

Article

Phase State Influence on Photoluminescence of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ Perovskites towards Optimized Photonics Applications

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Abstract: Perovskite halide has many advantages that attracted the attention of researchers in the last years, but many challenges prevent the use of halide perovskites in different applications. One of these challenges is the low thermal stability resulting in phase transitions with temperatures. Here, the photoluminescence (PL) characteristics and related phase transitions of different $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ ($\text{MA}(\text{Br}_x\text{I}_{1-x})_3$) perovskites structures have been investigated under a wide temperature range. The work that has been conducted demonstrates that under temperature, the exciton behavior of the halide anions, I and Br, has a considerable impact on structural phases and the fluorescence process. The obtained results for the temperature dependence of PL for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ showed a wide range of emission wavelengths, between 500–800 nm with a decrease in PL intensity with increasing temperature. In addition, the ratio of both bromine and iodine in $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ affects the range of phase transition temperatures, where at $x = 0.00, 0.25$, and 0.50 the first transition occurs below room temperature (orthorhombic to tetragonal) phase and the other occurs above room temperature (tetragonal to cubic) phase. Furthermore, increasing the proportion of bromine causes all the transitions to occur below room temperature. The presented findings suggest a suitable halide component under a temperature-controlled phase transformation to benefit these materials in photonics devices.

Keywords: perovskite; photoluminescence; phase transition; tunable energy; mixed-halide



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1. Introduction

Lead-halide hybrid perovskite crystals have emerged as promising materials due to their unique chemical and physical properties such as broad absorption range, bandgap tunability, high carrier mobility, relatively long carrier lifetime, long carrier diffusion length, low non-radiative recombination rates, balanced electron/hole transportation, high photo conversion efficiencies, and their relative ease of synthesis from simple starting materials through solution processing or vapor deposition [1–5]. Perovskite basically adopts a crystal structure consisting of corner-sharing TiO_6 octahedra in three dimensions, with Ca occupying the cuboctahedra cavity in each unit cell [6]. The same crystal structure is also found for a broad range of materials with ABX_3 stoichiometry [7], where A is an organic cation or an inorganic cation, B is a metal cation (e.g., Pb, Sn), and X is a halide anion (I, Br, Cl) dependent Goldschmidt's tolerance factor [8–10].

Methylammonium lead halide, MAPbX_3 , has received increasing attention as an absorber material for perovskite solar cells. The halide anion was the most efficiently varied component in hybrid perovskites. With the increasing atomic size of group VIIA ($\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$), the absorption spectra shifts to longer wavelengths with reduction in energy. This can be attributed to the decrease in electronegativity to better match that of Pb, effectively reducing ionic and increasing covalent character Iodide (I) [11,12]. MAPbI_3 crystallizes in the tetragonal phase at room temperature. The addition of iodine gives many advantages, the most important of which is the small value of the band gap, for example, in solar cells it helps by increasing their efficiency [4,13].

MAPbBr₃ is another model of the organic-inorganic halide perovskite (OIHP) group. It crystallizes in the cubic phase at room temperature. However, MAPbI₃ is more efficient than MAPbBr₃ in photovoltaics applications, whilst MAPbBr₃ is more stable in ambient conditions [14]. The value of bandgap MAPbI₃ is 1.51–1.55 eV, which is close to the optimal bandgap range for a single-junction solar cell is 1.1–1.4 eV, [15]. The ideal MAPbI₃ perovskite structure typically has the lowest bandgap and highest electron mobility. Distortions from the ideal symmetry cubic phase (space group Pm3m) have an impact on the bandgap and electronic transport properties, where the temperature change is one of the reasons for the transition [16]. MAPbBr₃ has a larger band gap (2.2 eV) than MAPbI₃, despite that MAPbBr₃ has better stability under air and moist conditions, compared to MAPbI₃.

Phase transition due to temperature variations of single crystal structure MAPb(Br_xI_{1-x})₃ has been studied by several groups of research. The phase transitions of MAPbI₃ from tetragonal to cubic at around 315–330 K and from orthorhombic to tetragonal 144–160 K [1,17] have been confirmed in different ways, approved by spectroscopic Ellipsometry techniques [18], and XRD technique [19], for single crystal MAPbBr₃ the phase transitions from cubic to tetragonal phase at around 230 K and then to orthorhombic phase around 150 K [19,20]. Temperature-dependent PL studies for thin film of MAPbI₃ showed the phase transitions followed by PL shifts [21–23]. Therefore, MAPb(Br_xI_{1-x})₃ perovskites with heating undergo two-phase transitions, orthorhombic (Pnm) to tetragonal (I4/mcm), then to cubic(Pm3m).

This study shows how to make high-quality perovskite films, as well as temperature-dependent PL and related phase transitions of different MAPb(Br_xI_{1-x})₃, and finally, how the anion ratio affects the activation energy value of MAPb(Br_xI_{1-x})₃.

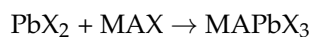
2. Materials and Methods

2.1. Materials

Lead(II) iodide (PbI₂, 99.999% trace metals basis); methylammonium iodide (MAI, 99.999% trace metals basis); lead(II) bromide (PbBr₂, 99.999% trace metals basis); and methylammonium bromide (MABr, 99.999% trace metals basis) used in this study were purchased from Sigma Aldrich and were used as received. All materials were used as received from the company with any further treatment or purification.

2.2. Methods

The studied films were basically formed by depositing the suitable mixture of the primary components CH₃NH₃X(MAX) and PbX₂ (X = Br, I), with the favorite stoichiometric ratios on glass substrate using single-source thermal evaporator system (Edwards 306 Coating System). The film could be experimentally synthesized using the two precursor (PbX₂) and (MAX) and summarized in the following reaction:



For example, to produce MAPbI₃, at first, glass substrate should be cleaned carefully and placed on a holder fronting the precursor sources. The material sources were first charged on a molybdenum boat sequentially with 46.10 mg (~0.1 mmol) of PbI₂ and 158.97 mg (~1.00 mmol) of (MAI). After having a relatively low pressure ~10⁻⁴ mbar in the vacuum chamber, the PbI₂ was first started to evaporate onto the glass. MAI was then evaporated on top of the evaporated PbI₂. After that, sample was taken out and annealed using a hot plate at 120 °C for 10 min. The film thickness was measured using a Dektak 150 stylus profiler (Bruker, Billerica, MA, USA). The schematic diagram of the thermal evaporation system parts is shown below in Figure 1.

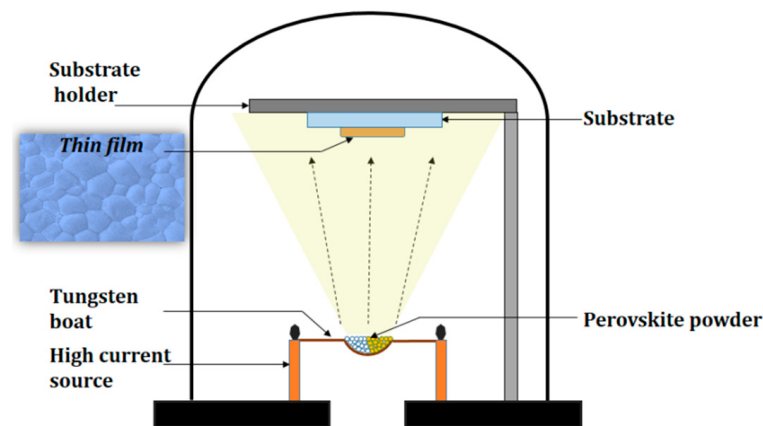
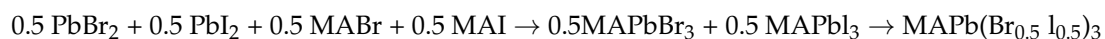


Figure 1. Schematic diagram of the thermal evaporation setup [10].

By repeating the previous method in the same way, another sample with different structure could be synthesized and summarized in the following reactions:



2.3. Characterization

2.3.1. Structural Characterization

All measurements were recorded at room temperature in an ambient environment. The morphology was investigated by using scanning electron microscopy (SEM-JEOL-7600F, JEOL, Japan) and the crystal phases of the films were verified (XRD—Miniflex 600, Rigaku, Japan) with copper K α radiation ($\lambda = 1.5418 \text{ \AA}$). The scanning angle (2θ) varied between 10° to 80° at a scanning rate (step size) of 0.02° at $3^\circ/\text{min}$.

2.3.2. Optical Characterization

For optical characterization, the absorption spectra of the samples were recorded by an ultraviolet-visible (UV-vis) spectrophotometer (V-670, JASCO, Tokyo, Japan). The PL spectra were obtained by using a fluorescence spectrophotometer (FP-8200, JASCO, Tokyo, Japan) over the wavelength range of 350–800 nm. For temperature-dependent emission, the sample holder temperature was controlled using CTI-Cryogenics (CTI, 8200, Helix Technology Corporation, Mansfield, Massachusetts, USA) over the temperature range of 10–400 K. The sample was placed on a copper sample holder to fit a $1 \text{ cm} \times 1 \text{ cm}$ slide and closed by a vacuum shroud. A schematic diagram of the low-temperature measurement setup is shown in Figure 2. The chamber is emptied after the vacuum pump connected to it is turned on, and the pressure reduces to approximately 8×10^{-3} . The compressor works to cool the environment that surrounds the sample.

(Cryodyne Refrigeration System Model 22) and (Lakeshore- Model 325 dual-channel) connected to the cold head and was used in monitoring and controlling the sample temperature. The sample was shined to be excited by continuous wave (CW) laser beam (Vortran Laser Technology, Inc., Rocklin, CA, USA) with a wavelength of $473 \pm 5 \text{ nm}$ with power controlled remotely to the desired level. The signals emitted by the samples were directed through an optical fiber to a computerized spectrograph (Ocean Optics QE65 Pro spectrograph) based on Spectra Suite Spectroscopy Software to read the data related to the sample PL spectroscopy.

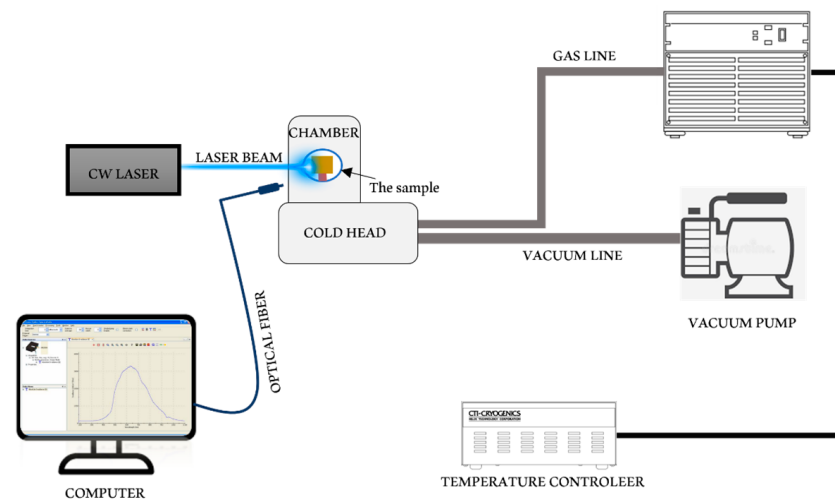


Figure 2. Schematic diagram of the low-temperature measurements setup.

3. Results and Discussion

3.1. Samples Morphology and Crystalline Structure

The sample of a surface morphology of prepared thin $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ films is shown in Figure 3. The perovskite material was distributed homogeneously and uniformly of the substrate surface with grains of an average length of 152 nm for MAPbBr_3 films. The average grain size appeared to be decreasing with decreasing (x) value. In Figure 3 for instance, the values of (74, 96, 125 nm) correspond to $x = (0.25, 0.50, 0.75)$, respectively. For MAPbI_3 perovskite, the average length of ~74 nm could be obtained. Perovskites cover the entire substrate surface completely for all samples prepared without the presence of voids, pits, or cracks.

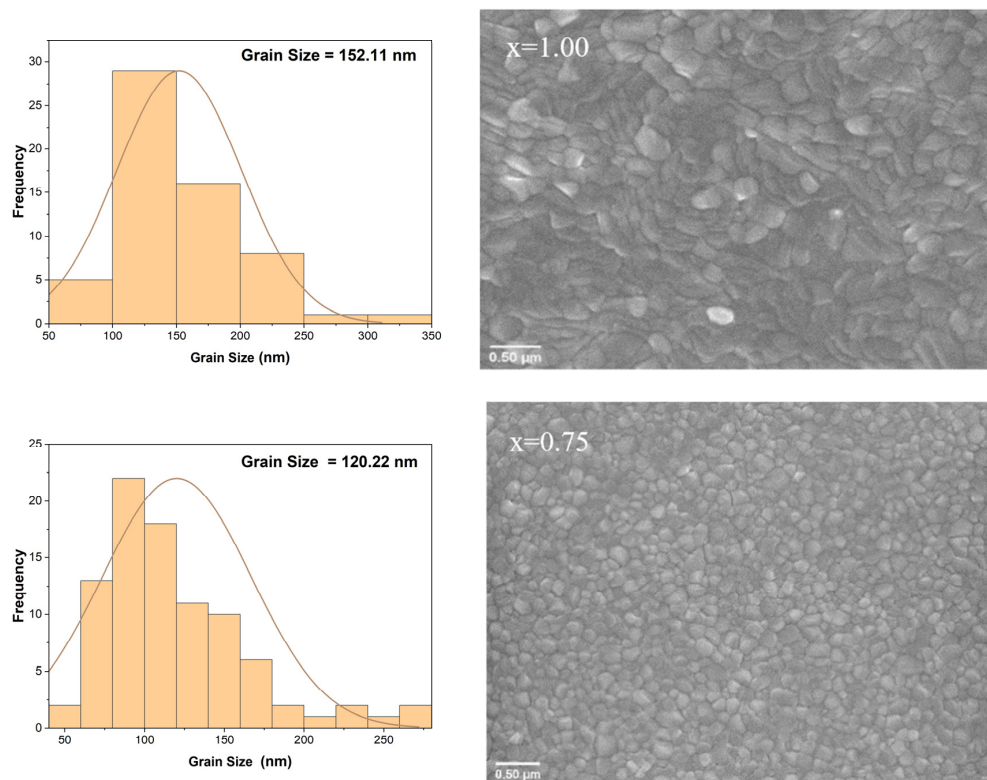


Figure 3. Cont.

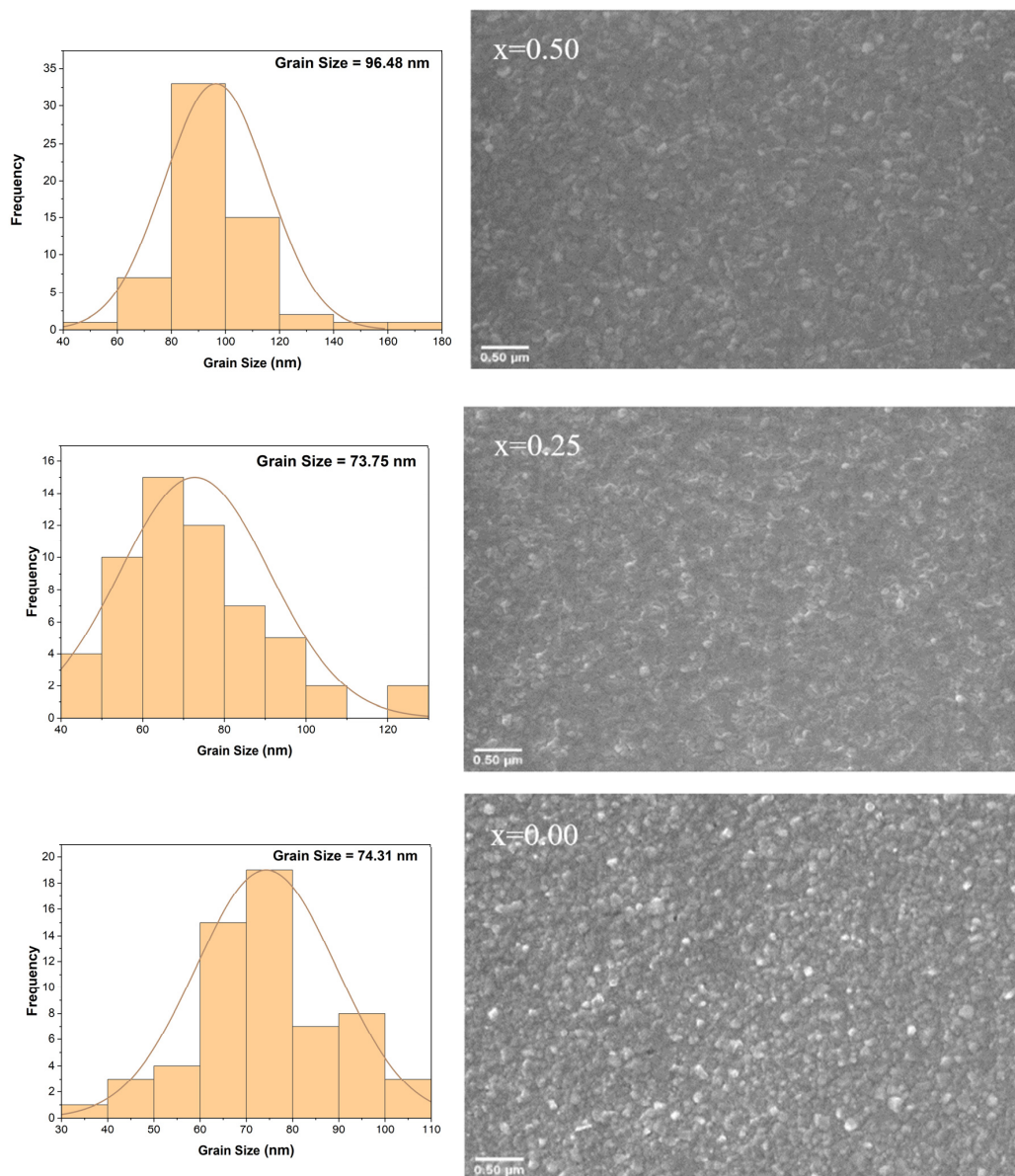


Figure 3. SEM images of the MAPb(Br_xI_{1-x})₃ thermally evaporated perovskite films.

Crystalline structures of MAPb(Br_xI_{1-x})₃ has been investigated at various values of x. Figure 4a shows the typical XRD pattern for studied samples at five values of X at room temperature. For MAPbI₃ (without Br), the planes (110), (220), and (310) belonging to the tetragonal structure [24], appear at around $2\theta \sim 13^\circ$, 27° , and 31° , respectively. By increasing the (Br) portion, the lattice parameters were affected, and these lines are getting shifted to appear at $2\theta \sim 14.21^\circ$, 29.42° , and 33.01° , respectively. Lattice parameters of the phases decrease with the increase in the total amount of bromine. For example, at $x = 1.00$, 0.75 the values of 2θ were around 14.08° , 29.24° and 32.84° which correspond to (hkl) values of (100), (200), and (210) which belong to cubic phase [25–27]. In this situation, the tetragonal superlattice phase disappeared. Values of 2θ and FWHM for each plane in five perovskites structures were tabulated in Table 1.

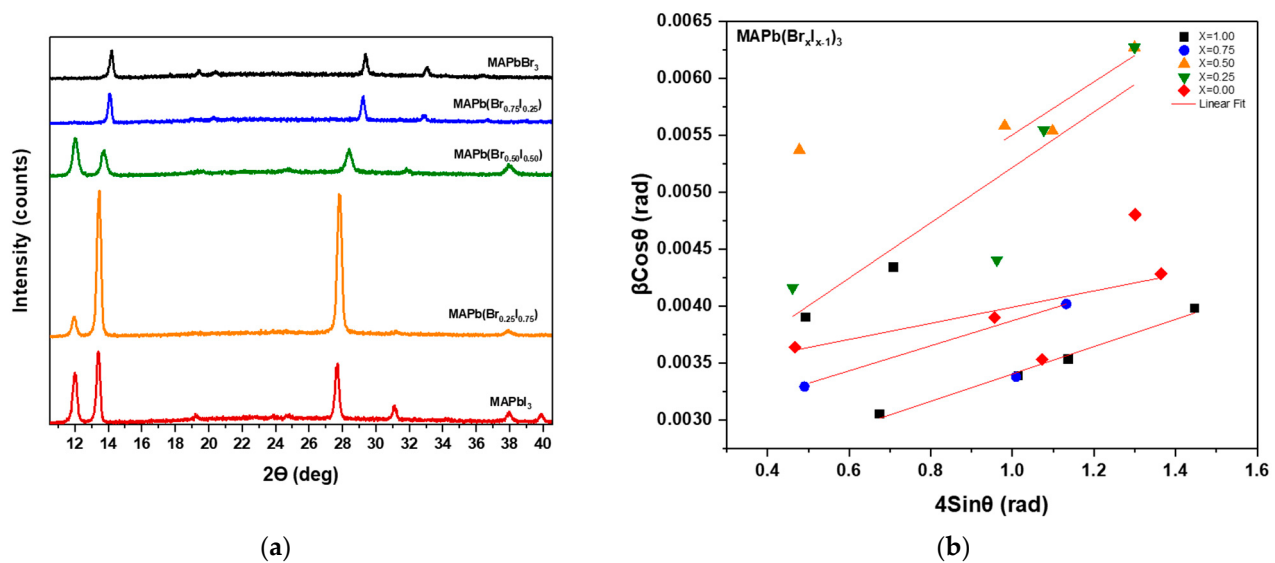


Figure 4. (a) XRD pattern and (b) W-H plot, of the MAPb(Br_xI_{1-x})₃ thin films.

Table 1. Values for an XRD pattern at three peaks.

Compound	Peak (1)		Peak (2)		Peak (3)	
	2θ (deg)	FWHM (meV)	2θ (deg)	FWHM (nm)	2θ (deg)	FWHM (nm)
MAPbBr ₃	14.21	0.193	29.42	0.2	33.01	0.217
MAPb(Br _{0.75} I _{0.25})	14.08	0.19	29.24	0.20	32.84	0.24
MAPb(Br _{0.50} I _{0.50})	13.72	0.31	28.39	0.33	31.24	0.22
MAPb(Br _{0.25} I _{0.75})	13.43	0.24	27.82	0.26	31.87	0.33
MAPbI ₃	13.4	0.21	27.67	0.23	31.11	0.21

To estimate the average grain size and strain of the films, a modified version of the Williamson–Hall (W–H) analysis, namely, the Uniform Deformation Model was employed. This model is governed by [28]:

$$\beta_{hkl} \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \quad (1)$$

where, β_{hkl} is the peak broadening, λ is the wavelength of incident radiation, ϵ is the strain, D is the crystallite size, and k is a constant (~ 0.9). The dislocation density (δ) is defined by $\delta = \frac{1}{D^2}$. The results obtained from Figure 4a and redrawn in Figure 4b according to the W–H plot have been tabulated and listed in Table 2, for the different values of Br_x, I_{1-x} compositions. The results show a reduction in the grain size, increase in the lattice strain, and dislocation density as the percentage of I increases.

Table 2. The X-Ray diffraction parameters estimated from the W–H plot.

MAPb(Br _x I _{1-x}) ₃	1	0.75	0.50	0.25	0.00
Crystallite size, D (nm)	59	51.35	43.6	46.21	42.2
Micro strain (ϵ) $\times 10^{-3}$	1.08	1.13	2.3	2.4	0.71
Dislocation density (δ) $\times 10^{-3}$ (nm) ^{−2}	5.45	5.28	14.96	8.44	6.46

3.2. Spectral Characteristics

Absorbance, emission, and PL properties were studied for MAPb(Br_xI_{1-x})₃ at various values of halides compositions. The absorbance was obtained using Ultraviolet-visible (UV-Vis) spectroscopy at room temperature and shown in Figure 5 from which data were

extracted to calculate the direct band-gap energy (E_g) using by the well-known Tauc Plot equation:

$$((\alpha h\nu)^\gamma = A(h\nu - E_g)) \quad (2)$$

where α is the absorption coefficient, A is a proportionality constant. Calculated E_g values are listed in Table 3. Blue shift in the absorption wavelength peaks (excitonic peaks), or increase in E_g value, as the Br percentage increases could be observed.

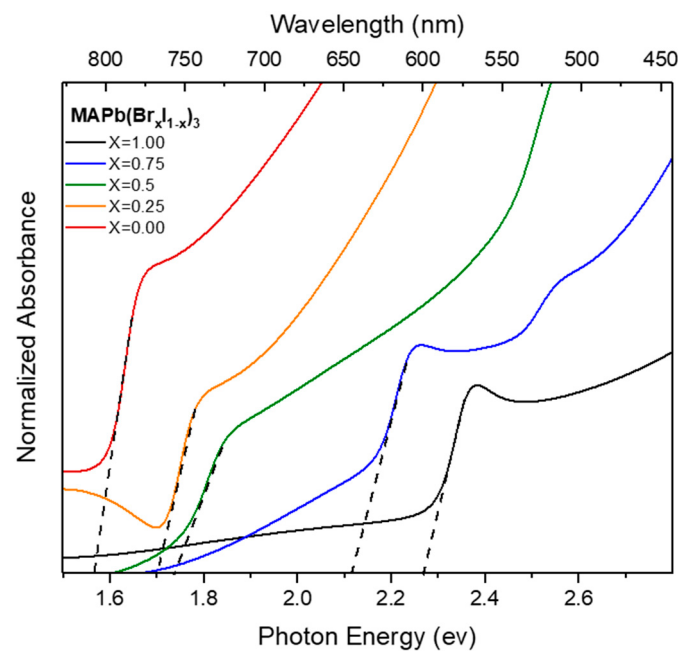


Figure 5. The absorbance values of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskite films.

Table 3. The Band-gap values and Wavelength position of peaks at room temperature.

$\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$	x Values				
	1.00	0.75	0.50	0.25	0.00
Energy bandgap (eV) at RT	3.54	3.35	2.8	2.99	1.56
Peak Emission (nm) at RT	541.45	715.85	728.2	743.39	765.85

The normalized emission spectrum was recorded for samples at room temperature. The emission wavelength peak of MAPbI_3 appears at around 760 nm and around 530 nm for MAPbBr_3 ; Figure 6, as agrees with others [19,29–31]. The peaks of emission for the rest of the samples with mixed halides were located between these two values. The related E_g is listed in Table 3. One could notice that the interval of peak values was not equal, or in other words, does not change systematically with x value. Peak values were aligned to the long wavelength side of the spectrum for the Br-free perovskite sample. This is an indication that the expected and recorded values of x were not very accurate. It means that some quantity of Br, but not I, that was confirmed by Energy-dispersive X-ray spectroscopy (EDX) results.

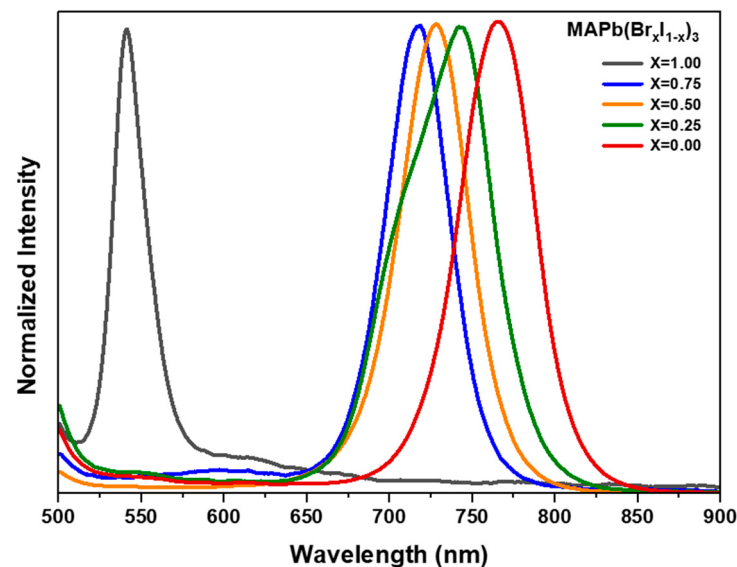


Figure 6. The Photoluminescence spectra of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskite films.

3.3. Temperature-Dependent of Phase Structure and PL for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ Perovskites

Temperature-dependent PL of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ has been studied over a wide range of temperature (10–400 K) under a low power density (7.9 mW cm^{-2}) CW laser beam of 473 nm excitation wavelength. Figure 7 shows a sample of PL recorded from $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ within 500–800 nm range of emission wavelength. The samples show an Inverse relationship between emission intensity and temperature, As the temperature increases, the value of the emission intensity decreases. On the other side, lowering temperatures lead to an increase in emissions intensity. The photoluminescence quantum yield (PLQY) with decreasing temperature is increasing, this increase leads to an increase in the intensity value of the PL, and the PLQY value is associated with radiative recombination and non-radiative recombination [32,33]. The charge carriers become less mobile with lower temperature, therefore they are frequently unable to reach the non-radiative recombination centers that are present in perovskite. Instead, they must recombine radiatively which gives rise to an increase in PLQY with decreasing temperature [34,35]. Phonon interactions have an effect on the luminescence and charge transport properties of these perovskites. Overall, the PL peak narrows as the temperature is lowered. It is the result of a decrease in the population of phonons, and therefore less homogenous broadening of the PL due to phonon coupling, as the temperature decrease [35].

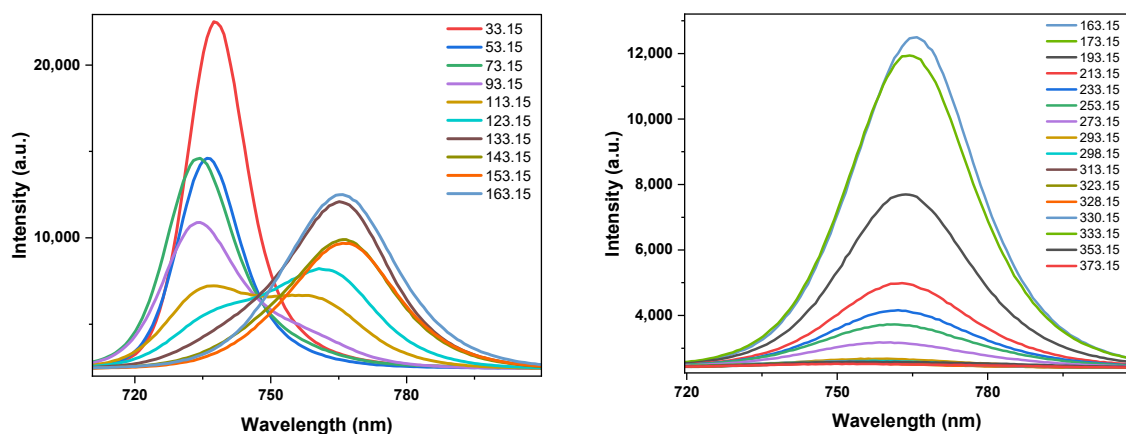


Figure 7. PL spectra of MAPbI_3 in the temperature range 33–353 K. excitation laser intensity of 7.9 mW cm^{-2} by 473 nm CW laser.

The trend of variation in emission wavelength due to the sample's temperature change does not obey the familiar manner of semiconductors. It was common in semiconductor materials that E_g decreases (result in red shifts of emission) as the temperature increases [36,37]. Whereas in studied perovskites with increasing temperature, blue shifts were observed with no continuity; Figure 8a–e. This unusual behavior was attributed to the stability of the maximum valence band [21] or due to irregular phase transition [21].

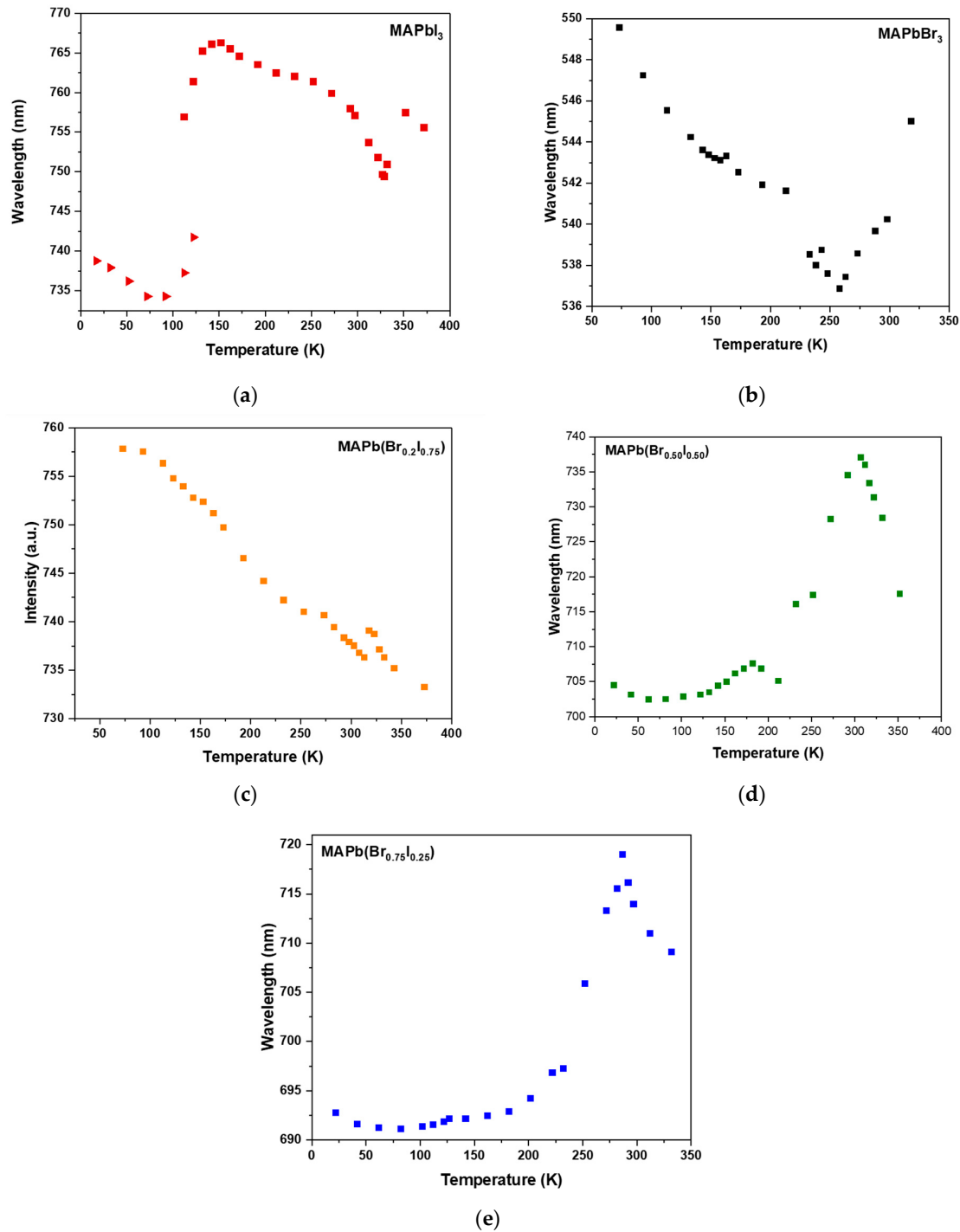


Figure 8. Temperature dependence of the emission band peak for the $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskite films, (a) for MAPbI_3 , (b) MAPbBr_3 , (c) $\text{MAPb}(\text{Br}_{0.25}\text{I}_{0.75})_3$, (d) $\text{MAPb}(\text{Br}_{0.50}\text{I}_{0.50})_3$, (e) $\text{MAPb}(\text{Br}_{0.75}\text{I}_{0.25})_3$.

MAPbBr_3 and MAPbI_3 pass through two-phase transitions with a temperature increase: from the orthorhombic to tetragonal phase and then, from the tetragonal to cubic

phases. For MAPbI₃ and MAPbBr₃, the first transition occurs around 150 K while and the second transition for MAPbI₃ occurs above room temperature around 330 K. However, MAPbBr₃ shows the second transition below room temperature around 230 K. This can occur because of the difference in ionic radius of the two halides [29,36–38]. Phase transition can follow by tracking the change in the position of the peak with increasing temperature. In addition, changing in the structural phase will lead to a change in the value of the energy bandgap and a change in the optical properties, which will notably affect the PL spectrum. Therefore, based on PL observations, phase structures could be recognized where the XRD data were used to know the phase type at room temperature, as shown in Figure 4.

Two emission bands have been observed from the MAPbI₃ samples at low temperature (<160 K) which was attributed to the coexisting of two (orthorhombic and tetragonal) phases simultaneously. The temperature ranges of the two phases coexisting start at 93 K and end at 156 K as shown in Figure 8a. Below this range, the material was in the orthorhombic phase and beyond that range it was in the tetragonal phase state. This means that there was a gradual transition along with slow wavelength variation of emission as indicated by two simultaneous bands of emission from the same intra-band transition on both sides of the structural phases [35]. Figure 7 shows that the intensity of the peak in the long wavelength band (LWB) will continue to increase as the temperature increases. The peak of the short wavelength band (SWB) decreases until it is no longer apparent, clearly at 133 K. With increasing temperature, a blue shift of SWB can be noticed up to 93 K.

Afterwards, a red shift was observed with heating the sample more until LWB starts glowing. Over this transition region, both SWB and LWB show a red shift as the temperature increases which agrees with other studies [16,21,37]. It is worth mentioning that a blue shift in the LWB maxima starts to occur after reaching 163 K of heating. It is expected that the LWB may be attributed to the tetragonal phase regime and the SWB to the orthorhombic phase. Therefore, the tetragonal phase dominates after the temperature exceeds 163 K. A blue shift in the LWB emission continues with increasing the temperature up to 330 K after which a red-shift occurs as the temperature reaches 350 K followed by blue shift again [1]. Over the red shift range (330–350 K), a transition from tetragonal phase state to the cubic one was expected.

For the MAPbBr₃ sample, the blue shift was observed as the temperature increases up to 157 K. Some fluctuation in the emission wave length was observed over a small range of temperature (157–163 K) which could be attributed to the beginning of the transition from the orthorhombic to the tetragonal phase of structure which was in agreement with others' studies [19,20,30,39,40]. A red shift in the emission appeared again over the temperature range of 257–317 K during which the structure started to take the cubic shape.

For MAPb(Br_xI_{1-x})₃, perovskites with mixed I and Br halides, the phase transition from the orthorhombic to the tetragonal phase occurs over the temperature range (120–160) K depending on the portion (*x*) value, Figure 8c–e. The phase transition from the tetragonal to the Cubic phase occurs over the temperature range (290–318) K. It is summarized in Table 4. Generally speaking, the addition of more Bromine (increase *x*) to the MAPb(Br_xI_{1-x})₃ results in reduced phase transformation temperature. MAPbI₃ and MAPbBr₃ shared the temperature transition from the tetragonal to the orthorhombic phase, but the mixture of bromine and iodine in perovskite led to a transition degree below 163 K. For the second transformation from the tetragonal to the cubic phase, the increase in bromine in MAPb(Br_xI_{1-x})₃ led to a decrease in the degree temperature of transformation, as shown in Table 4.

Table 4. The transition point with the temperature of MAPb(Br_xI_{1-x})₃ perovskite films.

MAPb(Br _x I _{1-x}) ₃	0	0.25	0.50	0.75	1
The transition from (orthorhombic to tetragonal) phase	163 ± 10		132 ± 10	122 ± 10	163 ± 10
The transition from (tetragonal to cubic) phase	330 ± 10	318 ± 10	312 ± 10	290 ± 10	263 ± 10

3.4. Activation Energy

Activation Energy (E_a) is the minimum amount of energy that must be provided to lead active atoms or molecules in the materials to undergo a chemical or physical reaction. The activation energy of different perovskite samples varies due to several reasons, including the difference in the structural phase with different external factors, the difference in the particle size of the film [41], and the difference in the temperature range. The E_a of MAPbI₃ in the tetragonal phase is 20 meV and increases to 200 meV in the cubic phase [1], where [40] concludes the value around 150 K is 29 meV for MAPbI₃ and 38 meV for MAPbBr₃. Another study calculated 65 meV for bulk [42] and 86.6 meV for a single crystal [43]. For CsPbBr₃ nanocrystals (NCs), E_a is 63.9 meV and decreases with increases the size of NCs to be 54.7, 43 and 35 meV [44]. Table 5 shows the values of E_a for some of the studied samples. An increase in E_a could be noticed as the portion of Br increases. This observation is consistent with the values of energy band gap. By temperature dependence of the integrated PL, emission intensities can be fitted using the Arrhenius equation [45].

$$I(T) = \frac{I_0}{1 + A \exp\left[-\frac{E_a}{k_B T}\right]} \quad (3)$$

where I_0 is the PL intensity at the lowest temperature and k_B is the Boltzmann constant. PL intensity is plotted as a function of temperature and calculated as the activation energy by the Arrhenius equation fitted. The resulting figures found from the above equation were plotted in Figure 9.

Table 5. E_a calculated by Arrhenius plots of perovskite films above 160 to 300 K range of temperature.

X	The Material	Activation Energy (meV)
0.00	MAPbI ₃	47
0.50	MAPb(Br _{0.50} I _{0.50}) ₃	67
1.00	MAPbBr ₃	71

As it is expected that the increase in bromine will lead to an increase in the value of E_a , this agrees with our results shown in Table 5.

Finally, parameter verification, optimization, and modification are fundamental to learning how to exploit the material's advantages in various applications. This paper provides an overview of MAPb(Br_xI_{1-x})₃ band gap expansion and activation energy change with anion ratio change between (Br, I), which aids in understanding halide perovskite and future development in this field. The thermal evaporation method of preparation yields high-quality nanocrystal films with no difficulties in preparation and no need for any solvent, facilitating their manufacture for different applications. Determining the type and percentage of the anion (x) helps to broaden the range of absorption and emission spectra, giving better efficiency in using it—for example, as sensors in solar cells with low energy consumption or use as active layers in photodetectors (highly efficient and polarization sensitive)—by taking advantage of the large absorption coefficients of perovskite that are controlled by the type and ratio of anion.

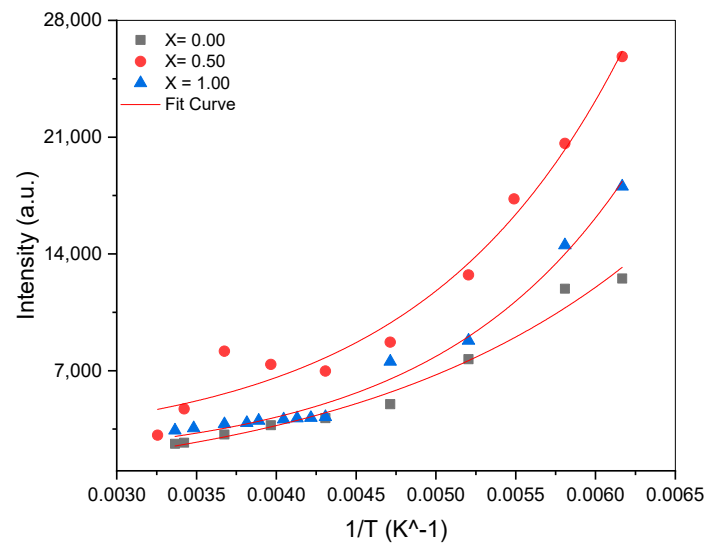


Figure 9. Temperature dependence of integrated PL intensity with Arrhenius equation fitting for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskite films.

4. Conclusions

The obtained results of temperature (18 to 373 K) dependence of PL for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites showed wide range of emission wavelengths: 500–800 nm with a decrease in PL intensity as the temperature increases. The phase transitions go along with temperatures variation for studied films, have been studied. The effects of anion replacement in $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ on phase transitions with temperature changes have been investigated. In general, there were two phase transitions for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ samples. One transition occurred below room temperature (orthorhombic to tetragonal) and the other occurred above room temperature (tetragonal to cubic) at $X = 0, 0.25$, and 0.50 , down room temperature at $X = 0.75$ and 1.00 . The temperature needed for such transitions can be controlled by varying the value of x (ratio of I to Br). In contrast to other semiconductor material, blue shifts in the emission wavelength were observed in the studied materials. A red shift could be noticed over the range of phase transition temperature. Over this range, a dual wavelength of emission was observed of MAPbI_3 . In addition, by the different ratios of X , the value of the activation energy of the perovskite changes, which increases with the increase in bromine. Therefore, the determination of a suitable halide component for a perovskite for controlling the phase structure, with temperature and activation energy value, helps to benefit these materials in photovoltaics or light-emitting devices.

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References

1. Milot, R.L.; Eperon, G.E.; Snaith, H.J.; Johnston, M.B.; Herz, L.M. Temperature-Dependent Charge-Carrier Dynamics in CH₃NH₃PbI₃ Perovskite Thin Films. *Adv. Funct. Mater.* **2015**, *25*, 6218–6227. [\[CrossRef\]](#)
2. Wang, H.; Zhou, M.; Luo, H. Electric-Field-Induced Dynamic Electronic Junctions in Hybrid Organic–Inorganic Perovskites for Optoelectronic Applications. *ACS Omega* **2018**, *3*, 1445–1450. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Ghaithan, H.M.; Qaid, S.M.H.; Alharbi, K.K.; Bin Ajaj, A.F.; Al-Asbahi, B.A.; Aldwayyan, A.S. Amplified Spontaneous Emission from Thermally Evaporated High-Quality Thin Films of CsPb(Br_{1-x}Y_x)₃ (Y = I, Cl) Perovskites. *Langmuir* **2022**, *38*, 8607–8613. [\[CrossRef\]](#)
4. Al-Asbahi, B.A.; Qaid, S.M.; Hezam, M.; Bedja, I.; Ghaithan, H.M.; Aldwayyan, A.S. Effect of deposition method on the structural and optical properties of CH₃NH₃PbI₃ perovskite thin films. *Opt. Mater.* **2020**, *103*, 109836. [\[CrossRef\]](#)
5. Verduci, R.; Romano, V.; Brunetti, G.; Yaghoobi Nia, N.; Di Carlo, A.; D'Angelo, G. Solar Energy in Space Applications: Review and Technology Perspectives. *Adv. Energy Mater.* **2022**, *12*, 2200125. [\[CrossRef\]](#)
6. Bhalla, A.; Guo, R.; Roy, R. The perovskite structure—A review of its role in ceramic science and technology. *Mater. Res. Innov.* **2000**, *4*, 3–26. [\[CrossRef\]](#)
7. Stoumpos, C.C.; Malliakas, C.D.; Kanatzidis, M.G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. *Inorg. Chem.* **2013**, *52*, 9019–9038. [\[CrossRef\]](#)
8. Zhou, Y.; Chen, J.; Bakr, O.M.; Sun, H.-T. Metal-Doped Lead Halide Perovskites: Synthesis, Properties, and Optoelectronic Applications. *Chem. Mater.* **2018**, *30*, 6589–6613. [\[CrossRef\]](#)
9. Li, C.; Lu, X.; Ding, W.; Feng, L.; Gao, Y.; Guo, Z. Formability of ABX₃ (X = F, Cl, Br, I) halide perovskites. *Acta Cryst. Sect. B Struct. Sci.* **2008**, *64*, 702–707. [\[CrossRef\]](#)
10. Ghaithan, H.M.; Qaid, S.M.H.; Alahmed, Z.A.; Hezam, M.; Lyras, A.; Amer, M. Anion Substitution Effects on the Structural, Electronic, and Optical Properties of Inorganic CsPb(I_{1-x}Br_x)₃ and CsPb(Br_{1-x}Cl_x)₃ Perovskites: Theoretical and Experimental Approaches. *J. Phys. Chem. C* **2021**, *125*, 886–897. [\[CrossRef\]](#)
11. Whitcher, T.J.; Gomes, L.C.; Zhao, D.; Bosman, M.; Chi, X.; Wang, Y.; Carvalho, A.; Hui, H.K.; Chang, Q.; Breese, M.B.H.; et al. Dual phases of crystalline and electronic structures in the nanocrystalline perovskite CsPbBr₃. *NPG Asia Mater.* **2019**, *11*, 70. [\[CrossRef\]](#)
12. Qaid, S.M.H.; Ghaithan, H.M.; Al-Asbahi, B.A.; Aldwayyan, A.S. Tuning of amplified spontaneous emission wavelength for green and blue light emission through the tunable composition of cspb(Br_{1-x}Cl_x)₃ inorganic perovskite quantum dots. *J. Phys. Chem. C* **2021**, *125*, 9441–9452. [\[CrossRef\]](#)
13. Park, B.W.; Seok, S.I. Intrinsic Instability of Inorganic–Organic Hybrid Halide Perovskite Materials. *Adv. Mater.* **2019**, *31*, 1805337. [\[CrossRef\]](#)
14. McGovern, L.; Futscher, M.H.; Muscarella, L.A.; Ehrler, B. Understanding the Stability of MAPbBr₃ versus MAPbI₃: Suppression of Methylammonium Migration and Reduction of Halide Migration. *J. Phys. Chem. Lett.* **2020**, *11*, 7127–7132. [\[CrossRef\]](#)
15. Chen, Q.; De Marco, N.; Yang, Y.; Song, T.-B.; Chen, C.-C.; Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y. Under the spotlight: The organic–inorganic hybrid halide perovskite for optoelectronic applications. *Nano Today* **2015**, *10*, 355–396. [\[CrossRef\]](#)
16. Dar, M.I.; Jacopin, G.; Meloni, S.; Mattoni, A.; Arora, N.; Boziki, A.; Zakeeruddin, S.M.; Rothlisberger, U.; Grätzel, M. Origin of unusual bandgap shift and dual emission in organic–inorganic lead halide perovskites. *Sci. Adv.* **2016**, *2*, e1601156. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Whitfield, P.S.; Herron, N.; Guise, W.E.; Page, K.; Cheng, Y.Q.; Milas, I.; Crawford, M.K. Structures, Phase Transitions and Tricritical Behavior of the Hybrid Perovskite Methyl Ammonium Lead Iodide. *Sci. Rep.* **2016**, *6*, 35685. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Jiang, Y.; Soufiani, A.M.; Gentle, A.; Huang, F.; Ho-Baillie, A.; Green, M.A. Temperature dependent optical properties of CH₃NH₃PbI₃ perovskite by spectroscopic ellipsometry. *Appl. Phys. Lett.* **2016**, *108*, 61905. [\[CrossRef\]](#)
19. Chen, C.; Hu, X.; Lu, W.; Chang, S.; Shi, L.; Li, L.; Zhong, H.; Han, J. Elucidating the phase transitions and temperature-dependent photoluminescence of MAPbBr₃ single crystal. *J. Phys. D Appl. Phys.* **2018**, *51*, 45105. [\[CrossRef\]](#)
20. Lehmann, F.; Franz, A.; Daniel, M.T.; Levchenko, S.; Unold, T.; Taubert, A.; Schorr, S. The phase diagram of a mixed halide (Br, I) hybrid perovskite obtained by synchrotron X-ray. *RSC Adv.* **2019**, *9*, 11151–11159. [\[CrossRef\]](#)
21. Kong, W.; Ye, Z.; Qi, Z.; Zhang, B.; Wang, M.; Rahimi-Iman, A.; Wu, H. Photoluminescence behavior upon crystal-phase. *Phys. Chem. Chem. Phys.* **2015**, *17*, 16405–16411. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Park, S.; Seo, Y.-S.; Ahn, C.W.; Woo, W.S.; Kyhm, J.; Lee, S.A.; Kim, I.W.; Hwang, J. Temperature-dependent optical properties of hybrid organic–inorganic perovskite single crystals (CH₃NH₃PbI₃ and CH₃NH₃PbBr₃). *J. Phys. D Appl. Phys.* **2019**, *52*, 335302. [\[CrossRef\]](#)
23. Schötz, K.; Askar, A.M.; Köhler, A.; Shankar, K.; Panzer, F. Investigating the Tetragonal-to-Orthorhombic Phase Transition of Methylammonium Lead Iodide Single Crystals by Detailed Photoluminescence Analysis. *Adv. Opt. Mater.* **2020**, *8*. [\[CrossRef\]](#)
24. Qaid, S.M.H.; Ghaithan, H.M.; Al-Asbahi, B.A.; Aldwayyan, A.S. Solvent Effects on the Structural and Optical Properties of MAPbI₃ Perovskite Thin Film for Photovoltaic Active Layer. *Coatings* **2022**, *12*, 549. [\[CrossRef\]](#)
25. Fan, P.; Gu, D.; Liang, G.-X.; Luo, J.-T.; Chen, J.-L.; Zheng, Z.-H.; Zhang, D.-P. High-performance perovskite CH₃NH₃PbI₃ thin films for solar cells prepared by single-source physical vapour deposition. *Sci. Rep.* **2016**, *6*, 29910. [\[CrossRef\]](#)
26. Shen, H. Materials Defect step controlled growth of perovskite MAPbBr₃ single crystal. *J. Mater. Sci.* **2019**, *54*, 11596–11603. [\[CrossRef\]](#)

27. Fru, J.N.; Nombona, N.; Diale, M. Characterization of Thin MAPb(I1-xBrx)3 Alloy Halide Perovskite Films Prepared by Sequential Physical Vapor Deposition. *Front. Energy Res.* **2021**, *9*, 196. [\[CrossRef\]](#)
28. Nath, D.; Singh, F.; Das, R. X-ray diffraction analysis by Williamson-Hall, Halder-Wagner and size-strain plot methods of CdSe nanoparticles- a comparative study. *Mater. Chem. Phys.* **2019**, *239*, 122021. [\[CrossRef\]](#)
29. Saxena, R.; Kangsabanik, J.; Kumar, A.; Shahee, A.; Singh, S.; Jain, N.; Ghorui, S.; Kumar, V.; Mahajan, A.V.; Alam, A.; et al. Contrasting temperature dependence of the band gap in CH₃NH₃PbX₃ (X = I, Br, Cl): Insight from lattice dilation and electron-phonon coupling. *Phys. Rev. B* **2020**, *102*, 81201. [\[CrossRef\]](#)
30. Liu, Y.; Lu, H.; Niu, J.; Zhang, H.; Lou, S.; Gao, C.; Zhan, Y.; Zhang, X.; Jin, Q.; Zheng, L. Temperature-dependent photoluminescence spectra and decay dynamics of MAPbBr₃ and MAPbI₃ thin films. *AIP Adv.* **2018**, *8*, 095108. [\[CrossRef\]](#)
31. Qaid, S.M.; Al Sobaie, M.S.; Khan, M.M.; Bedja, I.M.; Alharbi, F.H.; Nazeeruddin, M.K.; Aldwayyan, A.S. Band-gap tuning of lead halide perovskite using a single step spin-coating deposition process. *Mater. Lett.* **2015**, *164*, 498–501. [\[CrossRef\]](#)
32. Pereira, L.; Ferreira, I.; Thomaz, M.P. Temperature effects on fluorescence quantum efficiency of 9,10-diphenylanthracene. *J. Photochem.* **1978**, *9*, 363–367. [\[CrossRef\]](#)
33. An, P.; Thomson, S.; Tesa, M.; Gakamsky, A. *Temperature-Dependent Absolute Photoluminescence Quantum Yield Measurements of a Halide Perovskite Temperature-Dependent Absolute Photoluminescence Quantum Yield Measurements of a Halide Perovskite*. Edinburgh Instruments; Edinburgh Instruments: Livingston, UK, 2018; pp. 2–5.
34. Agrawal, G.P.; Dutta, N.K. Recombination Mechanisms in Semiconductors. *Long-Wavel. Semicond Lasers* **1986**, 70–141.
35. Wehrenfennig, C.; Liu, M.; Snaith, H.J.; Johnston, M.B.; Herz, L.M. Charge carrier recombination channels in the low-temperature phase of organic-inorganic lead halide perovskite thin films. *APL Mater.* **2014**, *2*, 081513. [\[CrossRef\]](#)
36. Phys, J.C.; Yamaguchi, A.; Uehara, R.; Yasuhara, S.; Hoshina, T.; Miyauchia, M. Temperature dependence on bandgap of semiconductor photocatalysts Temperature dependence on bandgap of semiconductor photocatalysts. *J. Chem. Phys.* **2020**, *152*, 231101.
37. Guha, S.; Rice, J.D.; Yau, Y.T.; Martin, C.M.; Chandrasekhar, M.; Chandrasekhar, H.R.; Guentner, R.; Scanduicci de Freitas, P.; Scherf, U. Temperature dependent photoluminescence of organic semiconductors with varying backbone conformation. *Phys. Rev. B* **2003**, *67*, 125204. [\[CrossRef\]](#)
38. Buckner, C.A.; Lafrenie, R.M.; Dénommée, J.A.; Caswell, J.M.; Want, D.A.; Gan, G.G. Structural Phase Transitions of Hybrid Perovskites CH₃NH₃PbX₃ (X = Br, Cl) from Synchrotron and Neutron Diffraction Data. *IntechOpen* **2016**, *11*, 13.
39. Tingting, Y.; Yan, J. Stability of CH₃NH₃PbBr₃ and evolution of H-bonding during its polymorphic transformations. In Proceedings of the 2017 Opto-Electronics and Communications Conference (OECC) and Photonics Global Conference (PGC), Singapore, 31 July 2017–4 August 2017.
40. Ruf, F.; Aygüler, M.F.; Giesbrecht, N.; Rendenbach, B.; Magin, A.; Docampo, P.; Kalt, H.; Hetterich, M. Temperature-dependent studies of exciton binding energy and phase-transition suppression in (Cs,FA,MA)Pb(I,Br)₃ perovskites. *APL Mater.* **2019**, *7*, 031113. [\[CrossRef\]](#)
41. Li, J.; Yuan, X.; Jing, P.; Mechanics, F.; Ji, L. Temperature-dependent photoluminescence of inorganic perovskite nanocrystal films. *RSC Adv.* **2016**, *6*, 78311–78316. [\[CrossRef\]](#)
42. Zhang, F.; Zhong, H.; Chen, C.; Wu, X.G.; Hu, X.; Huang, H.; Han, J.; Zou, B.; Dong, Y. Brightly luminescent and color-tunable colloidal CH₃NH₃PbX₃ (X = Br, I, Cl) quantum dots: Potential alternatives for display technology. *ACS Nano* **2015**, *9*, 4533–4542. [\[CrossRef\]](#)
43. Park, Y.; Jana, A.; Myung, C.W.; Yoon, T.; Lee, G.; Kocher, C.C.; Ying, G.; Osokin, V.; Taylor, R.A.; Kim, K.S. Enhanced photoluminescence quantum yield of MAPbBr₃ nanocrystals by passivation using graphene. *Nano Res.* **2020**, *13*, 932–938. [\[CrossRef\]](#)
44. Yuan, X.; Hou, X.; Li, J.; Qu, C.; Zhang, W.; Zhao, J.; Li, H. Thermal degradation of luminescence in inorganic perovskite CsPbBr₃ nanocrystals. *Phys. Chem. Chem. Phys.* **2017**, *19*, 8934–8940. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Ai, B.; Liu, C.; Deng, Z.; Wang, J.; Han, J.; Zhao, X. Low temperature photoluminescence properties of CsPbBr₃ quantum dots embedded in glasses. *Phys. Chem. Chem. Phys.* **2017**, *19*, 17349–17355. [\[CrossRef\]](#) [\[PubMed\]](#)

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