

RESEARCH ARTICLE

Vibrational Spectroscopic Insights into Capsaicin Doped Organic–Inorganic Hybrid Perovskite Single Crystals

Aiswarya M. ¹, P. Predeep ^{2,*}

ABSTRACT: Organic-inorganic hybrid perovskites have emerged as promising materials for high-performance optoelectronic devices due to their superior properties. Crystal quality plays a pivotal role in optimizing their performance. This study investigates the incorporation of Capsaicin ($C_{18}H_{27}NO_3$), a natural organic compound, as a dopant in methylammonium lead iodide (MAPbI₃) single crystals, synthesized through the inverse temperature crystallization method. Vibrational spectroscopic analyses were performed to understand the structural and functional impact of Capsaicin on crystal growth, nucleation, and quality. Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR) reveal significant enhancements in the structural stability and purity of MAPbI₃ crystals upon doping with Capsaicin. Powder X-ray diffraction (XRD) confirmed the improved phase purity, with impurity peaks observed in pristine MAPbI₃ eliminated in the doped crystals. The addition of Capsaicin was found to modulate the nucleation rate and enhance the growth rate, leading to larger, and high-quality crystals with improved stability. Vibrational spectroscopic studies further highlighted reduced water absorption and enhanced molecular interactions within the doped crystals. This work underscores the potential of Capsaicin as an effective organic ligand to regulate the crystallographic properties of hybrid perovskites. The findings pave the way for utilizing Capsaicin and similar organic additives in engineering optoelectronic materials with enhanced stability and efficiency. Future studies could explore the broader applications of Capsaicin-doped perovskites, particularly in photovoltaics and photodetectors, further advancing the field of hybrid perovskite research.

Keywords: Organic-inorganic hybrid perovskites, Capsaicin doping, Crystal stability, Vibrational spectroscopy.

Received: 20 January 2024; Revised: 17 February 2024; Accepted: 19 February 2024; Published Online: 01 March 2024

1. INTRODUCTION

Organic-inorganic hybrid perovskites have emerged as one of the most promising materials for next-generation optoelectronic devices. These materials have captivated researchers due to their outstanding properties, such as high light absorption, long carrier diffusion lengths, tunable bandgap, and remarkable defect tolerance [1]. The ability to fabricate these materials using cost-effective solution-based methods further adds to their appeal for a wide range of

applications, including solar cells, light-emitting diodes (LEDs), photodetectors, and lasers. Among the various perovskites, methylammonium lead iodide (MAPbI₃) stands out for its impressive performance and ease of synthesis [2, 3]. However, despite these advancements, achieving long-term stability and high crystallinity in perovskite single crystals remains a critical challenge.

The quality of perovskite single crystals is directly linked to their performance in optoelectronic devices. Defects and impurities in the crystal structure can act as non-radiative recombination centers, degrading device efficiency and stability [4]. To address these issues, researchers have employed various strategies, including compositional engineering, surface passivation, and the use of ligands and additives during synthesis. Among these, the use of organic ligands is particularly attractive as it can effectively regulate the nucleation and crystal growth processes. Organic ligands

¹ Department of Physics, National Institute of Technology Calicut, Kozhikode, India

² School of Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam 686560, Kerala, India

* Author to whom correspondence should be addressed:
aiswaryasan2@gmail.com (Aiswarya M.)

not only improve crystal quality but also enhance the stability of perovskite materials by mitigating environmental degradation caused by moisture, oxygen, and heat [5, 6].

In this study, capsaicin ($C_{18}H_{27}NO_3$), a natural organic molecule derived from chili peppers, has been used as a dopant to improve the quality and stability of MAPbI₃ single crystals [7]. Capsaicin is known for its unique molecular structure, which includes a long hydrophobic tail and multiple functional groups capable of interacting with the perovskite lattice [8]. This molecular architecture makes capsaicin an ideal candidate for modulating the growth of perovskite crystals. The incorporation of capsaicin in the precursor solution alters the nucleation dynamics, resulting in a reduced nucleation rate and enhanced crystal growth [9–11]. The outcome is a structurally stable, high-quality single crystal with fewer defects and superior phase purity.

The synthesis of perovskite single crystals doped with capsaicin was achieved through the inverse temperature crystallization (ITC) method. This technique, widely recognized for its ability to produce large and defect-free crystals, involves gradually increasing the temperature of the precursor solution to facilitate crystal growth [12–15]. By optimizing the concentration of capsaicin and the growth parameters, a 5 mm-sized capsaicin-doped MAPbI₃ single crystal was successfully obtained. Comparative analysis revealed that the incorporation of capsaicin not only improved the phase purity but also eliminated impurity peaks observed in the X-ray diffraction (XRD) pattern of undoped MAPbI₃ crystals.

Characterization techniques, including powder XRD, Fourier-transform infrared (FTIR) spectroscopy, and Raman spectroscopy, were employed to investigate the structural and vibrational properties of the doped crystals. XRD analysis confirmed the tetragonal crystal structure of MAPbI₃ with enhanced phase purity upon capsaicin doping. The FTIR spectrum revealed the absence of broad water absorption bands in capsaicin-doped crystals, indicating improved resistance to moisture-induced degradation. Raman spectroscopy provided insights into the bonding mechanisms and vibrational modes, further substantiating the structural stability imparted by capsaicin.

This study highlights the potential of using capsaicin as a natural, cost-effective dopant to enhance the crystallographic quality and environmental stability of organic-inorganic hybrid perovskites. The results pave the way for further exploration of bio-inspired molecules in the field of perovskite research. Such studies could lead to the development of advanced materials with tailored properties for specific optoelectronic applications. Future investigations could focus on optimizing the molecular interactions between capsaicin and the perovskite lattice, as well as exploring other natural ligands with diverse functional groups. This approach aligns with the broader goal of sustainable and green chemistry, promoting the use of eco-friendly materials in high-performance technologies. By combining soft crystallographic halide perovskites with exotic natural ligands like capsaicin, researchers can achieve significant improvements in device performance. This study not only

demonstrates the practical utility of capsaicin in perovskite engineering but also opens up new avenues for the integration of natural molecules into advanced material systems. The findings underscore the importance of innovative doping strategies in addressing the challenges of stability and efficiency in perovskite-based optoelectronics.

2. EXPERIMENTAL DETAILS

2.1. Materials

Chemicals: Capsaicin (natural, Sigma), Hydroiodic acid (HI) (40wt% in water, Sigma-Aldrich), Lead iodide (PbI₂ ≥99.99%, Sigma-Aldrich), Diethyl ether (anhydrous, ≥99.9%, Sigma-Aldrich), Methylamine (MA) (57wt% in water, TCI chemicals) and γ -Butyrolactone (GBL) (99%, TCI chemicals).

2.2. Single-Crystal Preparation of MAPbI₃ Perovskite

Mixing stoichiometric amounts of synthesised MAI and PbI₂ (99.99%, Sigma Aldrich) in γ -Butyrolactone (GBL) (99%, TCI chemicals) in a beaker at 60 °C for 10 hours with steady magnetic stirring yielded precursor solution of MAPbI₃. Here 1.23 Molar MAPbI₃ precursor solution was prepared. It was then kept at varied temperatures on a hot plate for 18 hours at a rate of 5 °C per 1 hour, ranging from 60 °C to 100 °C, to allow single crystals to develop (after filtration of solution using 0.22 μ m pore size Polytetrafluoroethylene (PTFE) syringe filter). The growth solution was kept at the proper temperature using a silicon oil bath to ensure constant temperature throughout the crystal development process. Three or four nucleation of MAPbI₃ single crystals were observed after 1hr within the 100 °C solution. One seed was kept to grow for further growth. It results in the formation of a 4mm sized single crystal of MAPbI₃ (Figure 1) after a period of 18 hour, which is then washed in diethyl ether and used for further studies.

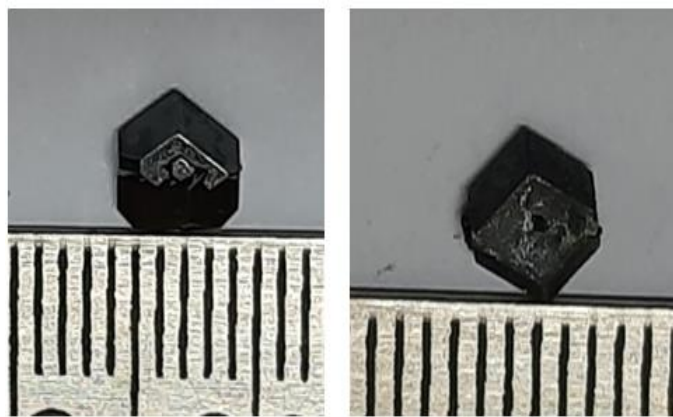


Fig. 1. Single crystal MAPbI₃ obtained by ITC (Inverse Temperature Crystallization) method.

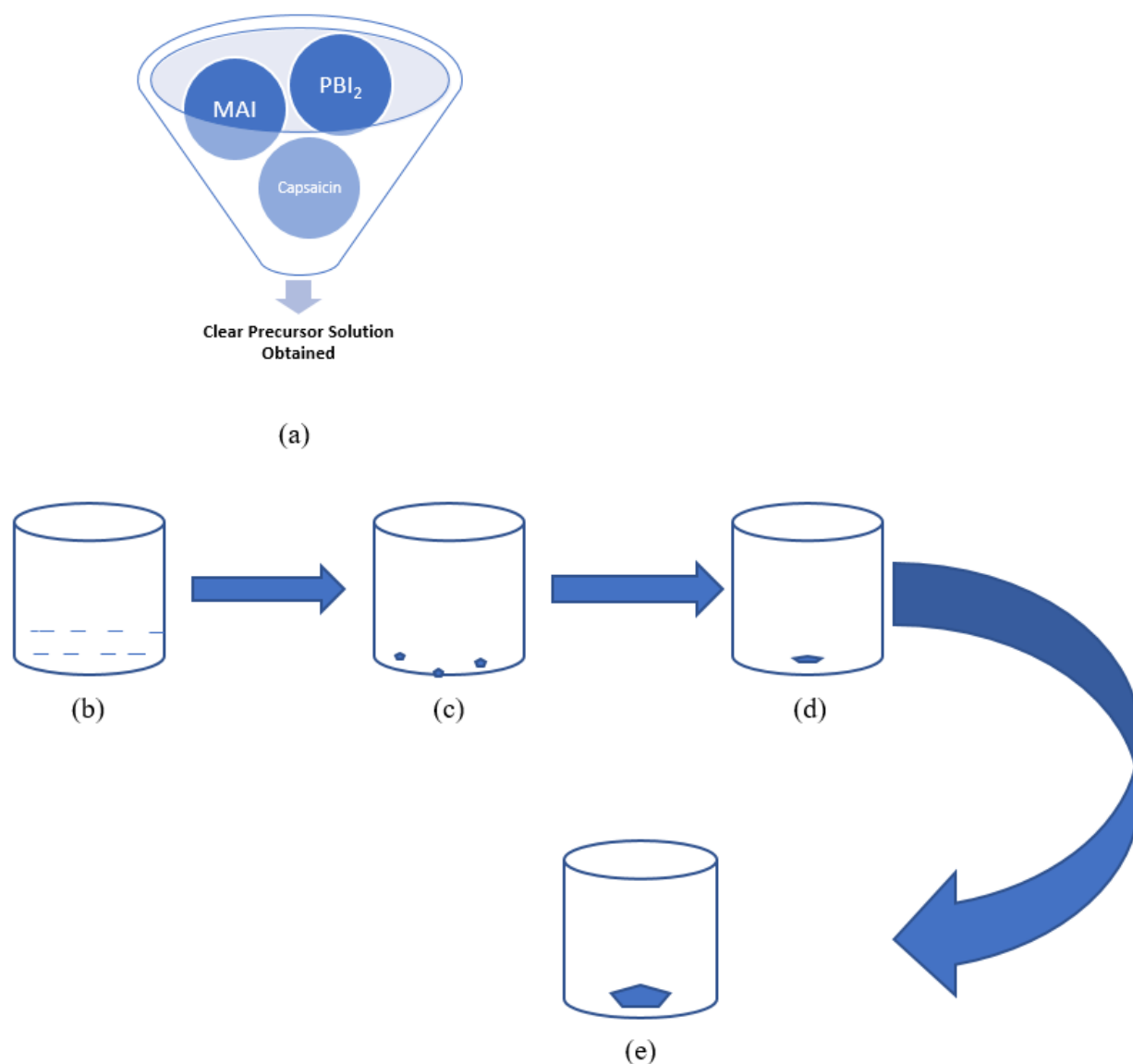


Fig. 2. Procedure for Crystal Growth- (a)Magnetic stirring at 60 °C (b) Clear Precursor Solution kept in silicon oil bath at proper temperature (c) Seed Crystals formed (c) Crystal kept for further growth (d) large single crystal.

2.3. Single-Crystal Preparation of Capsaicin doped MAPbI₃ Perovskite

A 1.23 M precursor solution was prepared by dissolving 1134.1 mg of PbI₂ and 391.066 mg of MAI in 2 ml of γ -butyrolactone (GBL). The solution was magnetically stirred at 60°C for 10 hours to ensure complete dissolution. Capsaicin (1.525 mg, corresponding to 0.1 wt% of the precursor) was then added to the solution, and stirring was continued at 60°C to achieve homogeneity. The solution was filtered using a 0.22 μ m PTFE syringe filter to remove any undissolved impurities.

The filtered solution was transferred to a silicon oil bath maintained at 100°C. A single nucleation was observed after 1 hour, and the crystal was left to grow over 12 hours, resulting in the formation of a 5 mm-sized single crystal (Figure 3). The grown crystal was washed with diethyl ether

and stored for further studies.

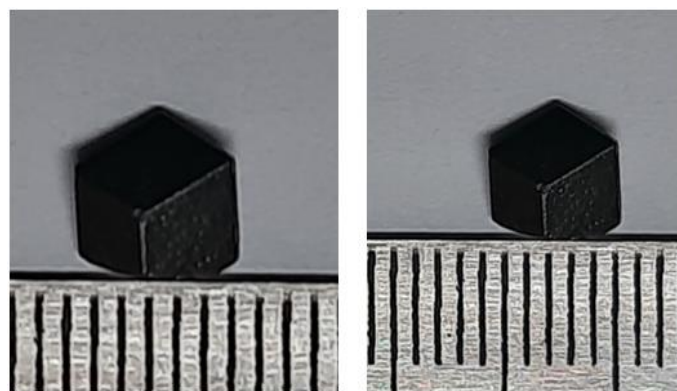


Fig. 3. Capsaicin doped MAPbI₃ single crystal obtained by ITC method.

2.4. Characterizations and measurements

Scientific instruments and equipment were used to analyse the crystal structure in detail. Powder X-ray diffraction of synthesised MAPbI₃ and Capsaicin doped MAPbI₃ single crystals were performed using a Rigaku Miniflex 600 X-ray diffractometer with CuK α radiation. For single crystal XRD measurements at room temperature, a Bruker Kappa Apex II ($\lambda=0.71073$ Å) X-Ray diffractometer was employed. A HORIBA LABRAM HR Evolution Raman Spectrometer was used to measure the Raman characteristics of the synthesised single crystals.

3. RESULTS AND DISCUSSION

The crystal structure of the synthesised MAPbI₃ sample was studied using powder X-ray diffraction studies. The XRD data collected was compared with the ICSD data. At 2θ values, 14.08° , 28.44° , 31.85° , 40.58° , and 43.19° of the MAPbI₃ tetragonal structure, a set of favorable orientations corresponding to the planes (110), (220), (310), (224), and (330) were detected. Minor peaks can also be found at 19.92° , 23.54° , 24.52° , 34.94° , 50.22° , and 52.54° , which are ascribed to the planes (112), (211), (202), (204), (404), and (336). The XRD pattern of MAPbI₃ shown in Figure 4 indicated two impurity peaks at 2θ values of 12.64° and 25.79° . These two impurity peaks (marked by *) corresponds to the PbI₂ contaminant present in the synthesised MAPbI₃ single crystal [15]. The phase purity and stability of the developed MAPbI₃ single crystal can be improved by the addition of Capsaicin.

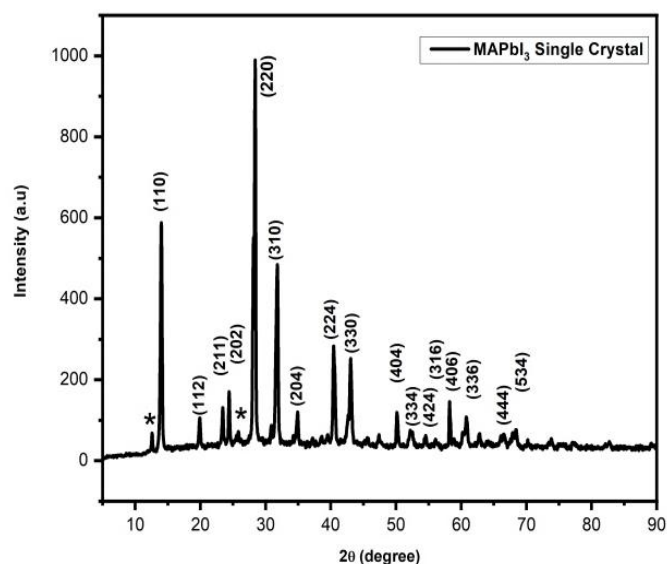


Fig. 4. Powder XRD pattern of MAPbI₃.

The active component of chilli peppers, Capsaicin (8-methyl-N-vanillyl-6-nonenamide), was utilized as an adjuvant to increase the crystal quality and stability of MAPbI₃

perovskite material. The addition of 0.1wt% Capsaicin to the above precursor solution decreases the nucleation rate and also increases the growth rate of the MAPbI₃ crystal than the above case. The powder X-Ray diffraction studies on the capsaicin doped MAPbI₃ sample shows the tetragonal structure of MAPbI₃ with phase purity and good quality. The impurity peaks present in the MAPbI₃ perovskite sample were completely removed in the Capsaicin doped MAPbI₃ single crystal and the crystal planes (532) and (600) were well defined within the Capsaicin doped MAPbI₃ XRD pattern (Figure 5). The XRD pattern peaks are well defined with appreciable intensity. Hence it is inferred that the phase purity and stability of the Capsaicin doped MAPbI₃ is better.

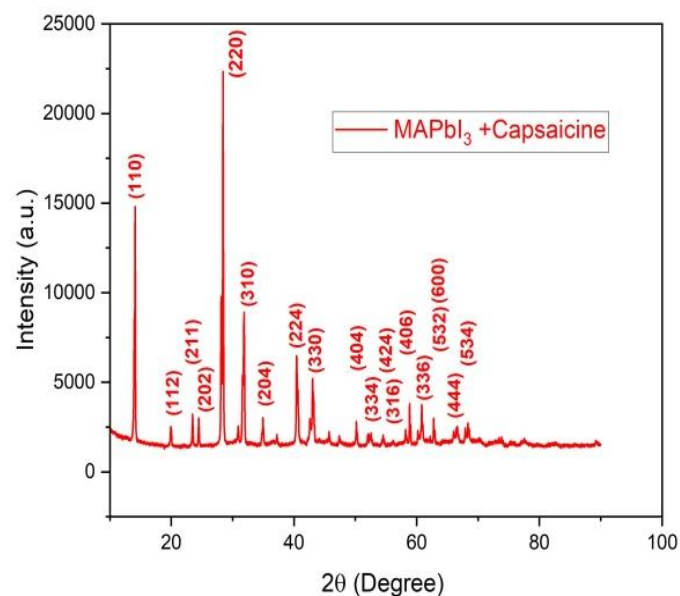


Fig. 5. Powder XRD pattern of Capsaicin doped MAPbI₃.

Fourier Transform Infrared Spectroscopy helps to find various molecular interactions in a particular sample. In this study, FTIR is used to investigate the structural details of capsaicin doped MAPbI₃ single crystals. Figure 6 shows the various vibrational bands of MAPbI₃ and capsaicin doped MAPbI₃ single crystal, which will help to study more about molecular structure change in MAPbI₃ single crystal by the incorporation of capsaicin as an additive. The powdered samples of crystals can be placed in the JASCO FTIR 4700 spectrometer to obtain the FTIR spectrum. The wide IR band observed at 3450 cm^{-1} represents the water absorption, which is due to residue water initially absorbed by the MAPbI₃ perovskites from the atmosphere [16,17]. At the same time, such a broad band is not intensely observed in the capsaicin doped MAPbI₃ single crystal shows the improvement in the crystal quality. FTIR spectrum also shows a correlation between the development of the band at 1518 cm^{-1} and the broad absorption mode of water at 3450 cm^{-1} [17]. The IR band at 1518 cm^{-1} belongs to the symmetric and asymmetric O-H stretching modes of water [16–18], which is found to be present only at MAPbI₃ single crystal and not in capsaicin doped MAPbI₃. The CH₃-NH₃⁺ bend mode at 1580 cm^{-1} and

$\text{CH}_3\text{-NH}_3^+$ rock mode at 1465 cm^{-1} of MAPbI_3 single crystal [17, 18] is also observed in capsaicin doped MAPbI_3 single crystal. The IR band present at 908 cm^{-1} and 943 cm^{-1} corresponds to $\text{CH}_3\text{-NH}_3^+$ rock mode is found in both crystals [16, 17]. The capsaicin-doped crystal lacks characteristic IR bands at 3450 and 1518 , which represents the bonding between H_2O and MA. The absence of these two peaks indicate the quality of the synthesized single crystal. Various absorption frequencies can be found out from each peak in the spectrum. This is shown in Table 1 with different bonding and nature of vibration.

Table 1. FTIR vibrational bands of MAPbI_3 single crystal.

Wavenumber (cm^{-1})	Type of bond	Vibration mode
3450	H_2O	Stretching
1580	NH^+	Bending
1518	H_2O	Bending
1465	$\text{CH}_3\text{-NH}_3^+$	Bending
1249	$\text{CH}_3\text{-NH}_3^+$	Rocking
943	$\text{CH}_3\text{-NH}_3^+$	Rocking
908	$\text{CH}_3\text{-NH}_3^+$	Rocking

A confocal Raman spectroscopic technique was utilized to solve the structural problems in MAPbI_3 and Capsaicin doped MAPbI_3 single crystal by using a HORIBA LABRAM HR Evolution Raman Spectrometer. On a microscopic scale, Raman spectroscopy is better to identify structural as well as compositional variations in the above synthesized single

crystals [19, 20]. The ligand mediated MAPbI_3 perovskite crystals show a high quality crystal structure and stability [21]. Raman spectroscopy helps systematic investigation of these properties. Raman measurements of MAPbI_3 single crystals were performed using an excitation wavelength of 600 nm with 10% of non-dispersive filter from a Diode pumped solid state laser. Grancini et al. published a famous study on the vibrational modes of MAPbI_3 single crystals, discovering two broad bands nearly at 110 cm^{-1} and 250 cm^{-1} [22].

Figure 7 exhibits the Raman spectra of MAPbI_3 and Capsaicin doped MAPbI_3 . In this study, the first Raman peak was obtained at 98 cm^{-1} , which corresponds to the stretching mode of Pb-I cage within the Capsaicin added MAPbI_3 perovskite crystal. It was found that the Pb-I stretching in the ligand added MAPbI_3 single crystal shows a very slight blue shift at the peak point when compared to the ordinary MAPbI_3 . This is due to the lattice strain at the crystal structure by the addition of capsaicin to the perovskite structure. Moreover the intense and the sharp peak at 98 cm^{-1} reveals a better crystallinity of the synthesized MAPbI_3 with capsaicin. The full width at half maximum of the peak at 98 cm^{-1} is reduced from 65.5 cm^{-1} to 26.6 cm^{-1} confirms that the Pb-I cage is a highly ordered structure in the capsaicin injected MAPbI_3 perovskite crystals. The obtained intensity increment in that particular peak of a Raman spectrum indicates that the fraction of substance in the MAPbI_3 sample contributing to that vibrational mode is increased. The experimentally found shoulder band at 66.4 cm^{-1} corresponds to the previously reported band at 56 cm^{-1} [23], which involves the bending of the I-Pb-I bonds and the subsequent liberation of the cations owing to inorganic cage deformation.

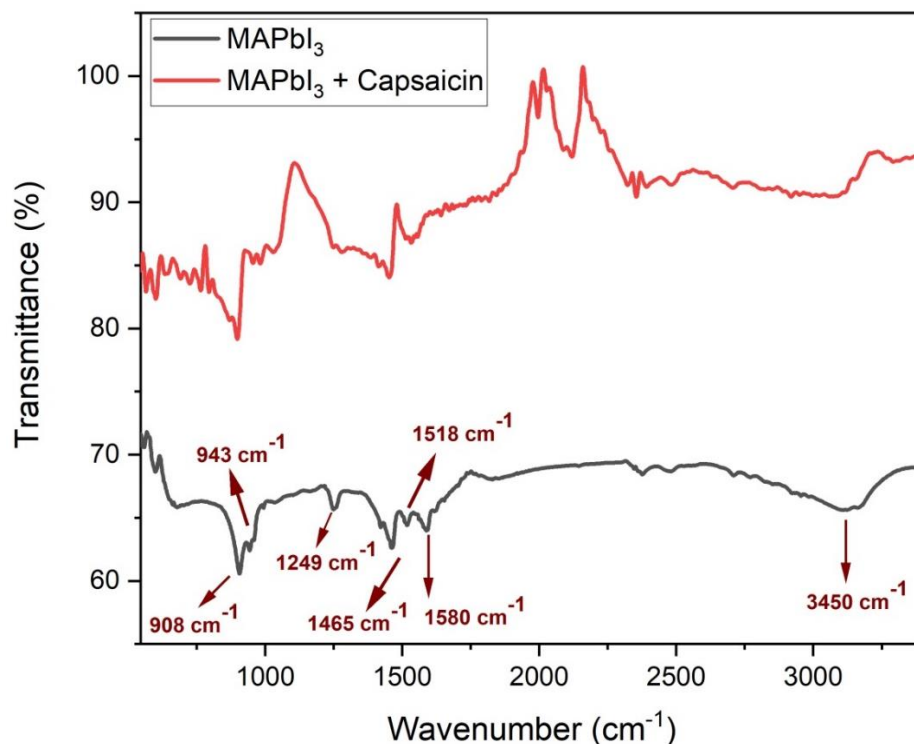


Fig. 6. FTIR Spectrum of MAPbI_3 and Capsaicin doped MAPbI_3 .

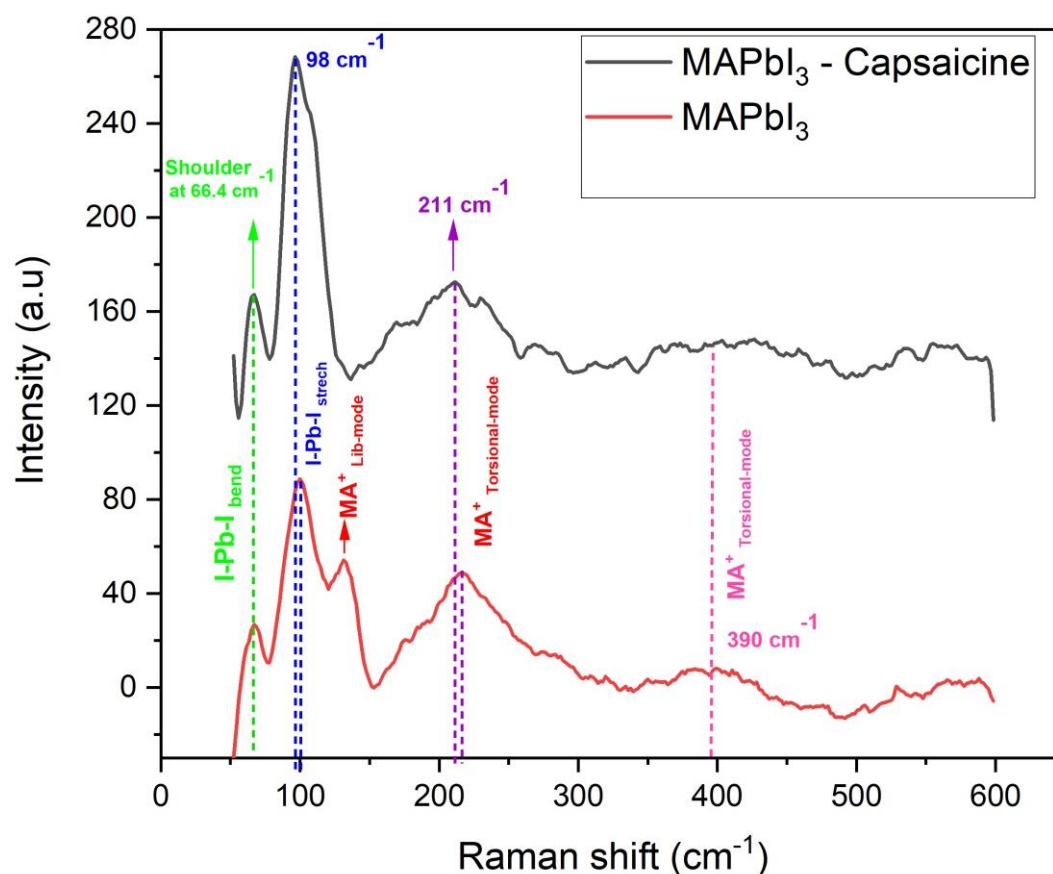


Fig. 7. Raman spectra of MAPbI₃ and Capsaicin doped MAPbI₃.

Raman spectroscopy is a useful method for investigating the vibrational structure and structural dynamics of MA in MAPbI₃ perovskite, and it complements static information by techniques such as X-ray diffraction. The Raman peak near at 129 cm⁻¹ is formed due to the liberation mode of organic cation MA in pure MAPbI₃ perovskite material. The frequency that corresponds to the liberation mode of the MA cation is fairly sensitive to the inorganic framework's local structure. In MAPbI₃ crystal structure each organic MA cation is exposed to a unique local environment, which has an impact on vibrational frequencies, particularly liberation vibrations. In that case, the expected band at 119 cm⁻¹ [24, 25] is shifted to 129 cm⁻¹, which is absent in the newly synthesized capsaicin added MAPbI₃. There is also a broad and unresolved pattern between 150 cm⁻¹ and 300 cm⁻¹, as well as a weak peak nearly at 390 cm⁻¹. The broad Raman peak at 211 cm⁻¹ corresponds to the torsional mode of the MA cation with slight difference in the peak position.

Raman intensity anticipated for torsional modes increases with structural disorder and huge variances in torsional frequencies reported in distinct MAPbI₃ crystal structures, according to several literatures [25]. Due to the considerable orientational mobility, the MA cations are distributed in a random orientation within the inorganic cage in the more disordered phase of MAPbI₃ [22] (at a temperature greater than 327 K the cubic phase shows the extreme case [26]). As a result of this, the Raman peak shows

a red-shift and broadening roughly at 211 cm⁻¹. The weak feature at 390 cm⁻¹ also corresponds to the torsional mode of MA organic cation, which is not specific in the Capsaicin doped one and is also broadened over the range 325 cm⁻¹ to 475 cm⁻¹. The torsional mode of the MA cations is thus attributed to the broad and unresolved band over the 300 cm⁻¹ to 475 cm⁻¹, and we suggest this mode as a possible marker of the orientational order of the organic cations in the material, and hence of the whole crystal.

The frequency of the MA torsional modes in crystal structures may be the result of two opposing effects related to the interactions between the cation and the inorganic cage. On the one hand, MA molecule deformation shifts the torsional mode toward higher frequencies; on the other hand, the creation of particular hydrogen bonding couplings, which are characteristic to these compounds, shifts this mode toward lower frequencies [22, 25].

When comparing the evolution of the Raman spectrum from "MAPbI₃" to "Capsaicin doped MAPbI₃" (see Figure 7), a distinct pattern emerges: (i) the band at around 98 cm⁻¹ blue-shifts, its intensity increases strongly and band width is narrowed; (ii) the peak at 211 cm⁻¹ is slightly blue-shifted; (iii) the band at around 129 cm⁻¹ is missing; (iv) the peak at around 390 cm⁻¹ is not well defined and dispersed throughout a large range. Finally, our findings reveal that doping causes structural changes in MAPbI₃, which may enhance its performance in various optoelectronic devices.

4. CONCLUSION

This study presents a comprehensive analysis of the effects of Capsaicin doping on the structural, vibrational, and crystallographic properties of organic-inorganic hybrid perovskite single crystals. Capsaicin, a natural organic molecule, was utilized as an additive in the synthesis of MAPbI₃ single crystals, resulting in significant improvements in crystal quality and stability. The incorporation of Capsaicin during the growth process reduced nucleation rates while enhancing growth rates, yielding larger and structurally robust crystals. Powder X-ray diffraction analysis demonstrated the elimination of impurity peaks present in pristine MAPbI₃ crystals, confirming improved phase purity. The emergence of well-defined crystal planes, such as (532) and (600), further highlighted the enhanced structural integrity of the doped crystals. Vibrational spectroscopic techniques, including Raman and FTIR spectroscopy, provided insights into the molecular interactions and vibrational modes of the doped crystals. A notable reduction in water absorption bands and the absence of certain vibrational modes associated with defects underscored the superior quality of Capsaicin-doped crystals compared to undoped MAPbI₃. The findings of this study emphasize the critical role of Capsaicin as a versatile ligand in regulating nucleation and growth processes, reducing crystallographic defects, and enhancing phase stability. These improvements hold significant promise for advancing the performance of perovskite-based optoelectronic devices, including solar cells, photodetectors, and light-emitting diodes. Future work should explore the application of similar organic dopants in perovskite systems, along with a deeper investigation into the optoelectronic properties of Capsaicin-doped materials. By integrating novel organic additives, the development of next-generation perovskite materials with exceptional stability and efficiency can be realized, revolutionizing the field of optoelectronics.

DECLARATIONS

Ethical Approval

Not Applicable

Funding

Not applicable

Availability of data and material

The data of the manuscript are available upon request.

Conflicts of Interest

The authors declare no conflicts of interests. The authors alone are responsible for the content and writing of this article.

Authors' contributions

All the authors contribute equally to the article, in writing and editing

REFERENCES

- [1] Liu, Y., Yang, Z. and Liu, S., **2018**. Recent progress in single-crystalline perovskite research including crystal preparation, property evaluation, and applications. *Advanced Science*, 5(1), p.1700471.
- [2] Lei, Y., Chen, Y. and Xu, S., **2021**. Single-crystal halide perovskites: opportunities and challenges. *Matter*, 4(7), pp.2266-2308.
- [3] Chen, Y., He, M., Peng, J., Sun, Y. and Liang, Z., **2016**. Structure and growth control of organic-inorganic halide perovskites for optoelectronics: From polycrystalline films to single crystals. *Advanced Science*, 3(4), p.1500392.
- [4] Yang, M., Tian, T., Feng, W., Wang, L. and Wu, W.Q., **2021**. Custom molecular design of ligands for perovskite photovoltaics. *Accounts of Materials Research*, 2(12), pp.1141-1155.
- [5] Hills-Kimball, K., Yang, H., Cai, T., Wang, J. and Chen, O., **2021**. Recent advances in ligand design and engineering in lead halide perovskite nanocrystals. *Advanced science*, 8(12), p.2100214.
- [6] Salih, M.N.M., ObaidAl-Husseini, Z.N. and Aljamali, N.M., **2018**. Formation of New Ligands Imine-(Oxazole, Thiazole, Thiophene) And Study of (Chemical Investigation and Chromatographic Applications). *International Journal of Engineering & Technology*, 7(4.36), pp.580-585.
- [7] Heuer-Jungemann, A., Feliu, N., Bakaimi, I., Hamaly, M., Alkilany, A., Chakraborty, I., Masood, A., Casula, M.F., Kostopoulou, A., Oh, E. and Susumu, K., **2019**. The role of ligands in the chemical synthesis and applications of inorganic nanoparticles. *Chemical Reviews*, 119(8), pp.4819-4880.
- [8] Xiong, S., Hou, Z., Zou, S., Lu, X., Yang, J., Hao, T., Zhou, Z., Xu, J., Zeng, Y., Xiao, W. and Dong, W., **2021**. Direct observation on p-to n-type transformation of perovskite surface region during defect passivation driving high photovoltaic efficiency. *Joule*, 5(2), pp.467-480.
- [9] Khan, B.A., Rashid, F., Khan, M.K., Alqahtani, S.S., Sultan, M.H. and Almoshari, Y., **2021**. Fabrication of

- capsaicin loaded nanocrystals: Physical characterizations and in vivo evaluation. *Pharmaceutics*, 13(6), p.841.
- [10] Cha, H., Bae, S., Lee, M. and Jeon, H., **2016**. Two-dimensional photonic crystal bandedge laser with hybrid perovskite thin film for optical gain. *Applied Physics Letters*, 108(18).
- [11] Guo, Y., Liu, C., Tanaka, H. and Nakamura, E., **2015**. Air-stable and solution-processable perovskite photodetectors for solar-blind UV and visible light. *The Journal of Physical Chemistry Letters*, 6(3), pp.535-539.
- [12] Espinosa, N., Serrano-Luján, L., Urbina, A. and Krebs, F.C., **2015**. Solution and vapour deposited lead perovskite solar cells: Ecotoxicity from a life cycle assessment perspective. *Solar Energy Materials and Solar Cells*, 137, pp.303-310.
- [13] Ben-Uliel, T., Aviv, H., Zhou, J., Li, M., Avadyayev, S., Kapon, O., Damle, V., Yi, C. and Tischler, Y., **2020**. Raman scattering obtained from laser excitation of MAPbI₃ single crystal. *Applied Materials Today*, 19, p.100571.
- [14] Pistor, P., Ruiz, A., Cabot, A. and Izquierdo-Roca, V., **2016**. Advanced Raman spectroscopy of methylammonium lead iodide: development of a non-destructive characterisation methodology. *Scientific Reports*, 6(1), p.35973.
- [15] da Silva Filho, J.M.C. and Marques, F.C., **2018**. Growth of perovskite nanorods from PbS quantum dots. *MRS advances*, 3, pp.1843-1848.
- [16] Pammi, S.V.N., Tran, V.D., Maddaka, R., Eom, J.H., Jung, J.S., Jeong, H.M., Kim, M.D., Pecunia, V. and Yoon, S.G., **2020**. Bromine Doping of MAPbI₃ Films Deposited via Chemical Vapor Deposition Enables Efficient and Photo-Stable Self-Powered Photodetectors. *Advanced Optical Materials*, 8(19), p.2000845.
- [17] Tang, X., Brandl, M., May, B., Levchuk, I., Hou, Y., Richter, M., Chen, H., Chen, S., Kahmann, S., Osvet, A. and Maier, F., **2016**. Photoinduced degradation of methylammonium lead triiodide perovskite semiconductors. *Journal of Materials Chemistry A*, 4(41), pp.15896-15903.
- [18] Guo, X., McCleese, C., Kolodziej, C., Samia, A.C., Zhao, Y. and Burda, C., **2016**. Identification and characterization of the intermediate phase in hybrid organic-inorganic MAPbI₃ perovskite. *Dalton Transactions*, 45(9), pp.3806-3813.
- [19] Das, R.S. and Agrawal, Y.K., **2011**. Raman spectroscopy: Recent advancements, techniques and applications. *Vibrational Spectroscopy*, 57(2), pp.163-176.
- [20] Pérez-Osorio, M.A., Lin, Q., Phillips, R.T., Milot, R.L., Herz, L.M., Johnston, M.B. and Giustino, F., **2018**. Raman spectrum of the organic-inorganic halide perovskite CH₃NH₃PbI₃ from first principles and high-resolution low-temperature Raman measurements. *The Journal of Physical Chemistry C*, 122(38), pp.21703-21717.
- [21] Zhang, H., Nazeeruddin, M.K. and Choy, W.C., **2019**. Perovskite photovoltaics: the significant role of ligands in film formation, passivation, and stability. *Advanced Materials*, 31(8), p.1805702.
- [22] Grancini, G., Marras, S., Prato, M., Giannini, C., Quarti, C., De Angelis, F., De Bastiani, M., Eperon, G.E., Snaith, H.J., Manna, L. and Petrozza, A., **2014**. The impact of the crystallization processes on the structural and optical properties of hybrid perovskite films for photovoltaics. *The Journal of Physical Chemistry Letters*, 5(21), pp.3836-3842.
- [23] Gottesman, R., Gouda, L., Kalanoor, B.S., Haltzi, E., Tirosh, S., Rosh-Hodesh, E., Tischler, Y., Zaban, A., Quarti, C., Mosconi, E. and De Angelis, F., **2015**. Photoinduced reversible structural transformations in free-standing CH₃NH₃PbI₃ perovskite films. *The Journal of Physical Chemistry Letters*, 6(12), pp.2332-2338.
- [24] Quarti, C., Grancini, G., Mosconi, E., Bruno, P., Ball, J.M., Lee, M.M., Snaith, H.J., Petrozza, A. and De Angelis, F., **2013**. The Raman spectrum of the CH₃NH₃PbI₃ hybrid perovskite: interplay of theory and experiment. *The Journal of Physical Chemistry Letters*, 5(2), pp.279-284.
- [25] Park, M., Kornienko, N., Reyes-Lillo, S.E., Lai, M., Neaton, J.B., Yang, P. and Mathies, R.A., **2017**. Critical role of methylammonium librational motion in methylammonium lead iodide (CH₃NH₃PbI₃) perovskite photochemistry. *Nano letters*, 17(7), pp.4151-4157.
- [26] Baikie, T., Fang, Y., Kadro, J.M., Schreyer, M., Wei, F., Mhaisalkar, S.G., Graetzel, M. and White, T.J., **2013**. Synthesis and crystal chemistry of the hybrid perovskite (CH₃NH₃)PbI₃ for solid-state sensitised solar cell applications. *Journal of Materials Chemistry A*, 1(18), pp.5628-5641.