Solvents driven structural, morphological, optical and dielectric properties of lead free perovskite CH$_3$NH$_3$SnCl$_3$ for optoelectronic applications: experimental and DFT study

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Abstract

Solvent engineering is a powerful technique to achieve high performance Organic-Inorganic Halide Perovskites (OIHPs) which emerged as a potential candidate for various optoelectronic applications. In the present work, lead free CH$_3$NH$_3$SnCl$_3$ perovskites were prepared using two different mixed solvents namely N, N-dimethylformamide (DMF): Dimethylsulfoxide (DMSO) and N, N-dimethylformamide (DMF): Acetonitrile (ACN). The effect of these two solvents mixture on the structural, morphological and optical properties of CH$_3$NH$_3$SnCl$_3$ was analysed. The obtained two perovskites samples were investigated by XRD, TGA, FESEM, EDAX, FT-IR, UV–vis spectroscopy (UV–vis), Photoluminescence spectroscopy (PL) and dielectric spectroscopy. To gain insight into the optical behaviour, the first principle calculations were also performed. FESEM images revealed a conspicuous variation for the two solvents. The DMF:ACN based perovskite possesses band gap more than that for DMF:DMSO based perovskite. The DFT calculations also show the same trend for the energy gap. PL emission is found to enhance in the case of DMF:DMSO based perovskite. The dielectric constant and dielectric loss values have demonstrated the influence of solvents. The analysis shows that among the two cases, the DMF: DMSO solvent mix is found to show results better than that of DMF: ACN case.

1. Introduction

Of late, the Organic-Inorganic Halide Perovskites (OIHPs) are the major scientific interest due to the high performance of next generation optoelectronic devices. OIHP light harvester has many applications in the field of optoelectronic devices such as solar cells, light emitting diodes (LEDs) and photodetectors. High absorption coefficient, low non-radiative recombination rate, tunable band gap, long carrier diffusion, charge carrier transport and high power conversion efficiency (PCE) non-radiative recombination rate, tunable band gap, long carrier diffusion length, charge carrier transport and high power conversion efficiency (PCE) are the outstanding properties of OIHP materials. These are much suitable for the solar cells. OIHP’s external quantum efficiency (EQE), lifetime photoluminescence and high colour purity are ideal for LEDs. The OIHP’s other properties such as fast photo responsibility, high ON-OFF ratio and low working voltage are appropriate for the photodetectors. Moreover, OIHP can be synthesized using lowcost starting materials and simple chemical methods at room temperature [1–6].

The OIHPs have ABX$_3$ structure, where A is larger organic cation (i.e., CH$_3$NH$_3^+$, HC(NH$_2$)$_2^+$ or Cs$^+$) which occupies the body-centred position with twelve X anions surrounding it. Typically B is a smaller divalent metal...
ion in the cube corners (i.e., Pb\(^{2+}\), Sn\(^{2+}\), Ge\(^{2+}\) or Sn\(^{3+}\)) and X is a mixture of monovalent anions in the face-centred positions (i.e., Cl, Br or I). In solar cells, the OIHP perovskite has received much attention in the past decade\(^{[2,7–10]}\) because within a few years, the PCE increases up to 15% by using a simple planer heterojunction incorporating CH\(_3\)NH\(_3\)PbI\(_{x}\)Cl\(_{3-x}\) layer\(^{[11]}\). Moreover, in recent years, there has been growing interest in perovskite light emitting diodes (PLEDs) because currently available commercial LEDs require high temperature and high vacuum process. Specifically, the emission color can be tuned by changing monovalent halide anion from Cl to Br or I\(^{[12–15]}\). Moreover, OIHPs emerged as high-performance photodetectors compared to commercial photodetectors\(^{[16–19]}\). Owing to the various applications, the OIHPs have gained wide attention for next-generation optoelectronic devices\(^{[20–22]}\). The above mentioned application of OIHPS, mainly depends on the method of synthesis and choice of the B and X atoms. Very importantly, as a powerful tool, solvent engineering is imperative to improve the stability of the prepared samples for all these applications. The choice of solvent for the precursor solution is a key factor to achieve the improved perovskite morphology. The solvent should be polar aprotic to dissolve the precursors. The solvents should have a low melting point, low volatility and reasonably moderate vapour pressure. The higher saturated vapour pressure of solvent can cause a lower boiling temperature and higher volatility which lead to fast crystallization, while higher boiling temperature can raise the temperature and time of crystallization. The solvents such as N, N-dimethylformamide (DMF), Dimethylsulfoxide (DMSO), γ-butyrolactone (GBL) and N-methyl-2-pyrrolidone (NMP) were widely used as effective solvents for CH\(_3\)NH\(_3\)PbX\(_3\)\(^{[23, 24]}\). However, all these solvents have a rather high boiling point and low vapour pressure which reduces the evaporation during preparation and hence it results in long drying times. The solubility of the precursor in DMF and DMSO is quite better than GBL and far superior to NMP. The boiling temperature of DMF (153 °C) is lower than the other solvents such as GBL (204 °C), DMSO (189 °C), NMP (202 °C) and so the crystal nucleus steadily grows to a substantial size. Though the vapour pressure of DMF is lower than that of DMSO, crystal nucleus of DMSO is smaller because the dimension of the crystal nucleus depends not only on solvent’s volatility but also on the strength of coordination with precursor and its respective crystallization route. The current and potential techniques of solvent engineering for good active layer morphology mainly depends on primary solvent, co-solvent and solvent additives\(^{[25]}\).

From the literature, it is obvious that the most studied and high efficient OIHPs material contains lead (Pb\(^{2+}\)) in their inorganic part which is a highly toxic metal\(^{[26]}\). In the replacement of lead-free or low toxic alternative, various approaches have been proposed. To the best of our knowledge tin (Sn) is the suitable material as it was considered as an environmental friendly alternative to lead. So, the tin-based OIHPS are proved to be suitable as lead free material for the solar cell, photodetector, LED and other optoelectronic devices. Several studies on the Sn-based OIHPS with I, Br and Cl were reported mostly for the solar cells\(^{[27–33]}\). However, influence of the solvent engineering of these materials on their optoelectronic properties were reported sparsely.

This paper focuses on the effect of solvent on the optoelectronic properties of Sn and Cl based OIHP (CH\(_3\)NH\(_3\)SnCl\(_3\)). The optoelectronic properties such as dielectric constant, dielectric loss, optical absorption, energy band gap and photoluminescence were studied for the Sn–Cl based OIHP. Moreover, the detailed literature review reveals that the analysis of the dielectric properties of CH\(_3\)NH\(_3\)SnCl\(_3\) perovskites are not reported so far. In the present study, to overcome the instability problems of Sn based OIHPS, mixed solvents were used. For the first time, two different solvent mixtures namely (DMF: DMSO) and (DMF: ACN) were used to prepare CH\(_3\)NH\(_3\)SnCl\(_3\) perovskite and the results are compared. There are a few reports on the use of ACN\(^{[34–36]}\). In our study, we used mixed solvents of DMF: ACN and compared the results with that of DMF: DMSO mixed solvents case. The boiling point of ACN is lower (82 °C) than that of the other two solvents used in our study. The intermolecular hydrogen bonding is an important solute-solvent interaction. This plays an essential role in changing the position of the energy levels and hence optical properties can be tuned. The present work aims to bring out the effect of mixed solvents on the optoelectronic properties of CH\(_3\)NH\(_3\)SnCl\(_3\).

2. Experimental procedure

2.1. Materials

The methylammonium chloride (CH\(_3\)NH\(_3\)Cl) 99% (Loba chemicals) and Tin Chloride (SnCl\(_3\)) 99% (Merck life science) were used as starting materials. The Acetonitrile (ACN), Dimethylsulfoxide (DMSO) and N, N Dimethylformamide (DMF) solvents were purchased from Avra chemicals.

2.2. Methods

The CH\(_3\)NH\(_3\)SnCl\(_3\) perovskite was synthesized by the procedure as given in the previous report\(^{[37]}\). First, the starting materials were dehydrated in a hot air oven. Sample 1 of CH\(_3\)NH\(_3\)SnCl\(_3\) was prepared using the solvents Dimethylformamide (DMF) and Dimethylsulfoxide (DMSO). The solution of 0.1 M of methylammonium
chloride (0.675 g) was prepared separately with the solvents namely N, N Dimethylformamide (5 ml): Dimethylsulfoxide (5 ml). Then, the solution of 0.1 M of tin chloride (1.895 g) was prepared separately with these two solvents. Next, the tin chloride solution was slowly added into the methylammonium chloride solution at a fixed temperature of 60 °C, which resulted in the formation of a white suspension. The white product was filtered by using PTFE filter paper with a 0.2 μm pore size. Finally, the powder obtained by precipitation was filtered and then powder was heated in a hot air oven at 100 °C for 12 h, 120 °C for 12 h, and 140 °C for 12 h to evaporate the solvents in the perovskite. Sample 2 of CH₃NH₃SnCl₃ was prepared using the solvents DMF and ACN following the procedure as described above for sample 1. However, in this case, the filtered product was placed at a fixed temperature of 70 °C in 12 h for initial evaporation of ACN solvents because the ACN boiling point is very low compared to DMF and DMSO solvents. To study the dielectric properties, the pellets were prepared using the hydraulic pellet press at the pressure 6 tons and then silver coated on both sides.

2.3. Characterization

For phase analysis, Bruker D8 advanced x-ray Diffractometer with Cu Kα radiation and high-speed wide angle lynx eye detector was used. TGA measurements were conducted in Q500 Hi–Res under an N₂ atmosphere to identify the chemical composition of the released gases during the thermal decomposition process. FESEM and EDX results were obtained with a CarlZeiss SUPRA 55VP. FTIR Spectrum was measured in transmittance mode using JASCO FT/IR 6300 type. The absorption spectrum was obtained out in the range of 300 to 700 nm using a SHIMADZU UV–vis 2600. The PL spectrum was recorded on an Agilent Carry Eclipse fluorescence spectrometer. The dielectric constant and dielectric loss were measured using a HIOKI 3532-50 LCR HITESTER.

3. Result and discussion

3.1. Structural studies

The XRD patterns of the two solvent engineered samples are displayed in figure 1. The XRD peaks matched with the cubic perovskite structure (space group Fm3m). There are no critical differences in the XRD peaks between the two samples, except a slight shift in the positions of the peaks. The XRD peaks are clearly observed for DMF: DMSO mixed solvents based CH₃NH₃SnCl₃ perovskite at the angles of 14.200, 20.050, 24.680, 28.470, 32.040 and 35.160, which matched with the (100), (110), (111), (220), (310) and (312) planes respectively. The XRD peaks for DMF: ACN mixed solvents based perovskite are located at the angles of 14.260, 20.150, 24.700, 28.480, 32.060 and 35.290 corresponding to (100), (110), (111), (220), (310) and (312) planes, respectively.

The assigned (110) and (220) peaks are indicative of the perovskite phase. Diffraction peaks as in good agreement with the previous reports [38–40]. The obtained crystal structure of perovskites depends upon the Goldschmidt tolerance factor \( t \) which is given by the following expression:

\[
t = \frac{(r_A + r_X)}{(\sqrt{2}(r_B + r_X))}
\]

where \( r_A, r_B \) and \( r_X \) is the ionic radii of A, B and X ions. If \( t > 1 \), the structure is tetragonal or hexagonal. If \( t = 0.9 \) to 1, the structure is cubic and for \( t < 0.9 \), it is in orthorhombic or rhombohedral structure. It is believed that the perovskites can be stabilized when ‘\( t \)’ is in the range of 0.813 – 1.107. In the present work, the Goldschmidt
tolerance factor $t$ is 0.9345 and so the samples should be in the cubic structure [41] and this is confirmed by the XRD data.

Octahedral factor ($\mu$) for the perovskite is determined by

$$\mu = \frac{r_B}{r_X}$$

where $r_B$ and $r_X$ are ionic radius of B and X ions respectively. The radius ratio $r_B/r_X$ for perovskite halides is between 0.377 and 0.895 [42]. For our samples, the calculated octahedral factor ($\mu$) is 0.5978 which indicates the octahedral coordination of the crystal structure.

The average crystallite size ($d$) of CH$_3$NH$_3$SnCl$_3$ were calculated using the Debye–Scherrer formula,

$$d = \frac{K\lambda}{\beta \cos \theta}$$

where shape factor $K$ is 0.89 Å, $\lambda$ is the wavelength of the incident beam and $\beta$ is the FWHM. The calculated average crystallite size of CH$_3$NH$_3$SnCl$_3$ (DMF: DMSO) and CH$_3$NH$_3$SnCl$_3$ (DMF: ACN) are 67 nm and 104 nm respectively.

### 3.2. Thermal gravimetric analysis

The thermal stability is assessed by TGA and the TGA spectrum which is shown in figure 2. The TGA curves show two distinct mass losses. The decomposition temperature of DMF: ACN based case is 194 °C which is higher than that of DMF: DMSO case (190 °C) indicating that both have the relatively good thermal stability. This is the first weight loss which is due to the removal of solvents trapped inside the sample powder. For DMF: DMSO case, the weight loss is 22.2% which begins at about 190 °C while the weight loss of 22% begins at 194 °C for DMF: ACN case. The next weight loss was observed at 320 °C (54.2%) and 325 °C (44.4%) for DMF: DMSO case and DMF: ACN case respectively and such a loss is attributed to loss of SnCl$_2$ residues and organic cations to some extent [43]. The TGA results of the present work reveals that the solvents have great influence on the crystal growth.

### 3.3. Morphological analysis

The morphologies of the solvents mixed perovskites were characterized by FESEM in order to analyze distribution of grains and visualize the crystallization process. The FESEM images are shown in figure 3. The magnification is given for 1 μm and 2 μm. The findings of morphology show irregularly shaped particles for both cases. The SEM images of both solvent cases reveal that the solvents have a significant impact on the morphology of the perovskites as some significant changes are identified in the FESEM images. It is known that the crystallization process of the perovskite can be adjusted by changing the solvent [44]. The changes in the SEM images may be due to the variation in the crystal growth when mixed with varied solvents. Within the same scale, we can observe that the particle formation is different. The elemental composition of the samples was analyzed with EDAX and presented in figure 4. The EDAX spectrum reveals the distribution of chloride, tin, carbon, nitrogen and hydrogen in the two samples. Quantitative analysis of the EDAX spectra shows that the atomic...
Figure 3. Field-Emission Scanning Electron Microscope (FESEM) images (a) 1 μm and (b) 2 μm top view of DMF: DMSO solvent mixed CH3NH3SnCl3 perovskites. (c) 1 μm and (d) 2 μm top view of DMF: ACN solvent mixed CH3NH3SnCl3 perovskites.

Figure 4. EDX of CH3NH3SnCl3 perovskites. (a) DMF: DMSO solvent mix. (b) DMF: ACN solvent mix.
ratios of Sn and Cl are 7%:20% for DMF: DMSO solvents mixed perovskite and 3%:9% for the DMF: ACN solvents mixed perovskite and weight percentage is given in the table S1 in the supplementary.

3.4. Analysis of FT-IR spectrum

The presence of CH$_3$NH$_3$Cl and SnCl$_2$ in DMF: DMSO and DMF: ACN solutions are further confirmed through the FTIR spectroscopy which is shown in figure 5. There is a characteristic band measured at 3354 cm$^{-1}$ corresponding to stretching vibration of N–H for both cases. In addition, the strong peak position between 3500 and 3300 cm$^{-1}$ is related to the N–H stretch vibrations which could be associated with the NH$_3^+$ group of the organic cation. The bands of both samples 2919 cm$^{-1}$ is identified to correspond to C–H stretching. This C–H stretching vibration is associated with a CH$_3^+$ group of the organic cation. The band at 1620 cm$^{-1}$ is identified as symmetry and asymmetry of N–H bend vibrations. The symmetry and asymmetry of C–H bond vibrations are located at 1548 cm$^{-1}$. From the spectrum, C–N stretching vibrations bands are detected at 1246 cm$^{-1}$. The bands at 666 cm$^{-1}$ correspond to C–Cl stretch which is associated with strong alkyl halide [38]. Thus the FTIR confirms the presence of all functional group of the CH$_3$NH$_3$SnCl$_3$ samples.

3.5. Optical absorption study

The absorption spectrum of the samples recorded by UV–vis absorption spectrometer is given in figure 6(a). The absorption onset is located at 471 nm for DMF: DMSO solvents mixed perovskite (sample 1) and at 439 nm for DMF: ACN mixed perovskite (sample 2). The absorption is slightly better for sample 1 than that of sample 2 and also we observe a variation in the band gap. The band gap $E_g$ was evaluated from the Tauc plot which is shown in figure 6(b). The band gap of CH$_3$NH$_3$SnCl$_3$ is 2.63 eV and 2.82 eV respectively for DMF: DMSO solvents mixed perovskite and DMF: ACN mixed perovskite. The variation in the band gap values may be attributed to the variation of crystal quality. Our band gap values are reasonably in good agreement with earlier report on CH$_3$NH$_3$SnCl$_3$ where DMF solvent is used ($E_g$ = 2.5 eV) [33]. According to the Schockly—Quessier limits, the materials possessing $E_g$ < 3 eV are suitable for the solar cells application. The previous studies reported the $E_g$ value which lies between 2.4–2.6 eV for the solar cell prepared with SnCl$_2$ based perovskites [32, 33]. In our study, we also observe that $E_g$ values for the SnCl$_2$ based perovskites are consistent with these reports and so, this confirms that the samples prepared are suitable for the solar cell. Our $E_g$ values are high compared to that of SnI$_2$ and SnBr$_2$ based perovskites. When compared to SnI$_2$ ($E_g$ = 1.2 eV) [27] and SnBr$_2$ ($E_g$ = 2.2 eV) [45] based perovskites, we have obtained high $E_g$ values for SnCl$_2$ based cases. The solar cell was fabricated and its characteristics are presented in the supplementary section (figures S1 and S2 is available online at stacks.iop.org/MRX/6/125921/mmedia).

3.6. Photoluminescence study

Figure 7 shows the photoluminescence spectrum for the two solvent based CH$_3$NH$_3$SnCl$_3$. It is to be noted that the PL peak of DMF: DMSO solvents mix is found to be broadened compared to that of DMF: ACN for which a sharp peak is exhibited. The broadening may be due to the presence of more intermediate energy levels between the valence band and conduction band. It is interesting to note that the emission wavelength of DMF: DMSO
based perovskites is at 516 nm while for DMF: ACN mixed solvent case, peak is located at 487 nm. Hence, it is clear that the DMF: ACN mixed perovskites shows the blue shift when compared with DMF: DMSO based perovskites. This speculates that even though the material is the same, the solvent mixed to the compound has the influence to augment the emission. Our emission results are comparable to other reports [5, 37, 46]. The FWHM calculated from the maximum emission peaks is 18 nm and 16 nm for DMF: DMSO and DMF: ACN solvents mixed perovskites respectively. If the value of this FWHM is less than 35 nm, it is suitable to fabricate efficient monochromatic LEDs with high luminous and high color purity [47]. We obtained a FWHM less than 35 nm and so we suggest that both solvent mixed CH$_3$NH$_3$SnCl$_3$ perovskites may be potential candidates for LED.

### 3.7. Dielectric properties

The dielectric permittivity and the dielectric loss were measured as functions of frequency from 1 MHz to 5 MHz at room temperature which are shown in figure 8. The dielectric constant decreases with increase in frequency for both cases. The dielectric constant for sample 1 is more than that of sample 2. For the DMF: DMSO mixed solvents based compound, the maximum value of dielectric constant is 169.37 at 2 MHz while for DMF: ACN mixed solvents based compound, the maximum dielectric constant is 147.57. We observe that dielectric loss is more for DMF: ACN case than that of DMF: DMSO case at all frequencies.
3.8. First principle calculations

To gain insight into the optical characteristics of the samples, we performed the first principle calculations to understand the electronic band structure and the band gap of DMF: DMSO and DMF: ACN solvent cases of CH$_3$NH$_3$SnCl$_3$. We used the mimic of CH$_3$NH$_3$SnCl$_3$ which is CsSnCl$_3$ in the cubic crystal structure (Space group no 221) because when Cs is replaced by MA, the electronic properties are strongly dependent on the inorganic components namely Sn and Cl$^-$ [48]. The self-consistent full potential linearized augmented plane wave (FP-LAPW) method based on the density functional theory (DFT) as implemented by the Vienna package code WIEN2k was used for the electronic band structure calculations. In this method, the crystal potential is treated without shape approximation and core electrons are treated relativistically and the scalar relativistic calculations are performed. Calculations were performed with a cutoff $R_{MT}K_{\text{max}} = 7$ where $R_{MT}$ is the minimum radius of the muffin-tin spheres and $K_{\text{max}}$ gives the magnitude of the largest k vector in the plane wave expansions. A dense mesh of 1 000 k points was used and the potential and charge cut-off G$_{\text{max}}$ was kept as 12. The exchange-correlation potential is evaluated by the Perdew–Burke–Ernzerhof Generalized Gradient Approximation (PBE-GGA). The integration over the irreducible Brillouin zone are performed using Monkhorst-Pack mesh. The self-consistency is achieved when total energy convergence is less than 10$^{-5}$ Ry and the charge convergence is less than 10$^{-4}$ e for the stability of the system. We used the experimental lattice parameter obtained from the XRD data to perform the electronic band structure calculations. The calculated electronic band structure of the two samples is presented in figures 9(a), (b). It is found that a direct band gap $E_g$ is located along the symmetry direction R and formed mainly between the Sn-5p state (conduction band minimum) and the Cl-3p state (valence band maximum). The $E_g$ values are 1.9 eV for DMF: DMSO and 2.1 eV for DMF: ACN. The computed band gap values for DMF: DMSO and DMF: ACN are in close agreement with our experimental values that obtained through UV–vis spectrum. Moreover, the trend in the variation of the band gap is also consistent.

4. Conclusions

In this study, we prepared lead-free methylammonium tin tri-chloride (CH$_3$NH$_3$SnCl$_3$) perovskites through DMF: DMSO and DMF: ACN mixed solvents to analyse the optical properties such as optical absorption, photoluminescence and dielectric constant. Typical remarkable variations are detected in the optical properties, when two different solvent mix are used for the preparation of CH$_3$NH$_3$SnCl$_3$. Among the two cases, mixed solvent of DMF: DMSO case exhibits better optical properties than the DMF: ACN mixed solvents. The absorption wavelength is relatively longer (471 nm) for DMF: DMSO solvents mixed perovskite compared to that of DMF: ACN mixed perovskite (439 nm). The room temperature PL emission falls at green for DMF: DMSO and at blue for the other. The DMF: DMSO case exhibits more dielectric constant than the other. Enhanced optical characteristics are essential for the optoelectronic devices and so, DMF: DMSO mixed perovskite is found to be a potential candidate for the device applications compared to the other.

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