of glassy materials has been studied and several micro fluorescent structured materials have been reported [VANGHELUWE, 2016; LIU, 2008; RICHTER, 2013]. Indeed, the DLW is a powerful technique that produces photoreduction of metallic ions into nanoclusters in photosensitive materials [LU et al, 2013].

Materials containing Ag nanostructures, here mentioned as silver nanoclusters (Ag NC's) and nanoparticles (Ag NP's), are promising candidates for future applications in light source [DÍEZ, 2009], second-harmonic generation [MALAKHO et al, 2008], laser illumination [HUA, 2017], white light generation [FARES et al, 2017] and photonic structures, such as waveguides [CHAN et al, 2013]. Such potentialities of Ag

NC's and NP's are due to their tunable spectral properties that strongly depend on their size and geometries [YU et al, 2018], that are commonly controlled by the concentration, melting temperature and thermal treatment [MA et al, 2017]. Furthermore, the obtention of luminescent Ag NC's with tunable optical properties may be induced by DLW technique, that offers a fast 3D modification.

To date, phosphate glasses have proven to be an attractive host for DLW micro-structuring as well as related applications [ROYON, 2010; DANTO, 2016; PAPON, 2013; PAPON, 2014]. Recently, Hssen and co-authors demonstrated the feasibility of Ag NC's doped fluorophosphate glasses for waveguide inscription, operating a Ti:Sapphire laser at 800 nm [FARES et al, 2017]. The advantages of these vitreous systems is that a high metal solubility is allowed by the high viscosity owing to the phosphate groups. Additionally, fluorophosphate glasses present chemical durability due to insoluble fluorides, low melting point temperature, stability against devitrification and low glass transition [ASEEV et al, 2012; PEYSE; LEE; DICKSON, 2002].

In this study, on the first part we present the synthesis of fluorescent Ag NC's in fluorophosphate glass, as well as the dependence of size NC's on the photoluminescent properties. We show a broad visible emission when the average diameter of the Ag NC's is about 2.3 nm. As a second part, we demonstrate for the first time the interaction of a near-infrared femtosecond (fs) pulsed laser in order to obtain three-dimensional patterned structures with strong fluorescent contrast in different irradiation conditions. In addition, by DLW technique we use the well organized Ag NC's to develop double tracked waveguide and its mode profile was elucidated as well.

6.2 Experimental section

6.2.1 Glass synthesis and spectroscopy characterization

The glass sample with the following molar composition: 45NaPO₃-25MgF₂-15CdF₂-10YF₃-5AgNO₃ was prepared by melt-quenching method using raw materials with high purity (99,9% Sigma-Aldrich). In a platinum crucible, 8 g of the mixed batch were melted at 1000 °C for 45 min in air atmosphere. After, the melted was poured out in a stainless steel mold preheated at 350 °C, 40 °C below the glass transition (390 °C),

presented elsewhere [FARES et al, 2017], and then, kept at this temperature for 5 h to avoid mechanical stress. For the sake of a better clarity, the sample is named as Ag5.

Transmission electron microscopy (TEM) was carried out using a equipment Philips CM200 operating at 200 kV and equipped with X-ray energy dispersive spectroscopy (EDS - Bruker model XFlash 6Ti30). Photoluminescence properties, excitation and emission spectra, were collected using a fluorimeter (Fluorolog Horiba Jobin Yvon) equipped with a Xenon lamp (450 W) and a photomultiplier tube (Ramamatsu R298). All measurements were obtained at room temperature.

6.2.2 DLW structures and waveguide fabrication

The glass sample was cut in a parallelepiped shape with dimensions of 7x4x2 mm and the optically polished in order to perform the laser writing. Following direct laser writing of the waveguides, the glass facets were polished in order to inject the laser and observe the guided mode profile. Direct laser writing was conducted using a Yb:KGW femtosecond oscillator from Amplitude system, delivering up to 2.6 W of average power, 9.8 MHz repetition rate, 390 fs pulse duration (FWHM) and emitting at 1030 nm. The laser irradiance were controlled with an acousto-optic modulator enabling the accumulation of $N=10^5$ - 10^6 pulses with energy pulses going from 20 nJ up to 150 nJ. The sample was placed on a high precision 3D translation stage (XMS-50 stages, Micro controller). Irradiation of the sample was performed using a microscope objective (Carl Zeiss, 20x - 0.75 NA) and the structures were written 200 μm below the surface.

By using back-and-forth displacements, 12 patterned structures were inscribed with different laser parameters. Three writing speeds were applied: 10, 50 and 100 $\mu\text{m/s}$, corresponding to 1.7×10^6 and 3.3×10^5 deposited pulses. For the waveguide inscription, a longitudinal line was drawn with speed of 300 $\mu\text{m/s}$. The mode profile of the WG was carried out using a red diode laser emitting at 630 nm. The signal of the guided light was collected by an objective (100x – 0.55 NA Mitutoyo) accopled on a CCD camera.

6.3. Results and discussion

6.3.1 Structural characterization of the Ag NC's and optical properties

Figure 6.1 shows the absorption spectrum of the sample. Only a strong absorption is seen between 200 and 400 nm, in which represents the cut-off of the host glass. This spectrum is quite similar to the absorption observed for the composition $50\text{NaPO}_3\text{-}25\text{ZnF}_2\text{-}15\text{CdF}_2\text{-}10\text{YF}_3$ (Chapter 4 – Figure 4.2b – blue line). Compared with an Ag NC's-free glass sample, Figure 4.2b (Black line), the absorption spectrum is shifted to longer wavelengths. This indicates the presence of Ag NC's absorbing in the UV wavelengths. Moreover, it is needed emphasize the absence of surface plasmon resonance (SPR) effect. It is already reported by Hssen et al. that SPR in fluorophosphate glasse this effect appears as a shape band at about 415 nm. Figure 6.2 shows the DSC curve of the sample Ag5. Glass transition temperature (T_g) is found at 401 °C and the beginning of the crystallization at 425 °C.

Figure 6.1. Absorption spectrum of the sample Ag5.

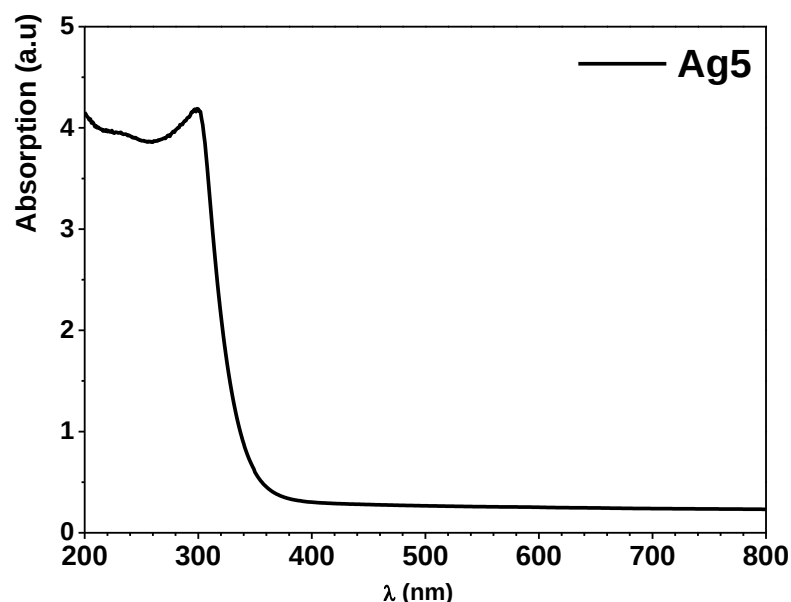


Figure 6.2. DSC curve of Ag5. The T_g is indicated by the intersection point between the two red lines at 421 °C. The onset of crystallization is at 483 °C and the maximum crystallization occurs at 512 °C.

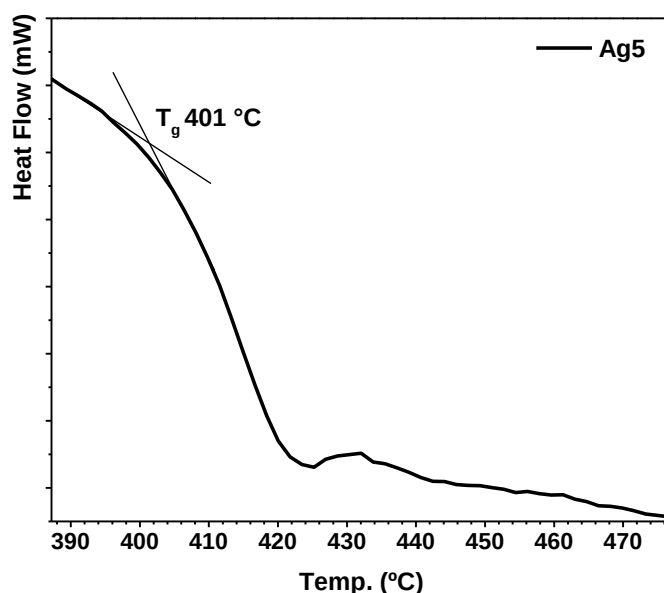
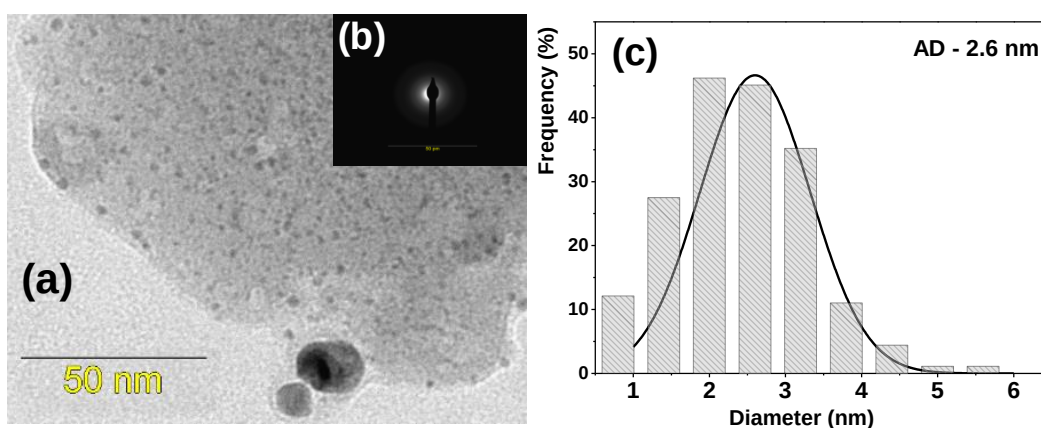


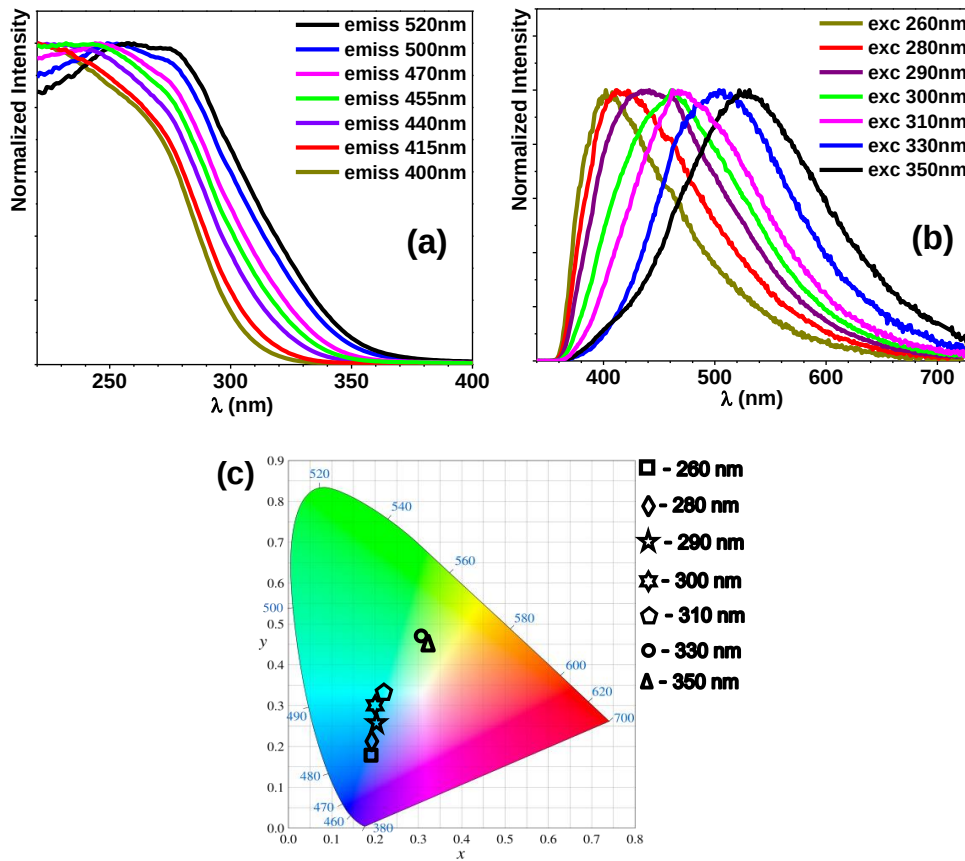
Figure 6.3 (a) shows the transmission electron microscopy (TEM) image of teeny piece crushed of the sample Ag5. As observed, the Ag NC's are homogeneously distributed on the glassy volume and the average size distribution is 2.6 nm, according to the histogram from the Figure 6.3c. To confirm the crystalline state of the Ag NC's, we perform selected area electron diffraction (SAED), as we can see on the Figure 6.3b, which shows concentric diffraction rings that is characteristic for amorphous materials. Recently, Hssen *et al.*, reported the growth of Ag NC's in fluorophosphate glasses [FARES *et al.*, 2017]. Still, according to Tikhomirov *et al.* [TIKHOMIROV *et al.*, 2010], in a glassy network containing alkali halide such as CdF_2 , the F^- vacancies disperse across the host volume, resulting in F^- nanoclusters, then the F^- negative reservoir attracts the Ag^+ ions, whose are reduced to form metallic silver. Most probably, the Ag remains as Ag^+ ions and Ag NC's. In this case, the Ag^+ ions persist owing to their solutibility on the glassy network, after, the combination of the reduced and nonreduced species (Ag^+ , Ag_0 , Ag_2^+ and others) takes place to guarantee the nucleation and growth of the nanoclusters.

Figure 6.3. Transmission electron microscopy (TEM) of the sample Ag5. Black spots characterize Ag NC's, whose show absence of cristalinity according to selected area electron diffraction (SAED), figure (b). Size distribution of the Ag NC's was obtained by analysis of 250 nanoclusters, figure (c).



The photoluminescence properties, excitation and emission of the Ag NC's are shown in Figure 6.4a and 6.4b, respectively. The precipitation of Ag^+ in different size NC's, by consequence, exhibits a large emission that extends along the visible range, when the excitation was carried out ranging from 260 to 350 nm. On the other hand, the excitation of the Ag NC's, covered the UV region from 220 to 367 nm (Figure 6.4a). The shape and position of the emission band match well with the earlier publication of Ag NC's in fluorophosphate glasses for white light emission [FARES et al, 2011]. The broad emission at the visible range result in a high colour rendering capability of Ag NC's, according to the chromaticity diagram CIE (Commission Internationale d'Eclairage), Figure 6.4c. The best wavelength for white visible emission was found to be at 350 nm.

Figure 6.4. (a) PLE of the sample collected at different emission; (b) PL at different excitation wavelength and chromaticity diagram (c).

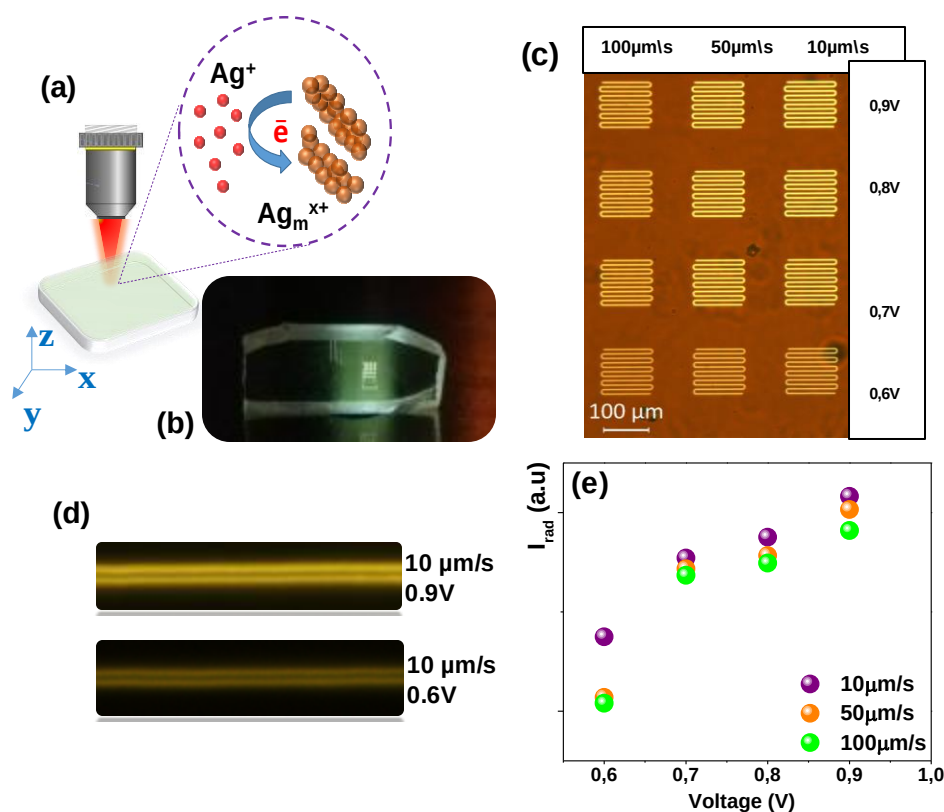


6.3.2 Micro-patterning of Ag NC's by DLW and optical characterization

The partial setup for DLW interaction is depicted on the Figure 6.5 (a). The sample was placed on a microscopy slide and irradiated perpendicularly with a fs laser focused by a microscope objective. Square linear structures of $100\ \mu\text{m} \times 100\ \mu\text{m}$ were written $200\ \mu\text{m}$ below the surface while changing the laser writing conditions. Micro fluorescent structures can be seen at the naked eyes under UV radiation, as we can see on the digital photography, Figure 6.5b. The process of DLW in silver containing glasses induced the reduction of the Ag^+ ions by ejected electrons in the center of the laser beam, then, after the heat caused by pulse-to-pulse accumulation, Ag metallic drift into the Ag nonreduced ions, forming Ag_m^{x+} species, as shown in Figure 3 (a), dashed circle. The Ag_m^{x+} species are formed around the interaction voxel [BELLEC et al, 2017]. Still, the number of Ag migration, by consequence the Ag_m^{x+} size, is function of the

number of pulses, repetition rate and irradiance. Figure 6.5c shows different bright structures for different writing parameters. According to that, it is expected a thicker line of nanoclusters to be formed at low speed of laser writing. This is emphasized in Figure 6.5d, where we can see a brighter double line when the energy deposited is higher comparing to the energy deposited in the conditions 10 μm and 0.8V. Indeed, the two Ag NC's tracks formed after DLW is due to a Gaussian profile of the laser beam which induces a photodissociation of the NC's in the central part of the direction of propagation [SMETANINA et al, 2016].

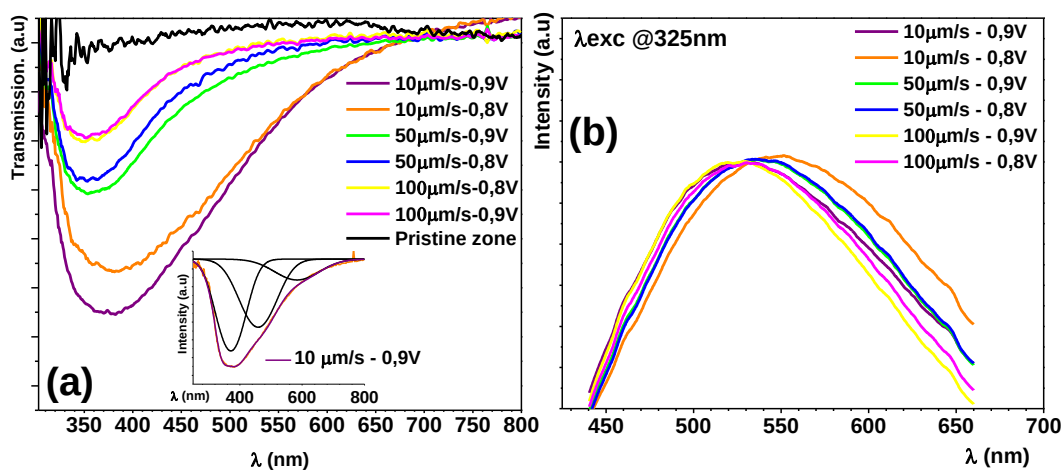
Figure 6.5.(a) Partial setup for direct laser writing (DLW). The laser was perpendicularly focused by an objective on the top level of the sample and the patterns were written by displacements on the xy plane; (b) digital picture from the sample under UV light exposure; (c) fluorescence under UV light of all patterns obtained after DLW. All patterns have the same dimensions $100 \times 100 \mu\text{m/s}$, and the horizontal and vertical distance among them is around $100 \mu\text{m/s}$; (d) expanded images for the patterns recorded at $10 \mu\text{m/s}$ at different voltages. All the images show double line of Ag nanocluster under UV irradiation in dark field; (e) integrated fluorescence intensity ranging from 0,6 to 0,9 V.



The photoinduced Ag NC's fabricated show broad absorption and remarkable emissions that extend until 660 nm, Figure 6.6a and b, respectively. For the micro-absorption analysis, a selected pristine zone from the glass does not show any absorption (black line – Figure 6.6a), on the other hand, different profile absorption was obtained for different writing parameters. The absorptions, specially at 50 and 10 $\mu\text{m/s}$ are enlarged compared to the 100 $\mu\text{m/s}$, indicating a size distribution for the Ag

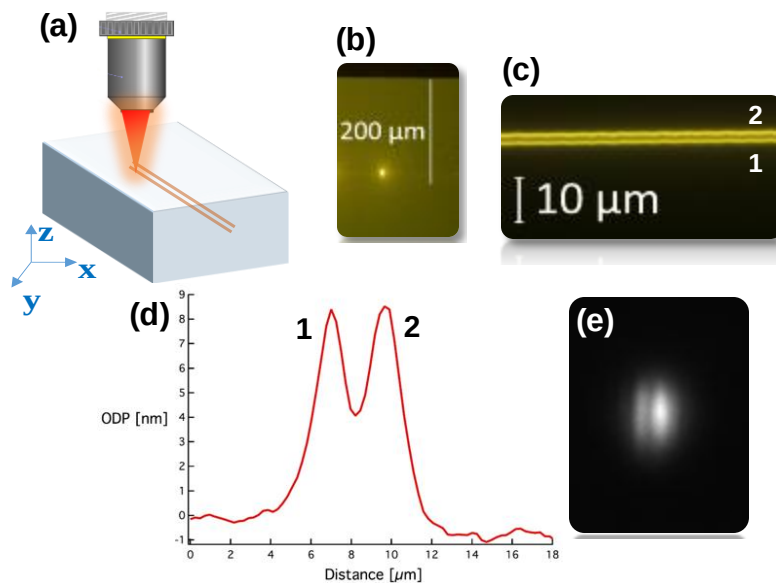
NC's after laser interaction. A parallel point of view may be mentioned by using the PLE on the bulk sample (Figure 6.4a), which shows a shifting from shorter to longer wavelengths. In this sense, we could expect a broad absorption when the tendency is to form big NC's (ideal conditions for low speed such as 10 $\mu\text{m/s}$) in high irradiance dose. As a result, the pattern recorded at 10 $\mu\text{m/s}$ shows a micro-absorption with maximum at 370 nm and extend with a large tail until 650 nm. However, the micro-absorption differs from the excitation spectra (Figure 6.4a) by a wider response in the visible region, this extension on the absorption may be the result of the bigger Ag NC's formation compared to the pristine glass (before DLW), which in turn, the driving force to the Ag NC's formation is the amount of Ag and heat treatment. The absorption spectrum for 10 $\mu\text{m/s}$ can be separated in three Gaussian components, as shown in the inset graph in Figure 6.6a. These three components indicate the presence Ag NC's responsible for the blue, green and red absorption on the Ag tracks. The emission spectra (Figure 6.6b) show a slight displacement upon excitation at 325 nm when the dose is increased. The bands have similar shape and cover a wide range of the visible region. The maximum wavelength of each band is centered between 525 and 550 nm and differs from each other in few nanometers. This result indicates that at different laser irradiance, the system produces an ensemble of different size NC's which emits in an specific region. Moreover, we should expect the same position of the bands on the emission spectra since the excitation was carried out at 325 nm, however, the slight displacement for low wavelength (redshift) indicates that the different size of Ag NC's may be activated in this wavelength.

Figure 6.6. (a) Transmission spectra recorded after different fs laser dose and (b) microfluorescence for the same parameters (except for the pristine zone not recorded).



As a second part of the experiments, we perform DLW along the larger surface of the sample (y axis), as shown schematically in Figure 6.7a. For the sake of brevity, it is shown only the waveguide (WG) recorded at 300 $\mu\text{m/s}$. The depth of the WG is about 200 μm from the surface, as we can see in Figure 6.7b. Likewise to the back-and-forth movement, the propagation of the laser beam produced double line of Ag NC's, Figure 6.7c. These double line are spaced roughly by 2.7 μm , according to a top view image. Although the Ag NC's seem to be homogeneously distributed along the two line, a slight deviation on the propagation axis of the laser beam, has contributed in micro-oscillations on the lines. Indeed, the line marked by the number 1 is thicker than the line number 2. Since this non-uniform spatial distribution of Ag NC's provides a non-uniform path for the light, the refractive index (Δn) interpolated across the two lines is affected.

Figure 6.7. (a) Partial configuration for WG writing. The y axis may be taken as reference for the laser propagation; (b) depth of the WG (side view); (c) double line of Ag NC's after laser passing at 300 $\mu\text{m/s}$; (d) refractive index profile after formation of Ag NC's double line and (e) mode profile of the WG under 630 nm laser input.



6.4. Conclusions

In summary, he studied in bulk and in microscale the optical properties of Ag NC's in fluorophosphate glass, and the dependence of these properties regarding the size distribution. In addition, we presented a high sensitive glass for DLW that produces fluorescent and organized microstructures owing to the photoreduction of the Ag⁺ ions. The distinct energy deposited by the pulse accumulation resulted in different spatial distribution of the Ag NC's leading to a slight distribution on the lines, as demonstrated by the back-and-forth patterns and the WG. Still, the WG written exhibited a monomode profile with a positive refractive index change after DLW passing. According to SHG mapping, the double track from the WG presented a non-homogeneous distribution of the Ag NC's, this behavior was induced by a different rate migration of these nanoclusters around the interaction voxel.

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General Conclusions

Fluoroindate and fluorophosphate glasses were prepared through the melting-quenching method. These two family of glasses were selected according to the physics and chemical properties. The low energy phonon matrix (fluoroindate) yielded a very intense upconversion emission for the sample with 7 mol% of Er^{3+} , in consequence, a high photocurrent was observed for low power excitation (22 mW). However, due to the low absorption and emission coefficient of the lanthanides, it is still far the application in spectral converters to increase solar cells efficiency. From the fluorophosphate glasses results, we conclude a size-dependence for the Ag NC's stabilization. The F^- ions played an important role on the Ag NC's reduction. In addition, the long molecular weight introduced by the metaphosphate groups may be a crucial reason for a non-agglomeration of Ag ions, since the phosphate groups may leave voids in the glass network. However, this is still in investigation in our research group. The dispersion of 5 mol% of Ag, seems to be an ideal concentration for Ag NC's obtention and SPR-free samples. This sample with 5 mol% showed a broadband emission that started in the UV region and extended until infrared at 730 nm. This broadband resulted from a size-distribution behavior in which the formation of nanoclusters responsible for the blue, green and red emission is observed. Still, silver nanoclusters showed an energy transfer (ET) to the rare-earths Pr^{3+} and Yb^{3+} . The composition with less amount of metaphosphate groups, allowed to disperse a less amount of silver, in consequence, 2 mol% was the optimum concentration to avoid the obtention of opaque glasses with SPR effect, as it was obtained for 4 and 10 mol%. However, the samples even for high amount present broadband emission in the visible range. For the last, very bright microstructures of silver were obtained after interaction of the sample with 5 mol% and the femtosecond laser. This sample showed to be a good candidate for waveguide application.

Appendix I

In this thesis, a special attention was given to fluoroindate and fluorophosphate glasses preparation, spectroscopy properties of the rare-earths Er^{3+} , Pr^{3+} , Yb^{3+} ; silver nanoclusters (Ag NC's) and applications shown in the chapter 2, 4, 5 and 6. However, the physics and chemical nature of the vitreous materials was not mentioned. Herein, we provide a deeper reading in glass science with the following references and references therein:

GUPTA, P. K. Non-crystalline solids: glasses and amorphous solids. Journal of non-crystalline solids. v. 195, pag. 158-164, 1996.

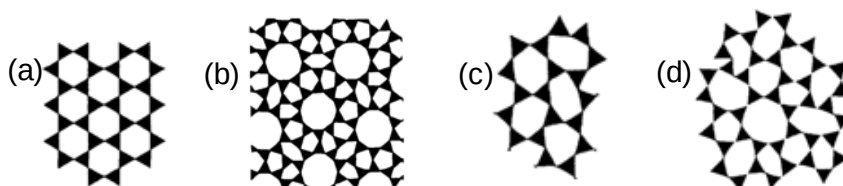
ZARZYCKI, J. Glasses and vitreous state. Cambridge University Press, 1991.

VARSHNEYA, A. Fundamentals of Inorganic Glasses. 1st edition. Academic Press, 1994.

NAPOLITANO, S.; GLYNOS, E.; TITO, N. B.; Glass transition of polymers in bulk, confined geometries, and near interfaces. Reports on Progress in Physics. v. 80, pag. 036603, 1-50, 2017.

To point out some basic aspects in glass, an easy and simple definition is given by Prabhat K. Gupta in his publication named “Non-crystalline solids: glasses and amorphous solids”. Besides, other definitions of glass and amorphous solids can be find in the same publication. For instance, we can understand a non-crystalline solids (glass) as a “solid with absence of long range positional order”. In other words, there is a lack of atomic periodicity that is observed in crystalline solids. Besides, glasses exhibit a glass transition (T_g). The lack of atomic periodicity rises from the fast cooling of the melted material during the glass formation. According to Gupta, the network of solids are portrayed in four different types: (a) crystalline; (b) quasi-crystalline; (c) non-crystalline topologically ordered and (d) topologically disordered, figure below.

Figure 1. Four different types of solid networks. Adapted from Gupta, 1996.



In general, glass is a liquid phase that is cooled below its freezing temperature. According to the figure below, the liquid phase (red line) is rapidly supercooled until it reaches the glass transition temperature (T_g). This temperature represents the temperature at which the supercooled liquid becomes a glass. A disordered network is preserved changing the liquid system to the glass system (blue line). Unlikely, when a liquid is cooled at a constant temperature until it reaches T_M , the disordered network becomes ordered and the glass system becomes a crystalline system (green line), where the molar volume is smaller compared to the glass one.

Figure 2. Temperature versus volume for a hypothetical glass system formation.

