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RELATÓRIO DE PÓS-DOCTORADO

**Estrutura, propriedades e estabilidade de perovskitas de iodeto de chumbo
contendo cátions orgânicos mistos**

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Número do Projeto: 4496

Modalidade: PD-III

Período: 01/02/2023 a 31/01/2025

Ilha Solteira - SP

Janeiro, 2025

Resumo

Perovskitas de haleto contendo cátions mistos são a base de muitos dispositivos optoeletrônicos, incluindo células solares, para as quais se obteve um salto de eficiência de conversão de energia de 3,8 para 26,7% em 15 anos. As perovskitas de haleto de cátions mistos possuem propriedades ajustáveis e maiores estabilidades que as composições puras. Em particular, atenção tem sido dada às aquelas formadas pela incorporação dos cátions orgânicos metilamônio (MA^+), formamidínio (FA^+) e guanidínio (GA^+) em uma única estrutura. Embora essas composições já venham sendo usadas em dispositivos, poucas informações estruturais sobre esses sistemas e suas propriedades intrínsecas e degradação térmica foram reportadas na literatura. Nesse sentido, a presente pesquisa versou sobre o estudo sistemático de diferentes composições de perovskitas de iodeto de chumbo contendo os cátions MA^+ , FA^+ e GA^+ obtidas via rota mecanoquímica, que possui vantagens por não usar solventes e resultar em pós mais estáveis em relação àqueles obtidos por rotas via solução. A execução do projeto trouxe avanços significativos na área do conhecimento, publicados em quatro artigos em revistas de alto impacto.

1. INTRODUÇÃO

A busca por fontes alternativas de energia é uma prioridade para o avanço ambientalmente sustentável da economia global. Há uma demanda crescente para o desenvolvimento de células solares mais baratas e com maior eficiência de conversão de energia solar. Nesse sentido, destacam-se as perovskitas de haleto (HPs), que podem ser usadas na fabricação de células solares com uma eficiência de conversão certificada de 26,7%, comparável a tecnologias de células solares comerciais baseadas em filmes finos, por exemplo, de silício, CdTe e GaAs [1]. Isso representa um ganho sem precedentes em cerca de 15 anos desde a primeira célula fabricada com esses materiais, em 2009, com eficiência de conversão de energia de 3,8% [2]. Em geral, as perovskitas híbridas de haleto possuem uma composição dada por ABX_3 e podem ser descritas como arranjos cristalinos nos quais um cátion orgânico A^+ (e.g. $A^+ = CH_3NH_3^+$, $[CH(NH_2)_2]^+$ e $[C(NH_2)_3]^+$) ocupa o centro da célula unitária formada pela ligação entre vértices de octaedros BX_6^{4-} (e.g. $B^{2+} = Sn^{2+}$ e Pb^{2+} e $X^- = Cl^-$, Br^- e I^-) [3]. Além das células solares, a enorme atenção dedicada a essas perovskitas também resultou em aplicações como LEDs e lasers [4] e detectores de radiação alfa, beta, gama e raios X [5], entre outros. Em parte, essa versatilidade e o avanço observado podem ser atribuídos à disponibilidade de composições possíveis (seja para sítios A, B e/ou X), às diversas rotas de síntese utilizadas (por soluções, reações em estado sólido) e à preparação desses materiais sob diferentes arquiteturas (como filmes finos, pós, monocristais, etc.).

Como arquétipo das HPs, o iodeto de chumbo e metilamônio ($CH_3NH_3PbI_3$, ou $MAPbI_3$) tem sido a base para diversos outros sistemas. Embora sua aplicação como material puro seja limitada, é possível ajustar suas propriedades usando a substituição por outros cátions. Em geral, as HPs de cátions mistos têm energias de *bandgap* ajustáveis e estabilidades aprimoradas [6]. Outra característica importante é do transporte de íons em tais materiais, que também pode ser modulada. Por exemplo, energias de ativação para transporte de íons são muito dependentes da natureza dos cátions substitutos [7]. Além disso, foi demonstrado que HPs de cátions mistos podem suprimir a segregação de haleto foto-induzida [8]. Essas abordagens surgem como uma alternativa para controlar a degradação indesejável e potencializar as propriedades das HPs, preservando importantes propriedades físicas alcançadas que possibilitarão a produção de dispositivos optoeletrônicos comerciais otimizados. A substituição parcial de metilamônio (MA^+) por formamidínio ($[CH(NH_2)_2]^+$, ou FA^+) pode levar a cristais altamente estáveis com mobilidade de portadores de carga melhorada [9,10], maiores comprimentos de difusão [10] e tempos de vida de portadores de carga [11] e migração

iônica reduzida [9]. Da mesma forma, a substituição parcial de MA^+ por guanidínio ($[\text{C}(\text{NH}_2)_3]^+$, ou GA^+) leva a materiais mais estáveis [12] e com maiores tempos de vida de portadores de carga altamente [13,14]. Para ambos os sistemas, eficiências aprimoradas e tensões de circuito aberto podem ser alcançadas em células solares. O uso simultâneo de cátions MA^+ , FA^+ e GA^+ também é relativamente comum. A incorporação de GA^+ no conhecido sistema de cátion triplo CsFAMA foi relatada para melhorar as tensões de circuito aberto e eficiência das células solares [15] e sua estabilidade enquanto reduz a histerese IV [16]. Um sistema do tipo $\text{GA}_y(\text{FAMA})_{1-y}\text{PbI}_x\text{Cl}_{3-x}$ foi proposto para a fabricação de células solares [17], sendo alcançada uma eficiência de 21,3% com a manutenção de mais de 95% do valor inicial após 35 dias expostas ao ar. Esses resultados demonstram que os três cátions orgânicos simultâneos utilizados são uma estratégia promissora para a fabricação de células solares. Um estudo preliminar no sistema $\text{GA}_x\text{FA}_x\text{MA}_{1-2x}\text{PbI}_3$ foi realizado pelo grupo, demonstrando características desejáveis como a possibilidade de ajuste fino das energias de *bandgaps* e de Urbach, baixa difusividade iônica e estabilidade térmica adequada [18]. No entanto, há ainda pouca literatura sobre a estrutura e propriedades intrínsecas de demais composições contendo esses três cátions orgânicos. Estudos dessa ordem também são relevantes no sentido de usar cátions advindos de fontes mais abundantes em comparação com o cério, ao qual tem sido dada maior ênfase em sistemas de cátions mistos.

Baseado no exposto, a principal motivação deste projeto de pesquisa foi a caracterização da estrutura e das propriedades intrínsecas do sistema $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$. A relevância da proposta aqui apresentada se apoia na contemporaneidade do tema e no fato de que dispositivos já estão sendo fabricados com composições similares, mas sem que informações importantes, como as transições de fase, energias de ativação para condução iônica e energias de *bandgap* tenham sido apropriadamente obtidas. Foram realizados estudos em amostras policristalinas espessas dessas composições, fabricadas a partir de pós sintetizados via rota mecanoquímica. Essa rota vem recebendo grande atenção [19] por aspectos de sustentabilidade pela redução de solventes e maior estabilidade dos pós de HPs em relação aos métodos via solução [20,21]. Esses pós podem ser utilizados para produção direta de dispositivos [22,23], e também são mais adequados para o armazenamento, pois as soluções de HPs podem sofrer vários efeitos de envelhecimento e degradação, resultando em mudanças importantes no desempenho e na reprodutibilidade dos dispositivos [24,25,26]. Por fim, células solares mais acessíveis, reprodutíveis, eficientes e estáveis usando filmes finos preparados a partir de precursores obtidos de pós de perovskita redissolvidos, além de que tem havido uma

tendência crescente de usar pós diretamente na síntese de filmes [27]. Os resultados dessa pesquisa de ciência básica sobre o sistema em questão forneceram dados importantes para traçar o perfil fundamental das propriedades de dispositivos fabricados com o mesmo.

2. OBJETIVOS, HIPÓTESES E QUESTÕES A SEREM RESPONDIDAS

2.1 Objetivos

- 1) Sintetizar pós de perovskitas do sistema $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ por via mecanoquímica e pastilhas policristalinas com esses para estudar a estrutura, propriedades elétricas e optoeletrônicas intrínsecas e estabilidade dessas perovskitas;
- 2) Caracterizar a estrutura e composição de fases (estruturas cristalinas das perovskitas formadas, parâmetros de rede, presença de fases secundárias e/ou de precursores não reagidos) usando difração de raios X, as transições de fase (temperaturas e entalpias de transição) por calorimetria exploratória diferencial, a microestrutura (morfologia de grãos e porosidade) por microscopia eletrônica de varredura, as propriedades optoeletrônicas (energias de *bandgap* e de Urbach) por espectroscopia de refletância difusa de UV/Vis, as propriedades elétricas (condutividade elétrica, permissividade elétrica, energias de ativação, densidade de portadores e mobilidade de portadores) por espectroscopia de impedância e eletrometria I-V.
- 3) Estudar as vias de degradação térmica e a cinética de degradação das perovskitas de cátions mistos usando tratamentos térmicos por tempos e temperaturas distintos, acompanhando as mudanças estruturais e de composições de fases (via difração de raios X) e da microestrutura (via microscopia eletrônica de varredura) que ocorrem em virtude dos respectivos tratamentos térmicos.

2.2 Questões e hipóteses

- a) Qual o efeito dos tipos e concentrações de cátions orgânicos sobre a estabilidade de composições do sistema $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$?
- b) É possível obter propriedades finamente ajustáveis, como temperaturas de transição, permissividades elétricas e energias de ativação, com o sistema $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$?
- c) Como ocorre e com que velocidade se dá a degradação induzida por temperatura das perovskitas de cátions mistos?

No contexto das propriedades intrínsecas do sistema em questão, uma vez tendo sido notada a possibilidade de ajuste para composições intermediárias do tipo $\text{GA}_x\text{FA}_x\text{MA}_{1-2x}\text{PbI}_3$,

espera-se que isso possa ser estendido para maiores intervalos de propriedades considerando que os extremos dados por $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ e $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ são relativamente distintos. Por exemplo, $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ têm baixo limite de solubilidade ($x \sim 0.25$) e energia de *band gap* crescente com x , enquanto $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ forma soluções sólidas para todo o intervalo de composições e energia de *band gap* decrescente com x . Um estudo dessa ordem pode fornecer informações relevantes para a previsão de propriedades em sistemas de cátions mistos, haja vista que os cátions orgânicos nesses sistemas podem gerar efeitos sobre as propriedades que não são, a priori, compatíveis com os comportamentos esperados. Por exemplo, o cátion GA^+ (278 pm) é consideravelmente maior do que o cátion FA^+ (245 pm). Quando substituindo parcialmente os cátions MA^+ (217 pm), por argumentos do fator de tolerância de Goldschmidt, seria esperado que o GA^+ tivesse um efeito maior sobre a temperatura de transição entre as estruturas tetragonal e cúbica do que o FA^+ . Porém, é verificado experimentalmente o inverso. Por sua vez, a degradação térmica de perovskitas de haleto de diferentes composições vem sendo bastante estudada [28,29,30,31,32], porém, exceto por uns poucos resultados [33], pouco se conhece sobre como diferentes cátions orgânicos em sistemas mistos podem impactar a estabilidade térmica das perovskitas. Em geral, nota-se que a decomposição térmica nas perovskitas de haleto segue uma lei cinética de primeira ordem e que há aumento da estabilidade nos sistemas mistos. Resultados prévios do grupo mostram que essas tendências ocorrem e que a estabilidade é otimizada em sistemas triplos, mas, dependendo da composição, a degradação térmica é intensificada e pode ser ainda mais rápida que nos sistemas puros, com mudança da cinética de decomposição para uma lei de segunda ordem. Considerando isso, espera-se que um estudo da cinética de decomposição térmica forneça dados que permitam o design de composições com estabilidade térmica otimizada.

3. MATERIAIS E MÉTODOS

A proposta inicial consistia da execução deste projeto de pesquisa ao longo de quatro semestres, segundo o cronograma a seguir. Entretanto, as etapas programadas foram todas executadas e já publicadas durante o primeiro ano de fomento da pesquisa, conforme mencionado na seção 4. Resultados. A descrição dos experimentos a seguir versa sobre a metodologia geral empregada nos estudos. Aspectos específicos dos procedimentos são encontrados nos artigos publicados, em anexo neste relatório.

ATIVIDADE	SEMESTRE			
	1	2	3	4
1. Revisão e atualização bibliográfica	X	X	X	X
2. Síntese e caracterização das perovskitas	X	X		
3. Ensaios de degradação térmica		X	X	
4. Organização e tratamento de dados		X	X	X
5. Redação de artigos e do relatório final		X	X	X

3.1. Síntese das pastilhas policristalinas

Inicialmente, os pós das composições foram ser preparados pela rota mecanoquímica. Para cada composição, foram pesadas quantidades dos precursores iodeto de chumbo (PbI_2), iodeto de metilamônio (MAI), iodeto de formamidínio (FAI) e iodeto de guanidínio (GAI) nas proporções desejadas. Os precursores foram misturados manualmente e moídos usando gral e pistilo de ágata natural por aproximadamente 50 min em condições ambientes. Os pós foram peneirados em peneira 250 μm (60 mesh) e depois aquecidos para homogeneização e alívio de tensões por ~ 6 horas a 60 $^{\circ}\text{C}$. Com os pós de cada composição, foram feitas pastilhas pela adição de ~ 150 mg à cavidade circular de um molde metálico de 10 mm e posterior prensagem do pó em 250 MPa com auxílio de uma prensa hidráulica. Por fim, as pastilhas foram sinterizadas em forno elétrico a 120 $^{\circ}\text{C}$ por 2h.

3.2. Caracterização das amostras

As análises de difração de raios X (DRX) foram realizadas em um difratômetro Rigaku Ultima IV com radiação $\text{CuK}\alpha$ ($\lambda = 1,5406 \text{ \AA}$), sob 40 kV e 20 mA, em varredura contínua ($2^{\circ} \text{ min}^{-1}$), com 2θ de 10 a 60 $^{\circ}$, à temperatura ambiente. As medidas de calorimetria exploratória diferencial (DSC) foram realizadas em um DSC 25 - TA Instruments de -90 a 100 $^{\circ}\text{C}$, com taxa de aquecimento de 5 $^{\circ}\text{C min}^{-1}$, sob atmosfera de nitrogênio. As imagens da microestrutura das amostras foram obtidas em microscópio eletrônico de varredura (MEV) Zeiss EVO LS15, com feixe de tungstênio, operando na faixa de tensão entre 10 e 20 kV, por análise de elétrons secundários. Os espectros de refletância difusa (UV/Vis) foram coletados em um espectrofotômetro Shimadzu UV-2600, na faixa de 200 a 1100 nm, no modo de baixa velocidade com intervalo de dados de 1 nm. Para as medidas elétricas, uma matriz de 10 x 10 eletrodos circulares de ouro de $\sim 0,6$ mm de diâmetro será depositada no topo das pastilhas usando uma máscara de cobre, enquanto um eletrodo de ouro inferior será depositado sobre toda a superfície da amostra. As medições de espectroscopia de impedância (IS) foram

realizadas em um sistema fechado Displex ARS CSW-202 usando um medidor LCR Agilent 4284A para medir a condutância (G) e susceptância (B) nas faixas de frequência de 10^2 a 10^6 Hz e de temperatura de -173 a 107 °C. Todas as medições elétricas foram realizadas no vácuo e no escuro para evitar efeitos externos usando um sistema fechado Displex ARS CSW-202. Dados de corrente em função do potencial (eletrometria I-V) foram coletados usando um eletrômetro Keithley 6517B. As medidas foram realizadas em condições ambiente, no escuro. Os dados foram coletados em ciclos de faixa de -6 a +6 V e vice-versa com uma taxa de varredura de $0,1 \text{ V.s}^{-1}$ e em potencial ascendente de 0 a +20 V com uma taxa de varredura de $0,1 \text{ V.s}^{-1}$ e de 0 a + 30 com taxa de varredura de 0.5 V.s^{-1} .

3.3 Degradação térmica

Ensaio de degradação térmica foram conduzidos em composições selecionadas utilizando tratamentos térmicos entre 150 e 200 °C. As amostras foram analisadas via difração de raios X em intervalos predefinidos para acompanhamento das modificações estruturais e das composições de fases. Uma rotina de condições de tempo/temperatura de tratamento e os intervalos entre coletas de dados, já empregada no grupo em um estudo preliminar, é mostrada na tabela abaixo. A cada intervalo predefinido, as amostras são removidas do forno de tratamento e resfriadas rapidamente. Coletas de dados via difração de raios X foram feitas no equipamento mencionado anteriormente, em varredura contínua (2° min^{-1}), com 2θ de 10 a 15° , à temperatura ambiente. Após as medidas, as amostras são novamente inseridas no forno para continuidade do tratamento térmico. A visualização da microestrutura de amostras degradadas será feita por microscopia eletrônica de varredura em amostras selecionadas após tempos de tratamento a serem definidos posteriormente.

T (°C)	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₀	t ₁₁	t ₁₂	Total
150	3h	7h	8h	9h	9h	9h	9h	11h	10h	13h	11h	11h	110h
160	5h	6h	8h	5h	5h	4h	9h	10h	6h	7h	-	-	65h
170	4h	4h	2h	6h	5h	5h	8h	5h	-	-	-	-	39h
180	2h	2h	2h	2h	2h	2h	3h	3h	-	-	-	-	18h
190	1h	1h	1h	1h	1h	1h	1h	1h	-	-	-	-	8h
200	0.5h	0.5h	0.5h	0.5h	0.5h	0.5h	0.5h	0.5h	-	-	-	-	4h

4. RESULTADOS E DISCUSSÃO

No que diz respeito às questões formuladas na proposta inicial desse projeto, indicadas no subitem 2.2, os objetos da questão b), isto é, a obtenção de propriedades finamente ajustáveis, como temperaturas de transição, permissividades elétricas e energias de ativação, com o sistema $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$, foram tratados majoritariamente nos artigos publicados nas seguintes referências:

- F. B. Minussi, R. M. Da Silva and E. B. Araújo, Differing effects of mixed A-site composition on the properties of hybrid lead iodide perovskites, *J. Phys. Chem. C*, 2023, **127**, 8814-8824.
- F. B. Minussi, R. M. Silva and E. B. Araújo, Composition-property relations for $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ perovskites, *Small*, 2024, **20**, 2305054.
- F. B. Minussi, R. M. Silva and E. B. Araújo, Interplay between cation composition and charge transport characteristics in $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ halide perovskites, *Applied Physics Letters*, 2024, **124**, 153901.

Por sua vez, os aspectos sobre as questões a) e c), versando sobre a estabilidade e degradação térmica do sistema $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$, foram abordados no estudo publicado em:

- F. B. Minussi, R. M. Silva, J. F. Carvalho and E. B. Araújo, Thermal degradation in methylammonium–formamidinium–guanidinium lead iodide perovskites, *J. Mater. Chem. C*, 2024, **12**, 5138-5149.

Cópias desses artigos estão em anexo ao final desse relatório.

5. OUTRAS PUBLICAÇÕES

Além dos artigos acima referidos, diretamente relacionados ao presente projeto, outros artigos em perovskitas de haleto, abaixo listados, foram publicados durante o período de pós-doutorado:

- F. B. Minussi and E. B. Araújo, On the prospects of high-entropy organic A-site halide perovskites, *Phys. Chem. Chem. Phys.*, 2024, **26**, 26479–26488.

- F. B. Minussi, R. M. Silva, J. C. S. Moraes and E. B. Araújo, Organic cations in halide perovskite solid solutions: exploring beyond size effects, *Phys. Chem. Chem. Phys.*, 2024, **26**, 20770–20784.
- F. B. Minussi, R. M. Da Silva and E. B. Araújo, Does it mix? Insights and attempts to predict the formability of single phase mixed A-cation lead iodide perovskites, *Inorg. Chem. Front.*, 2023, **10**, 6129–6133.

Ademais, outros artigos, abaixo listados, foram publicados em colaboração com projetos desenvolvidos no grupo:

- F. B. Minussi, F. V. A. Borges and E. B. Araújo, Charge transport and dielectric characteristics of $\text{Sm}_x\text{Bi}_{1-x}\text{FeO}_3$ thin films from the perspective of grain and grain boundary properties, *J. Phys. D: Appl. Phys.*, 2023, **56**, 355302.
- R. K. Mishra, F. B. Minussi, P. Kumari, R. R. Shahi and E. B. Araújo, Synthesis and functional properties of $(\text{Al}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2}\text{Ti}_{0.2})_3\text{O}_4$ high entropy spinel oxide, *Journal of Physics and Chemistry of Solids*, 2024, **194**, 112249.

6. ORIENTAÇÕES

Durante o período do presente projeto, o pesquisador atuou ou ainda atua como coorientador em dois projetos de iniciação científica, do mesmo aluno, e um projeto de mestrado, listados abaixo:

- Rogério Marcos da Silva Jr. *Propriedades de perovskitas de iodeto de chumbo e metilamônio parcialmente substituído com guanidínio, etilamônio e acetamidínio* (iniciação científica), de 08/2023 a 07/2024.
- Rogério Marcos da Silva Jr. *Triagem da formação e estabilidade de fases de perovskitas de haleto contendo cátions orgânicos mistos* (iniciação científica), início em 08/2024 com previsão de finalização em 07/2025.
- Rafaela Coutinho de Oliveira Santos. *Descrição físico-química de perovskitas do sistema $\text{AC}_x\text{MA}_{1-x}\text{PbI}_3$* (mestrado em Ciência dos Materiais), início em 03/2024 com previsão de finalização em 02/2026.

7. COMENTÁRIOS DO SUPERVISOR

O projeto de pós-doutorado do Dr. Fernando Brondani Minussi foi muito bem executado, com autonomia, evolução científica e um desempenho muito acima da média. O cronograma do projeto foi cumprido com êxito e todas as etapas previstas no plano de trabalho inicial foram cumpridas adequadamente, com a obtenção de um volume surpreendente de resultados que proporcionou avanços consideráveis na compreensão dos problemas em torno das perovskitas híbridas estudadas. O relatório apresentado foi muito bem redigido e resumiu os principais resultados obtidos no período sobre os estudos de diferentes composições de perovskitas de iodeto de chumbo contendo os cátions MA^+ , FA^+ e GA^+ . Os estudos promoveram avanços significativos na área do conhecimento e resultaram na publicação de importantes artigos científicos em periódicos internacionais de alto fator de impacto. Considero aprovado o relatório científico apresentado e parabeno o Dr. Fernando pelo excelente trabalho realizado.

8. REFERÊNCIAS

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Differing Effects of Mixed A-Site Composition on the Properties of Hybrid Lead Iodide Perovskites

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Cite This: *J. Phys. Chem. C* 2023, 127, 8814–8824



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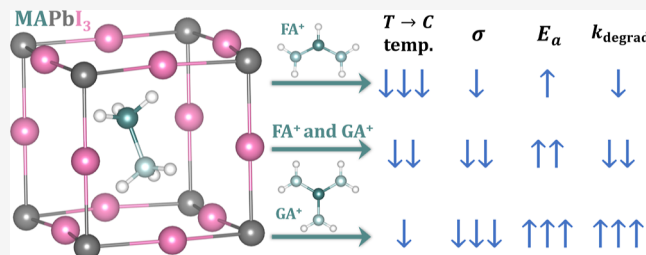


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Supporting Information

ABSTRACT: Halide perovskites (HPs) appeared as a revolutionary class of relevant optoelectronic materials. Optimizing these materials involves developing mixed formulations currently used in many of the most efficient HP-based devices. Mixing A-site organic cations has been a widely used strategy to achieve the desired characteristics in these perovskites. Few of the reported works were devoted to understanding the effects of different organic cations on the properties of the resulting HPs. In the present work, we report a detailed study on the structural, thermal, and electrical properties and degradation assays in HPs with mixing A-site organic cations at the MAPbI_3 , $\text{FA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$, $\text{GA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$, and $\text{GA}_{0.05}\text{FA}_{0.05}\text{MA}_{0.90}\text{PbI}_3$ compositions. The results show that the charge transport properties change consistently with the A-site cation size. However, the structure and phase transitions are unusually affected by the composition, suggesting that other characteristics of substituent cations are relevant to the behavior of the resulting materials. Finally, thermal degradation tests reveal that, contrary to general expectations, not all mixed compositions are more stable than their related pure HPs. More than that, the order of degradation kinetics may also depend on the type of substituent cation. The results elucidate the particularities of each type of organic cation on the properties of mixed perovskites and advance knowledge about these relevant materials.



1. INTRODUCTION

The formulation of mixed-component halide perovskites (HPs) is one of the ways to achieve optimized characteristics for optoelectronic applications in devices based on this revolutionary class of materials. Most efficient devices fabricated with HPs today employ mixed systems, including the currently most efficient perovskite solar cells.^{1–4} A compositional variety of the ABX_3 HP compounds can be explored considering the mixtures of several perovskites instead of single compounds. Consequently, the component substitution effect on the characteristics of HPs and their devices has been widely evaluated.^{5–13} In HPs with A-site cation substitutions, using organic cations mainly, investigations were conducted in systems of the types $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$,^{14–18} $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$,^{19–24} $\text{DMA}_x\text{MA}_{1-x}\text{PbI}_3$,^{25–27} $\text{EA}_x\text{MA}_{1-x}\text{PbI}_3$,^{28,29} and $\text{GA}_x\text{FA}_x\text{MA}_{1-2x}\text{PbI}_3$.³⁰ In these systems, MA^+ , FA^+ , GA^+ , DMA^+ , and EA^+ are the methylammonium, formamidinium, guanidinium, dimethylammonium, and ethylammonium cations, respectively. These A-site organic cations are the most common and often used in HP formulations. Generally, the degree of substitution in these mixed systems affects characteristics such as the structure, phase transition temperatures, dielectric permittivities, charge carriers, ion dynamics, and photoluminescence. However, only a few works sought to directly prove the effects of the type of substitution of the A-site cation on the characteristics of hybrid HPs. In this sense, it

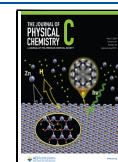
was demonstrated that substituting organic cations of different sizes leads to lattice strain, potentially inducing phase transitions, and constitutes a route to tune the band gap energies of resulting materials.³¹ Recent results suggest that internal interactions between different bulky organic A-site cations in mixed-cation systems improve trap-state densities, Urbach energy, and carrier transport in related films.³² Furthermore, organic cations of different acidities may cause changes in the thermal stability of the HPs.³¹ Also, even though not restricted to organic cations only, there are indications in the literature that the nature of the A-site cation controls the open-circuit voltage of perovskite solar cells.³³

Despite the current knowledge about the effects of substituent organic cations on HPs, studies on systems substituting cations with different concentrations and complex compositions and properties are primarily associated with the devices and not with the perovskites themselves. In such cases, rationalizing what effect a particular substituent might have on the resulting material is difficult. Studies of this order become

Received: February 20, 2023

Revised: April 7, 2023

Published: April 28, 2023



relevant since the optimization of perovskite performance in a given application is achieved by fine-tuning their characteristics, which can be achieved by choosing appropriate compositions. For example, an expected increase in lattice size with the increasing substitution degree and substitution of the cation radius was demonstrated in equimolar substituted MAPbI₃-based materials.³⁴ Also, the combination of theoretical and experimental techniques verifies the proportionality between iodide ion transport suppression and the size difference between MA⁺ and substituent cations in similar HPs.³⁵ In systems such as Cs_xMA_{1-x}PbI₃, Cs_xFA_{1-x}PbI₃, and FA_xMA_{1-x}PbI₃, the optical and transport band gaps depend on the substituting cation.³⁶ Although a justification based on the size of the cations involved is reasonable in these cases, other particular cases seem to be affected by other factors. For example, under light-induced degradation, it was found that partial substitution of MA⁺ cations with larger ones resulted in a decreased degradation rate. Still, no direct correlation with the substituent size was observed.³⁴ It indicates that other characteristics of the larger cations, such as polarity and hydrogen bonding capabilities, may play a role in the mixed-cation HPs' properties. It demonstrates that there are fundamentally different aspects arising from incorporating different cations in a perovskite matrix that, along with some currently unknown features, deserve to be studied.

Considering the above-depicted scenario, we studied how different mixed compositions of the same concentrations can affect the perovskite matrix of MAPbI₃ (otherwise referred to as MAPI). To do so, we chose two double-cation compositions, namely, GA_{0.10}MA_{0.90}PbI₃ (or GA0.10) and FA_{0.10}MA_{0.90}PbI₃ (or FA0.10), and a triple-cation composition given by GA_{0.05}FA_{0.05}MA_{0.90}PbI₃ (or TC). We studied the crystalline structure, phase transitions, dielectric and charge transport behavior, and HP compositions' thermal stability using a wide combination of techniques and experiments. For the properties associated with charge transport, there seems to be a direct correlation with the average size of the substituent ions. However, the results also demonstrate that changing the substituent organic cations can lead to unpredictable effects, especially concerning the mixed-HP structure, dielectric behavior, and thermal stability.

2. METHODS

2.1. Sample Synthesis. To synthesize the samples, initially, the amounts of the precursors lead iodide (PbI₂, Sigma-Aldrich, 99%), methylammonium iodide (CH₃NH₃I or MAI, Sigma-Aldrich, 98%), formamidinium iodide (CH₃(NH₂)₂I or FAI, Sigma-Aldrich, 99%), and guanidinium iodide (C(NH₂)₃I or GAI, Sigma-Aldrich, 99%) were weighted in desired proportions (see [Supplementary Note 1](#)). The precursors were manually mixed and ground to react in a natural agate mortar for about 1 h under ambient conditions in a controlled temperature room (~298 K or 25 °C) and with relative humidity below 30%. The resulting black powders of perovskites were sieved in a 250 μm aperture sieve (60 mesh), dried, and annealed for 6 h at 333 K (60 °C) in a laboratory oven with periodic (once an hour) stirring. Powders were stored in PVC film-sealed hermetic amber glass flasks kept in a desiccator, filled with silica gel granules, and covered with black opaque plastic foils. Pelletized powders were produced with approximately 150 mg of the powders uniformly spread into a 10 mm diameter circular cavity of a metallic mold and compacted with a pressure of about 250 MPa. Lastly, the

pellets were sintered in an electric furnace at 393 K (120 °C) for 2 h and slowly cooled to room temperature inside the electric furnace. Several pellets of each composition were synthesized and used in the following procedures.

2.2. Characterizations. The crystalline structure of the materials was characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with CuK_{α1} radiation ($\lambda = 1.5406$ Å) at about 295 K (22 °C), under 40 kV and 20 mA, with a continuous scan (2° min⁻¹), in the range of 2 θ from 10 to 50° under controlled conditions (dark, at approximately 295 K and relative humidity below 30%). Differential scanning calorimetry (DSC) measurements were performed in a DSC 25—TA Instruments from 183 to 373 K (−90 to 100 °C), with a 5 K min⁻¹ heating rate, under a nitrogen atmosphere, using about 10 to 15 mg of pellet fragments in aluminum crucibles. For electrical measurements, a matrix of 8 × 8 circular gold electrodes of about 0.6 mm diameter was sputtered on top of the perovskite pellets using a shadow mask, while a bottom gold electrode was deposited over the entire sample surface. Impedance spectroscopy (IS) measurements were performed in a Displex ARS CSW-202 closed system using an Agilent 4284A LCR meter to measure the conductance (*G*) and susceptance (*B*) in the frequency range of 10³ to 10⁶ Hz. For dielectric permittivity analyses, data were collected on cooling and heating regimes under a temperature rate of 1 K min⁻¹ in the 100 to 300 K range. Before starting measurements under heating, the samples were kept at 100 K for 30 min. For temperature-dependent conductivity analyses, dielectric permittivity and impedance data were collected at heating under continuous temperature variation of 0.3 K min⁻¹ in the 300 to 380 K range. All electrical measurements were carried out in a vacuum and in the dark to avoid external effects using a closed Displex ARS CSW-202 system. Several electrodes were tested before starting the experiment, and impedance spectra were collected to ensure choosing a representative electrode of the overall sample's electrical characteristics. Steady-state current–voltage (*I*–*V*) data were collected using a Keithley 6517B electrometer under controlled conditions. Direct and reverse measurements were performed from −6 to +6 V with a 0.2 V s⁻¹ scan rate. Forward measurements were performed from 0 to +20 V with a scan rate of 0.2 V s⁻¹. Ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy data were collected on a Shimadzu UV-2600 spectrophotometer, from 200 to 1100 nm, using the slow speed mode with a 1 nm data interval. The microstructure images of the samples were obtained in a Zeiss EVO LS15 scanning electron microscope, with a tungsten beam operating in the voltage range between 10 and 20 kV, by secondary electron analysis (SE mode).

2.3. Thermal Degradation Protocol. Each pellet composition was placed in a 60 × 15 mm glass Petri dish and heated for up to 110 h at 423 K (150 °C) in an electric oven under ambient air in the dark. After predefined intervals, the samples were removed from the oven and rapidly cooled to 295 K. XRD data were collected after each of these intervals, using the same experimental setup and conditions described in the previous section, in the range of 2 θ from 10 to 15°. Precautions were taken so that always the same faces of the samples were exposed to air during the heat treatment in the oven. The XRD data were always collected on that same face, with care always taken to position the samples in the same arrangement in the sample holder.

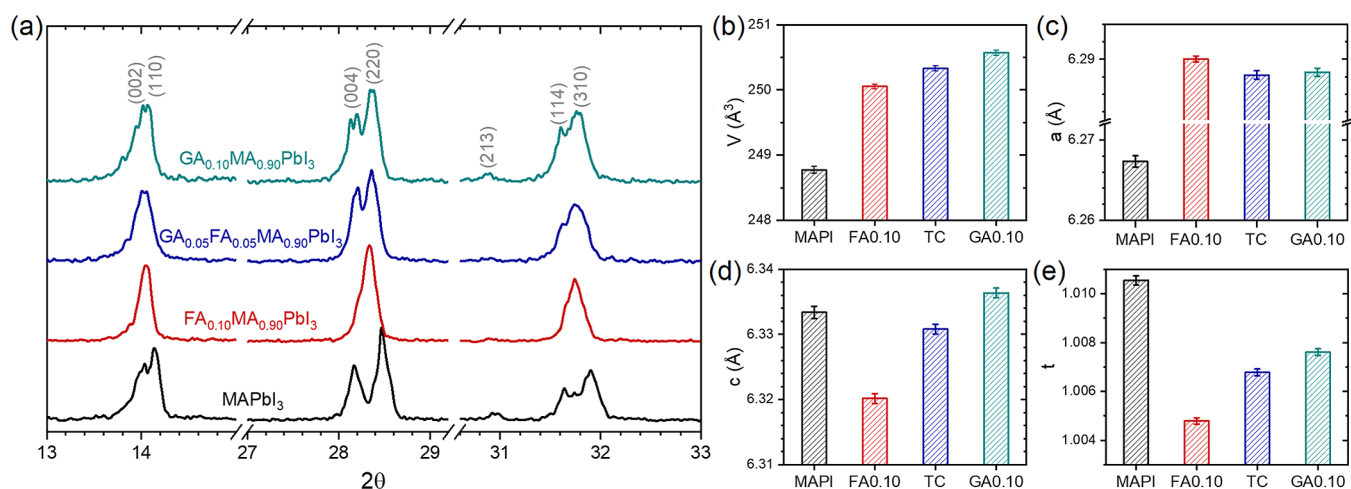


Figure 1. (a) XRD patterns of the studied compositions. Only the 2θ ranges of main peaks are shown. The crystal characteristics (b) cell volume, (c) lattice parameter a , (d) lattice parameter c , and (e) tetragonality factor $t = c/a$ were calculated using the relations $a = a'/\sqrt{2}$ and $c = c'/2$ of a pseudocubic representation, where a' and c' are the parameters obtained through the Le Bail fit of XRD data using the $I4cm$ space group.

3. RESULTS AND DISCUSSION

The first characteristic under study was the structure of the obtained perovskites. Figure 1 shows the XRD patterns of the studied compositions. From the XRD patterns in Figure 1a, typical profiles of tetragonal perovskites were observed in all compositions. Standard features include peaks relative to reflection by the (002) and (110) planes quite close together but separated, observed at $\sim 14.0^\circ$. This same characteristic can be observed in the peaks of (004) and (220) reflections at ~ 28.0 – 28.5° and in the peaks (114) and (310) reflections at ~ 31.5 – 32.0° . Furthermore, it should be noted that the small peak at $\sim 30.8^\circ$ was associated with reflection from the (213) plane. In this sense, it is clear that, at the temperature at which the data were taken, the studied compositions correspond to perovskite structures of the tetragonal lattice, as expected by results in the literature.^{16,24,30} As discussed in the following, from the obvious changes caused by the substituents in comparison with pure MAPbI_3 , and lack of secondary phases (complete XRD data are shown in Supplementary Note 2), it is concluded that the substituent cations were properly inserted into the perovskite lattice. Considering that the materials syntheses occurred using a mechanochemical route without any solvents or high temperatures, it is safe to assure that the perovskites used in this work had compositions very close to the nominal intended ones.

Based on the experimental XRD patterns, we performed Le Bail fits to obtain the crystal characteristics of studied compositions (details also given in Supplementary Note 2). In Figure 1b, it is evident that there is an increase in the unit cell volume as a function of the increase in the average effective ionic radius of the A-site cations (Supplementary Note 3), as expected. For clarity, MA^+ , FA^+ , and GA^+ effective ionic radii are around 217, 253, and 278 pm, respectively.³⁵ However, lattice parameters a and c in Figure 1c,d show an unexpected behavior that differs from the average cation size. In these cases, the $\text{FA}_{0.10}$ composition presents simultaneously the highest value of a and the lowest value of c , suggesting that FA^+ cations cause a differentiated distortion in the perovskite matrix structure. In other words, this means that the replacement of MA^+ by FA^+ is more effective in making the tetragonal structure closer to the cubic structure than the replacement of MA^+ by GA^+ . It was evidenced by the fact that

the $\text{FA}_{0.10}$ composition has the lowest tetragonality factor among those studied (Figure 1e). A direct consequence is that, for this composition, the diffractogram peaks are closer than the observed for the other compositions. Another peculiar consequence is that since the tetragonal lattice is “more cubic” in $\text{FA}_{0.10}$, its tetragonal-to-cubic ($T \rightarrow C$) transition temperature tends to be the lowest among the studied compositions. For a better investigation, $T \rightarrow C$ transition temperatures were estimated via DSC (details are given in Supplementary Note 4). Figure 2 summarizes these results.

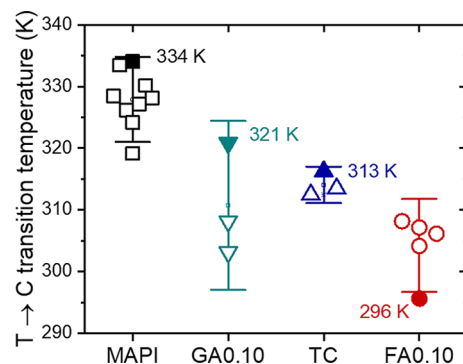


Figure 2. Tetragonal-to-cubic transition temperature of studied compositions. Full dots and their numbers are from data obtained in this work, while hollow dots are from the literature, as described in Supplementary Note 4.

From the previous discussion, it was found that the $\text{FA}_{0.10}$ perovskite possesses the lowest $T \rightarrow C$ transition temperature among the studied compositions. It seems consistent with the observed trend compared with results in the literature. Thus, it can be concluded that FA^+ cations seem to be more efficient than GA^+ cations in stabilizing the cubic phase of MAPbI_3 . It is interesting from a technological perspective in perovskite solar cells, given that the highest efficiencies and stability tend to be obtained in cubic perovskites, as well elaborated recently.³⁷ However, this result is contrary to the expectations predicted by these compositions' theoretical Goldschmidt tolerance factor (see Supplementary Note 3). For common inorganic compounds, the tolerance factor is a good tool to predict,

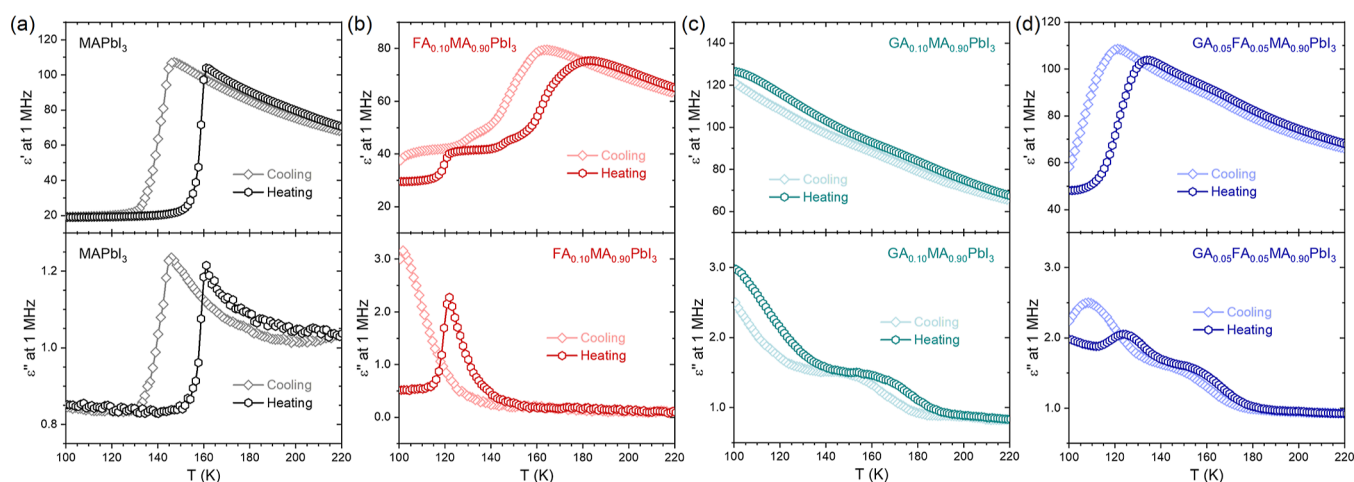


Figure 3. Temperature dependencies of the real (ϵ') and imaginary (ϵ'') dielectric permittivity at 1 MHz measured on cooling and heating for the (a) MAPbI₃, (b) FA_{0.10}MA_{0.90}PbI₃, (c) GA_{0.10}MA_{0.90}PbI₃, and (d) GA_{0.05}FA_{0.05}MA_{0.90}PbI₃ compositions.

among others, the effect of the A-site composition on the structure of a given ABX₃-type composition.^{38,39} This is partly because elemental ions can be satisfactorily assumed to be spherically symmetric chemical species, and for a given set of oxidation numbers, the main character to be modified is the ion size. However, in hybrid HPs, such a scenario becomes less predictable. This stems from the fact that organic cations have different effective ionic radii, diverse point groups, and dipole moments capable of performing different numbers of hydrogen bonds with the inorganic matrix formed by the BX₆ octahedra, among others. The tolerance factor and its modifications are widely studied in HPs,^{40,41} and its limitations are known. In any case, the result corroborates the motivation for studies like the present one and should encourage new experimental investigations. Finally, the results shown in Figures 1 and 2 suggest that the TC triple-cation composition shows intermediate characteristics between the GA_{0.10} and FA_{0.10} double systems, which is advantageous for allowing the rational design of compositions to obtain desired properties.

Figure 3 shows the real (ϵ') and imaginary (ϵ'') components of the dielectric permittivity as a function of temperature at 1 MHz, obtained under heating and cooling. Data at other frequencies and temperatures are shown in Supplementary Note 5. The following discussions refer to analyses done under heating.

In Figure 3a, the abrupt change in both components of dielectric permittivity at around 160 K shows the typical behavior of the orthorhombic-tetragonal ($O \rightarrow T$) phase transition for the pure MAPbI₃,⁴² associated with the disruption of the cooperative ordering of MA⁺ cations.^{29,43,44} As for the FA_{0.10}MA_{0.90}PbI₃ composition, different transitions below 200 K may occur, as observed in Figure 3b. In the FA_xMA_{1-x}PbI₃ system, several structures and transitions have been proposed in the literature.^{17,18} It can be argued that the changes in the temperature profile of the dielectric permittivity curves compared to MAPbI₃ are partly due to the possible existence of a large-cell cubic (LC) intermediate phase between the orthorhombic and tetragonal phases.¹⁷ In this sense and based on our experimental data, we estimate that the respective transitions occur approximately in $O + LC \xrightarrow{120\text{ K}} LC \xrightarrow{145\text{ K}} LC + T \xrightarrow{170\text{ K}} T$. In principle, the transition $O \rightarrow O + LC$ occurs below 100 K,¹⁷ that is, outside our measurement range. Hence, considering Figure 3a,b and

the aforementioned discussion, it can be inferred that the disappearance of the orthorhombic phase is accompanied by a peak in $\epsilon''(T)$ curve, while the appearance of the tetragonal phase is accompanied by a rapid increase in $\epsilon'(T)$. It should be noted that this increase in $\epsilon'(T)$ is much more subtle in FA_{0.10} than in MAPbI₃, as evidenced by the peak's broadening, which might be associated with the change (restriction) in the rotation of the MA⁺ cations when mixing with other cations, as already proposed for the FA_xMA_{1-x}PbI₃ system¹⁷ and others, such as EA_xMA_{1-x}PbI₃,²⁹ FA_xMA_{1-x}PbBr₃,⁴⁵ and DMA_xMA_{1-x}PbBr₃.⁴⁶ In these systems, it is generally shown that the activation energy for the rotation of MA⁺ cations increases, causing a disorder at low temperatures and consequent transition broadening. Furthermore, the $\epsilon'(T)$ peak is shifted to higher temperatures in FA_{0.10} compared to MAPbI₃.

In composition GA_{0.10}, the $\epsilon'(T)$ peak in Figure 3c, in principle related to the appearance of the tetragonal phase, is not even observed in the range of the studied temperatures in the present work. It suggests that, contrary to that noted for FA_{0.10}, the tetragonal phase becomes stable at lower temperatures than in MAPbI₃. This agrees with that observed for the GA_xMA_{1-x}PbI₃ system.²⁴ It should also be noted that the $O \rightarrow T$ transition temperature is progressively reduced with increasing x in the EA_xMA_{1-x}PbI₃ system.²⁹ This shows that different cations can cause contrasting changes in the relative stability of different structures of a perovskite. Finally, for the triple-cation composition TC, the $\epsilon'(T)$ peak in Figure 3d occurs at a much lower temperature than in MAPbI₃. Note that there is also a subtle peak in $\epsilon''(T)$ at this composition. Considering these observations, it appears that GA⁺ cations are more dominant than FA⁺ cations concerning the effect on the dielectric behavior of the perovskite matrix. This may be associated with the fact that GA⁺ cations (higher effective radius, zero dipole moment) are more distinct from MA⁺ (lower effective radius, higher dipole moment) than FA⁺ cations (intermediate effective radius and dipole moments). In addition, there is a greater approximation between the peaks of $\epsilon'(T)$ and $\epsilon''(T)$ in TC, which makes this composition particularly similar to MAPbI₃ in this regard and different from FA_{0.10}. Unfortunately, in GA_{0.10}, it is impossible to infer whether these peaks are close or not. Furthermore, we regret the lack of crystallographic data that would allow us to describe

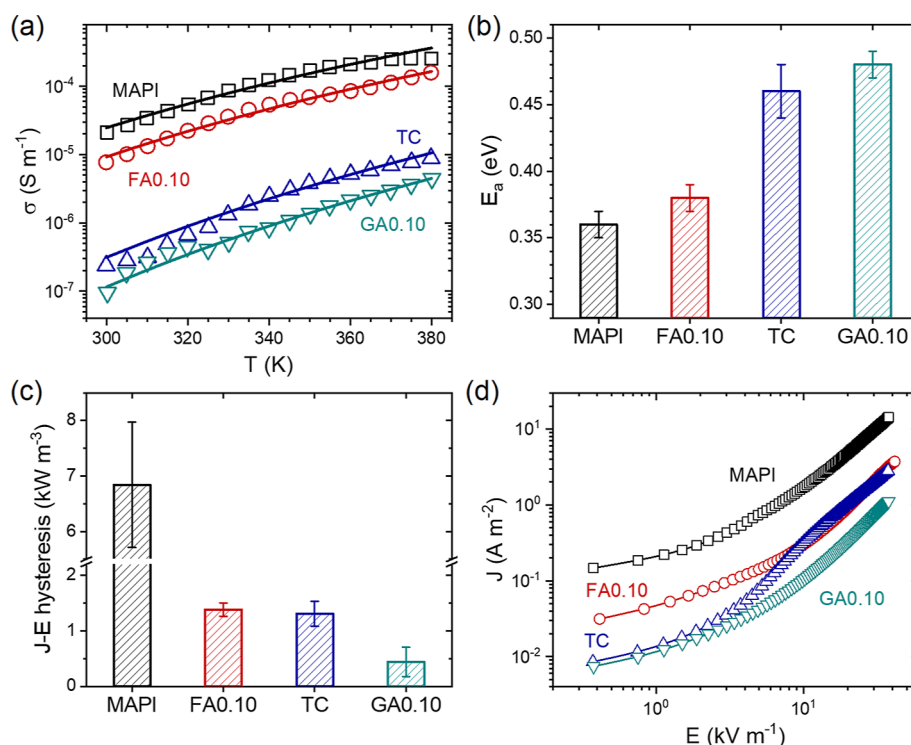


Figure 4. (a) Ionic conductivities of the studied compositions as a function of temperature. Dots are the experimental data, and lines are calculated curves from parameters obtained through the Arrhenius equation. (b) Activation energies for ionic conduction. (c) J - E hysteresis of the studied compositions with a scan rate of 0.2 V s⁻¹ at room temperature. Values are the mean from five measurements, and error bars are the respective standard deviation. (d) Current density as a function of the external electric field. Curves are the mean from the five measurements.

the possible structures in the GA0.10 and TC compositions at low temperatures to highlight their similarities and differences. As a result, we could not assign a physical meaning to the subtle shoulder at $\epsilon''(T)$ at about 160 K in the GA0.10 and TC compositions. This shoulder exists only in compositions containing GA⁺, and therefore, we suppose it relates to a structural change caused by these cations in the perovskite matrix. Lastly, the $\epsilon'(T)$ peaks in TC and FA0.10 compositions are slightly broader than in MAPbI₃. We speculate that the MA⁺ cations are less restricted to rotate in these mixed compositions. Additional investigations should be conducted to understand better the effects of GA⁺ and FA⁺ cations on the dielectric behavior in triple systems of the type GA_{*x*}FA_{*y*}MA_{1-*x-y*}PbI₃.

As materials for optoelectronic applications, understanding charge transport characteristics is important in HPs. Thus, Figure 4 summarizes the electrical characterizations of the studied compositions. Figure 4a shows the temperature dependence of the conductivity (σ), calculated from impedance spectroscopy data (details are given in Supplementary Note 6). Recently, it was shown that the electrical response resulting from impedance spectroscopy is mainly controlled by the transport of ions, not electronic carriers.^{47,48} Considering this fact, it can be concluded that the conductivity as a function of temperature for the studied materials consists of ionic conductivity, especially when the measurements are performed in the dark.⁴⁹ From the results, it is clear that the composition of the A-site cation greatly influences the ionic conductivity of the studied compositions, as evidenced by pure⁵⁰ and mixed^{24,35} systems. A reduction is noted with an increase in the average size of substituent cations. Over the entire temperature range, the ionic conductivity decreases in

the order MAPI > FA0.10 > TC > GA0.10, possibly due to the increase in the lattice strain caused by the substituent cations. Then, we modeled the temperature dependence of the ionic conductivity using the well-known Arrhenius-type equation $\sigma T = \sigma_0 \exp(-E_a/kT)$, where σ_0 is a pre-exponential constant, E_a is the activation energy for ion conduction, and k is the Boltzmann constant. Figure 4b summarizes the obtained activation energy values. As expected from the literature,³⁵ we obtained a trend where the ion transport activation energy increases with the A-site cation average size, possibly due to the local distortion of the PbI₆ lattice due to cation mismatch. The range of E_a values found in our work is commonly associated with iodide ion/vacancy diffusion,^{51,52} and for the GA⁺ cation substitution, it was proposed that the increased E_a is due to structural changes leading to a curved path that is bowed out of the Pb/I plane.³⁵ Extending these ideas to the other compositions, we conclude that GA⁺ cations are more effective in mitigating the diffusion of iodide defects than FA⁺ in mixed-cation lead iodide perovskites. We expect the lead and A-site ion/defect diffusion to also be restricted in the mixed systems, particularly in the GA⁺-containing ones.

In the ion migration context, it is important to mention that ionic conductivity and its activation energy have well-known implications, among which are the stability of HPs and their J - E (or J - V) hysteresis. The former will be considered later. Concerning the J - E hysteresis, growing understanding points toward its detrimental effect on reliability, reproducibility, and operational stability in perovskite solar cells.⁵³ Here, instead of determining the typical hysteresis index in solar cells, we studied the J - E hysteresis from current-voltage data collected with direct and reverse measurements on the sample pellets of each composition, as recently employed.^{24,54} The J - E

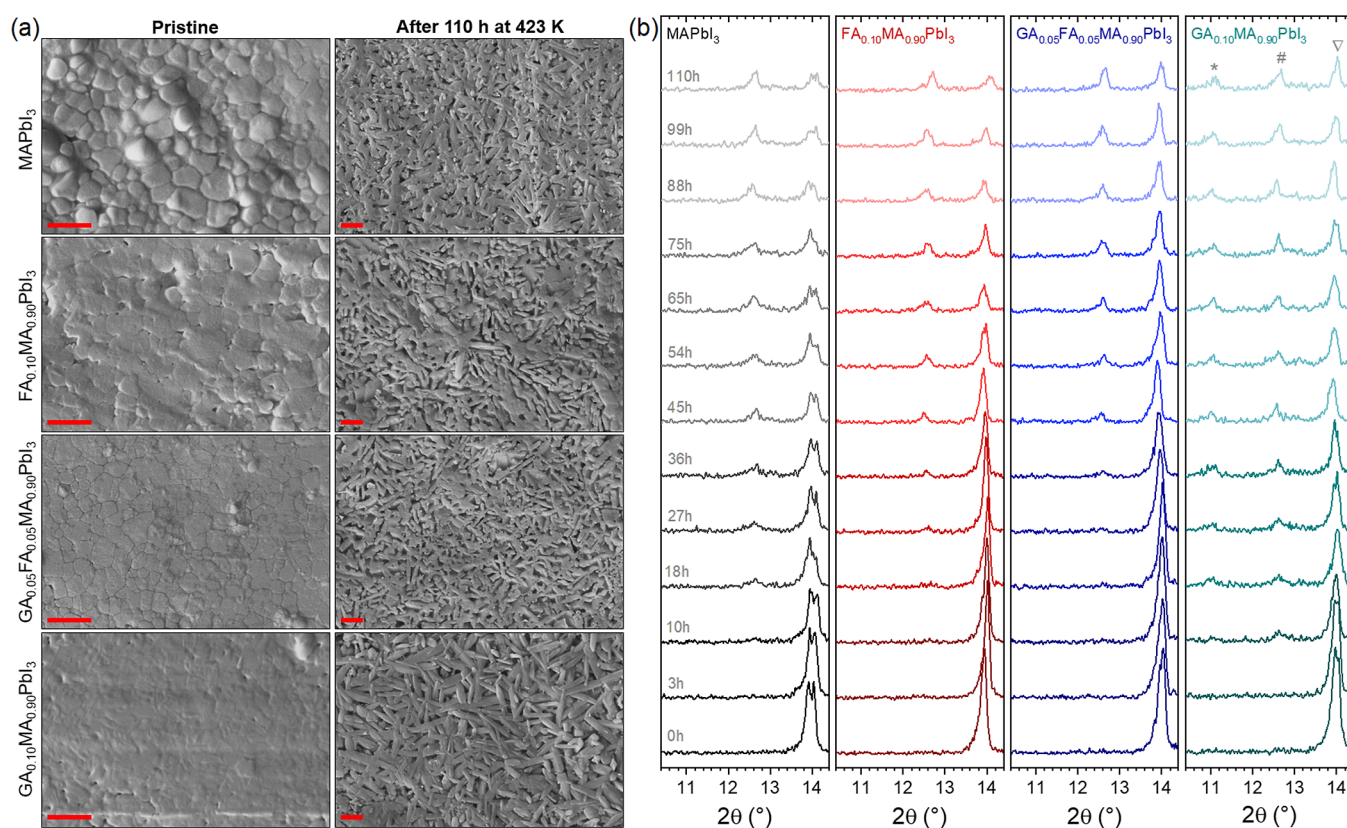


Figure 5. (a) Representative SEM images of the surface of each perovskite composition before and after thermal treatment at 423 K for 110 h. Scale bar: 2 μm. (b) XRD profiles at low angles showing progressive changes occurring throughout the thermal treatment. Assigned peaks are due to (*): GAPbI₃, (#): PbI₂, and (▽) perovskite phases.

hysteresis results are shown in Figure 4c (additional details are given in Supplementary Note 7). Considering that mobile ions are widely accepted to play a major role in the hysteresis phenomenon in HPs,^{55,56} it is not surprising that our results show that the hysteresis is remarkably mitigated in all mixed-cation compositions when compared to pure MAPbI₃. It should be stressed that, when studying such hysteresis, factors such as the scan rates, sample thicknesses, and electrode materials and configurations are important for quantitative considerations. However, as we used equal temperature and scan rate conditions for all samples of very similar thicknesses and have the same electrode configuration, the relative comparison is reasonable, at least from a qualitative perspective. We emphasize that a better *J*–*E* hysteresis trend with the A-site cations average size, as noted for the results of ionic transport properties, might be observed for the maximum hysteresis values tracked using several scan rates. Such determination is, for now, beyond the scope of this work. Lastly, the properties of electronic charge carrier transport can be studied using forward current–voltage measurements. In this regard, Figure 4d shows the positive branch of *J*–*E* curves of the studied compositions (complete data are given in Supplementary Note 8). Similar data in HPs are often modeled using the well-known space charge-limited current (SCLC) approach. However, the common features of Mott–Gurney (*J* ∝ *V*²) and trap-filling (*J* ∝ *V*^{*n*}) regimes (for *n* > 2), typically observed when a given semiconductor material/device follows the classical SCLC behavior, could not be identified in our results for any composition under the employed measurement conditions. Indeed, as high ionic contributions to electric

currents are expected in these materials, the application of the SCLC model may not be possible to extract relevant charge transport parameters under steady-state conditions.^{57–59} In contrast, our data suggest a *J* ∝ *V*^{*n*} proportionality (with *n* ∼ 1.5) in several measurements, especially for higher electric fields. In this case, ballistic or quasi-ballistic transport may be in effect, as identified in thick-HP samples.⁶⁰ Also, considering ionic transport contributions on the *J*–*E* hysteresis of our samples and the previous discussion, the diffusion currents cannot be disregarded in certain cases, and, therefore, the application of more robust models based on drift-diffusion equations would be necessary. In this sense, it is evident that the attribution of a particular charge transport regime in our samples is quite complex, beyond the complexity intended for the present work. For now, brief qualitative interpretations are used to analyze the A-site composition-dependent results, for which a drop in the current density as a function of the increase in the average size of the A-site cations is observed. In principle, the current densities are due to the transport of both ionic and electronic charge carriers, where both the carrier mobilities and densities must be considered. From the perspective of ion transport, the previously discussed trend clearly states that the ionic contributions are reduced with increasing A-site cation average sizes, possibly resulting from reduced ion/vacancy mobility. In turn, considering that the band gap energies are fairly close in the studied system, of about 1.5 to 1.6 eV^{16,23,30} (see Supplementary Note 9), with measurements conducted in the dark and at the same temperature, no appreciable difference is expected in the carrier densities in thermal equilibrium with the perovskite

lattice. Hence, similar electronic charge carrier densities possibly are present in all studied compositions. In this case, eventual differences in electronic contributions to electric currents in our samples must be due to the effect of composition on electronic mobility. In theory, it would be expected that the structural distortions caused by the incorporation of bulky organic cations would result in greater carrier scattering, decreasing electronic mobility. Although reasonable, it should be emphasized that this simplistic explanation is difficult to verify, given that, for a given HP composition, reported charge-carrier mobility values span over large ranges.⁶¹ Thus, we speculate that electronic currents also decrease according to the same trend as ionic currents. In theory, both characteristics benefit the materials in question, given that low dark currents are usually desirable. In addition, although we did not obtain data in this sense, results show that the trap densities are lower in the mixed-cation systems than in the respective pure composition, where the triple system is the one with the lowest trap density among the studied compositions.³² By analogy, we hypothesize that the change, particularly clear at mid-electric fields ($\sim 5 \text{ kV cm}^{-1}$), in the behavior of the J – E curve in the TC composition, may be related to a lower trap density compared to the other compositions. It should be stressed that, in general, the TC composition seems to show intermediate electric characteristics between the FA0.10 and GA0.10 compositions. This trend follows the same predicted by the average size of the substituent cations. Therefore, it is reasonable to conclude that the electrical properties of HPs are controlled, at least partially, by the structural distortions caused by the size differences of such cations rather than by their other properties.

Finally, the thermal stability of the studied mixed systems was studied. Temperature-accelerated degradation tests are an excellent tool to understand the intrinsic stability of perovskites and seek improvement strategies. This topic is of great relevance given that the rapid degradation of HPs and their devices is possibly the major obstacle to large-scale commercialization today. Greater stabilities against environmental stressors, including heat, humidity, light, and oxygen, are often observed in mixed-cation systems.⁶² The mitigating ionic transport or increasing configurational entropy generally explains the thermal stability in HPs. Although extensively studied, few results are found in the literature seeking to understand the effect of different A-site substituents on their thermal stability and degradation behavior. In the present work, thermal degradation was studied by monitoring the microstructure and structure of the studied composition. Figure 5 summarizes the microstructure and structure results of the analyzed samples under different conditions characterized by SEM images and XRD patterns.

Figure 5a shows representative SEM images of the microstructure of pristine and thermally treated samples at 423 K for 110 h. After heat treatment, the previously dense microstructure with defined grains becomes full of voids spaced by elongated microconstituents. Thermal degradation of MA^+ -based HPs can occur according to some main reactions,^{63,64} given by $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{s}) \rightarrow \text{CH}_3\text{NH}_3\text{I}(\text{g}) + \text{PbI}_2(\text{s})$, $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{s}) \rightarrow \text{CH}_3\text{NH}_2(\text{g}) + \text{HI}(\text{g}) + \text{PbI}_2(\text{s})$, and $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{s}) \rightarrow \text{CH}_3\text{I}(\text{g}) + \text{NH}_3(\text{g}) + \text{PbI}_2(\text{s})$. The definition of the major reactions among these has been extensively studied,^{65–67} and the details will not be discussed here. The relevant point to consider is the mass loss of organic volatiles, possibly leading to the origin of the voids on the surface while

leaving solid PbI_2 . The development pathway of the surface microstructure during degradation can occur, in principle, by layer-by-layer decomposition, from the surface inward, or be initiated in internal defects close to the surface and break it from the inside outward.⁶⁸ Considering any differences between the compositions, these microstructural aspects should be studied in the future. In addition to the pristine samples, XRD data were collected for the heat-treated samples to understand the formation of different phases along the thermal degradation. Figure 5b shows the obtained XRD profiles of the studied samples heat treated at 423 K at different times. In this figure, the peaks observed at $2\theta \sim 14.0^\circ$ refer to the perovskite phase, while the peaks at $2\theta \sim 12.5^\circ$ and $2\theta \sim 10.0^\circ$ were associated with the PbI_2 and the non-perovskite phase GAPbI_3 , respectively. The XRD profiles of all pristine samples (non-heat treated) only contain peaks from the perovskite phase, but secondary phases appeared in thermally treated samples, depending on the treatment time. The results show a progressive decrease in the perovskite phase followed by a progressive increase over time in the peak associated with PbI_2 . As expected and is well known, the observation is a direct consequence of eliminating volatile species, especially those related to MA^+ cations, according to the abovementioned reactions. However, in composition GA0.10, a distinct peak at $\sim 11.0^\circ$ due to the GAPbI_3 phase is formed progressively. A priori, this fact is surprising considering that this composition is well below the predicted solubility limit for the $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ system of $\sim 25\%$ or $x = 0.25$.^{20,24} However, evidence of the formation of GAPbI_3 even below the solubility limit is also found in the literature for materials studied under forced³⁴ and non-forced degradation conditions.⁵⁴ It suggests that guanidinium-containing compositions may be subject to different degradation routes of the perovskite matrix.

The degradation of the perovskite phase was followed to better understand the thermal degradation kinetics of the studied samples. Although it seems obvious, this approach differs from most works that also address the problem via XRD, in which the degradation monitoring has been done mainly by the progressive formation of PbI_2 .^{69–71} From a theoretical perspective, this difference in approach is motivated by the consideration that not all thermal degradation pathways result in the formation of PbI_2 . Some examples might include forming point defects from both full and partial Schottky defects with low formation energies.⁷² In these cases, the crystalline quality loss potentially affects the peak of the perovskite phase in the diffractograms without necessarily forming PbI_2 . From an experimental view, we noticed in our data that there was a drop in the area of the perovskite peaks before the PbI_2 peak could be identified in the XRD diffractograms, which agrees with the hypothesis presented previously. Furthermore, the hypothetical formation of GAPbI_3 from the perovskite matrix in GA0.10 composition can follow a reaction of the type $\text{GA}_{0.10}\text{MA}_{0.90}\text{PbI}_3 \rightarrow z \text{GAPbI}_3 + (1 - z)\text{GA}_{0.1-y}\text{MA}_{0.9+y}\text{PbI}_3$, where $y = 0.09z/(1 - z)$. It is clear in this reaction that there is a decrease in the amount of perovskite without concomitant PbI_2 formation. Considering this discussion, perovskite degradation extent $\alpha(t)$ was associated with the reduction of the perovskite peak area in the diffractograms through the expression $\alpha(t) = 1 - A(t)/A_0$, where $A(t)$ is the perovskite peak area after a given degradation time t and A_0 is the initial perovskite peak area. A similar approach was employed elsewhere.⁷³ It

should be stressed that several possible degradation pathways can occur simultaneously, together leading to a progressive drop in the perovskite peak area. Furthermore, when GAPbI_3 precipitates, not only is the amount of perovskite phase reduced but there is also a change in the composition of the solid solution, which makes the scenario even more complex. The separation of all these possible processes and their consequences cannot be done based solely on our XRD data and is outside the scope of this work. The interest here is limited to the global visualization of perovskite degradation in the form of α variation as a function of thermal treatment time.

Figure 6a shows the evaluated degradation $\alpha(t)$ at different thermal treatment times at 423 K for the studied samples. The

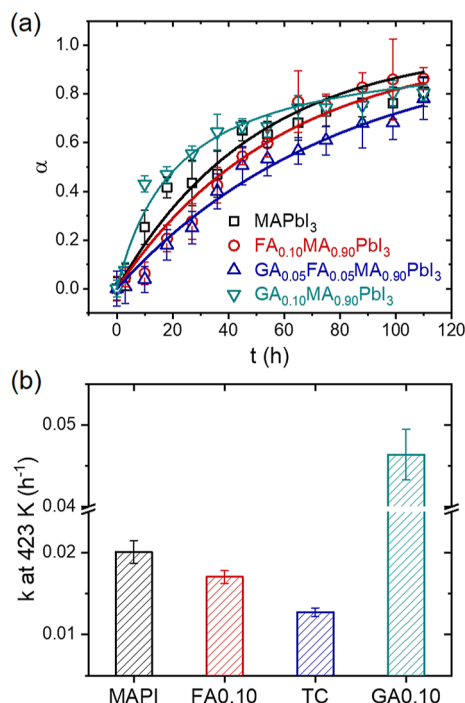


Figure 6. (a) Variation of the degradation $\alpha(t)$ at different thermal treatment times at 423 K. Symbols are experimental data, and lines are theoretical fits using the equations discussed in the main text. The error bars are the standard deviations obtained from calculating the perovskite peak areas on the diffractograms. (b) Calculated kinetic constants k for each composition at 423 K.

first pertinent observation is that, in all compositions, α increases progressively with advancing time since the beginning of the experiments, as expected. Second, the visual inspection of the experimental data suggests that the FA0.10 and TC compositions are more stable than pure MAPbI_3 , the latter being the most stable among those studied. However, the degradation of the GA0.10 composition is the fastest among those studied, which goes against the expectations from a general rule of high entropy gain in mixed perovskites leading to enhanced thermal performance.⁷⁴ Third, for the MAPI , FA0.10 , and TC compositions, the variation of α with the treatment time could be adjusted with a first-order reaction kinetic law, similar to what has already been reported in the literature in similar compositions of HPs.^{69,70} Indeed, the theoretical fit of the experimental data for these three compositions could be adequately determined with an equation of the type $\alpha(t) = 1 - \exp(-kt)$, derived from a first-order differential kinetic law, where k is the kinetic

constant at a given temperature. However, there is a clear difference in the degradation kinetics of GA0.10 , whose experimental data could not be adjusted with the above-mentioned equation. For this composition, the variation of $\alpha(t)$ could only be fitted following a relation of the type $\alpha(t) = kt/(1 + kt)$, derived from a second-order differential kinetic law (the derivation of rate laws and fitting parameters are given in [Supplementary Note 10](#)). This result is reasonable considering the existence of an additional perovskite decomposition pathway (GAPbI_3 segregation). To our best knowledge, there are no reports in the literature on the thermal decomposition in HPs whose thermal degradation kinetics follows a second-order rate law. Curiously, under similar conditions (heating in the air), a zeroth-order thermal degradation reaction kinetics was observed in mixed-HP thin films.⁷³

Figure 6b summarizes the kinetic constants quantification of the studied compositions, calculated from the theoretical fits. Not surprisingly, the determined k values reflect the qualitatively predicted order of stability against thermal degradation, such that, at the study temperature, the k values follow the order $\text{GA0.10} > \text{MAPI} > \text{FA0.10} > \text{TC}$. Thus, it is possible that HPs that exhibit additional degradation pathways are less stable than thermal decomposition. In this sense, perhaps it can be generalized that compositions containing a high concentration of bulky cations, such as GA^+ , in which there is a low solubility limit, present lower thermal stability under certain circumstances. It would be interesting to test, with a similar approach, systems such as $\text{EA}_x\text{MA}_{1-x}\text{PbI}_3$ and $\text{DMA}_x\text{MA}_{1-x}\text{PbI}_3$, whose predicted solubility limits are of the order of $x \sim 0.4$ ²⁹ and $x \sim 0.2$,²⁶ respectively, to verify this hypothesis. Despite this, it should be noted that the TC composition did not show a formation of GAPbI_3 , which indicates that this segregation should only occur in compositions with higher concentrations of GA^+ . Probably, due to even higher entropic stabilization in the triple system, this composition is stable enough to prevent appreciable segregation of GAPbI_3 . Still, besides GA0.10 presenting the higher k , it is not possible to state that this is due to a low stability against the volatilization of organic cations or if there is a major effect due to the existence of the additional perovskite decomposition pathway. It does not occur or was not observed in the other compositions. Furthermore, it is not possible to infer which volatile species are formed by thermal decomposition in all studied compositions. Even though volatilization, mainly of species associated with MA^+ cations, is expected, we cannot rule out a wide range of different chemical species being formed, either by the volatilization of species associated with FA^+ and GA^+ cations or by the products formed by the parallel reaction between the various possible chemical species.^{65,75,76} Finally, it is common sense that the thermal decomposition reactions in solid materials occur essentially in a localized manner on the surface and that the continuation of the decomposition would depend on the diffusion of species from the bulk to the surface. Thereby, it could be expected that GA0.10 , whose ionic transport rate is the smallest among the studied compositions, would be the most stable, but the exact opposite has been observed. These aspects will be addressed in a study currently in progress.

4. CONCLUSIONS

In summary, we observed that the triple-cation system seems to show some intermediate characteristics between the double-

cation systems, which is interesting from the perspective of allowing the rational design of compositions for property optimization. In particular, the charge transport properties seem dictated by the mean effective ionic radius of the substituent cations in the studied compositions. However, structural aspects, such as tetragonality factors and structures and phase transitions, both at high and low temperatures, are not shown to be related solely to the size of substituent cations. Further investigations, including of other substituent cations, must be done to elucidate the reason for these behaviors. Finally, striking differences in the effect of the A-site cations occurred in the thermal degradation of the perovskites. Not only was it shown that the mixed composition GA0.10 is less stable than pure MAPI but also that there is an additional pathway of degradation of the perovskite phase due to the segregation of GAPbI₃. As a result, there was possibly a change from a first-order degradation kinetics regime in MAPI, FA0.10, and TC to a second-order one in GAPbI₃. The thermal stability trend, indicated by kinetic constant values at 423 K, suggests that a combination of factors should be considered in explaining the results. Overall, the results presented here provide a robust basis for developing new strategies for mixing A-site cations in HPs and advancing the understanding of such systems.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c01179>.

Precursor and perovskite masses, XRD data and Le Bail fits, effective A-site ionic radius and related tolerance factors, DSC data and analysis, dielectric permittivity behavior, temperature-dependent conductivities, direct and reverse *I*–*V* measurements and *J*–*E* hysteresis, forward *J*–*E* curves, band gap energies, and thermal degradation kinetics data (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP (Project: 2017/13769-1) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, CAPES (CAPES-PRINT Project: 88881.310513/2018-01). The first author was granted CAPES (Finance Code 001). The authors would like to thank Elton José de Souza for support with SEM measurements and José Luiz Vilches for support with DSC measurements.

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Composition-Property Relations for $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ Perovskites

Fernando Brondani Minussi,* Rogério Marcos Silva Jr., and Eudes Borges Araújo

Halide perovskites are materials for diverse optoelectronic applications owing to a combination of factors, including their compositional flexibility. A major source of this diversity of compositions comes from the use of mixed organic cations in the A-site of such compounds to form solid solutions. Many organic cations are possible for this purpose. Although significant progress is made over years of intensive research, the determination of systematic relationships between the compositions and properties of halide perovskites is not exploited accordingly. Using the MAPbI_3 prototype, a wide range of compositions substituted by formamidinium (FA^+) and guanidinium (GA^+) cations are studied. From a detailed collection of experimental data and results reported in the literature, heat maps correlating the composition of $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ solid solutions with phase transition temperatures, dielectric permittivity, and activation energies are constructed. Considering the characteristics of organic cations, namely their sizes, dipole moments, and the number of N—H bonds, it is possible to interpret the heat maps as consequences of these characteristics. This work brings a systematization of how obtaining specific properties of halide perovskites might be possible by customizing the characteristics of the A-site organic cations.

Most of the compositional diversity of HPs comes from varying the A-site cations solid solutions, in particular of organic nature, such as methylammonium (MA^+), formamidinium (FA^+), guanidinium (GA^+), ethylammonium (EA^+), dimethylammonium (DMA^+), imidazolium (IM^+), and acetamidinium (AC^+).^[11–28] At present, essentially all top-efficiency HP-based materials and devices use at least one of these organic cations. The properties of common APbI_3 -based materials can be designed by fine-tuning the A-site composition using these organic cations, with formamidinium and guanidinium possibly the most studied and satisfactorily applied in devices. In general, compared to the prototype MAPbI_3 , compositions of the type $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ and $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ have lower transition temperatures between the tetragonal and cubic phases, mitigated ionic transport, higher charge carrier lifetimes, and greater stability against environmental agents. The highest perovskite solar cells (PCE) fabricated with HPs are based on FA^+ -containing compositions^[29] and using

GA^+ in HPs can effectively lead to defect passivation.^[30] Not surprisingly, MA^+ , FA^+ , and GA^+ triple cation perovskites were successfully applied in solar cells, leading to PCEs above 21% retaining at least 90% for more than 800 h.^[31,32] Differences in cation sizes and concepts of the physical chemistry of mixtures may explain these general trends. However, it was recently highlighted^[33] that some observed trends do not strictly follow general expectations using the mentioned cations. For example, although FA^+ is smaller than GA^+ , it was found that FA^+ is more efficient than GA^+ in reducing the tetragonality factor and stabilizing the cubic phase of the MAPbI_3 matrix, which is not what it could be predicted based on tolerance factors of the structures. Also, it was shown that the thermal stability of compositions containing only GA^+ could be lower than that of pure MAPbI_3 , even though arguments from the number of hydrogen bonds would suggest the opposite.^[29,30] From a broader perspective, these results demonstrate that understanding the characteristics of organic cations that lead to changes in the properties of the resulting HP demands greater attention. This same idea was highlighted recently, emphasizing a better understanding of the structure-interaction-property-performance-stability correlations conferred by A cations is still somewhat lacking.^[29] Currently,

1. Introduction

In the last decade, halide perovskites (HPs) became a consolidated group of materials progressively finding application in several optoelectronic devices.^[1–5] In solar energy conversion,^[6–8] a field in which HPs are known to probably have found their most prolific niche, certificated efficiencies close to or above 26% in solar cells using them as active layers have been consistently reported in recent years.^[9] This is mainly due to the enormous flexibility of synthesis routes, compositions, and structures obtained with these materials.^[10]

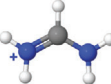
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DOI: 10.1002/sml.202305054

Table 1. Relevant characteristics of the A-site organic cations used in this work. Blue, grey, and white spheres represent nitrogen, carbon, and hydrogen, respectively. *From ref. [30] **Calculated values for APbI₃ compositions, with $r_{\text{Pb}} = 119$ pm and $r_{\text{I}} = 220$ pm.^[48]

Organic cation	Representation	Structure	r_{A} [pm] *	τ **	μ [D] *	n_{NH}
methylammonium	MA ⁺		217	0.912	2.17	3
formamidinium	FA ⁺		253	0.987	0.60	4
guanidinium	GA ⁺		278	1.039	0	6

A-site cation size, dipole moment, dynamic motion, and capability of forming hydrogen bonds, which relate to the number of N—H bonds, are among the most important characteristics under consideration when dealing with organic cations in HP.^[34–43] Still, a clear systematization of their correlations and effects in specific properties seems far from achieved. From our perspective, this is a consequence of the current literature mainly focusing on obtaining better devices. By doing so, a great deal of Information is collected regarding properties of applied importance, such as PCE, hysteresis index, fill factors, etc., using complex HPs compositions and where the additional layers must be considered. There is no doubt about the amazing technological development of HP-based devices over the past few years. Still, this pace may have compromised the non-empirical understanding of the underlying causes of the obtained properties. Taking inspiration from a recent perspective,^[44] if there is a relationship between A-site characteristics and the properties of HP, would it be possible to design a perfect combination of A-site cations for halide perovskites?

As a starting point to answer the question and to obtain a better visualization of the effect of different cations on the fundamental properties of halide perovskites, we report in the present work a systematic study on the physical properties of a broad set of $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ solid solutions. We constructed extensive maps that correlate A-site composition with phase transition temperatures, ionic transport activation energies, and dielectric permittivity from the reported data in the literature and additional obtained experimental results. The obtained results reinforce expected ionic transport activation energy trends and dielectric permittivity varying closely with the organic cation size and intrinsic dipole, respectively. However, the temperatures for orthorhombic $\rightarrow$ tetragonal $\rightarrow$ cubic phase transitions do not seem to correlate to one single A-site organic cations characteristic, revealing a much more complex scenario where various characteristics might be responsible for determining the stable crystal symmetry of HP solid solutions. This work consolidates a large set of scattered data in the literature on how FA⁺ and GA⁺ cations can affect the fundamental properties of HP solid solutions. It expands the property tuning of HP compositions based on MA⁺, FA⁺, and GA⁺ cations.

2. Results and Discussion

Initially, we make a brief description of the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system in terms of characteristics commonly associated with the A-site organic cations, namely their effective ionic radius (r_{A}), dipole moments (μ), and the number of N—H bonds (n_{NH}), summarized in **Table 1** for the cations used in the present work. From r_{A} , the well-known Goldschmidt tolerance factor can be calculated from its definition, given by $\tau = (r_{\text{A}} + r_{\text{X}})/\sqrt{2}(r_{\text{B}} + r_{\text{X}})$, where r_{B} and r_{X} are the effective ionic radius of B and X, respectively. In general, perovskites are expected to form when $0.8 < \tau < 1.0$, where values close to the lower and upper limits lead to tilted (orthorhombic and tetragonal) and cubic perovskites, respectively.^[34] Despite its limitations, especially for predicting the formability of perovskites from iodides,^[45] the Goldschmidt tolerance factor is still a valuable tool for first estimating perovskite forming compositions. In the case of MAPbI₃, FAPbI₃, and GAPbI₃, the experimentally observed room temperature structures are respectively tetragonal, cubic (but metastable)^[46] and 1D (non-perovskite),^[47] in accordance to τ -based predictions.

From the characteristics in **Table 1**, the molar ratio weighted values for the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system were calculated in the range of our interest in this work, with $0.0 \leq x + y \leq 0.3$. For a better visual inspection, the calculated r_{A} , τ , μ and n_{NH} values of solid solutions in the form of heat maps are shown in **Figure 1**. It is important to notice that all compositions are in the τ range from 0.91 to 0.95 and experimentally form perovskite structures, as observed in the literature^[13,16,25] and discussed in the following. Despite that, $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ compositions start segregating GAPbI₃ for $x \approx 0.25$ and above.^[16,21] Even though we did not test $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions with $x \geq 0.25$, we considered that the triple cation solid solutions would also form GAPbI₃ in this composition range of GA⁺ contents. Some possible consequences of μ and n_{NH} trends are discussed throughout the following paragraphs.

Before considering the properties of the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system, we should mention that one of the most important properties for optoelectronic applications of halide perovskites is their band gaps. In these materials, the band structure is formed mainly by ions in sites B and X, such as Pb²⁺ and I[−], which form the lower conduction and higher valence bands, respectively.^[49]

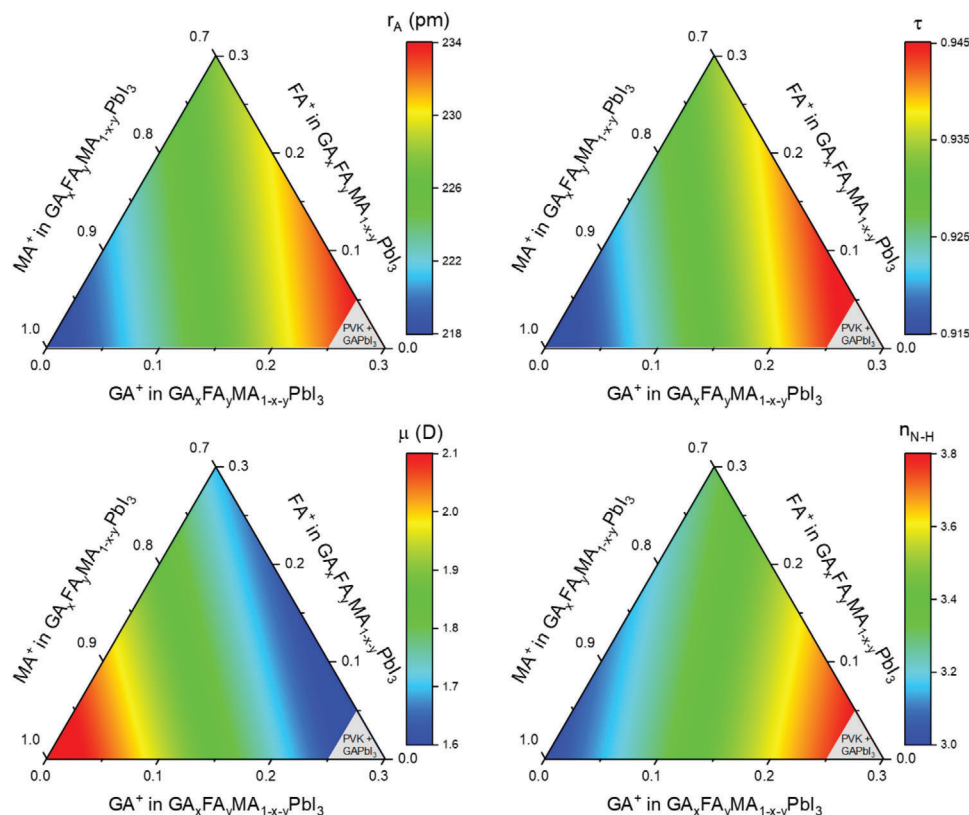


Figure 1. Heat maps for $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ properties regarding the A-site organic cation characteristics. Grey triangles are considered beyond the solubility limit of GA^+ at the perovskite (PVK) host lattice, which coexists with the non-perovskite GAPbI_3 secondary phase.

In this sense, for example, the replacement of Pb^{2+} by Sn^{2+} ^[50] and I^- by Br^- ^[51] are ways of significantly altering the band gaps of the materials. However, as the orbitals of A-site cations do not effectively form the band structure of halide perovskites, modifying these cations only indirectly affects these properties,^[49] often of little intensity. Partial substitution in systems formed by the three cations here results in very close bandgaps, with variations of less than 0.1 eV between different compositions.^[11,12,17,25] Thus, to maintain the focus on the properties that can be more significantly altered by changing the cations of A-site, we chose to reserve our discussion on other characteristics that, in a certain way, have been less explored in the literature.

Regarding other properties of halide perovskites, most of the data concerning $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions that can be found in the literature were obtained for the $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ and $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ systems and some information on $\text{GA}_x\text{FA}_x\text{MA}_{1-2x}\text{PbI}_3$. To have a better exploration of the intermediate triple cation compositions, we synthesized and characterized sixteen $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions along the $x = 2y$ (GA^+ -rich), $x = y$ and $y = 2x$ (FA^+ -rich) series. **Figure 2a** shows the X-ray diffraction patterns of the studied materials at different compositions, where the typical main peaks associated with perovskite phases are present at the regions of $\approx 14.0^\circ$, $28.0\text{--}29.0^\circ$, and $31.5\text{--}32.5^\circ$. No peaks related to secondary phases (GAPbI_3 at $\approx 11.0^\circ$ and PbI_2 at $\approx 12.5^\circ$) were observed, indicating that all compositions are pure perovskite phases. It is well known that MAPbI_3 is tetragonal (β phase) at room temperature and

transitions to cubic (α phase) approximately at 330 K.^[52] From the perspective of X-ray diffraction (XRD) patterns in **Figure 2a**, one of the features that can be used to distinguish tetragonal and cubic symmetries is if the peaks at these regions are single or multiple. For example, for the tetragonal symmetry (based on $I4cm$ space group), two peaks of (004) and (220) are encountered at the $28.0\text{--}29.0^\circ$ region, whereas for the cubic symmetry (based on $Pm\bar{3}m$ space group), a single peak of (200) reflection is present. Also, for the tetragonal symmetry, a small peak at $\approx 31.0^\circ$ related to the (213) planes can be identified, which is absent for the cubic symmetry. From the XRD patterns, it can be clearly seen that the compositions with lower substitution contents exhibit the typical tetragonal features, which progressively shift to the cubic features as the substitution degree increases. In this sense, substituting MA^+ by FA^+ and GA^+ stabilizes the cubic phase, as expected from results in similar systems,^[13,21,33] meaning that the temperature of tetragonal-to-cubic ($\beta \leftrightarrow \alpha$) phase transitions decreases.

To estimate the $\beta \leftrightarrow \alpha$ phase transition temperature of studied materials, the samples were characterized using the differential scanning calorimetry (DSC) technique. The results shown in **Figure 2b** corroborate the expected trend of decreasing $\beta \leftrightarrow \alpha$ transition temperature as the substitution content increases. Comparing the results shown in **Figure 2a,b**, we could state which compositions are tetragonal or cubic at room temperature (≈ 300 K). **Figure 2c** shows the lattice parameters, tetragonality factor, and cell volume as a function of the substitution

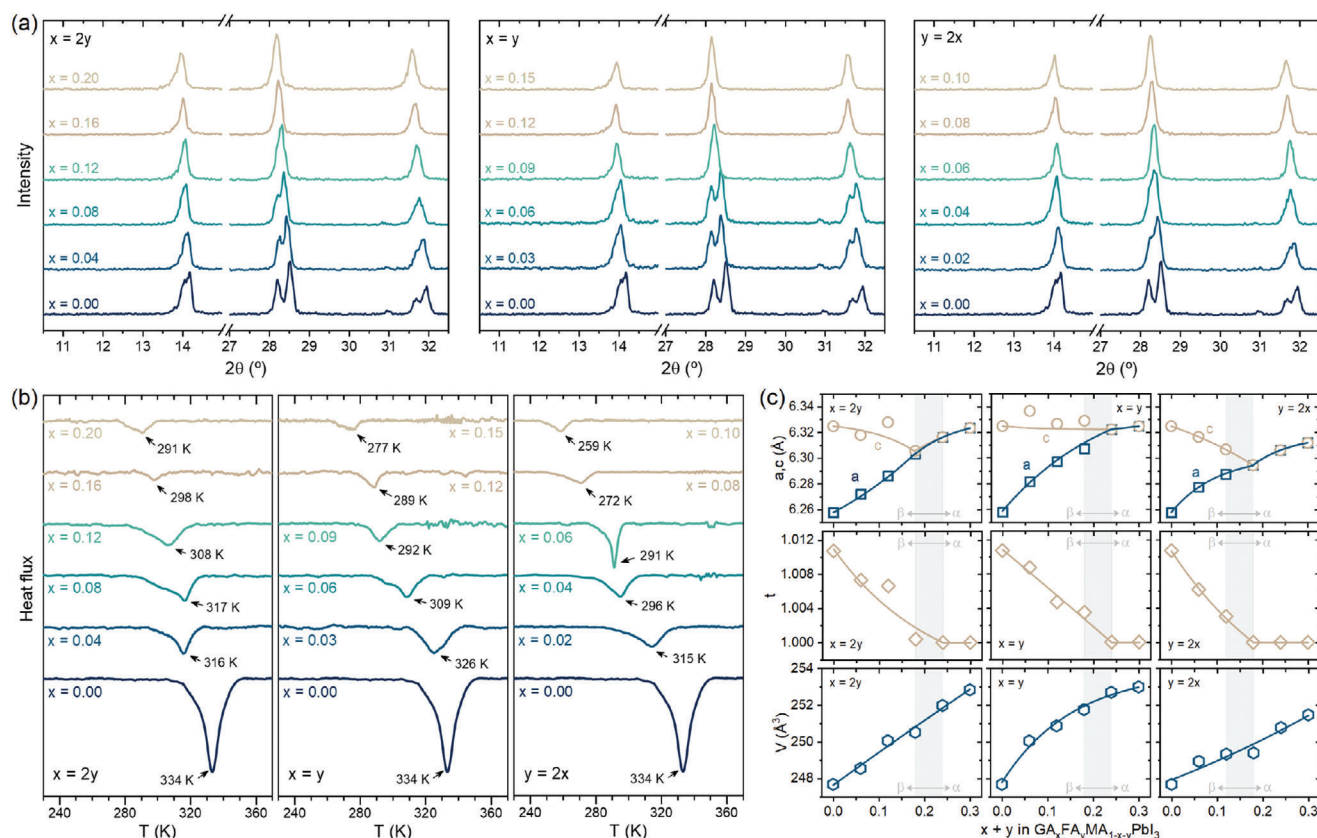


Figure 2. a) X-ray diffraction patterns of synthesized $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions. Only the 2θ ranges of main peaks are shown. b) DSC thermograms on heating of the studied compositions. c) Lattice parameters a and c , tetragonality factor $t = c/a$, and cell volume V as a function of the substitution degree. For the compositions of tetragonal symmetry (β range), the parameters shown were calculated using the relations $a = a'/\sqrt{2}$ and $c = c'/2$ of a pseudocubic representation, where a' and c' are the parameters obtained through the Le Bail fit of XRD data using the $I4cm$ space group. For the compositions of cubic symmetry (α range), the values were obtained directly through the Le Bail fit of XRD data using the $Pm\bar{3}m$ space group. Lines are guides to the eyes. In all graphs, MAPbI_3 ($x = 0.00$) data is repeated for better comparison.

degree, obtained from Le Bail fits (see Note S1, Supporting Information). For all series of compositions, there is a progressive increase in lattice parameter a and a decrease in lattice parameter c as the substitution degree increases, which translates into decreasing the tetragonality factor (t), as expected from the changes in $\beta \leftrightarrow \alpha$ transition temperatures. Naturally, cell volume (V) smoothly increases with the substitution degree due to both FA^+ and GA^+ cations being larger than MA^+ . It has to be mentioned that the lattice parameters change continuously with the replacement of MA^+ by FA^+ and GA^+ , showing that the formed materials are indeed solid solutions and that no solubility limit of the components was reached, corroborating the inexistence of secondary phases in XRD patterns and at scanning electron microscopy images (Note S2, Supporting Information).

An interesting feature regarding the changes in $\beta \leftrightarrow \alpha$ transition temperatures is that FA^+ -rich compositions seem more effective in stabilizing the cubic phases. The decrease in this transition temperature with an increasing degree of substitution appears steeper in the order FA^+ -rich > even FA^+/GA^+ > GA^+ -rich, which aligns with other results.^[33] To have a better perspective on this matter, we collected several $\beta \leftrightarrow \alpha$ transition temperatures of $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions from the literature (data organized in Note S3, Supporting Information), including

results obtained in the present work, and constructed a heat map to highlight the transition-composition trends in this system, as shown in Figure 3. The visual analysis points toward the same trend of $\beta \leftrightarrow \alpha$ transition temperatures decreasing with the substitution degree, with FA -rich compositions possessing the lowest in this system.

The cation size at the A site is one factor that most affects perovskites' stable symmetry. Small cation tends to be smaller than the cage formed between the PbI_6 octahedra in the perovskite matrix, causing their tilting and distorting the structure, commonly leading to orthorhombic or tetragonal symmetries. By introducing larger cations, the degree of distortion becomes smaller until eventually it reaches an optimal size, and the structure will have an undistorted, cubic symmetry. If the cations are larger than the cage, the octahedra cannot maintain 3D connectivity, and the material ceases to be a perovskite. This can be represented by the tolerance factor, as discussed earlier. In this sense, it would be expected that the degree of perovskite tilting is smaller the larger the size of the substituent cations, which in the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system occurs in compositions rich in GA^+ . As the tilting is lower, the temperature required to reach the cubic phase would tend to be lower in these compositions, which was not verified when comparing r_A and τ with the trends

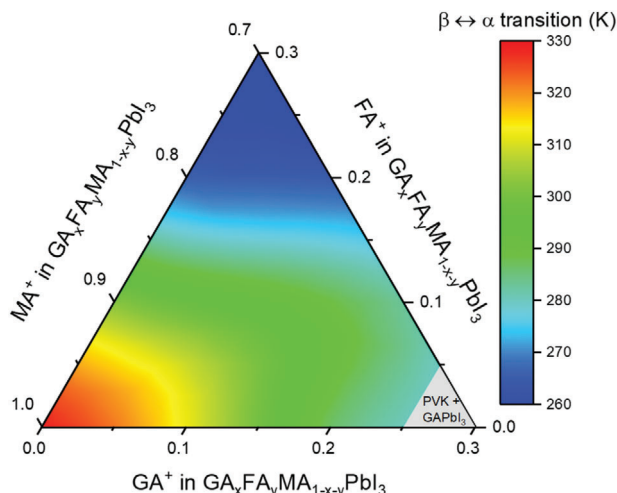


Figure 3. Composition map for tetragonal-to-cubic phase transition temperatures in the $GAXFAyMA_{1-x-y}PbI_3$ system. Note S3 (Supporting Information) includes all data.

of $\beta \leftrightarrow \alpha$ transition temperatures. There is abundant evidence of the importance of increasing entropic factors arriving from the mixing of A-site cations and cation dynamics in stabilizing the cubic phase of HPs.^[29,53–55] Knowing that GA^+ has more N–H bonds than FA^+ , it would be expected that GA^+ to form more hydrogen bonds with the iodide ions of the PbI_6 framework and be less free to rotate. Therefore, its contribution to the entropic stabilization of the cubic phase through orientational disorder will be less than the FA^+ cation, which has fewer N–H bonds and is possibly less restricted rotation. Noteworthy, FA^+ cations are reported to display much faster reorientation times than MA^+ ,^[56,57] which is possibly a positive entropy contribution to cubic phase stabilization. Also, GA^+ cations were reported to possess higher rotational times than FA^+ and MA^+ cations.^[58] Considering these ideas, FA^+ -rich compositions would display lower $\beta \leftrightarrow \alpha$ transition temperatures than the GA^+ -rich, as indeed observed. Hence, we hypothesize that the size effects of GA^+ cations on stabilizing the cubic phase are somewhat hindered by their high number of N–H bonds and a consequent capability of forming hydrogen bonds. Going further in this rationale, a large cation with fewer N–H bonds might be even more effective in stabilizing the cubic phase in solid solutions. This hypothesis is supported when we compare the compositions $FA_{0.10}MA_{0.90}PbI_3$ ($\beta \leftrightarrow \alpha$ at ≈ 300 K) and $GA_{0.10}MA_{0.90}PbI_3$ ($\beta \leftrightarrow \alpha$ at ≈ 310 K) with $DMA_{0.10}MA_{0.90}PbI_3$ ($\beta \leftrightarrow \alpha$ at ≈ 275 K)^[22] and $EA_{0.09}MA_{0.91}PbI_3$ ($\beta \leftrightarrow \alpha$ at ≈ 290 K),^[24] where DMA^+ ($r_A = 272$ pm and $n_{NH} = 2$) and EA^+ ($r_A = 274$ pm and $n_{NH} = 3$) are larger than FA^+ and almost the same sizes of GA^+ , but with less N–H bonds. Either way, it has to be mentioned that, in general, the highest material (defect formation energy, activation energy for ion migration, charge carrier lifetime) and device (power conversion efficiency, open-circuit voltage, short-circuit current) values are obtained in cubic perovskites,^[59] which makes cubic phase stabilization of particular interest for most applications. We conclude that FA^+ cations are more efficient than GA^+ cations in stabilizing the cubic phase, which is in line with FA -based compositions used in the most efficient HP solar cells.

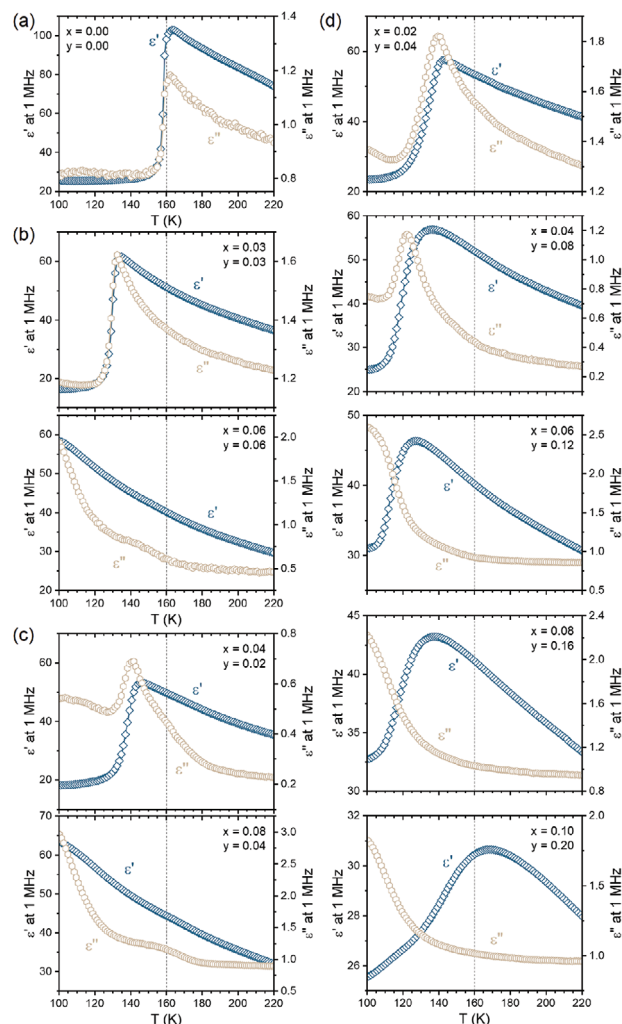


Figure 4. Real and imaginary dielectric permittivity, $\epsilon'(T)$ and $\epsilon''(T)$ respectively, at 1 MHz frequency as a function of temperature on heating for a) $MAPbI_3$, b) GA^+ -rich, c) $FA^+ = GA^+$, and d) FA^+ -rich compositions. The light dashed line is a reference temperature of the $\gamma \leftrightarrow \beta$ phase transition of pure $MAPbI_3$ for comparison.

Figure 4 shows the real and imaginary dielectric permittivity as a function of temperature on heating at 1 MHz frequency, $\epsilon'(T)$ and $\epsilon''(T)$ respectively, for $MAPbI_3$, GA^+ -rich, equal FA^+ and GA^+ amounts, and FA^+ -rich compositions. These characterizations were carried out to study the phase transitions at low temperatures. Note S4 (Supporting Information) includes a complete dielectric permittivity data set as a temperature function at frequencies ranging from 1 kHz to 1 MHz. In **Figure 4a**, the orthorhombic-tetragonal ($\gamma \leftrightarrow \beta$) phase transition observed for pure $MAPbI_3$ occurs at ≈ 160 K and is accompanied by an abrupt change in the peaks of the real dielectric permittivity $\epsilon'(T)$ and in the imaginary dielectric permittivity $\epsilon''(T)$.^[33,60] These results agree with those recently reported to describe the orthorhombic-tetragonal transition on heating for mixed organic cations HPs.^[14,33] For the GA^+ -rich composition series ($x = 2y$), the introduction of substituents causes a progressive drop in the transition temperature of the $\gamma \leftrightarrow \beta$ phase transition, as shown

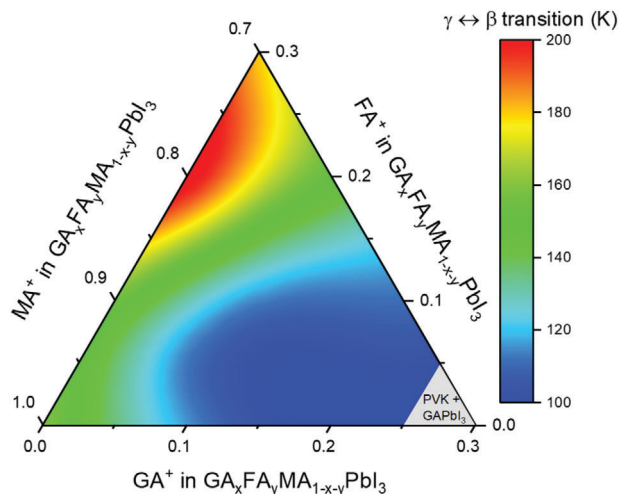


Figure 5. Composition map for low-temperature phase transition temperatures in the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system. The $\gamma \leftrightarrow \beta$ notation in the present case refers to the temperature where the tetragonal phase starts (on heating) or ceases (on cooling) to be the single phase in equilibrium. The complete data used to construct this map is provided in Note S5 (Supporting Information).

in Figure 2b, so that in $x = 0.08$, $y = 0.04$ the tetragonal phase seems to remain stable even below 100 K. Figure 4c shows the same behavior occurring in the $\text{FA}^+ = \text{GA}^+$ series ($x = y$), in which it is observed that in $x = 0.06$, $y = 0.06$ the tetragonal phase also seems to be maintained even below 100 K. These results are in agreement with what was observed in compositions of the type $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$, where a point of maxima at $\epsilon'(T)$ is already shifted down 100 K in $x = 0.10$.^[33] However, for the FA^+ -rich series ($y = 2x$), the drop in the $\epsilon'(T)$ peak in Figure 4d around the phase transition is much less intense when compared with the other series. In none of these compositions was there stabilization of the tetragonal phase below 100 K, and in addition, it is noted that between the compositions $x = 0.06$, $y = 0.12$ and $x = 0.08$, $y = 0.16$, there is a relative increase in the maximum temperature of $\epsilon'(T)$, which grows even more with increasing degree of substitution. Also, attention is drawn to the fact that the peaks of which the maximum points of $\epsilon'(T)$, and $\epsilon''(T)$, are consistently separated from each other and the change of $\epsilon'(T)$ with temperature becomes more and more broadened. Both observations are probably related to the coexistence of the orthorhombic and tetragonal phases in a certain range of temperatures or the existence of intermediate phases between these two, as observed in the $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ system, depending on the degree of substitution.^[14] The increase in the transition temperature after a certain degree of substitution is also observed in this system.^[14,15]

Considering the results shown in Figure 4, there seems to be a trend that compositions containing high GA^+ contents are more efficient in stabilizing the tetragonal phase at low temperatures than those rich in FA^+ , in agreement with previous results.^[33] This corroborates the previously found tendency that GA^+ is less efficient in stabilizing the cubic phases than FA^+ , which implies that GA^+ stabilizes the tetragonal phase more than FA^+ at high temperatures. To better visualize these trends, we constructed in Figure 5 a heat map of the $\gamma \leftrightarrow \beta$ transition temperature using the data organized in Note S5 (Supporting Information). Unfortunately,

we could not access the transition temperatures below 100 K. Moreover, data on transitions of this nature in compositions containing guanidinium are somewhat scarce in the literature, preventing us from getting more details on how changes in compositions containing high levels of GA^+ affect phase transitions at low temperatures. Having that said, the observed trends are quite clear in showing that FA^+ -rich and GA^+ -rich compositions, a priori, have essentially opposite behaviors.

Low-temperature phase transition between orthorhombic and tetragonal phases in MAPbI_3 is known to be an order–disorder transition,^[24,61,62] where nearly free-to-rotate MA^+ cations at the tetragonal phase undergo cooperative ordering at orthorhombic phase. In this scenario, several different and connected effects play a role, including steric hindrance of rotational motion, dipole–dipole interactions, hydrogen bonds, and inorganic cage deformation.^[35,56,63] Due to this intricate scenario, a generalization of what A-site cation properties are effectively responsible for the observed differences between FA^+ and GA^+ cations is not feasible with existing data. Considering that these cations are under the same trend of r_A , μ and n_{NH} changes, we would expect effects at different intensities, but not opposite effects. It is also peculiar that the $\text{EA}_x\text{MA}_{1-x}\text{PbI}_3$ system show $\gamma \leftrightarrow \beta$ transition temperatures above 120 K for x values up to 0.21,^[24] which indicate a severely less intense effect of EA^+ cations in tetragonal phase stabilization when compared to GA^+ cations, even though their sizes are almost the same. To explain these differences, the number of N–H bonds and especially their dipole (apolar GA^+ versus 4.49 D for EA^+ ^[30]) differences must also play an important role. All that said, current information points to a scenario where the effects of substituting cations in MA^+ dynamics changing is important, as the dynamics of these cations themselves.

In the context of real dielectric permittivity, the values close to room temperature are of scientific and technological importance due to their possible relation with charge carrier stabilization and mobility, thereby affecting the functioning of HP devices. Figure 6 shows the frequency dependence of ϵ' at 300 K of studied $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ materials. Complete data at different temperatures are given in Note S6 (Supporting Information).

Under a given frequency and temperature, the ϵ' value represents the sum of different polarization mechanisms, generally due to space charge, dipolar, ionic, and electronic contributions. In HPs, the main contributions to ϵ' arise from the polarization due to mobile ionic charge carriers, the orientation of intrinsic organic cation dipoles, PbI_6 off-center distortion, and displacement of electron clouds.^[64] For pure MAPbI_3 , an experimental value of ϵ' at 1 MHz of ≈ 50 is commonly found,^[60,61] although individual contributions are relatively dispersed in ranges of values.^[64] Either way, for all compositions, increasing frequency causes a decrease in ϵ' values, which is the expected behavior due to inhibition of mobile ions space charge polarization with low relaxation frequencies. When comparing the compositions along the studied series at high frequencies, there is a clear trend of ϵ' decreasing with the substitution degree. Considering that all these compositions are made of the same elements and built with the same PbI_6 inorganic framework, we can rule out that changes in PbI_6 off-center distortion and displacement of electron clouds are among the main reasons behind this trend. Consequently, the reduced ϵ' values with substitution content can only be explained based on the contributions of the orientation of A-site

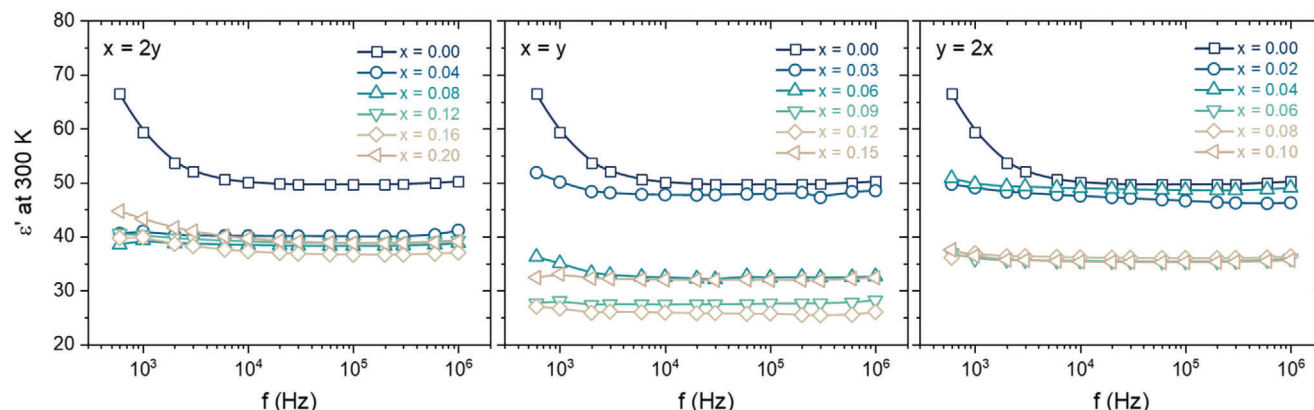


Figure 6. Frequency-dependence of the real dielectric permittivity at 300 K of the studied $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions.

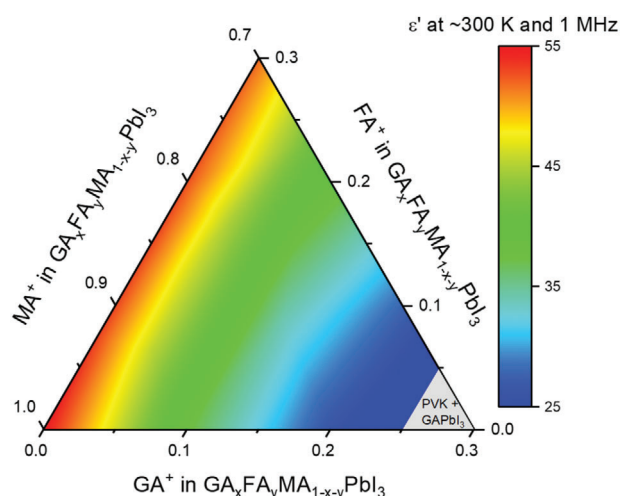


Figure 7. Composition map for the real dielectric permittivity at 1 MHz and 300 K. The data used to construct the heat map is given in Note S7 (Supporting Information).

organic cation dipoles to the material's polarization. This follows the general expectations as both GA^+ and FA^+ cations have lower dipole moments than MA^+ cations, thus diminishing the contributions of this type of polarization. For GA^+ -rich compositions, a substitution content of only $x + y = 0.06$ is enough to cause a steep ϵ' reduction. For $\text{FA}^+ = \text{GA}^+$ compositions, a considerable ϵ' reduction is only obtained for $x + y = 0.12$. On the other hand, the ϵ' drop for FA^+ -rich compositions occurs only after reaching a substitution content of $x + y = 0.18$. This trend suggests that GA^+ cations are more effective in reducing the permittivity of HP than FA^+ cations. This is possibly a direct consequence of GA^+ cations having lower dipole moments than FA^+ cations. For a broader perspective on this topic, **Figure 7** shows a constructed heat map summarizing the composition dependence of dielectric permittivity ϵ' at 1 MHz and 300 K temperature. Note S7 (Supporting Information) presents the summary of the data used to construct this map.

The dependence of ϵ' on the composition in the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system emphasizes the downward trend in GA^+ -rich compositions, as expected by the dipole moment

values of the cations. Despite the agreement, in comparison to GA^+ -rich compositions, there also seems to be a tendency that in FA^+ -rich ones, this reduction in ϵ' is very small, if any, considering that the dipole moment of FA^+ is quite low. In terms, it is possible that not only the value of the dipole moments of the cations in question but other factors are also involved. Using Debye's theory for the contribution of free-to-rotate dipoles to ϵ' ,^[14,65] it can be argued that not only the values of the dipoles but also the dynamics and density of dipoles are relevant to understanding the behavior of the permittivity. Given this, it must also be weighed that GA^+ cations are larger than FA^+ cations and, therefore, must cause some restriction to the rotation of MA^+ dipoles in neighboring cells and, consequently, the contribution of MA^+ itself to ϵ' should decrease. Note that in the $\text{EA}_x\text{MA}_{1-x}\text{PbI}_3$ system, there is initially an increase of ϵ' with x , possibly due to the fact that the EA^+ cation dipoles are quite large. However, at higher concentrations, the value of ϵ' starts to decrease possibly due to the hindering of MA^+ dynamics,^[24] corroborating with the possible restriction effect caused by GA^+ . Overall, the trends obtained suggest that the dipoles of substituting cations play a major role in explaining how ϵ' is affected by them, but secondary effects arising from the dynamics of the present cations have also to be considered, where the size of cations is possibly the most relevant parameter.

The last property under study is ionic transport, particularly the activation energies for such. Mobile ions in HPs are well known to be linked with operational instability in devices and degradation processes, making this topic of great importance. **Figure 8** shows the Arrhenius plots of ion conductivity and respective activation energies of the studied $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions. The used data and calculation details are given in Note S8 (Supporting Information).

The first important observation is the trend of conductivity values decreasing with the substitution content in all series of compositions. This is the expected behavior and can be attributed to the decrease of point defect density due to stabilization via entropy of mixing. In turn, the extent to which temperature affects conductivity is quantified by the activation energy, which relates to the energy barrier of ion/defect motion in a jump process between two positions of local potential minima. The obtained activation energies are all in the range usually attributed to the transport of iodide ions/vacancies.^[66] We also note that the

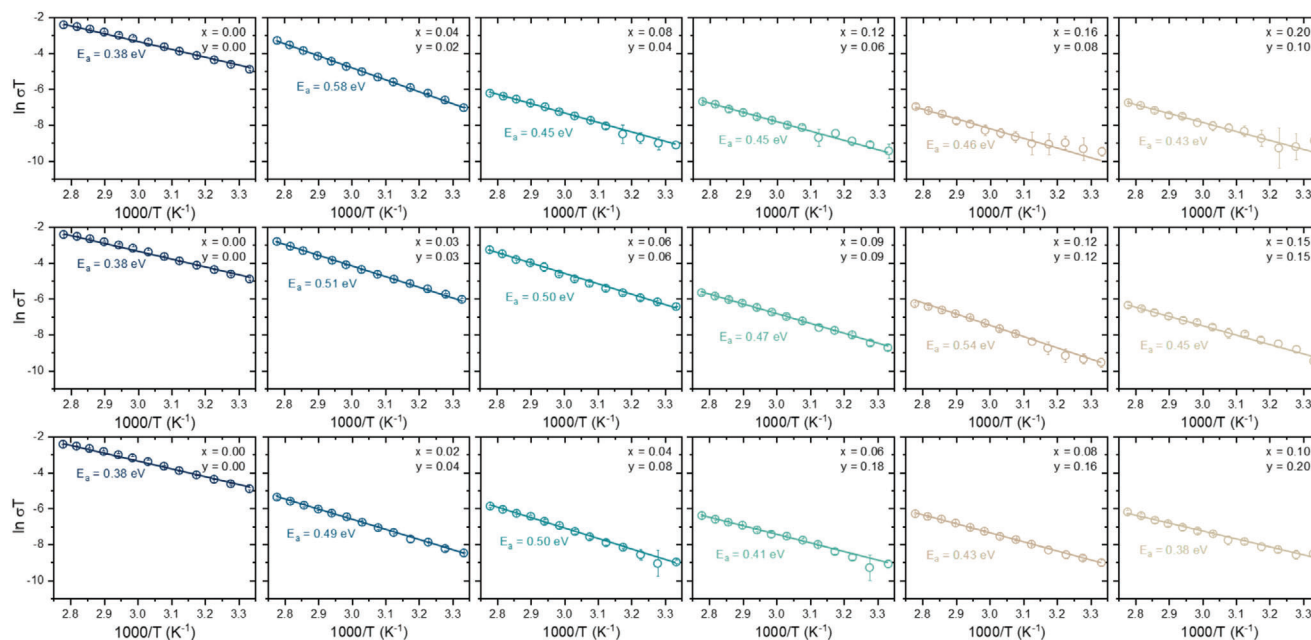


Figure 8. Arrhenius plots of conductivity of the different studied $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions. Lines are theoretical fits, and numbers are the calculated activation energies of each composition.

activation energies in all mixed compositions are higher than in pure MAPbI_3 , which is again the expected result as both FA^+ and GA^+ cations are larger than MA^+ .^[67] The results do not allow us to differentiate how FA^+ and GA^+ cations affect the activation energies. Ion transport may depend on several features, such as the crystal structure, local strains, migration path anisotropy, and whether the conduction occurs in grains or grain boundaries. In this sense, establishing trends in how compositions affect activation energies depends on a large amount of data to balance these different effects. Fortunately, plenty of activation energy values are available in the literature on compositions within the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system, many of which are organized in Note S9 (Supporting Information). A heat map constructed from these data is shown in **Figure 9**.

The dependence of activation energies on the composition suggests a trend of GA^+ being more effective than FA^+ in increasing the values of activation energies. This is the expected result when considering other results in the literature.^[33,67] It was proposed that GA^+ cations induce structural changes leading to a curved diffusion path that is bowed out of the Pb/I plane.^[67] Hence, larger cations should intensify this structural change, leading to higher activation energies. Eventually, considering hydrogen bonds of organic cations with iodide ions as indicative of structural integrity, one may expect these iodide ions to be more restricted in their crystal positions, which would act as an additional factor of activation energy increase. In any case, the size of the cations and the number of N-H bonds would favor GA^+ as more effective in raising the activation energy of the solid solutions under study.

The body of our results, altogether with existing literature data, suggests some property-composition correlations that can be explained fairly well by the characteristics of A-site organic cations. **Table 2** summarizes the main findings.

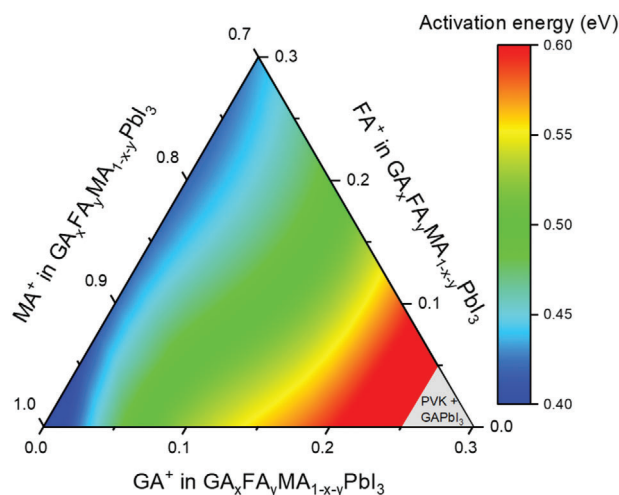


Figure 9. Composition map for ionic transport activation energies of the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system. The data used to construct the heat map are shown in Note S9 (Supporting Information).

Despite the possible advances in systematizing current data, some potential limitations must be mentioned. First, given the lack of similar data, the construction of heat maps was only possible using results collected with different experimental/theoretical approaches and conditions, which is inevitably a source of differences. For example, to study the tetragonal-cubic phase transition, we used data obtained under both heating and cooling experiments, where thermal hysteresis effects provoke the temperature measured to be different. Second, additional differences can be introduced if materials are studied in thin films or bulk single/polycrystals. The differences in ion

Table 2. Possible effects of A-site characteristics on some properties of hybrid halide perovskites solid solutions.

Property	Effect of substituent A-site characteristic
$\beta \leftrightarrow \alpha$ transition	Temperature decreases with cation size and increases with the number of N—H bonds
$\gamma \leftrightarrow \beta$ transition	An intricate combination of cation sizes, dipoles, and number of N—H bonds; more data is needed to isolate possible variables
Dielectric permittivity	Decreases with decreasing cation dipole and increasing cation size
Activation energy	Increases with cation size; may be intensified by the number of N—H bonds

conductivity and activation energies in grains and grain boundaries should be considered when dealing with single and polycrystals. In addition, effects arising from strains in thin films can make their properties different from their bulk polycrystalline analogs. Third, a question is pertinent: are the simple molar ratio weighted values good descriptors? This has been a standard way of calculation for the effective ionic radius, but as far as we know, this or any other averaging method was never employed for HPs. Also, additional studies may be an effective strategy, including other potential descriptors, such as the globularity of organic cations, number of double bonds, partial charges at nitrogen atoms, etc. We should also mention that although there is much discussion about the relevance of hydrogen bonds in the properties of halide perovskites, there is also a contrary position suggesting that these bonds do not even exist in these materials.^[68] Finally, our approach to correlate the characteristics of A-site cations with the properties of resulting HPs solid solutions is heavily descriptive and qualitative, which may not be optimal. However, we tried to employ principal component analyses to obtain quantitative relations. Even though the results were mathematically interesting, they were not physically representative since r_A , μ and n_{NH} are directly related to the group of cations used in our work (the higher r_A , the higher is n_{NH} and the lower is μ). For a better picture of any relations, a broader set of A-site organic cations should be used to have these characteristics more “independent” from each other. In this matter, cations such as trimethylsulfonium ($r_A = 244$ pm, $\mu = 1.08$ D and $n_{NH} = 0$), imidazolium ($r_A = 258$ pm, $\mu = 1.99$ D and $n_{NH} = 2$), dimethylammonium ($r_A = 272$ pm, $\mu = 1.93$ D and $n_{NH} = 2$), and ethylammonium ($r_A = 274$ pm, $\mu = 4.97$ D and $n_{NH} = 3$) might be good candidates. Using fluorinated molecules may also be interesting to change μ keeping n_{NH} constant without appreciably changing r_A , even though additional interactions may be introduced,^[69] making the scenario even more complicated. In summary, the study presents a broad view of composition-property relations in HPs, giving reasonable interpretations, insights, and trends of a complex and promising system, considering a robust set of physical properties obtained in the present work and those reported in the literature.

3. Conclusion

From an extensive experimental characterization of a robust set of samples and analysis of the available data in the literature for the GA^+/FA^+ -substituted $MAPbI_3$ -based system, we were able to obtain composition-property maps and insights into the correlations with the characteristics of substituent A-site organic cations. A qualitative description of results suggests that the tem-

perature of the tetragonal-cubic phase transition is reduced with increasing cation size. However, this effect is possibly hindered when the number of N—H bonds, the capability of forming hydrogen bonds, is high, making FA^+ cations more effective in reducing this temperature than GA^+ . Regarding the orthorhombic-tetragonal phase transition, it was found that GA^+ cations tend to reduce the phase transition temperature, whereas FA^+ cations decrease it slightly but then increase it at high substitution contents. For these reasons, making clear correlations based on existing data was impossible. Due to the lower electric dipole and larger size, the dielectric permittivity decreases more with GA^+ than with FA^+ substitution. Finally, GA^+ cations are also more effective than FA^+ in increasing activation energies, possibly due to the larger size and number of N—H bonds. These results consolidate a conceptual base for designing compositions in halide perovskites with organic cations.

4. Experimental Section

Sample Synthesis: To synthesize $GA_xFA_yMA_{1-x-y}PbI_3$ ($0 \leq x + y \leq 0.3$, for $x = 2y$, $x = y$ and $y = 2x$) samples, initially, amounts of the precursors lead iodide (PbI_2 , Sigma-Aldrich, 99%), methylammonium iodide (CH_3NH_3I or MAI, Sigma-Aldrich, 98%), formamidine iodide ($CH(NH_2)_2I$ or FAI, Sigma-Aldrich, 99%), and guanidinium iodide ($C(NH_2)_3I$ or GAI, Sigma-Aldrich, 99%) were weighted in desired proportions (see Note S10, Supporting Information). The precursors were manually mixed and ground to react in a natural agate mortar for about one hour under ambient conditions in a controlled temperature room (≈ 298 K) and relative humidity below 30%. The resulting black powders of perovskites were sieved in a 250 μm aperture sieve (60 mesh), dried, and annealed for 6 h at 333 K in a laboratory oven with periodic (once an hour) stirring. Powders were stored in PVC film-sealed hermetic amber glass flasks kept in a desiccator, filled with silica gel granules, and covered with black opaque plastic foils. Pelletized powders were produced with ≈ 180 mg of the powders uniformly spread into a 10 mm diameter circular cavity of a metallic mold and compacted with a pressure of ≈ 250 MPa. Last, the pellets were sintered in an electric furnace at 393 K for 2 h and slowly cooled to room temperature inside the electric furnace. Several pellets of each composition were synthesized and used in the following procedures. Exemplary samples are shown in Note S11 (Supporting Information).

Characterizations: The crystalline structure of the materials was characterized by XRD using a Rigaku Ultima IV diffractometer with CuK_α radiation ($\lambda = 1.5406$ Å) at ≈ 295 K, under 40 kV and 20 mA, with a continuous scan (2° min^{-1}), in the range of 2θ from 10 to 50° under controlled conditions (dark, at ≈ 300 K and relative humidity below 30%). DSC measurements were performed in DSC 25 TA Instruments from 183 to 373 K with a 5 K min^{-1} heating rate, under a nitrogen atmosphere, using ≈ 10 to 15 mg of pellet fragments in aluminum crucibles. For electrical measurements, a matrix of 8×8 circular gold electrodes of ≈ 0.6 mm diameter was sputtered on top of the perovskite pellets using a shadow mask, while a bottom gold electrode was deposited over the entire sample surface. Impedance

spectroscopy measurements were performed in a Displex ARS CSW-202 closed system using an Agilent 4284A LCR meter to measure the conductance (G) and susceptance (B) in the frequency range of 6.10^2 to 10^6 Hz. Data were collected on heating regimes under a temperature rate of 1 K min^{-1} from 100 to 220 K range and 0.3 K min^{-1} from 300 to 360 K range. All electrical measurements were carried out in vacuum and dark conditions to avoid external effects using a closed Displex ARS CSW-202 system. Several electrodes were tested before starting the experiment, and impedance spectra were collected to ensure choosing a representative electrode of the overall sample's electrical characteristics. The microstructure images of the samples were obtained in a Zeiss EVO LS15 scanning electron microscope (SEM), with a tungsten beam operating in the voltage range between 10 and 20 kV, by secondary electron analysis (SE mode).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP (Project: 2017/13769-1), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, CAPES (CAPES-PRINT Project: 88881.310513/2018-01). The first author was granted CAPES (Finance Code 001) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (151319/2023-5). The authors would like to thank Mr. Elton José de Souza for support with SEM measurements, Mr. José Luiz Vilches for support with DSC measurements and Dr. Andressa Oliveira de Lima for performing the principal component analysis.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

F.B.M. dealt with the conceptualization, methodology, investigation, writing-original draft, writing-review, and editing. R.M.S. dealt with the investigation, writing-review, and editing. E.B.A. did the conceptualization, methodology, investigation, writing-review, editing, and project administration.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

activation energies, formamidinium, guanidinium, halide perovskites, methylammonium, permittivity, phase transitions

Received: June 15, 2023
Revised: September 21, 2023
Published online:

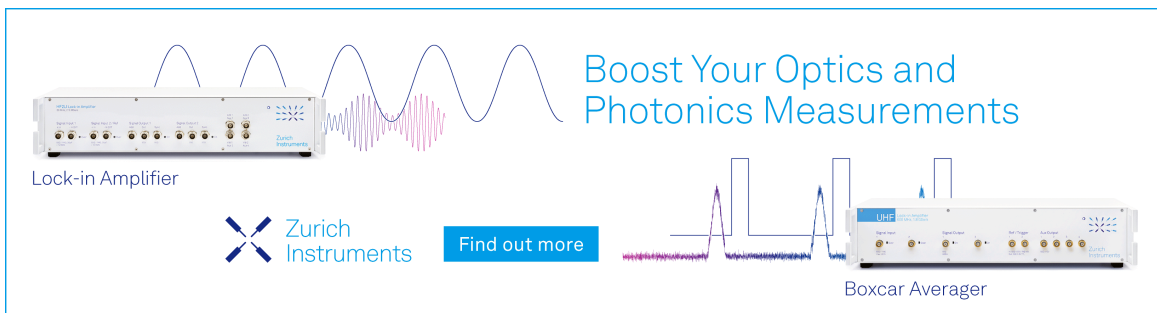
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Interplay between cation composition and charge transport characteristics in $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ halide perovskites

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Cite as: Appl. Phys. Lett. **124**, 153901 (2024); doi: [10.1063/5.0200610](https://doi.org/10.1063/5.0200610)

Submitted: 27 January 2024 · Accepted: 31 March 2024 ·

Published Online: 9 April 2024



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ABSTRACT

Halide perovskites (HPs) are a well-known class of mixed electronic and ionic conductors with diverse applications in optoelectronic devices. The simultaneous transport of ionic and electronic carriers has beneficial and detrimental effects depending on the intended applications. There is an extensive understanding of the charge transport characteristics in HPs since the phenomenon is of applied relevance. However, considering that several applications use compositions containing mixed cations, a deeper understanding of how the degree of substitution and the characteristics of the substituent cations affect the charge transport characteristics is needed. To this end, we experimentally studied the ionic conductivity (σ_{ion}), current–voltage hysteresis (J – E hysteresis), mobility (μ_e) and density (n_e) of electronic carriers, and bandgap energies (E_g) of up to 24 compositions of methylammonium lead iodide partially substituted with guanidinium and formamidinium. The results indicate that σ_{ion} , J – E hysteresis, and μ_e decrease with the degree of substitution, with the J – E hysteresis being smaller the larger size of the substituent cation. At the same time, σ_{ion} appears to be lower in compositions with equimolar substituents, in which the entropy of mixing is maximum. On the other hand, a slight increase in n_e was observed with the substitution degree, showing highest values for FA^+ -rich compositions, where E_g is the lowest. The results advance the understanding of how it is possible to customize charge transport properties through the rational design of compositions in HPs.

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The mixed component formulation is one engineering strategy to design the properties of halide perovskites, which emerged as a promising class of semiconductor materials for third-generation photovoltaic devices.^{1–3} One of the main ways of design compositions comes from the partial substitution of cations in the A-site of perovskites with formula ABX_3 (mainly $\text{B} = \text{Pb}^{2+}$, Sn^{2+} , and $\text{X} = \text{I}^-$, Br^- , Cl^-).^{4,5} Among the A-site cations, methylammonium (MA^+), formamidinium (FA^+), and cesium (Cs^+) are mainly used in solid solutions with each other and with other cations, such as guanidinium (GA^+), ethylammonium (EA^+), and dimethylammonium (DMA^+).⁴ In photovoltaic devices, most of the current top efficiency halide perovskite solar cells, as of now at certified efficiencies of 26.1%,⁶ make use of mixed A-site compositions.^{7,8} It is widely recognized that these materials have mobile ions that can participate in charge transport, leading to not only diverse detrimental effects, such as operational instabilities, hysteresis, and degradation, but also new applied perspectives.⁹ As mixed electronic and ionic conductors, understanding compositional effects

on transport relative to different charge carriers is challenging. Although it is recognized that the formulation of mixed cation systems is an efficient way to mitigate ion transport,¹⁰ the effects of different organic cations and how their characteristics affect the relative transport of charge carriers remain without being studied in detail.

Although several works on charge transport characteristics involving mixed-cation hybrid perovskites and their effects have been conducted recently,^{11–16} the literature has not yet reported systematic studies in a broader chemical space or on more ionic and electronic transport parameters. The present work conducted meticulous research on a series of different compositions of triple-cation $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system to map their physical properties as a function of cation substitution. For this purpose, impedance spectroscopy, current–voltage, and UV-Vis diffuse reflectance data were collected in up to 24 compositions, which, together with literature data, were used to obtain composition-charge transport property maps and correlate and understand how the charge transport characteristics,

namely, the ionic conductivity, current–voltage hysteresis, electronic charge carrier mobility, carrier density, and bandgap energies in halide perovskites are affected by the substitution degree and properties of substituting GA^+ and FA^+ cations.

The compositions of the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system studied in the present work were prepared from a mechanochemical route, as reported in our previous publication.¹¹ In addition to the first set of samples prepared previously ($0 \leq x + y \leq 0.3$, with $x = y$, $x = 2y$, and $y = 2x$), $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ ($x = 0.04, 0.08, 0.15$, and 0.20) and $\text{FA}_y\text{MA}_{1-y}\text{PbI}_3$ ($y = 0.05, 0.15, 0.20$, and 0.30) compositions were also prepared to the present study.

For the sample preparation, the precursors lead iodide (PbI_2 , Sigma-Aldrich, 99%), methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$ or MAI, Sigma-Aldrich, 98%), formamidinium iodide [$\text{CH}(\text{NH}_2)_2\text{I}$ or FAI, Sigma-Aldrich, 99%], and guanidinium iodide [$\text{C}(\text{NH}_2)_3\text{I}$ or GAI, Sigma-Aldrich, 99%] were weighed in the appropriate proportions. The precursors were manually mixed and ground to react in a natural agate mortar for about one hour under ambient conditions in a controlled temperature room ($\sim 25^\circ\text{C}$) and relative humidity below 30%. The resulting black powders of perovskites were sieved in a $250\text{ }\mu\text{m}$ aperture sieve (60 mesh), dried, and annealed for 6 h at $\sim 60^\circ\text{C}$ in a laboratory oven with periodic (once an hour) stirring. Pelletized powders were produced with approximately 150 mg of the powders uniformly spread into a 10 mm diameter circular cavity of a metallic mold and compacted with a pressure of about 250 MPa. Finally, the pellets were sintered in an electric furnace at 120°C for 2 h and slowly cooled to room temperature inside the electric furnace. The obtained pellets in the first set of samples can be visualized in supplementary material Note 11 of the reported early article.¹¹ All additional samples show the same visual aspect.

X-ray diffraction and scanning electron microscopy were used for the structural and microstructural characterizations, respectively. These results were summarized in supplementary material Note 1. For electrical measurements, gold electrodes of about 0.6 mm diameter (supplementary material Note 2) were sputtered on top of the perovskite pellets, while a bottom gold electrode was deposited over the entire sample surface. Impedance spectroscopy (IS) measurements were performed in an Agilent 4284A LCR meter coupled to a Displex ARS CSW-202 closed system to measure the conductance and susceptibility in the frequency range of 5×10^2 – 10^6 Hz. All data were collected at $\sim 27^\circ\text{C}$. All electrical measurements were carried out in a vacuum and dark to avoid external effects using a closed Displex ARS CSW-202 system. Steady-state current–voltage (I – V) data were collected using a Keithley 6517B electrometer under controlled conditions. Cycles of up (-6 to $+6$ V) and down ($+6$ to -6 V) measurements were performed with a 0.1 V s^{-1} scan rate. Forward measurements were performed from 0 to $+30$ V with a scan rate of 0.5 V s^{-1} . Up to six electrical measurements were performed on each sample to ensure the reproducibility. UV-Vis diffuse reflectance spectroscopy data were collected on a Shimadzu UV-2600 spectrophotometer, from 200 to 1100 nm, using the slow speed mode with a 1 nm data interval.

The ionic conductivity (σ_{ion}) of studied materials was evaluated using impedance spectroscopy measurements, given that electrical response in halide perovskites studied through IS experiments is dominated by the transport of ions,^{17,18} even more so when measurements are performed in the dark.¹⁹ In the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system, the temperature-dependent conductivity results obtained through IS were shown to follow a $\sigma T = \sigma_0 \exp(-E_a/RT)$ behavior, with activation

energies (E_a) of the order of 0.4–0.6 eV, both expectedly attributed to the transport of ions.¹¹ The details to obtain σ_{ion} are given in supplementary material Note 3. Figure 1 shows an ion conductivity map summarizing the obtained results. In MAPbI_3 -based perovskites, ionic conduction occurs mainly through the migration of I^- vacancies (V_{I}^-).²⁰ In this sense, the ionic conductivity can be expressed by $\sigma_{\text{ion}} = qn_{\text{ion}}\mu_{\text{ion}}$, where n_{ion} and μ_{ion} are, respectively, the density and mobility of mobile iodide ions (vacancies), and q is the elementary charge. Therefore, in general, the lower the V_{I}^- concentration, the lower the σ_{ion} in MAPbI_3 -based perovskites. The partial substitution of MA^+ by other cations causes an increase in entropy of mixing and configurational entropy, which should reduce the concentration of defects associated with ionic transport. Consequently, this entropic stabilization decreases ionic conduction, as pure MAPbI_3 has the highest values among the studied compositions. Furthermore, it is commonly noted that activation energies for ionic transport increase with the difference in size between the host ion and the substituent, so GA^+ substituted compositions display higher activation energies than FA^+ -substituted.^{11,12,21} This is due to the greater lattice distortion caused by GA^+ (278 pm), larger than FA^+ (253 pm) and MA^+ (217 pm),²² which effectively decreases ionic mobility, given by the Nernst-Einstein relation, $\mu_{\text{ion}} = qD_{\text{ion}}/k_B T$, where k_B is the Boltzmann constant, T is the temperature, and D_{ion} is the ion diffusivity coefficient, expressed by $D_{\text{ion}} = D_0 \exp(-E_a/k_B T)$, where D_0 is a constant. Despite this, the visual comparison of σ_{ion} in FA-rich and GA-rich compositions in the diagram in Fig. 1 is rather difficult. However, it is clear that the lowest σ_{ion} appears to be those of triple cations, in particular those close to equimolar substituent compositions. In fact, for a given substitution content, the compositions with an equimolar degree of substituting cations possess the highest entropy of mixing, which stabilizes the crystal and possibly provokes the density of point defects to be smaller, thus leading to the lowest σ_{ion} . Hence, the effect of decreasing the concentration of defects seems to be mainly responsible for the drop in σ_{ion} in relation to pure MAPbI_3 .

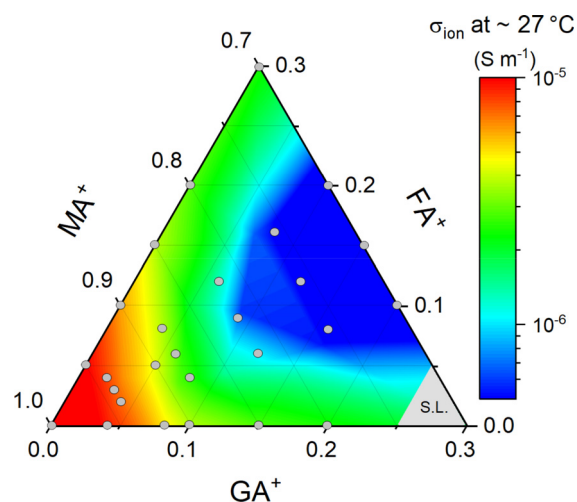


FIG. 1. Ion conductivity map for the studied triple-cation $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system. The data used to compose this map are given in supplementary material Note 4. Dots denote the compositions used to construct the map. The S.L. triangle denotes the region of compositions above the solubility limit of this system.²³

One of the main consequences attributed to ion transport in halide perovskites materials and devices is the well-known I - V hysteresis, which may lead to operational instabilities and degradation.⁹ Hence, inhibiting I - V hysteresis is highly desirable. To this end, we evaluated the power losses per volume unit (J - E hysteresis, where J is the current density and E is the applied electric field, given by $E = V/L$, where V is the applied voltage and L is the distance between electrodes, i.e., the sample thickness) in one cycle by measuring the differences between the current-voltage curves in up and down regimes using a slow scan rate (0.1 V s^{-1}) to enhance the effects of slow ionic currents, as employed elsewhere.^{21,24,25} A systematic set of I - V curves recorded from negative to positive and from positive to negative voltages was obtained for the different compositions. The I - V curves obtained for all compositions were summarized in supplementary material Note 5. From the geometrical parameters (sample thickness and electrode area), the data were used to compose the J - E hysteresis map shown in Fig. 2.

All mixed-cation compositions displayed a lower J - E hysteresis compared to pure MAPbI₃, following the reduced ionic conductivity observed previously. When different effects of the types of cations are considered, the tendency for lower J - E hysteresis values to occur in GA⁺-rich compositions compared to FA⁺-rich becomes clear. In other words, GA⁺ appears more effective in mitigating hysteresis than formamidinium. Taking this and the comparison with Fig. 1, justified based on the likely reduction of point defects in equimolar substituent compositions, the results suggest that the main reason for the drop in hysteresis is the reduction in ionic mobility. Thus, the mitigation of J - E hysteresis appears to be more intense the greater the effective ionic radius of the substituent cation.

To study the transport properties of electronic charge carriers, we employed steady-state measurements under a constantly increasing voltage regime. In this case, we used a fast scan rate (0.5 V s^{-1}) condition to reduce the contributions of ionic currents on the charge transport and prevent extensive ion accumulation at the electrode/sample interface, interfering in the electronic charge collection. Ideally, ion conduction processes can only be eliminated in these experiments by

applying pulsed current-voltage sweeps, as demonstrated elsewhere.^{26,27} Still, for a comparative study, the employed approach is reasonable. The procedure to extract the main electronic carrier parameters, e.g., electronic charge carrier mobility and density, from current density vs voltage data ($J \propto V^n$) of halide perovskite materials and devices is commonly modeled, with the necessary criticism, using space-charge limited-current (SCLC) models.^{26–29} One of the features of this model is the transition from an Ohmic regime ($n = 1$) at low voltages to a trap-filling regime at intermediate voltages ($n > 2$) and, at higher voltages, to the actual SCLC regime ($n = 2$), which can be given by the well-known Mott-Gurney law, $J = 9\epsilon_0\epsilon'\mu_e V^2/8L^3$, ϵ_0 is the permittivity of free space, ϵ' is the relative dielectric permittivity of the material (supplementary material Note 7), and μ_e is the electronic charge carrier mobility. However, only a few of our curves could be modeled using the SCLC model. For the ones that could not, we observed that $\log J$ vs $\log V$ curves have linear regions of slopes close to 1.5, characteristic of ballistic conduction regimes.^{30,31} The changes in the aspects of the J - V behavior of the samples might be due to the relative differences between the densities of electronic carriers, mobile ions, and trap.^{26,27} Henceforth, to model these curves, we employed a similar methodology described in Ref. 32 and substituted the Mott-Gurney term by a subtle modification of the ballistic-like expression obtained in Ref.,³³ leading to the equation $J = \epsilon_0\epsilon'\mu_e(4\pi^2k_BTV/q + \sqrt{2V_0}V^{3/2})/L^3$, where V_0 is the onset voltage in the transition from the Ohmic to the ballistic-like transport. The experimental curves are given in supplementary material Note 8. Results are summarized in Fig. 3.

The obtained electronic charge carrier mobility values in Fig. 3 agree with the wide range of values reported in the literature using several techniques.³⁴ A remarkable reduction in electronic charge carrier mobility is observed with increasing substitution degree. This effect can be explained based on more effective scattering of charge carriers through lattice distortion and heterogeneity in the mixed-cation compositions. The higher the degree of substitution, the more heterogeneous the material is. Surprisingly, there appears to be no difference between the types of substituents, at least for the present case, such

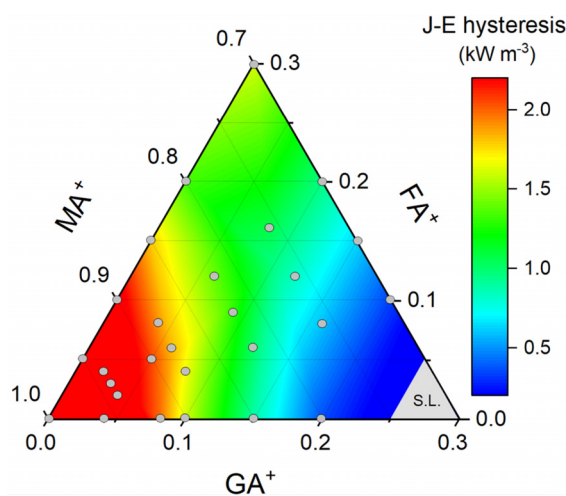


FIG. 2. J - E hysteresis map for the studied $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system, constructed from data shown in supplementary material Note 6.

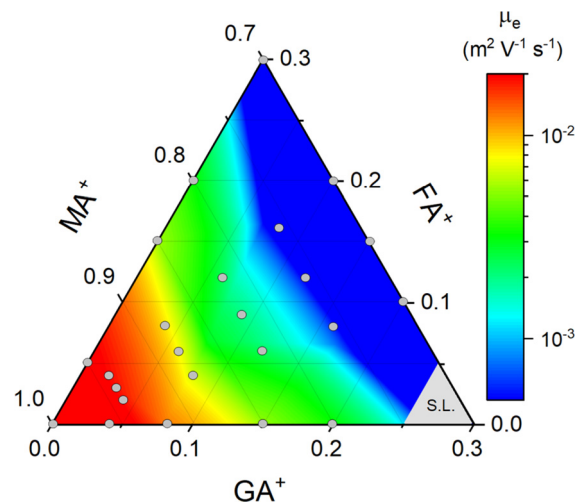


FIG. 3. Electronic charge carrier mobility map for the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system. The data used to construct this map come from those presented in supplementary material Note 9.

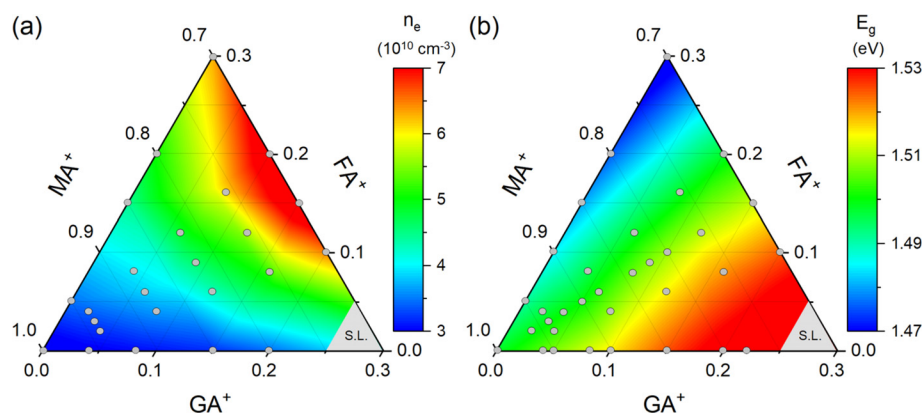


FIG. 4. (a) Intrinsic electronic charge carrier concentration and (b) bandgap energy (E_g) maps for the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system. The data used in this figure comes from those given in supplementary material Note 11 and supplementary material Note 12.

that only the degree of substitution affects the mobility of the carriers. Noteworthy, it is not possible to differentiate between hole and electron mobilities with I - V measurements using the present setup, but both mobilities are reported to be within the same range of values in halide perovskites.³⁴ Hence, we expect electron and hole mobilities to be greatly reduced with increasing substitution degree.

Finally, we estimated the intrinsic electronic charge carrier concentration (n_e). To do so, we evaluated the electronic conductivity (σ_{elec}) at low voltage (Ohmic) regimes in I - V data (supplementary material Note 10) using the expression $\sigma_{\text{elec}} = JL/V = q\mu_e n_e$, where we employed the μ_e values experimentally previously obtained in the relation $n_e = \sigma_{\text{elec}}/q\mu_e$. Based on these results, Fig. 4(a) summarizes the electronic charge carrier concentration map for the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system.

As can be seen, values of n_e on the order of 10^{10} – 10^{11} cm^{-3} were obtained, within the broad range of values usually encountered in halide perovskites.³⁵ More importantly, all values are very similar, almost equal within the inherent imprecision of employed methodology, with a minor trend of increasing n_e values with the substitution degree, slightly in favor of FA^+ -rich compositions. The intrinsic, nearly free electronic charge carrier densities in thermal equilibrium with the lattice at the dark depend on the bandgap energy, non-stoichiometry (doping) defects, and additional donor-acceptor states. As the conduction and valence band structures in lead iodide perovskites are formed by lead and iodide orbitals,³⁶ the effect of A-site cations is only indirect. In principle, it does not result in a great change between compositions of mixed cations, typically ranging from 1.5 to 1.6 eV. Usually, a minor increase in bandgap energies is observed with the substitution of MA^+ by GA^+ ,^{37,38} and with substitution by both GA^+ and FA^+ cations,³⁹ which leads to a decrease in the density of charge carriers from the Fermi distribution. On the other hand, substitution by only FA^+ is reported to decrease the bandgap,^{40–42} which should increase the carrier density. These trends are clearly displayed in Fig. 4(b). We disregard non-stoichiometry defects to play a major role in differentiating the compositions because we employed the same mechanochemical route to synthesize our materials. On the other hand, stoichiometric defects, such as Frenkel and full and partial Schottky defects, that introduce acceptor and donor states through the formation of diverse interstitials and vacancies⁴³ and possibly contribute to increase the density of charge carriers, are intrinsically present. However, as we discussed previously, the mixed compositions are expected to possess fewer point defects and consequently show fewer donor-acceptor

states. Taking all the things considered, the minor trend of electronic charge carrier density increasing with the substitution degree seems to be explained by other phenomena, although the reason for a greater increase effect in n_e , if any, in FA^+ -rich compositions may be related to their lowest bandgap values.

In conclusion, using a broad range of compositions on the system $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$, we showed that the ionic conductivity, J - E hysteresis, and electronic charge carrier mobility are reduced in solid solutions, while the electronic charge carrier density is slightly larger. The level of this decrease seems to be proportional to the substitution degree. Ionic conductivities are lower in equimolar solid solutions, possibly due to entropic stabilization and reduced defect density. At the same time, the J - E hysteresis is lower in GA^+ -rich compositions due to the lowering of ion mobility due to higher activation energies. The substitution of MA^+ greatly reduces electronic charge carrier mobilities because of the greater scattering of carriers by increasing lattice heterogeneity. The intrinsic dark electronic charge carrier densities display much less intense variations with composition, which might be because the bandgap energies are very close within the studied system. Our results enhance the current knowledge of the composition-electrical property relations in halide perovskites.

See the supplementary material for details on structural and microstructural characterization, the geometry of the electrodes, ionic conductivity determination and data, up and down I - V measurements, J - E hysteresis data, forward I - V measurements, data of electronic charge carrier mobilities and densities, and bandgap energies.

This research was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP Project: 2017/13769-1), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES-PRINT Project: 88881.310513/2018-01), and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (151319/2023-5). The authors thank Mr. Elton José de Souza for supporting SEM experiments and Mrs. Lais Conservan Nogueira and Professor José Antonio Eiras for supporting ultraviolet-visible (UV-Vis) measurements.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

F. B. Minussi: Conceptualization (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Validation (lead); Visualization (lead); Writing – original draft (lead); Writing – review & editing (lead). **R. M. Silva, Jr.:** Investigation (supporting); Writing – review & editing (supporting). **E. B. Araújo:** Conceptualization (supporting); Formal analysis (supporting); Funding acquisition (lead); Investigation (supporting); Methodology (supporting); Project administration (lead); Resources (lead); Supervision (lead); Validation (supporting); Visualization (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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PAPER



Cite this: *J. Mater. Chem. C*,
2024, 12, 5138

Thermal degradation in methyammonium–
formamidinium–guanidinium lead iodide
perovskites†

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The stability of hybrid halide perovskites (HPs) is one of the main factors hindering their potential commercial application. Numerous environmental agents are known to degrade HPs and their devices, including temperature, which can cause chemical modifications even at operational temperatures. Thermal degradation has been the subject of major studies in pure and HP-related compounds that have paved the way for a deep understanding of the phenomenon. However, thermally induced modifications in mixed-cation HPs have not been addressed in detail yet. In the present work, we report a systematic study of thermal degradation over a wide range of compositions of methyammonium lead iodide (MAPbI₃) partially substituted by guanidinium (GA⁺) and formamidinium (FA⁺), using diverse experimental techniques and thermal treatment conditions. The results indicated that mixed-cation HPs were more stable than pure MAPbI₃. Thermal degradation followed the volatilization of MA⁺ and MA⁺-related chemical species with PbI₂ consequently appearing; however, GA⁺-rich compositions could suffer from an additional degradation pathway by the segregation of non-perovskite GAPbI₃, reducing the material's thermal stability. This process also provoked a change in the degradation kinetic law. Remarkably, the simultaneous substitution with FA⁺ inhibited the formation of GAPbI₃, even in compositions with high GA⁺ contents. Our work advances the crucial understanding of thermal degradation processes and how to increase the thermal stability of halide perovskites.

Received 27th January 2024,
Accepted 5th March 2024

DOI: 10.1039/d4tc00395k

rsc.li/materials-c

1. Introduction

Hybrid halide perovskites have been intensively studied in the last decade and have emerged as a revolutionary semiconductor with several outstanding properties for optoelectronic and photovoltaic applications. Despite the high performance of perovskite-based photovoltaic devices, several barriers must be overcome for large-scale commercial deployment. The degradation of the physical properties of devices based on halide perovskites is a complex problem and a real obstacle to overcome. Profoundly understanding these degradation mechanisms remains a significant challenge.

Halide perovskites have the general chemical formula of the type ABX₃, where A denotes a monovalent cation, B a divalent cation, and X a halide anion composed of a tridimensional arrangement of corner-sharing PbX₆ octahedra, and have found many applications in optoelectronic and electrochemical devices, including solar cells, LEDs, lasers, X-ray and nuclear radiation detectors, sensing, photocatalysis, and organic synthesis.^{1–9} Despite the unprecedented success in inexpensive laboratory applications, the low stability of halide perovskite materials and devices is one of the main bottlenecks for their definitive commercial usage.^{10–12} Among the possible degradation stressors are humidity, oxygen, light, high temperatures and thermal stresses, bias voltages, and interfacial reactions between layers in perovskite devices.^{13–15} At present, the longest-lasting halide perovskite solar cell possesses a predicted lifetime of about five years under continuous operation at 35 °C,¹⁶ much lower than the desired times of at least 10 years, without even considering that humidity, light, and temperature fluctuations in real conditions could reduce this value. Furthermore, the solar cell in question is all-inorganic, much more stable but less efficient than the state-of-the-art organic–inorganic halide perovskite solar cells,^{17–21} for which retentions of initial efficiencies are generally lower than 80%

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after less than one year, even in strictly controlled environmental conditions. In this sense, to develop commercially competitive solar cells and other perovskite optoelectronic devices, efforts should be directed toward increasing the efficiency of inorganic perovskite devices and increasing the stability of hybrid perovskite devices. For such, one of the main strategies is the formulation of mixed compositions.^{22,23}

Generally, mixed compositions possess higher stabilities²⁴ due to the positive entropy of mixing leading to free energy reduction. It was experimentally found that entropy is the main stabilizing factor in MAPbX_3 (MA^+ = methylammonium, CH_3NH_3^+) perovskites.²⁵ Although this often happens,^{22–24} it has been observed, for example, that solid solutions containing guanidinium (or GA^+) may display time,²⁶ light,²⁷ and temperature²⁸ dependent segregation of guanidinium-related non-perovskite phases (possibly GAPbI_3) even below the solubility limit of GA^+ in the host perovskite. This segregation could be expected in compositions of guanidinium concentrations above the solubility limit.²⁹ The segregation of imidazolium and dimethylammonium-related non-perovskite phases may also appear under light-induced degradation.²⁷ On the other hand, this phenomenon seems less common in compositions containing formamidinium (or FA^+) cations, possibly due to the closer MA^+ and FA^+ radii and the fact that FA^+ is also a perovskite-forming cation. Despite this, the segregation of the non-perovskite $\delta\text{-FAPbI}_3$ phase coexisting with $\delta\text{-CsPbI}_3$ was observed in some compositions of the type $\text{Cs}_x\text{MA}_y\text{FA}_{1-x-y}\text{PbI}_3$ submitted to different light, thermal, and humidity conditions.³⁰ This secondary phase segregation may negatively affect the stability and efficiency of materials and devices.³¹

Regarding the thermal stability of halide perovskites, initial studies^{32–34} reported that methylammonium lead iodide, MAPbI_3 , decomposes by the reaction $\text{MAPbI}_{3(\text{s})} \rightarrow \text{CH}_3\text{NH}_{2(\text{g})} + \text{HI}_{(\text{g})} + \text{PbI}_{2(\text{s})}$. A general thermal decomposition reaction of the type $\text{CH}_3\text{NH}_3\text{PbX}_{3(\text{s})} \rightarrow \text{CH}_3\text{NH}_{2(\text{g})} + \text{HX}_{(\text{g})} + \text{PbX}_{2(\text{s})}$, where $\text{CH}_3\text{NH}_3 = \text{MA}^+$, was considered to interpret the thermal degradation kinetics and phase evolution in MAPbCl_3 , MAPbBr_3 , and MAPbI_3 , which may happen even at temperatures as low as 60 °C.³⁴ At the same time, it was experimentally and theoretically demonstrated that MAPbI_3 decomposes following the reaction $\text{CH}_3\text{NH}_3\text{PbI}_{3(\text{s})} \rightarrow \text{CH}_3\text{I}_{(\text{g})} + \text{NH}_{3(\text{g})} + \text{PbI}_{2(\text{s})}$.³⁵ Later, it was proposed that the actual degradation path depends on the thermal degradation conditions,^{36–38} so that the preferential formation of $\text{CH}_3\text{I}_{(\text{g})}$ and $\text{NH}_{3(\text{g})}$ occurs at temperatures below 350 °C.³⁸ For all purposes, computational methods, such as density functional theory (DFT) and molecular dynamics (MD) calculations, are valuable tools for predictions and mechanistic insights related to the degradation and stability of halide perovskites and related materials.^{39–43} Although the thermal stability and thermal degradation kinetics have been studied in other perovskites and perovskite-like materials with different A-site cations, such as Cs^+ , formamidinium (or FA^+), and tetramethylammonium,^{44–47} and some mixed-systems,^{28,30,48,49–53} studies on the systematized effects of A-site solid solutions containing different cations and concentrations on the thermal stability of halide perovskites are still scarce. It was recently noted that,

chemically, the thermal degradation induction of a secondary phase segregation acts as an additional perovskite degradation route, which provokes a change from first to second-order degradation kinetics and an unexpectedly higher thermal degradation rate.²⁸ This phenomenon was observed at 150 °C in $\text{GA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$ and indicated that the sole substitution by guanidinium led to a decrease in the thermal stability of the resulting material in comparison to MAPbI_3 . On the other hand, the compositions $\text{FA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$ and $\text{GA}_{0.05}\text{FA}_{0.05}\text{MA}_{0.90}\text{PbI}_3$ showed lower thermal degradation kinetics than pure MAPbI_3 . This intriguing scenario suggests that not all mixed-cation compositions are more stable than their analog pure compounds, as observed elsewhere.³⁰

From a thermally induced degradation perspective, although much information is available, mostly on how devices behave with time under thermal stress, fundamental insights, for example, on activation energies for thermal degradation in mixed-cation compositions, microstructural aspects, and differences in volatiles eliminated between different compositions, have not been adequately explored. This information is crucial for better understanding which compositions and characteristics of the substituent cations lead to the greatest stabilities to allow the best chemical design of halide perovskites for reliable long-term application in devices. Nevertheless, despite the greater focus of the current literature on FA^+ -based perovskite solar cells, the top efficiency solar cells today still contain the less stable MA^+ cations.^{54,55} Considering this scenario, in the present work we used a combination of different experimental techniques, including X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and mass spectrometry-coupled thermogravimetry analysis, to systematically investigate the degradation conditions with time and temperature considering a robust set of compositions of the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system. The results show that mixed-cation halide perovskites generally exhibit higher thermal stability with lower degradation rate constants. However, guanidinium-rich compositions show increased rate constants due to GAPbI_3 segregation triggered by the volatilization of MA^+ and related molecules. The formation of this secondary phase can be severely mitigated by partial substitution with FA^+ . Unexpectedly, the activation energies for thermal degradation were found to decrease with increasing the radius of the substituting cations. Our findings provide insights on the essential compositional design principles for achieving high thermal stability in halide perovskites.

2. Experimental

For the present study, different samples of the $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ system in the composition range $0 \leq x + y \leq 0.3$ were prepared from the precursors lead iodide (PbI_2 , Sigma-Aldrich, 99%), methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$ or MAI , Sigma-Aldrich, 98%), formamidinium iodide ($\text{CH}(\text{NH}_2)_2\text{I}$ or FAI , Sigma-Aldrich, 99%), and guanidinium iodide ($\text{C}(\text{NH}_2)_3\text{I}$ or GAI , Sigma-Aldrich, 99%). The precursors were manually mixed and ground to react in a natural agate mortar for about

1 h under ambient conditions in a controlled temperature room ($\sim 25\text{ }^{\circ}\text{C}$) and in relative humidity below 30%. The resulting black powders of perovskites were sieved in a $250\text{ }\mu\text{m}$ aperture sieve (60 mesh), dried, and annealed for 6 h at $60\text{ }^{\circ}\text{C}$ in a laboratory oven with periodic (once an hour) stirring. Pelletized powders were produced with 150–160 mg of the powders uniformly spread into a 10 mm diameter circular cavity of a metallic mold and compacted with a pressure of about 250 MPa. Lastly, the pellets were sintered in an electric furnace at $120\text{ }^{\circ}\text{C}$ for 2 h and slowly cooled to room temperature inside the electric furnace. Several pellets of each composition were synthesized and used in the present study.

The crystalline structure of the materials was characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.5406\text{ }\text{\AA}$), under 40 kV and 20 mA, with continuous scanning ($2^{\circ}\text{ min}^{-1}$), under controlled conditions (dark, at approximately $22\text{ }^{\circ}\text{C}$ and relative humidity below 30%), in the range of 2θ from 10° to 16° . The microstructure images of the samples were obtained using a Zeiss EVO LS15 scanning electron microscopy (SEM) system, with a tungsten beam operating in the voltage range between 10 and 20 kV, by secondary electron analysis. Coupled energy-dispersive X-ray spectroscopy (EDS) analysis was performed using an Oxford Instruments INCA x-act system. Iodine and lead elemental composition estimations were based on EDS analyses in regions of $1278 \times 684\text{ }\mu\text{m}$. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449 F3 Nevio analyzer under nitrogen flux, using an open $85\text{ }\mu\text{L}$ alumina crucible filled with powdered perovskite masses of about 15 mg, from $30\text{ }^{\circ}\text{C}$ to $330\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ proceeded by a 90 min isotherm at $330\text{ }^{\circ}\text{C}$. Coupled mass spectroscopy (MS) analysis was performed using a QMS 403 C Aëolos spectrometer using an electron multiplier detector, under nitrogen flux, in an m/z ion scanning range of 0.02, integration time per m/z of 200 ms, detector voltage of 2500 V, and analyzed m/z range from 40 to 160.

For the thermal degradation experiments, the pellets were placed in a $60 \times 15\text{ mm}$ glass Petri dish and heated for up to 110 h at $150\text{--}200\text{ }^{\circ}\text{C}$ in an electric oven under ambient air in the dark. After predefined intervals, the samples were removed from the oven and rapidly cooled to $\sim 22\text{ }^{\circ}\text{C}$ and XRD, SEM, and EDS data were collected. Precautions were taken so that the same faces of the samples were always exposed to air during the heat treatment in the oven. Except when intentionally desired, the XRD data were always collected on those same faces, with care always taken to position the samples in the same arrangement in the sample holder.

3. Results and discussion

To understand the degradation behavior of different mixed-cation compositions, possible temperature-induced GAPbI_3 segregation in GA^+ -containing compositions and its consequences, the first set of experiments aimed to track time-temperature phase changes and determine the rate

constants (k) at different temperatures for MAPbI_3 (MAPI), $\text{FA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$ (FA0.10), $\text{GA}_{0.05}\text{FA}_{0.05}\text{MA}_{0.90}\text{PbI}_3$ (TC), and $\text{GA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$ (GA0.10) compositions. We estimated the degradation rate constants by tracking the time-dependent vanishing of XRD peaks related to the perovskite crystalline phase when submitted to the thermal treatments at different temperatures. For this study, the degradation extent is described by the expression $\alpha(t) = 1 - A(t)/A_0$, where $A(t)$ is the perovskite XRD peak area (integrated intensity) after a given degradation time t , and A_0 is the initial perovskite peak area, which has been previously used to model the different effects of mixed A-site compositions of HPs.²⁸ The foregoing analysis of the XRD data was based on the 10° to 15° range, which contains the signature peaks of relevant phases related to the studied materials. Ideally, the complete diffractograms should be used for such; however, due to the number of diffractograms needed for the present work (more than 400), it would have been unfeasible to collect the complete diffractograms for all composition-time-temperature conditions. Extensive elaborations of the limitations of the use of areas in this type of study, and how to deal with them, can be found elsewhere.^{47,57} Despite that, other similar studies were based in the area of the selected XRD peaks.^{48–50} Potential quantitative errors are clear and so making direct comparisons between the various results present in the literature is difficult as the results are highly sensitive to experimental conditions, material architecture, and the methods used in data analysis. This is exemplified by the number of different models that can be employed to interpret results.⁴⁷ However, the results presented here were obtained using the same methodology, so a self-comparison is quite reasonable. That said, the time and temperature-dependent XRD data used in this study are summarized in Supplementary Note 1 (ESI[†]), while details of the modeling used are given in Supplementary Note 2 (ESI[†]).

Fig. 1a shows the degradation extent as a function of time, $\alpha(t)$, for the MAPbI_3 , $\text{FA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$, $\text{GA}_{0.05}\text{FA}_{0.05}\text{MA}_{0.90}\text{PbI}_3$, and $\text{GA}_{0.10}\text{MA}_{0.90}\text{PbI}_3$ samples at different temperatures in the $150\text{--}200\text{ }^{\circ}\text{C}$ range. In addition to the fact that the degradation rate increased with temperature for all compositions, the most important observation was that the time-dependent degradation extent profiles of the compositions MAPI, FA0.10, and TC were similar, but different from those observed for GA0.10. Similarly, as recently observed,²⁸ in the present work, the thermal degradation in the first three compositions seemed to follow a first-order kinetics since it followed a linear behavior in a plot of $\ln(1-\alpha)$ versus t . In contrast, the latter followed a second-order reaction kinetics according to linearization of the data in a plot of $1/(1-\alpha)$ versus t . In fact, in the respective diffractograms, at all temperatures between $150\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$, increasing the thermal treatment time for the composition GA0.10 was accompanied not only by the intensification of the peak associated with PbI_2 simultaneously with the decrease in peak associated with perovskite but also a concurrent emergence and peak intensification associated with GAPbI_3 . On the other hand, in MAPI, FA0.10, and TC, only the signs of the emergence and increase of the PbI_2 and the vanishing of the

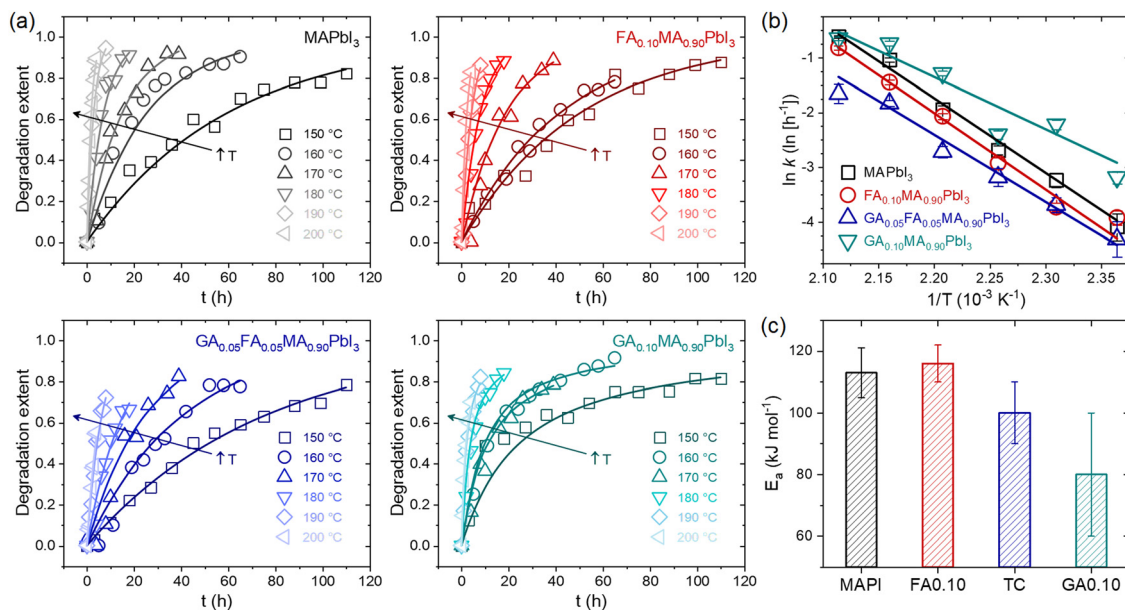


Fig. 1 (a) Degradation extent $\alpha(t)$ of the MAPbI₃ (MAPI), FA_{0.10}MA_{0.90}PbI₃ (FA0.10), GA_{0.05}FA_{0.05}MA_{0.90}PbI₃ (TC), and GA_{0.10}MA_{0.90}PbI₃ (GA0.10) compositions as a function of time at different temperatures. Dots are the data obtained from XRD measurements. Lines are reconstructed curves using the rate constants extracted from respective linear fits (details in Supplementary Note 2, ESI†). (b) Temperature dependency of the rate constants in the form of linearized Arrhenius plots. Lines are linear fits using an Arrhenius model. (c) Activation energies for thermal degradation obtained from linear fits for the Arrhenius plot data.

perovskite were present. Again, two simultaneous thermal degradation pathways led to the change from a first to a second-order reaction kinetics in the studied mixed-cation halide perovskites.

Fig. 1b shows plots of $\ln(k)$ versus $1/T$ to compare the relative thermal stabilities of the studied compositions. The results, in the form of a linearized Arrhenius plot, are given in the rate constant perspective, whereby the thermal stability of the studied compositions followed the order GA0.10 < MAPI < FA0.10 < TC over the entire temperature range. To obtain the activation energies for thermal degradation (E_a), we modeled the temperature dependency of the rate constant with an Arrhenius equation of the form $k = k_0 \exp(-E_a/RT)$, where k_0 is a constant, R is the universal gas constant, and T is the temperature. The results are given in Fig. 1c. The MAPbI₃ activation energy was about 110 kJ mol⁻¹, in agreement with values from 80 to 120 kJ mol⁻¹ reported in the literature.^{34,35,56,57} Considering the error bars, there seemed to be a trend of the activation energies lowering with the average size of the A-site cations. The commonly used effective ionic radii of MA⁺, FA⁺, and GA⁺ are 217, 253, and 278 pm,⁵⁸ respectively. Hence, the average A-site cation size increased in the order MAPI < FA0.10 < TC < GA0.10. When the substituting and host cations have different radii, a lattice distortion is accompanied by a crystal strain, which should increase the system's accumulated elastic energy. In other words, the enthalpy of mixing was possibly positive for all the mixed-cation compositions, as expected from the theoretical results.⁵⁹ Hence, with the increasing difference between the cations, the greater the enthalpy of mixing. Since the activation energy is

related to the enthalpy changes between the reactants and the transition state, it was unsurprising that the activation energy decreased with the average size of the substitute cation. Although contradictory at first glance, the compositions FA0.10 and TC had lower k values than pure MAPI because they were entropically stabilized (which reduces the k_0 term) and did not have additional degradation pathways, as was the case for GA0.10. This hypothesis is corroborated by the fact that, among the studied compositions, the highest mixing entropy occurred for TC, which was the one with the lowest k value. The difficulties in assigning the significance of activation energies in solid-state decomposition reactions is worth pointing out.⁶⁰ Also, depending on the methods used, one of more activation energies could be obtained, indicating reactions with multiple steps.⁴⁶ With the employed analysis, we could not distinguish processes with several steps, hence the results may reflect an average of more than one step or of the rate-limiting step. This would complicate the scenario if compositions had more than one volatile component. But, as will be shown, the thermally induced mass loss was largely due to the elimination of MA⁺-related species. Hence, whatever the significance of the decomposition activation energy for the MAPbI₃-based materials, it was clear that the composition effects were solely based on the kinetics of MA⁺-related decomposition and not on other volatiles.

A critical aspect of processes in solid-state materials is the microstructural changes that occur during the reactions. To track these changes, we collected SEM images of samples of the studied compositions submitted to thermal treatment at 200 °C for up to 4 h. Fig. 2a shows the SEM microstructure images of

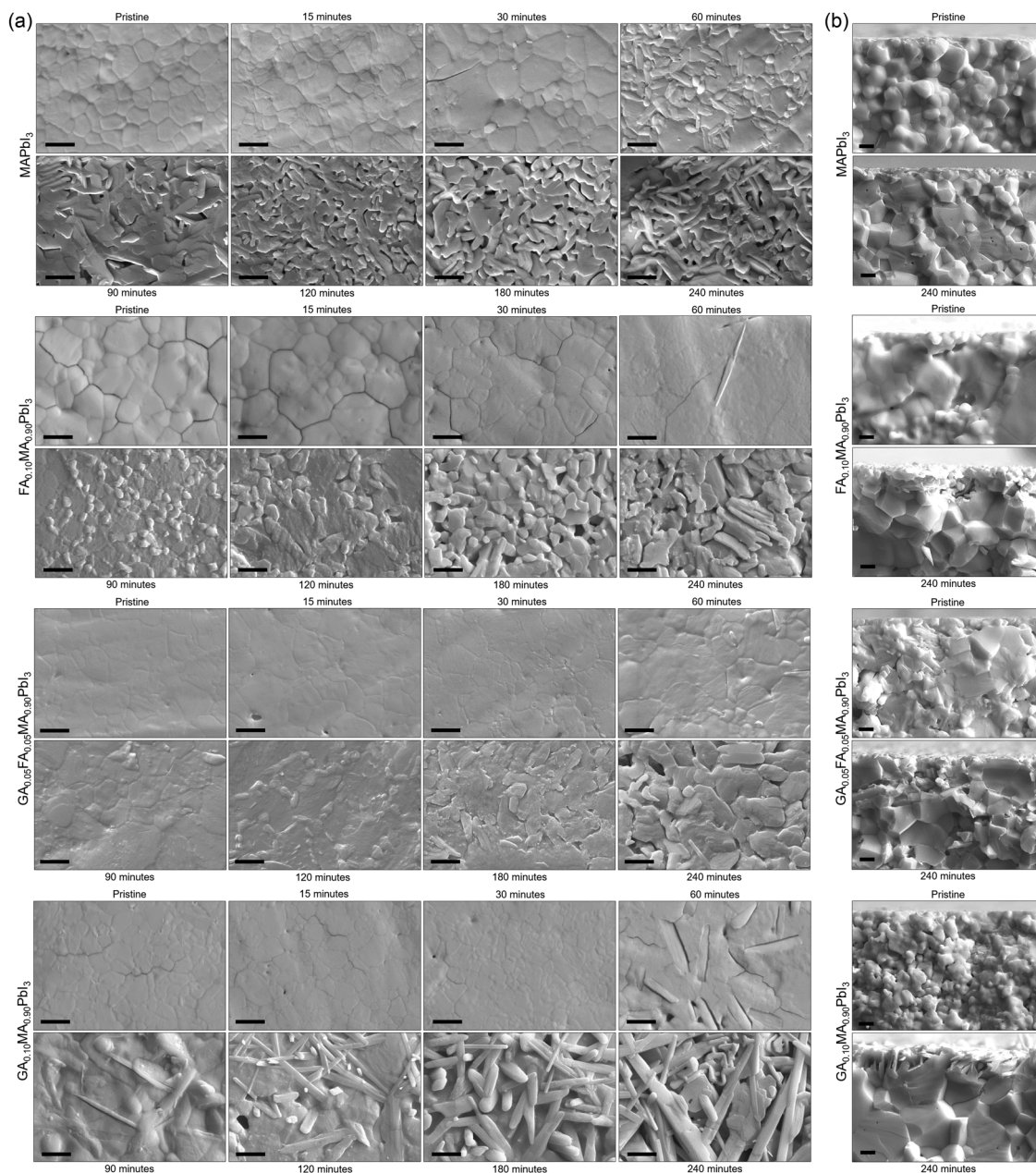


Fig. 2 (a) Representative SEM images of surface microstructural variation with time at 200 °C. (b) Cross-section near to the surface images of the samples in pristine and degraded conditions. In all images, scale bars are 2 μm.

the studied samples as prepared and after thermally treated at different times at 200 °C. For all compositions, we observed a general behavior of appearance and increasing volume fraction of secondary phases from the initially dense and homogeneous microstructures. At later stages, voids started to appear, resulting in a completely modified surface. One interesting aspect was that the formation of voids was severely delayed in the mixed-cation compositions. For pure MAPI, voids could be clearly identified after 90 min of thermal treatment. For the other compositions, these voids were only present after at least 120 min, with the extreme case being that for TC, where voids could only be identified after 240 min (4 h). Not surprisingly,

this was the composition with the lowest thermal degradation rate constant. Another interesting aspect was that for MAPI, FA0.10, and TC, the first secondary phases appeared to be round-shaped and somewhat bright, possibly related to the PbI₂ phase identified in the XRD data. On the other hand, for GA0.10, the first secondary phase appeared to have an elongated shape, which was only later followed by the presence of the round-shaped segregates. This elongated microconstituent had the same aspect as the secondary phases present in GA_xMA_{1-x}PbI₃ compositions above the solubility limit of GA⁺.⁶¹ Hence, as expected, we conclude that these different segregates that appeared in GA_{0.10}MA_{0.90}PbI₃ were due to

GAPbI₃. The appearance of PbI₂ in the microstructure of lead iodide-based perovskites is a common feature when the materials eliminate volatiles from the reactions mentioned earlier. It suggests that these processes start at the surface, giving rise to the formation of PbI₂ segregates, while, at later stages, the internal layers start to degrade as well, forming the voids. This observation agrees with the demonstration that the degradation of MAPbI₃ is initiated at the surfaces and progresses toward the bulk of the material.⁶² For GA_{0.10}MA_{0.90}PbI₃, the fact that GAPbI₃ segregates appeared before or simultaneously to PbI₂, not after, was also observed in the XRD data and suggests that both degradation pathways occur somewhat independently, as will be discussed ahead.

Fig. 2b summarizes the SEM cross-section images of the as-prepared sample and after being thermally treated at 200 °C for 240 min. These images were obtained to understand how deep the thermally induced formation of voids was across the bulk. At the deeper layers away from the surface, the only microstructural change appeared to be due to continued sintering, *i.e.*, densification and grain growth processes. In this sense, microstructural changes indicative of thermal degradation processes, the formation of secondary phases, and voids appeared to be restricted to only a few microns at the surface of the samples. This expected behavior is typical of the inherent diffusional restrictions of solid-state materials. To be released, the volatiles must reach the surface. The initial components at the surface are readily prompted to react, but the deeper components must diffuse over increasing distances to react. On the other hand, the role the local atmosphere and its dynamics play in the rate of degradation must be questioned. It is known that molecular oxygen contributes to the decomposition of MAPbI₃.⁶³ As shown in Supplementary Note 3 (ESI†), the comparison between the visual aspects and diffractograms of the sample's directly exposed and non-exposed surfaces shows that thermal degradation was severely reduced at the non-exposed surface. This could be mainly attributed to the continuous convection of oxygen and moisture and the impossibility of achieving equilibrium at the exposed surface. In turn, on the non-exposed surface, a state of equilibrium could be reached as the gases released by the material might be trapped in the grooves between the sample and the sample holder (glass), preventing the progression of thermal decomposition reactions. This exemplifies why encapsulation should be necessary for halide perovskite devices whenever possible.

In addition to modifying the phase composition and microstructure of the materials under heat treatment, it is also essential to understand the chemical changes that result from thermal degradation. As emphasized, it is notable that hybrid perovskites based on lead iodide leave solid PbI₂ as one of the degradation products through the elimination of volatiles. To understand these transformations, we performed EDS measurements of the surface of the samples, as shown in Fig. 2, to estimate the iodine-to-lead ratio as a function of time. Fig. 3 shows the EDS iodine/lead molar ratio quantification as a function of heat treatment time.

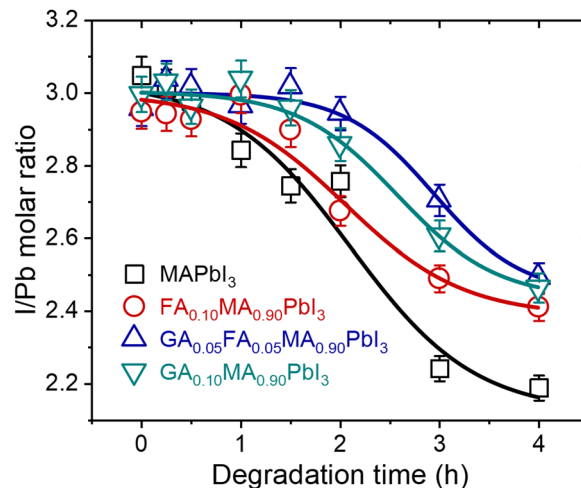


Fig. 3 Surface EDS iodine-to-lead molar ratio quantification as a function of time for samples treated at 200 °C. Lines were added as guides for the eyes.

For all compositions, the iodine-to-lead molar ratio varied from an initial value of 3 to values theoretically tending to 2. Although the quantitative limitations of estimating the chemical composition through EDS results are recognized, it is notable in our results that the mixed-cation compositions presented a lower I/Pb molar ratio reduction rate than pure MAPbI₃. After 4 h of heat treatment, the I/Pb molar ratio in the mixed-cation samples was 2.4 to 2.5, while in MAPbI₃ it was 2.2. These results suggest that entropic stabilization in mixed-cations compositions strongly mitigates the elimination of volatiles by the materials. This was true even for GA0.10, even though it was the composition with the highest thermal degradation rate constants. This is a robust indication that the thermal degradation in this composition is strongly affected by the concomitant segregation of GAPbI₃ and is not only due to the elimination of volatiles.

Considering the above results, we also tracked the correlated mass changes during the thermal treatments. The results from thermogravimetric analyses under two heating regimes, shown in Fig. 4a, clearly corroborated that the mass loss rate in MAPbI₃ was much higher than in the other compositions. Not surprisingly, the relative mass loss was also the highest for MAPbI₃ after the experiment.

With the clear perspective of gases being released from the materials, it must be asked if there are differences in the gas profile with time/temperature and from one composition to another. The mass spectra were periodically collected during the thermogravimetric experiments. The results are shown in Fig. 4b. For all the compositions, the main relevant peaks to appear had the same *m/z* values of 58, 127, and 142. It is also clear that no other peaks appeared within the time/temperature of the thermal treatment; the only variations corresponded to the intensities of the peaks. Noteworthy, the peak at *m/z* = 127 was the most intense in all compositions, but in the guanidinium-containing ones, the relative intensity of the peak at *m/z* = 58 was higher than the others. These peaks could all be

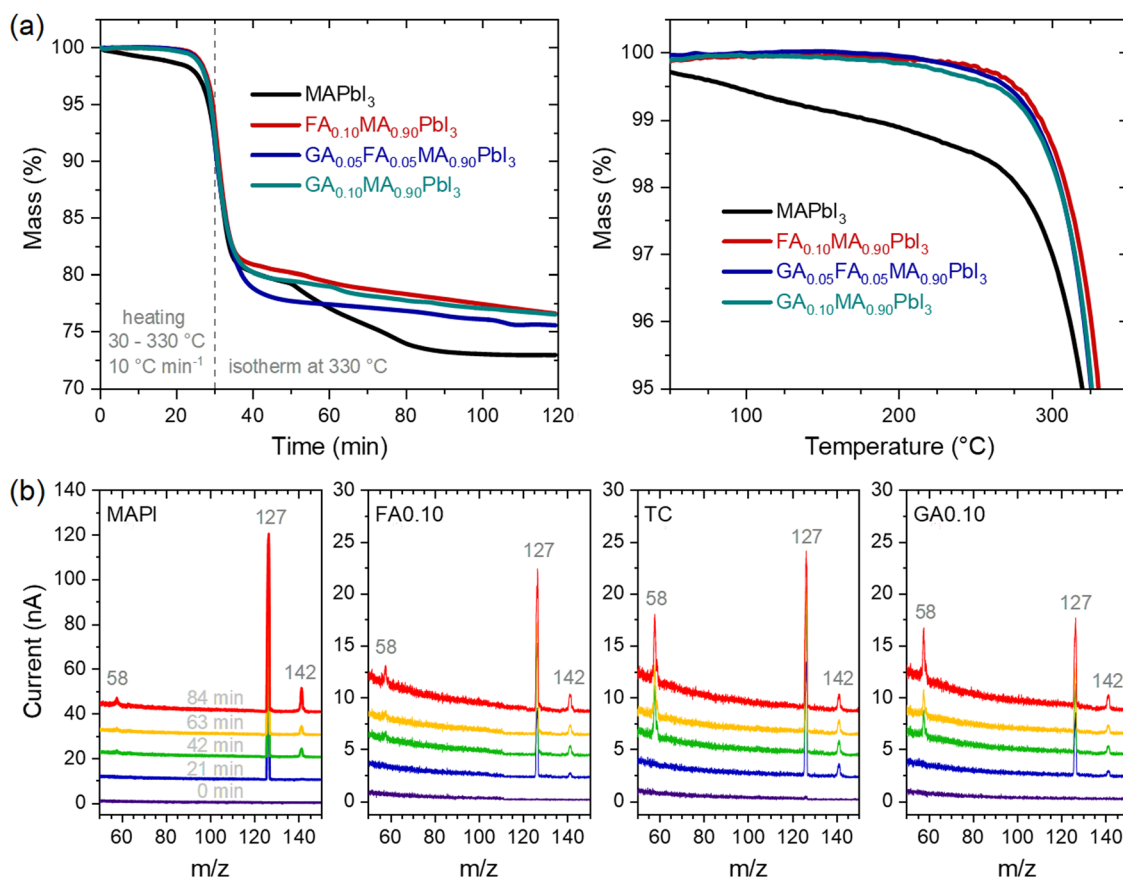


Fig. 4 (a) Mass percentage as a function of time (left) and temperature (right) under heating in two regimes. The figure on the right is a zoomed-in version for better visualization of the composition differences. (b) Cumulative mass spectra in the m/z range from 50 to 150 collected at different times under heating. Vertical shifts between the spectra were made intentionally for better visualization of the results.

attributed, directly or indirectly, to the initial decompositions of methylammonium cations to NH_3 and CH_3I .³⁵ The peaks at $m/z = 127$ and 142 were respectively due to I^+ and CH_3I^+ ions formed from CH_3I , while the peak at $m/z = 58$ was due to $\text{C}_3\text{H}_8\text{N}^+$ ions, attributed to the presence of $(\text{CH}_3)_3\text{N}$ formed from the reaction of trapped NH_3 molecules with the host methylammonium cations of the perovskite. A corroboration of this pathway was given by observing the peak at $m/z = 42$ (Supplementary Note 4, ESI†) associated with $\text{C}_2\text{H}_4\text{N}^+$ ions, also arising from $(\text{CH}_3)_3\text{N}$. The changes in the relative intensities between the peaks in the different compositions may be due to the observed ions coming from other sources, for example, I^+ from I_2 , and from kinetic/thermodynamic modifications that lead to certain pathways and products being preferred over others. One corroboration for such is that MAPI presented a two-step mass loss attributed to the sequential release of CH_3I and NH_3 ,³⁵ while the mixed-cation compositions displayed a single-step mass loss regime. Although the present results do not allow establishing these distinctions, it is clear that even though the nature of the FA^+ and GA^+ cations present differently affected the thermal stability of the material, there was no evidence, at least in the temperature range studied and the detection limit of the equipment, that these cations were degraded or eliminated during the thermal treatment. For

example, the thermal degradation of formamidinium cations has been reported to lead to the formation of *sym*-triazine, for which related peaks would be present at $m/z = 54$ and 81 ,⁴⁴ both of which were absent in our results. With that in mind, it is quite likely that the mass loss resulting from thermal degradation in our materials was largely due to the elimination of methylammonium. In fact, methylammonium is very well known to be volatile, while formamidinium and guanidinium could be expected to be much less susceptible to being released from the halide perovskites because they are larger, less acidic, and capable of forming more hydrogen bonds than methylammonium. It should be noted that the final mass of MAPI was 73% of the initial mass, which was close to the theoretical remaining mass of 74.3% considering the complete release of organic molecules. For the other compositions, between 75% and 77% of the initial masses remained after the thermal treatment. Simple mass balances indicate that this difference was due to non-volatile GA^+ - and FA^+ -related molecules.

Regarding, again, the segregation of GAPbI_3 in the composition $\text{GA}_{0.10}$, one of the outcomes of the previous results pointed toward the following scenario. When the material is subjected to thermal degradation, there is a major volatilization of MA^+ and derived molecules but much less, if any, of GA^+ . When this occurs, the mole fraction of GA^+ increases. Although

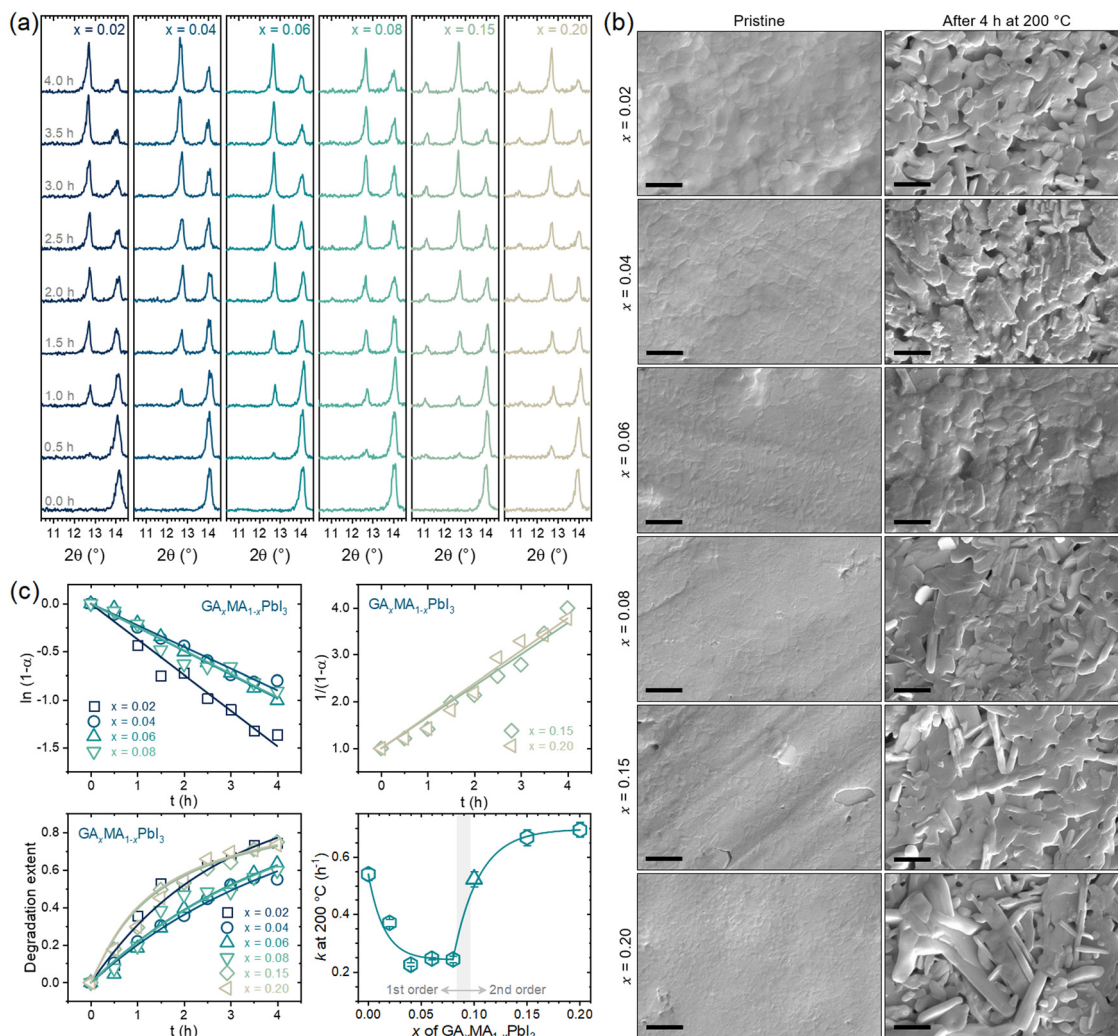


Fig. 5 (a) XRD results of $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ compositions thermally treated for different times at 200 °C. (b) Representative SEM images of the surface microstructure of the samples in the pristine and degraded conditions. In all images, scale bars are of 2 μm . (c) Linear fits of $\ln(1-\alpha)$ versus t to obtain the thermal degradation rate constants at 200 °C, experimental degradation extent $\alpha(t)$ with reconstructed curves, and composition dependency of the rate constants.

the extent of the damage, that is, the volume of material subject to thermal degradation, is small, there may not be the time necessary for the redistribution of GA^+ cations, such that in the degraded layers, the concentration of GA^+ becomes much higher than that in the bulk of the material. If the proper conditions were to be achieved, *i.e.*, a local supersaturation, there may be GAPbI_3 segregation. In this case, for compositions with high initial GA^+ concentrations, a smaller degradation extent would be required to reach local GA^+ supersaturation and trigger GAPbI_3 segregation. Also, it must be considered that the higher the concentration of GA^+ , the greater the mitigation of ion transport^{64,65} therefore, the more difficult (slow) the redistribution of ions would be, translating into the local concentration of GA^+ increasing quicker. Given this plausible scenario, we studied the thermal degradation behavior of $\text{GA}_x\text{MA}_{1-x}\text{PbI}_3$ compositions with x up to 0.20.

Fig. 5a presents the XRD results of the compositions subjected to a thermal treatment of up to 4 h. For all compositions,

there was a clear vanishing of the perovskite peak at $\sim 14^\circ$ with the appearance and intensification of the PbI_2 peak at $\sim 12.5^\circ$ with the thermal treatment time. For the compositions with $x = 0.15$ and 0.20, there was also a prompt appearance and intensification of the peak at $\sim 11^\circ$ attributed to GAPbI_3 . This is the same behavior previously observed for $x = 0.10$. For $x = 0.06$ or lower, no GAPbI_3 peaks could be identified, while for $x = 0.08$, the GAPbI_3 peak appeared, but only at later degradation times. These results indicate a GA^+ concentration threshold, around $x = 0.08$, below which there appears to be no segregation of GAPbI_3 . The same conclusions can be drawn from the surface SEM images of the pristine and fully degraded samples, as shown in Fig. 5b, where it can be noted that for compositions with x up to 0.06 there were no elongated microconstituents indicative of GAPbI_3 , which could be seen for compositions with $x = 0.08$ or higher. This follows the proposed idea of its formation being because of volatilizing MA^+ cations and aligns with GAPbI_3 being formed concomitantly to PbI_2 , not

consequently to it. The two phases are formed simultaneously but independently, starting from the same chemical phenomenon. We obtained the degradation extent with the XRD data as a function of time and respective rate constants. The results are given in Fig. 5c.

One of the most important aspects to note is that for the compositions with low GA^+ concentration ($x \leq 0.08$), the degradation was found to follow a first-order kinetics while a second-order kinetics was followed for the compositions with high GA^+ concentration ($x \geq 0.15$). Hence, as a general rule, it can be concluded that the segregation of GAPbI_3 provokes a change from a first- to a second-order reaction kinetics. From our results, this was not true only for the composition with $x = 0.08$, which might be due to the comparatively low GAPbI_3 segregation or because it was formed only at later stages of degradation. When we include the previous results for $x = 0.10$, we also noted a clear and expected trend of larger rate constants for compositions where GAPbI_3 was extensively formed, leading to second-order reaction kinetics.

Now, following earlier results with the TC composition, which showed the highest thermal stability (lowest rate constant), we wanted to further explore the behavior of the thermal degradation kinetics in other compositions with equal amounts of GA^+ and FA^+ ($\text{GA}_x\text{FA}_x\text{MA}_{1-2x}\text{PbI}_3$ system). From the XRD results shown in Fig. 6a, we note that all compositions displayed the same behavior of vanishing perovskite peaks with the appearance and intensification of PbI_2 peaks. One surprising feature was that compositions with $\text{GA}^+ = \text{FA}^+$ up to 0.15 did not segregate GAPbI_3 . Other compositions of the type $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$, with $x = 2y$ and $y = 2x$, were tested using the same approach (see details in Supplementary Note 5, ESI†).

Surprisingly, none of the compositions, even the ones with a total substitution content of up to 0.30, showed any signals for GAPbI_3 segregation. This remarkable result suggests that FA^+ strongly inhibits the formation of GAPbI_3 . We wonder if this also holds for other compositions with large cations, such as ethylammonium and dimethylammonium. This will be the subject of future work.

Fig. 6b shows the thermal degradation extents and rate constants of $\text{GA}_x\text{FA}_x\text{MA}_{1-2x}\text{PbI}_3$ compositions obtained from the XRD data. The results for the other $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ compositions are given in Supplementary Note 5, (ESI†). In all cases, the degradation behavior could be modeled assuming first-order reaction kinetics, which is consistent with the fact that none showed the segregation of GAPbI_3 . Also, increasing the substitution contents decreased the rate constants, as observed in the literature,⁴⁸ when no secondary phases other than PbI_2 were formed.

Lastly, to better understand the effect of composition on the thermal stability of the halide perovskite system under study, we constructed a ternary diagram to correlate the guanidinium and formamidinium contents with the rate constant of thermal degradation. To do so, we organized all the previous results at 200 °C and complemented the data with additional experiments in $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ compositions at the same temperature (Supplementary Note 6, ESI†). The results, in the form of a heat map, are summarized in Fig. 7.

The general trend observed was a lowering of the rate constant with increasing the substitution contents. This can be explained based on the entropic stabilization of mixed-cation compositions aligned with the reduced molar fraction of the volatile component, *i.e.*, the methylammonium cations.

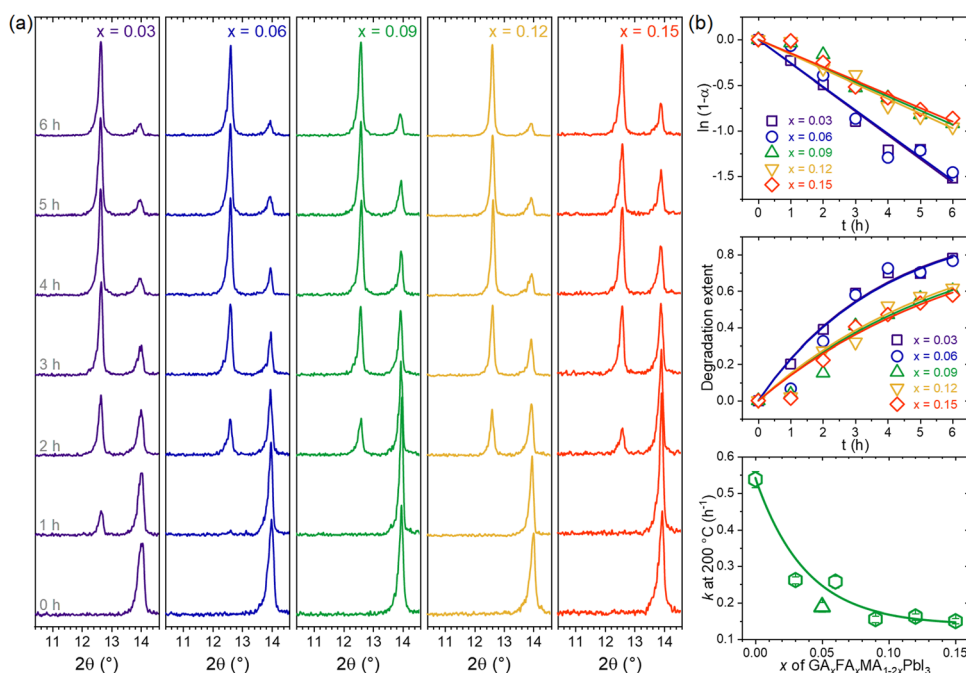


Fig. 6 (a) XRD results of $\text{GA}_x\text{FA}_x\text{MA}_{1-2x}\text{PbI}_3$ compositions treated for various times at 200 °C. (b) Linear fits used to obtain the thermal degradation rate constants at 200 °C, experimental degradation extent data with reconstructed curves, and composition dependency of the rate constants.

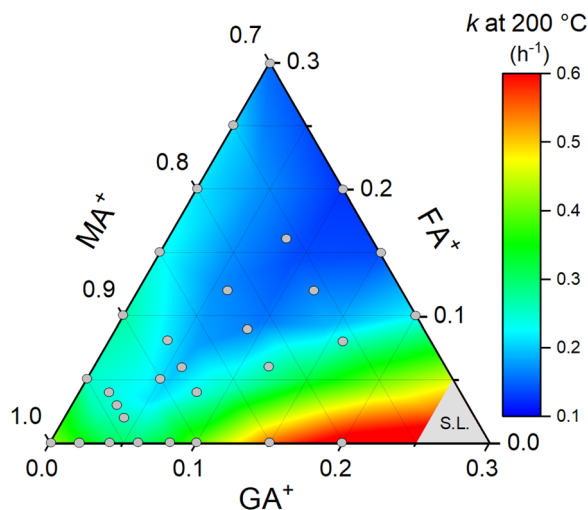


Fig. 7 Composition map for the thermal degradation rate constants at 200 °C for $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$ perovskites. Gray circles are the compositions for which we obtained experimental rate constants. The data are presented in Supplementary Note 7 (ESI†). The region denoted as S.L. were compositions above the solubility limit,²⁹ not considered in this work. To construct the heat map, a smoothing parameter of 0.5 and total points increase factor of 1 were used to highlight the composition-dependent trends of the rate constants.

This effect was intensified in the compositions with close to equimolar fractions of guanidinium and formamidinium, which showed the lowest rate constant values and, thereby, highest thermal stabilities, possibly due to increased entropic stabilization contributions. On the other hand, the guanidinium-rich compositions had higher rate constants. This may derive from the fact that guanidinium cations are large and destabilize the system through highly endothermic mixing, but certainly, the main reason for this is the segregation of GAPbI_3 in compositions with high guanidinium contents. Lastly, it should be stressed that even though this study was conducted in thick samples, the trends in Fig. 7 would possibly be the same in thin films since the degradation processes are restricted to the surface.

4. Conclusions

Using a broad range of time and temperature conditions for thermal degradation, experimental techniques, and compositions based on the system $\text{GA}_x\text{FA}_y\text{MA}_{1-x-y}\text{PbI}_3$, we showed that, in general, mixed-cation halide perovskites possess lower degradation rate constants, indicative of higher thermal stabilities. However, guanidinium-rich compositions tend to display higher rate constants. Mass loss processes seem localized at the surfaces and vastly controlled by the release of methylammonium and related chemical species, leaving solid-state PbI_2 . For some guanidinium-rich compositions, the volatilization of methylammonium triggered the segregation of GAPbI_3 , acting as an additional thermal degradation pathway that led to lower thermal stability. Contrary to expectations, the activation energies for thermal degradation seemed to decrease with

substitution by cations larger than methylammonium, possibly due to endothermic mixing. In this sense, higher thermal stabilities might be controlled by the positive entropy of mixing, which also explains why the compositions with equimolar substitution degrees possessed lower degradation rate constants. Noteworthy, compositions with both FA^+ and GA^+ tended to be much less prone to segregate GAPbI_3 , even for high GA^+ contents. This work provides a conceptual basis for the important design variables that need to be considered to achieve high thermal stabilities in halide perovskites.

Author contributions

F. B. Minussi: conceptualization, methodology, validation, formal analysis, investigation, writing – original draft, writing – review and editing, and visualization. R. M. Silva Jr.: investigation, writing – review and editing. J. F. Carvalho: conceptualization, methodology, validation, investigation, resources, writing – review and editing, and funding acquisition. E. B. Araújo: conceptualization, methodology, resources, writing – review and editing, supervision, project administration, and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP Project: 2017/13769-1), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES-PRINT Project: 88881.310513/2018-01), and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (151319/2023-5). The authors thank Mr Elton José de Souza for supporting SEM experiments and CRTI for the measurements of TGA coupled to mass spectroscopy.

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