

Article

RETRACTED: Improving the Structural, Optical and Photovoltaic Properties of Sb- and Bi- Co-Doped MAPbBr₃ Perovskite Solar Cell

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Abstract: We prepared 1% Bi- and (0, 0.5%, 1% and 1.5%) Sb- co-doped MAPbBr₃ films by a sol-gel spin coating technique. For the first time, the detailed structural properties including grain size, dislocation line density, d-spacing, lattice parameters, and volume of co-doped MAPbBr₃ films have been investigated. XRD confirmed the cubic structure of MAPbBr₃ with high crystallinity and co-doping of Bi and Sb. The 1% Bi and 1% Sb co-doping have a surprising effect in MAPbBr₃ structures, such as large grain size (59.5 nm), d-space value (6.23 Å), small dislocation line dislocation ($2.79 \times 10^{18} \text{ m}^{-2}$), and small lattice parameters ($a = b = c = 6.3 \text{ Å}$) and volume of unit cell. The detailed optical properties, including energy band gap (E_g), refractive index (n), extinction coefficient (k) and dielectric constant (ε), which are very important for optoelectronics applications, were investigated by UV-Vis spectroscopy. The film of 1% Bi and 1% Sb co-doped MAPbBr₃ showed good optical response including small E_g, high n, low value of k, high real and low imaginary parts of dielectric constant, making it good for solar cell applications. Solar cells were fabricated from these films. The cell fabricated with pure MAPbBr₃ has J_{sc} of 8.72 mA cm⁻², FF of 0.66, Voc of 1.29 V, and η of 7.5%. All the parameters increased by co-doping of Bi and Sb in MAPbBr₃ film. The cell fabricated with 1% Bi and 1% Sb co-doped MAPbBr₃ film had high current density (12.12 mA-cm⁻²), open circuit voltage (Voc), fill factor (0.73), and high efficiency (11.6%). This efficiency was 65% larger than a pure MAPbBr₃-based solar cell.

Keywords: perovskite solar cell; MAPbBr₃; Sb; Bi; co-doping



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1. Introduction

In recent years, energy shortages are the primary problem hindering global development and peace, and have become a focus of concern around the world [1]. The high demand for energy will make it a major problem in the future. To overcome the energy shortfall, it is necessary to expand native energy resources like hydropower, solar and wind. Among these sources the most important alternative is solar energy which is classified as a huge renewable resource. One hour of solar energy received by the globe is enough to supply the world's energy requirement for a year. This is an unlimited source of energy which is available at no cost. This energy can directly be converted into electricity by solar cells. Therefore, researchers from all over the world show great interest in developing new solar cells with high efficiency and low cost. Since 1888, where the first solar cell was built by physicist Aleksandr Stoletov, work continues to develop solar cells in a variety of specifications including, efficiency, ease of manufacturing, flexible work, etc. [1]. Currently, silicon-based solar cells capture the market. These solar cells are costly compared

to their efficiency and, therefore, these cells still cannot replace fossil fuels. Therefore, researchers are looking for other low-cost and efficient solar cells like dye-sensitized solar cells (DSSCs), quantum dot solar cells (QDSCs), perovskite solar cells (PSCs), and full organic PV (OPV) solar cells. Because of their instability and low efficiency, these cells may not have reached the market or have just been launched in tiny niche sectors. Among the several types of currently available PV systems, those depending on halide PSCs have piqued the scientific community's interest since they have the potential to provide higher efficiency at a cheap cost. As hybrid organic inorganic methylammonium lead (MAPb) halides in a perovskite crystal structure are identified as a potential material for solar cells, it will take around a decade to produce these. Their highest recorded efficiency for a small area cell is 25.5% [2]. These hybrid solar cells are the combination of inorganic and organic semiconductor materials. Lightweight, inexpensive, flexible, and robust characteristics make them a promising candidate for PV devices. It is critical to choose the right electrical structure for inorganic semiconductor materials in hybrid solar cells if you want to improve performance [3]. Enrique Hernández-Balaguera et al. [4,5] established a connection between perovskite memory effects, anomalous evolution or non-predictable response of the transient, structural complexity of PSCs, CPE features in IS, fractional dynamics, J–V hysteresis and Cole-Cole dielectric mode. In the few years since their discovery, MAPb halide PSCs have become more efficient and advanced more rapidly than any other solar cell. The outstanding performance of these cells has sparked interest in optoelectronics applications such as lasers, light-emitting diodes, and photodetectors [6]. This material has impressive properties for photovoltaic applications, like cheap fabrication costs, simplicity of manufacturing and production. Furthermore, at room temperature, they have a cubic structure and are thought to be more thermally stable under specific atmospheric circumstances. HOIPs, on the other hand, often have a low carrier concentration, which results in limited electrical conductivity [7]. This makes achieving high efficiency challenging for them. Different approaches have been made to increase the efficiency and stability of these materials. Among them, doping is found to be good for improving the efficiency and stability of the cell. It tunes the band gap and also increases the electrical properties of perovskite material. To gain tunability on electrical characteristics, controlled doping for halide perovskites is desirable. Until now, the most widely used doping methods for hybrid perovskites have relied on the injection of heterohalide atoms or organic anions to modify the band gaps. Recently, heterovalent doping techniques for modulating electrical and optical properties in halide perovskites have been presented [8]. Substitutions that are heterovalent to minimise the toxicity of Pb, Sb^{3+} and Bi^{3+} have been used in the perovskite (PVK) framework [9] and to improve efficiency. Jun Yin et al. [10] reported that doping of Bi^{3+} ions into CsPbBr_3 perovskite reduces the photoluminescence quantum yield from 78% to 8%. Snaith et al. found a high disorder of electronic and low PL intensity and carrier lifetime due to doping of Bi^{3+} into MAPbBr_3 [11]. On the basis of these studies, Kanemitsu et al. [12] have observed an improved Urbach tail with no high change in E_g . Miyasaka et al. [13] have also found that the E_g of CsPbBr_3 is not significantly changed by Bi doping but the fermi level is increased to 0.6 eV. Bi-based PVKs have been widely explored and proven for a variety of optoelectronic applications up to now. Both Sb^{3+} and Bi^{3+} contain fully occupied s^2 shells, resulting in optoelectronic characteristics that are quite comparable. Furthermore, Sb-based PVKs have already been used in solar cells and LEDs, and have tremendous potential [14]. Solar cells based on MAPbBr_3 with Sb^{3+} and Bi^{3+} doping displayed good stability for more than 40 days when exposed to humidity and ambient air at room temperature, according to a study [15]. Furthermore, even after 21 days of storage in the air, the gadget displays very little performance loss. Furthermore, it has been demonstrated that adding heterovalent Bi^{3+} to methylammonium lead-bromide based perovskite (MAPbBr_3) precursor solutions can result in MAPbBr_3 charge doping. With a dilute Bi^{3+} concentration, the mobility of perovskite can be increased electrically. As a result, bismuth-based halide perovskites/derivatives remain intriguing for future study in photovoltaics and other semiconductor-based technologies [15].

As Pb is not stable and is a toxic material, therefore, a strategy has been followed to substitute Pb by Bi, Sn or Sb. However, the efficiency of the cell is found to be reduced. In this paper, we have used a co-doping concept in MAPbBr₃ material. We have doped a constant amount of Bi and varied the amount of Sb with Pb in MAPbBr₃ crystal. Bi increases the optical property and Sb increases the electrical property. Therefore, it is suggested that this co-doping will improve the photovoltaic property of MAPbBr₃. Also, this material can be used in photo detectors and LEDs etc. because this co-doping has increased the structural, optical and photovoltaic properties of MAPbBr₃. To the best of our knowledge this work has not yet been addressed.

2. Materials and Methods

The sol gel method was used for the preparation of MAPbBr₃ in which SbCl₃ and BiCl₃ are doped into PbBr₃, where dimethylformamide (DMF) was used for the fabrication of doped MAPbBr₃. A 1:1 molar ratio of MABr was dissolved into PbBr₂ and after that in 2 mL of dimethylformamide, and MAPbBr₃ solution was obtained. For co-doping purposes, we added 1% BiCl₃ along with different concentrations of SbCl₃ like (0.5%, 1% and 1.5%) in the solution of MABr and PbBr₂ with DMF. We stirred this solution at room temperature for night, and a homogeneous precursor solution named as perovskite solution was obtained which was deposited on glass/FTO/TiO₂ substrate at 4000 rpm using a spin coater. TiO₂ film was prepared according to our published paper [16]. The deposited films were annealed at 100 °C in the muffle furnace for 10 min. Spiro-OMeTAD of 72 mg, TBP having 36 µL, and stock solution having a value of 22 µL of 520 mg mL⁻¹ lithium bis-(trifluoromethyl sulfonyl) imide in acetonitrile in 1 mL of chloro-benzene was dissolved to obtained the hole transport material. Finally, after successful evaporation, we obtained an 80 nm layer of Au on the device top. The 0.16 cm² was the main active area of the solar cells.

X-ray diffraction analysis (XRD) (PANanalytical, D/Max-III, Almelo, The Netherland) was used to characterize the synthesized crystal structure of the undoped and co-doped MAPbBr₃. Optical properties were characterized by UV-Vis spectroscopy (Shimadzu UV-2101, Kyoto, Japan). A solar simulator (100 mW/cm² irradiance, measured on the AM 1.5 spectrum) was used to characterized the solar cells efficiency.

3. Results and Discussion

3.1. X-ray Diffraction (XRD) Analysis

The XRD pattern of 1% Bi and (0%, 0.5%, 1% and 1.5%) Sb co-doped MAPbBr₃ films is shown in Figure 1. All the films have cubic perovskite structure. Sharp peaks in all the diffractograms represent improved crystallinity of the thin film material.

The structure and symmetry of the impact phase is reflected by the peak's position. That strongly agrees with a previous study of cubic MAPbBr₃ single crystals [17]. The diffraction directions of MAPbBr₃ at 2θ values 14.18°, 28.56° and 46.47° are attributed to (100), (111), and (320) diffraction planes, respectively. These confirmed the formation of MAPbBr₃. When 1% Bi is doped in MAPbBr₃ film, the observed peaks at 2θ values are 14.22° (100), 28.63° (111), and 46.49° (320) in comparison with undoped MAPbBr₃ peaks at higher angles. The reason behind this progress is the increased internal stress that occurred because of lattice shrinkage [3]. The intensity of peak is increased due to doping. This confirmed the substitution of Bi in MAPbBr₃ lattice. By the doping of 1% Bi along with (0.5% and 1%) Sb in MAPbBr₃ film, the observed peaks at 2θ values are [14.28° (100), 28.69° (111), and 46.55° (320)] and [14.29° (100), 28.70° (111), and 46.56° (320)], respectively. The shift in peaks toward the higher angle and higher intensity confirmed the doping of Sb. Since no extra peaks related to Bi-Sb, Sb-Pb etc. are observed this confirmed the complete doping of Sb and Bi. As the peak intensity is high due to doping, this indicated the improvement in crystallinity of the films. A higher structure factor is obtained when the required number of atoms are occupied for the group due to Wyckoff positions and, as a result, there is higher intensity. When the co-doping amount of Sb is increased i.e., 1% Bi and 1.5% Sb, then peak intensity is decreased pointing out the decrease in crystallinity. This shows that a higher

doping level causes loss of crystallinity of the MAPbBr₃ film. Also, due to high doping amount, a new peak of MAPbBr₃ is observed with (222) reflection plane. This shows that at high doping concentration, the re-crystallization of MAPbBr₃ is occurred due to which the intensity of the peak is decreased and a new peak is formed. Thus, we recommend 1% Bi and 1% Sn co-doping is good for enhancement in crystallization of MAPbBr₃ film.

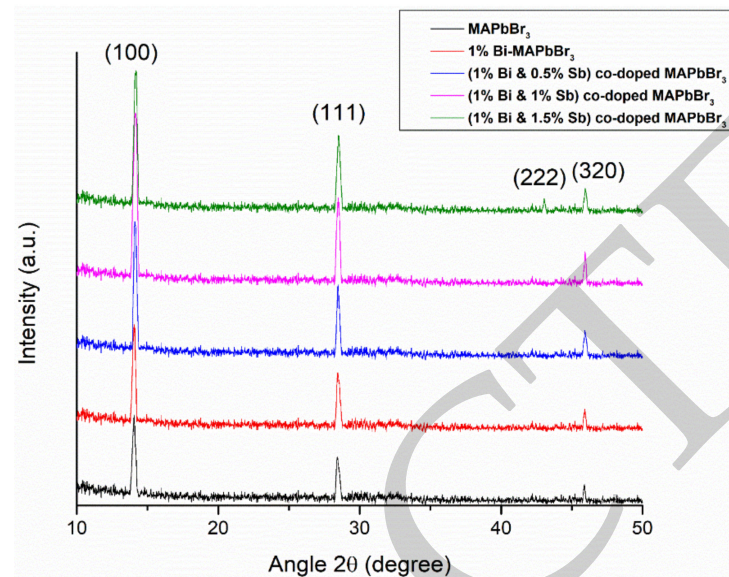


Figure 1. X-ray diffraction (XRD) of pure MAPbBr₃ and co-doped (1%Bi & 0.5%, 1% and 1.5% Sb)-MAPbBr₃.

3.1.1. Grain Size and Density of the Dislocation Line

Grain size (*D*) is an important parameter which affects the electrical properties of film. High grain size refers to low resistivity because electrons can easily move from grain to grain. The *D* of films is calculated from the following equation [18]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where, β is known as the full width at half maximum (FWHM), λ is a wavelength, and θ is the Bragg's angle. The diameter of individual grains of sediment is called grain size while dislocation line density refers to the defects or irregularity belonging to the crystalline structure. In other words, dislocation line density (δ) is inverse of the square of the grain size which can be calculated by this formula [19]:

$$\delta = \frac{1}{D^2} \quad (2)$$

δ is used for calculation of defects in the sample. The films will be of better quality if it has low δ value [20].

Figure 2 shows the graph of *D* and δ . The pure MAPbBr₃ has grain size 43 nm and dislocation line density $5.5 \times 10^{18} \text{ m}^{-2}$. At 1% Bi doping *D* increased from 43 to 56.5 nm and δ decreased from 5.5×10^{18} to $3.2 \times 10^{18} \text{ m}^{-2}$. Similarly, at co-doping of 1% Bi along with (0.5%, 1%) Sb, the grain size further increases and δ is decreased. The increment in grain size and reduction in dislocation line density resulted in the improvement in crystallinity at grain side boundaries and also due to the lattice position which is properly held by Bi atoms substitution in the MAPbBr₃ film [21]. At co-doping 1% Bi and 1.5% Sb, *D* is decreased. For the large amount of Sb, free spaces are not available. Therefore, Sb dispersed and reduction in grain size is observed. The low value of *D* refers to the loss in crystallinity and reduced electrical properties.

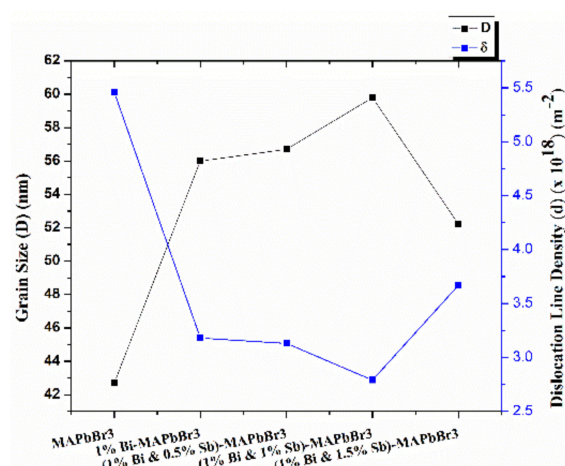


Figure 2. The D and δ variations for pure MAPbBr₃ and co-doped (1% Bi and 0.5%, 1% and 1.5% Sb)-MAPbBr₃.

3.1.2. Lattice Constants ($a = b = c$)

Lattice constants give information about the unit cells. Lattice constants of pure MAPbBr₃ and co-doped 1% Bi and (0%, 0.5%, 1% and 1.5% Sb)-MAPbBr₃ are calculated from Equation (3) [22]:

$$a = d \sqrt{h^2 + k^2 + l^2} \quad (3)$$

where, a and (h, k, l) are lattice parameters, Miller indices. d is inter-planer distance which is calculated by Bragg's law:

$$2d \sin \theta = n\lambda \quad (4)$$

The lattice parameter (shown in Figure 3) of 1% Bi and (0%, 0.5%, 1%, 1.5%) Sb co-doped MAPbBr₃ films are 6.24 Å, 6.22 Å, 6.20 Å, 6.194 Å and 6.194 Å, respectively. This shows that Bi does not replace the Pb atoms in the structure. It is present in the interstitial sites. At (0.5% and 1%) Sb doping the lattice parameters are decreased. This is because the size of Sb is smaller than Pb. The smaller size creates the interstitial stress which decreases the lattice parameters. At 1% Bi and 1.5% co-doping, the lattice parameters remain the same.

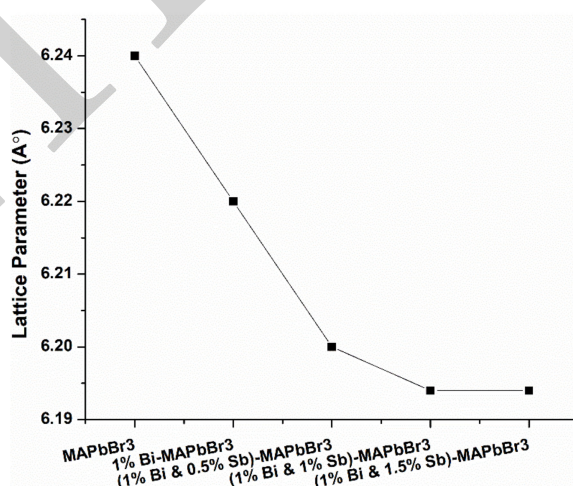


Figure 3. Lattice constants of pure MAPbBr₃ and co-doped (1%Bi and 0.5%, 1% and 1.5% Sb)-MAPbBr₃.

3.1.3. Volume versus Number of Samples

Volume of the pure and co-doped MAPbBr₃ with Bi and Sb are calculated by the relation (5) [23]:

$$\text{volume} = a^3 \quad (5)$$

The volume of a unit cell is decreased with doping as shown in Figure 4.

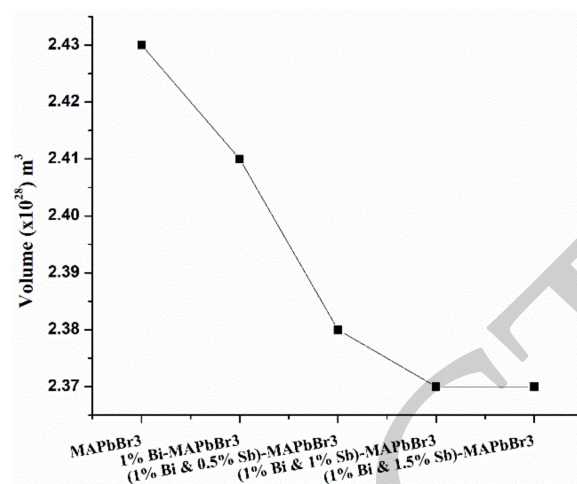


Figure 4. The volume of pure MAPbBr₃ and co-doped (1% Bi and 0.5%, 1% and 1.5% Sb)-MAPbBr₃.

3.2. Ultraviolet–Visible (UV–Vis) Analysis

UV visible spectroscopy is an analytical technique used for the measurement of absorbance and transmittance of light. The wavelength range of the UV visible region is from 100 to 800 nm whereas most of the spectrometers have a working area from 300 to 1100 nm. The UV visible spectroscopy has as its foundation electronic transition as light falls on the material, electrons absorb it and jump from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This absorption should be equal to the difference of energy between HOMO and LUMO. Fluorescence spectroscopy and absorption spectroscopy are almost opposite to each other, because the transition from excited to the ground state are dealt with through fluorescence spectroscopy; on the other hand the ground state to the excited state's transitions is dealt with through absorption spectroscopy. With the wavelength range from 300 to 900 nm, a SCHIMADZU UV-vis 1800 spectrophotometer was used to examine the photosensitive characterization of CH₃NH₃PbBr₃ perovskite. The efficiency of photovoltaic cells was improved by the band gap which was also important for determining the absorbing part of the solar spectrum [24].

3.2.1. Band Gap Energy (E_g)

The value of band gap energy (E_g) is determined from a graph plotted between $(\alpha h\nu)^{1/2}$ and $(E = h\nu)$, as shown in Figure 5.

Where h , α , and ν are the constant of Plank, coefficient of absorption, and light's frequency, respectively. The E_g value is measured by Equation (6) given below:

$$\alpha h\nu = A(h\nu - E_g)^m \quad (6)$$

where A refers to a constant and m is the exponent which is known as a numerical constant, and the value of m defines the nature of the transition; m takes a value of 1/2, and 2 for direct and indirect allowed transitions, respectively; m takes a value of 3/2 and 3 for direct and indirect forbidden transitions, respectively [20].

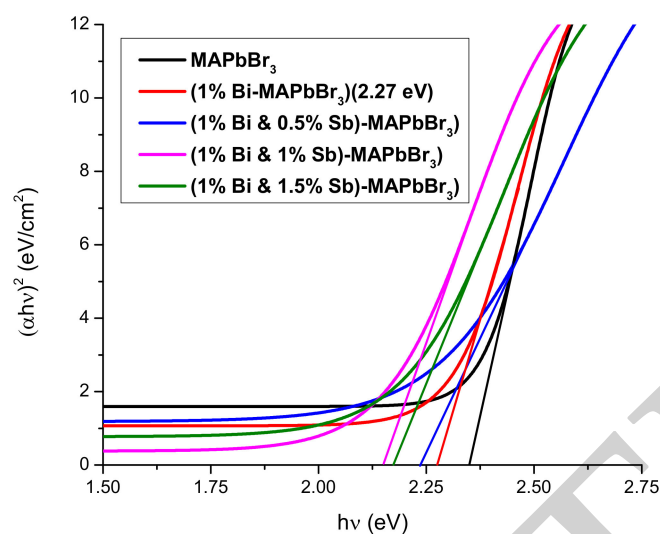


Figure 5. E_g of pure MAPbBr₃ and 1% Bi and (0%, 0.5%, 1%, 1.5%) Sb co-doped MAPbBr₃ films.

The E_g of pure MAPbBr₃ is 2.35 (eV), as shown in Figure 5. The 1% Bi doping in MAPbBr₃ has reduced the E_g to 2.27 eV. The reduction in E_g is taking place because crystallite size is increased with doping in MAPbBr₃. Also, the reduction in band gap refers to the introduction of the intermediate energy levels which are introduced in MAPbBr₃ by the substitution of Bi. At the co-doping of 1% Bi and (0.5% and 1%)-Sb in MAPbBr₃, the E_g further decreased to 2.23 and 2.14 eV, respectively. Carrier concentration is also decreased by the doping of Bi and Sb which is also responsible for lowering the band gap value. The continuously decreasing value of band gap can also be attributed to the improvement in crystallinity of the MAPbBr₃ thin film. This inverse relation of band gap with the doping is well matched with previous studies on MAPbBr₃ film [25]. Moreover, the small band gap value hinders the formation of deep-level traps which reduce the carrier lifetime of the solar cells [26]. The D band position of Bi- and Sn-doped Pb-based halides moves towards lower energy which is attributed to the ligand–metal charge–transfer transition because of the decrease of optical electronegativity from Pb to Bi or Sn. Because of the rising ionisation energy of metal ions, this drop in E_g is predicted for the charge-transfer band. As a result, the D band's transition energy varies not only with the ionisation energy or oxidation state of metal ions, but also with the optical electronegativity of halide ions, implying that the D band arises from the halide-metal charge-transfer transition and is responsible for the decrease in E_g [27]. When Bi and Sb are doped in MAPbBr₃ perovskite then they move in the body-centered position. Since Pb has +2 states and Bi has +3 states, therefore, electron concentration increases are defects that are introduced. Defect diffusion is substituted by a collective motion of atoms near the defect; doping density fluctuations generate cavities for Bi and Sb particle migration with low energy and low pre-exponential factor, lowering E_g [28]. At 1.5% Sb along with a constant amount of Bi the band gap slightly increased and shifted to 2.17 eV, respectively. At higher doping, the D is reduced due to which band gap value is decreased.

3.2.2. Refractive Index

Bending of light rays when it passes from one medium to another medium is measured by refractive index (n) which is the fundamental property of optical materials. Time duration of traveling of light through a medium is shown by refractive index. The progression in the refractive index for the optical materials is essential for many applications. The ionic electronic polarizability and local field inside the material is related to the optical refractive index which plays a key role in finding the electrical properties of materials. That is why the calculation of a refractive index is very important and a lot of investigations on this parameter have been carried out for many purposes [29].

The refractive index is calculated by Reddy et al. [30] with a modified form of the Hervé and Vandamme relation [31]

$$n = \sqrt{1 + \left(\frac{A}{3.72\Delta\chi^* + B} \right)^2} \quad (7)$$

where A and B are constant having values of 13.6 and 3.4 eV, respectively. $\Delta\chi^*$ is the optical electro negativity of anion and cation, respectively, which is calculated by the following relation [32]:

$$E_g = 3.72 (\Delta\chi^*) \quad (8)$$

By putting the value of A, B and $\Delta\chi$ in Equation (12), we obtain the refractive index of pure MAPbBr₃ as 2.57. By doping of 1% Bi in MAPbBr₃, the refractive index increased and reached 2.6. Similarly, the refractive index of 1% Bi⁺ (0.5%, 1%, and 0.5%) Sb co-doped MAPbBr₃ films are 2.61, 2.65 and 2.63, respectively, (shown in Figure 6).

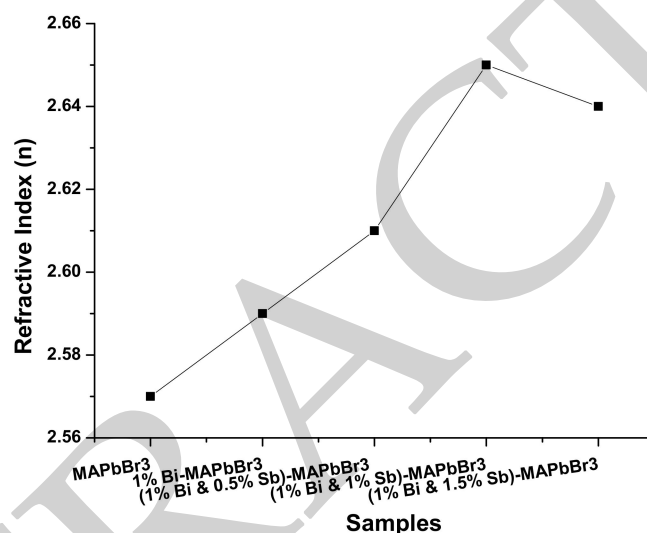


Figure 6. Refractive index pure MAPbBr₃ and 1% Bi and (0%, 0.5%, 1%, 1.5%) Sb co-doped MAPbBr₃ films.

The 'n' is increased in a non-linear manner with doping. The difference in 'n' is linked to the occurrence of a suboxide film that should form near to the base for all coatings [33]. The decrease in 'n' is due to the increase in apparent bandgap. The higher doping concentration creates the denser medium, thus more light bends so a high refractive index is observed. At 1% Bi and 1% Sb co-doping, a high value of 'n' is achieved. This refers to the fact that more light is scattered at this doping level and is good for solar cells. By the different doping concentration of Bi and Sb in the pure MAPbBr₃ film a slight difference in the refractive index occurs. First of all, anomalous dispersion occurs through which the increasing doping effect leads to increase in the refractive index in the MAPbBr₃ structure, and after normal dispersion occurs through which higher concentration of doping results in a decrease in the refractive index. The increase in the refractive index by increasing the doping concentration leads to the increased polarizability of higher atomic radius. Optical surface dispersion reduction occurs due to higher doping which is also the main reason for the reduced refractive index, and optical losses that also occur by the reduction in surface roughness and improvement in concentration.

3.2.3. Extinction Coefficient (k)

The extinction coefficient of pure MAPbBr₃ and 1% Bi and (0%, 0.5%, 1% and 1.5%) Sb co-doped MAPbBr₃ films is calculated by the following formula:

$$k = n / \Delta\chi^*{}^\gamma \quad (9)$$

Which gives a relation between refractive index n and electronegativity difference $\Delta\chi^*$. The value of γ is -0.32 . In Table 1 variation in k with doping has been observed and as shown a minimum value of k is observed in (1% Bi and 1% Sb) co-doped MAPbBr₃ film. By the reduction of optical losses with surface optical dispersion, extinction coefficient decreased which is quite similar to the refractive index; the major reason for the reduction is the increment in the carrier concentration and reduced surface roughness. Therefore, it is concluded that the chemical composition of the MAPbBr₃ changed by a different doping concentration of Bi and Sb [20].

Table 1. E_g , k , n and dielectric constants of undoped and Bi- and Sb- co-doped MAPbBr₃ films.

Sample	E_g (eV)	n	k	ϵ_r	ϵ_i
MAPbBr ₃	2.35	2.57	2.16	1.94	11.4
1% Bi-MAPbBr ₃	2.27	2.59	2.21	1.82	11.5
(1% Bi & 0.5% Sb)-MAPbBr ₃	2.23	2.61	2.23	1.84	11.6
(1% Bi & 1% Sb)-MAPbBr ₃	2.14	2.65	2.13	2.49	11.3
(1% Bi & 1.5% Sb)-MAPbBr ₃	2.17	2.64	2.22	2.04	11.7

3.2.4. Dielectric Constant

The polarity of a medium is measured by the dielectric constant which is proportional to the polarizability of solid material. In this situation, it is very important to know the real and imaginary parts of the dielectric constant. The dielectric constant in terms of real and imaginary parts is defined as [34]:

$$\epsilon = \epsilon_r + i\epsilon_i \quad (10)$$

where imaginary and real parts of dielectric constant are expressed as follows [35]:

$$\epsilon_r = n^2 - k^2 \quad (11)$$

$$\epsilon_i = 2nk \quad (12)$$

The speed of light is defined by the real part, which tells us how much it slows down the speed of light in a material. The imaginary part defines dielectric material, the electric field through which energy is absorbed due to dipole motion. The loss factor is determined by the ratio of ϵ_r and ϵ_i [36]. Photon energy ($h\nu$) has high influenced on the real (ϵ_r) and imaginary parts (ϵ_i) of the dielectric constant. All films absorb the visible region of light according to E_g . Therefore, films have high optical conductivity in the visible region. Here, the real part is decreased which refers to the decrease of speed of light in a medium. Therefore, the scattering is high. Similarly, the imaginary part is increased with doping which refers to the increase in the absorption of light. When more light will absorb then a large number of electrons and hole pairs are generated, so a large current will flow through the circuit. This will affect the current density of the solar cell and ultimately increase the efficiency of the cell. By different doping concentration the optical conductivity of the material is change. In spite of this, a very interesting thing is observed in all samples: that the values of ϵ_r are higher in comparison to ϵ_i , which simply indicates that by increasing the different doping concentration the values of ϵ_r and ϵ_i are also changed. The difference between the optical conductivity of the real and imaginary parts is directly linked with the positional densities (DOS) associated in the energy band gaps of the film [35]. A strong relation between photons and electrons in the visible region by the real part (ϵ_r) and the

imaginary part (ϵ_i) is shown in (Table 1). The calculated optical properties are summarized in Table 1.

3.3. J-V Curve of MAPbBr₃ with Doping

Figure 7 shows the J-V curve of undoped and Bi- and Sb- co-doped MAPbBr₃-based solar cells. With the help of the J-V curve, the values of short circuit current density (J_{sc}), fill factor (FF), open circuit voltage (V_{oc}), and efficiency η (%) of different solar cells are calculated and given in Table 2.

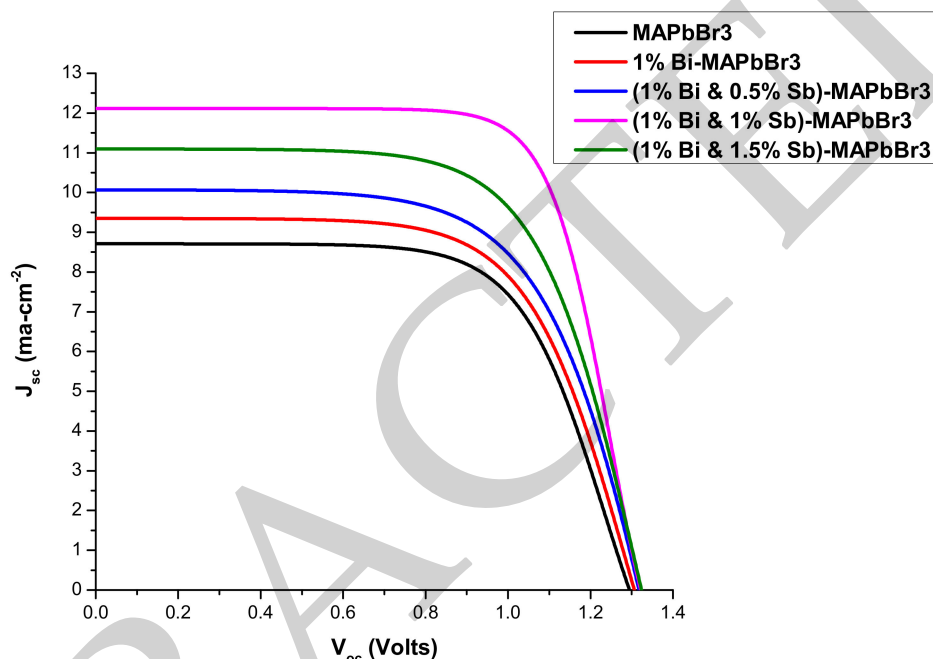


Figure 7. J-V curve of pure MAPbBr₃ and 1% Bi and (0%, 0.5%, 1%, 1.5%) Sb co-doped MAPbBr₃ based solar cells.

Table 2. J-V parameters of MAPbBr₃ and 1% Bi and (0%, 0.5%, 1%, 1.5%) Sb co-doped MAPbBr₃ solar cells.

Samples	J_{sc} mA/cm ²	V_{oc} (V)	FF	Efficiency η %
MAPbBr ₃	8.72	1.29	0.66	7.5
1% Bi-MAPbBr ₃	9.34	1.3	0.65	7.9
(1% Bi & 0.5% Sb)-MAPbBr ₃	10.06	1.31	0.64	8.5
(1% Bi & 1% Sb)-MAPbBr ₃	12.12	1.32	0.73	11.6
(1% Bi & 1.5% Sb)-MAPbBr ₃	11.09	1.32	0.66	9.65

The value of J_{sc} is 8.72 mA cm⁻², FF is 0.66, V_{oc} is 1.29 V, and η is 7.5% for pure MAPbBr₃. By doping 1% Bi, V_{oc} = 1.3 V, J_{sc} = 9.34 mA cm⁻², and as a result the efficiency is increased from 7.5% to 7.9%; Bi increases the conductivity and crystallinity of MAPbBr₃ as explained in the XRD graph. Due to high crystallinity, structural defects are reduced. Also, Bi increases the electron transport properties. Due to these high transport properties, J_{sc} is increased and as a result, efficiency is increased. At the doping of (0.5% and 1%) Sb along with constant concentration of 1% Bi in the pure MAPbBr₃ film, efficiency is enhanced from 7.5% to 8.5% and 11.6%, respectively. The efficiency has greater value for doped samples than for undoped MAPbBr₃ film. The increment in efficiency is because of higher carrier density. It has been observed that the efficiency is decreased to 9.65% from 11.7% by the doping of 1.5% Sb along with 1% Bi in the pure MAPbBr₃ film. Reduced charge carrier collection efficiency is responsible for the reduction of J_{sc} , η , FF, and V_{oc} . At this doping

concentration, grain size and crystallinity of MAPbBr₃ is decreased and new peak along the (222) plane of reflection occurs due to structural defects, according to the XRD result. These defects have increased the recombination rate which has been confirmed by decreasing the value of FF. Therefore, the efficiency is decreased.

4. Conclusions

Pure and Bi- and Sb- co-doped MAPbBr₃ films were deposited on FTO glass substrates by a sol-gel spin coating technique. XRD confirmed the doping of Bi and Sb in MAPbBr₃. The film of 1% Bi and 1% Sb co-doped MAPbBr₃ has high crystallinity, large grain size, and small lattice parameters. This film has low E_g (2.14 eV) due to which deep-level traps are reduced and recombination rate is decreased. The fabricated solar cells with this 1% Bi and 1% Sb co-doped MAPbBr₃ film showed high values of J_{sc} (12.12 mA·cm⁻²), V_{oc} (1.32 V), FF (0.73) and efficiency (11.6%) as compared to other solar cells. This high efficiency is due to the high crystallinity and low recombination rate.

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References

1. Upadhyaya, A.; Negi, C.M.S.; Yadav, A.; Gupta, S.K.; Verma, A.S. Synthesis and characterization of methylammonium lead iodide perovskite and its application in planar hetero-junction devices. *Semicond. Sci. Technol.* **2018**, *33*, 065012. [\[CrossRef\]](#)
2. Jeong, J.; Kim, M.; Seo, J.; Lu, H.; Ahlawat, P.; Mishra, A.; Yang, Y.; Hope, M.A.; Eickemeyer, F.T.; Kim, M.; et al. Pseudo-halide anion engineering for α -FAPbI₃ perovskite solar cells. *Nature* **2021**, *592*, 381–385. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Ma, H.; Yip, H.L.; Huang, F.; Jen, A.K.Y. Interface engineering for organic electronics. *Adv. Funct. Mater.* **2010**, *20*, 1371–1388. [\[CrossRef\]](#)
4. Hernández-Balaguera, E.; Arredondo, B.; del Pozo, G.; Romero, B. Exploring the impact of fractional-order capacitive behavior on the hysteresis effects of perovskite solar cells: A theoretical perspective. *Commun. Nonlinear Sci. Numer. Simul.* **2020**, *90*, 105371. [\[CrossRef\]](#)
5. Hernández-Balaguera, E.; Del Pozo, G.; Arredondo, B.; Romero, B.; Pereyra, C.; Xie, H.; Lira-Cantú, M. Unraveling the key relationship between perovskite capacitive memory, long timescale cooperative relaxation phenomena, and anomalous J–V hysteresis. *Solar RRL* **2021**, *5*, 2000707. [\[CrossRef\]](#)
6. Xing, G.; Mathews, N.; Lim, S.S.; Yantara, N.; Liu, X.; Sabba, D.; Grätzel, M.; Mhaisalkar, S.; Sum, T.C. Low-temperature solution-processed wavelength-tunable perovskites for lasing. *Nat. Mater.* **2014**, *13*, 476–480. [\[CrossRef\]](#)
7. Dong, Y.; Zhao, Y.; Zhang, S.; Dai, Y.; Liu, L.; Li, Y.; Chen, Q. Recent advances toward practical use of halide perovskite nanocrystals. *J. Mater. Chem. A* **2018**, *6*, 21729–21746. [\[CrossRef\]](#)
8. Li, W. Formability, synthesis and properties of perovskite-type oxynitrides. *Mater. Sci.* **2015**, *9*, 1–170.
9. Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenber, A.; Katsiev, G.; et al. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **2015**, *347*, 519–522. [\[CrossRef\]](#)
10. Yin, J.; Ahmed, G.H.; Bakr, O.M.; Brédas, J.L.; Mohammed, O.F. Unlocking the effect of trivalent metal doping in all-inorganic CsPbBr₃ perovskite. *ACS Energy Lett.* **2019**, *4*, 789–795. [\[CrossRef\]](#)

11. Nayak, P.K.; Sendner, M.; Wenger, B.; Wang, Z.; Sharma, K.; Ramadan, A.J.; Lovrinčić, R.; Pucci, A.; Madhu, P.K.; Snaith, H.J. Impact of Bi³⁺ heterovalent doping in organic–inorganic metal halide perovskite crystals. *J. Am. Chem. Soc.* **2018**, *140*, 574–577. [[CrossRef](#)] [[PubMed](#)]
12. Yamada, Y.; Hoyano, M.; Akashi, R.; Oto, K.; Kanemitsu, Y. Impact of chemical doping on optical responses in bismuth-doped CH₃NH₃PbBr₃ single crystals: Carrier lifetime and photon recycling. *J. Phys. Chem. Lett.* **2017**, *8*, 5798–5803. [[CrossRef](#)] [[PubMed](#)]
13. Lozhkina, O.A.; Murashkina, A.A.; Shilovskikh, V.V.; Kapitonov, Y.V.; Ryabchuk, V.K.; Emeline, A.V.; Miyasaka, T. Invalidity of band-gap engineering concept for Bi³⁺ heterovalent doping in CsPbBr₃ halide perovskite. *J. Phys. Chem. Lett.* **2018**, *9*, 5408–5411. [[CrossRef](#)] [[PubMed](#)]
14. Wang, R.; Wang, J.; Tan, S.; Duan, Y.; Wang, Z.K.; Yang, Y. Opportunities and challenges of lead-free perovskite optoelectronic devices. *Trends Chem.* **2019**, *1*, 368–379. [[CrossRef](#)]
15. Ramoser, S. Fabrication and testing of organo-lead halide perovskite solar cell and lead-free perovskite solar cells. *Tech. Chem. Inst. Chem. Technol. Mater.* **2015**, *9*, 512–520.
16. Khan, M.I.; Bhatti, K.A.; Qindeel, R.; Althobaiti, H.S.; Alonizan, N. Structural, electrical and optical properties of multilayer TiO₂ thin films deposited by sol–gel spin coating. *Results Phys.* **2017**, *7*, 1437–1439. [[CrossRef](#)]
17. Bakri, A.S.; Sahdan, M.Z.; Adriyanto, F.; Raship, N.A.; Said, N.D.M.; Abdullah, S.A.; Rahim, M.S. Effect of annealing temperature of titanium dioxide thin films on structural and electrical properties. *AIP Conf. Proc.* **2017**, *1788*, 030030–030038.
18. Ahmed, M.; Bakry, A.; Shaaban, E.R.; Dalir, H. Structural, electrical, and optical properties of ITO thin films and their influence on performance of CdS/CdTe thin-film solar cells. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 11107–11118. [[CrossRef](#)]
19. Williamson, G.; Hall, W. Discussion of the theories of line broadening. *Acta Met.* **1953**, *1*, 90006.
20. Mehmood, B.; Khan, M.I.; Iqbal, M.; Mahmood, A.; Al-Masry, W. Structural and optical properties of Ti and Cu co-doped ZnO thin films for photovoltaic applications of dye sensitized solar cells. *Int. J. Energy Res.* **2021**, *45*, 2445–2459. [[CrossRef](#)]
21. Moss, T. Relations between the refractive index and energy gap of semiconductors. *Phys. Status Solidi B* **1985**, *131*, 415–427. [[CrossRef](#)]
22. Fru, J.N.; Nombona, N.; Diale, M. Synthesis and characterisation of methylammonium lead tri-bromide perovskites thin films by sequential physical vapor deposition. *Phys. B Condens. Matter* **2020**, *578*, 411884. [[CrossRef](#)]
23. Wang, Y.; Lü, X.; Yang, W.; Wen, T.; Yang, L.; Ren, X.; Wang, L.; Lin, Z.; Zhao, Y. Pressure-induced phase transformation, reversible amorphization, and anomalous visible light response in organolead bromide perovskite. *J. Am. Chem. Soc.* **2015**, *137*, 11144–11149. [[CrossRef](#)]
24. Sheng, R.; Ho-Baillie, A.; Huang, S.; Chen, S.; Wen, X.; Hao, X.; Green, M.A. Methylammonium Lead Bromide Perovskite-Based Solar Cells by Vapor-Assisted Deposition. *J. Phys. Chem. C* **2015**, *119*, 3545–3549. [[CrossRef](#)]
25. Singh, M.; Goyal, M.; Devlal, K. Size and shape effects on the band gap of semiconductor compound nanomaterials. *J. Taibah Univ. Sci.* **2018**, *12*, 470–475. [[CrossRef](#)]
26. Liu, G.; Kong, L.; Gong, J.; Yang, W.; Mao, H.K.; Hu, Q.; Schaller, R.D.; Dera, P.; Zhang, D.; Liu, Z.; et al. Pressure-Induced Bandgap Optimization in Lead-Based Perovskites with Prolonged Carrier Lifetime and Ambient Retainability. *Adv. Funct. Mater.* **2016**, *27*, 1604208. [[CrossRef](#)]
27. Tsuboi, T.; Sakoda, S. Electronic structure of the Tl⁺ center in KCl. II. Relation to the D band. *Phys. Rev. B* **1980**, *22*, 4972. [[CrossRef](#)]
28. Lushchik, A.; Feldbach, E.; Kotomin, E.A.; Kudryavtseva, I.; Kuzovkov, V.N.; Popov, A.I.; Seeman, V.; Shablonin, E. Distinctive features of diffusion-controlled radiation defect recombination in stoichiometric magnesium aluminate spinel single crystals and transparent polycrystalline ceramics. *Sci. Rep.* **2020**, *10*, 7810–7819. [[CrossRef](#)]
29. Bahadur, A.; Mishra, M. Correlation between refractive index and electronegativity difference for ANB8-N type binary semiconductors. *Acta Phys. Pol. A* **2013**, *123*, 737–740. [[CrossRef](#)]
30. Reddy, R.R.; Gopal, K.R.; Narasimhulu, K.; Reddy, L.S.S.; Kumar, K.R.; Reddy, C.K.; Ahmed, S.N. Correlation between optical electronegativity and refractive index of ternary chalcopyrites, semiconductors, insulators, oxides and alkali halides. *Opt. Mater.* **2008**, *31*, 209–212. [[CrossRef](#)]
31. Herve, P.; Vandamme, L. General relation between refractive index and energy gap in semiconductors. *Infrared Phys. Technol.* **1994**, *35*, 609–615. [[CrossRef](#)]
32. Longman, R. Bonding energy levels and bonds in organic solids. *Longman Sci. Technol.* **1990**, *3*, 1–249.
33. Murphy, A. Band-gap determination from diffuse reflectance measurements of semiconductor films, and application to photoelectrochemical water-splitting. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1326–1337. [[CrossRef](#)]
34. Khan, M.I.; Naeem, M.; Mustafa, G.M.; Abubshait, S.A.; Mahmood, A.; Al-Masry, W.; Al-Garadi, N.Y.A.; Ramay, S.M. Synthesis and characterization of Co and Ga co-doped ZnO thin films as an electrode for dye sensitized solar cells. *Ceram. Int.* **2020**, *46*, 26590–26597. [[CrossRef](#)]
35. Aydin, C. Synthesis of Pd: ZnO nanofibers and their optical characterization dependent on modified morphological properties. *J. Alloys Compd.* **2019**, *777*, 145–151. [[CrossRef](#)]
36. Caglar, M.; Ilican, S.; Caglar, Y.; Yakuphanoglu, F. Electrical conductivity and optical properties of ZnO nanostructured thin film. *Appl. Surf. Sci.* **2009**, *255*, 4491–4496. [[CrossRef](#)]