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PHOTO - ENHANCED RESISTANCE SWITCHING BEHAVIOUR IN $(PEA)_2CuCl_4$ 2-DIMENSIONAL PEROVSKITE

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Abstract

The structural tunability and optical and thermal properties allured interest in hybrid perovskites. $(PEA)_2CuCl_4$ a lead-free 2D organic-inorganic hybrid perovskite of band gap 2.91eV, was synthesised, and its optical and electrical characterisations were reported in this work. The temperature-depended optical characteristics show a shift in absorbance and transmittance, indicating the thermochromic nature of the material due to the non-rigid copper ion and subsequent Jahn-Teller distortion arising on heating. The morphological analysis confirmed uniformity of $(PEA)_2CuCl_4$ thin film. The structural analysis confirmed that the material belonged to an orthorhombic non-centrosymmetric crystal structure, and the hysteresis loop obtained in capacitance versus applied voltage characteristics supported the ferroelectric behaviour of the material. Current versus voltage characteristics of $(PEA)_2CuCl_4$ show resistance switching behaviour promising for memory device application. The switching behaviour was analysed in light and dark environments. The light environment enhanced resistance switching in the material.

Index Terms: C-V hysteresis loop, Copper halide perovskite, Island morphology, Non-centrosymmetric, Rietveld refinement, Resistance switching, Thermochromic properties.

1. INTRODUCTION

Halide perovskites show interesting physical properties such as high absorption coefficient, ambipolar charge transport, tunable band gap, low exciton binding energy, ferroelectricity, etc. [1-7]. Miyasaka et al. in 2009 applied methylammonium lead iodide ($MAPbI_3$) and methylammonium lead bromide ($MAPbBr_3$) perovskites to sensitise to TiO_2 (titanium dioxide) for visible light with maximum efficiency of 3.8% [8]. Later, in 2011 park et al. synthesised $MAPbI_3$ nanocrystals and applied them in the solar cell, which showed an efficiency of 6.5% [9]. Followed by these, a hand full of innovative works came out using halide perovskites in solar cells, light-emitting diodes (LEDs), photodetectors, memory devices, field effect transistors, batteries and piezoelectric energy harvesters [10-16]. Even though the material performs well, chemical instability and lead toxicity retract its mass commercialisation [17-19].

Stability was attained by developing 2-dimensional (2D) perovskites [20, 21]. Ruddelson-popper(RP) and Dion-Jacobson (DJ) are the two important types of 2D perovskite structures, A_2MX_4 and AMX_4 respectively, where A is largely organic or inorganic cations (e.g.: MA^+, FA^+ (formamidinum), Cs^+ (caesium), PEA^+ (phenyl ethyl ammonium)etc.) and M is the metallic smaller cation (Pb^{2+}, Sn^{2+} (tin), Cu^{2+} (copper)etc) and X is the halide anion .Cl^{-1} (chloride), Br^{-1}, I^{-1} [22, 23]. Also, lead toxicity can be stamped out by replacing it with metallic cations such as Sn, bismuth (Bi), (Cu), germanium (Ge) etc. [24-27]. Cu-based halide perovskite is a better choice in this scenario because it forms a 2D environment-friendly perovskite [28, 29].

A number of Cu-based perovskite materials were reported to be flexible with temperature and light, showing thermochromism and photochromism [30, 31]. Non-rigid nature of Cu ion with electronic configuration $3d^9$ is responsible for this behaviour [32]. Li et al. reported the thermochromic behaviour of different Cu-based halide perovskites in smart windows [33]. B. G. H. M. Groeneveld et al. reported a photochromic phenomenon in 2D Cu-based perovskites [34]. Also, organic cations with phenyl ring showed high moisture stability compared to the commonly used methylammonium cation, which reported better performance [35, 36]. A. O. Polyakov et al. reported the coexistence of ferroelectricity and ferromagnetism in $(PEA)_2CuCl_4$ RP-perovskite. According to them, octahedral tilting and twisting in the structure of $(PEA)_2CuCl_4$ can naturally give rise to polarisation [37]. In this work, a stable $(PEA)_2CuCl_4$ 2D perovskite was synthesised, and its temperature-dependent optical characteristics, electrical characteristics and effect of photons on the resistance switching mechanism were studied.

2. EXPERIMENTAL SECTION

2.1 Materials used

phenyl ethyl amine(PEA) (99%, Sigma Aldrich), Copper (2) chloride ($CuCl_2$) (98%, Sigma Aldrich), con. Hydrochloric acid (HCl) (35% in distilled water, Merck), ethanol (99.8%, HI Media), N, N-Dimethylformamide (DMF) (99.9%, Merck) and distilled water, Fluorine doped tin oxide coated glass substrates (FTO glass substrate).

2.2. Methods

2 molar(M) solution of HCl and PEA were dissolved in distilled water and ethanol respectively and stirred at 0°C for 40 minutes. Then, the acidic solution was added and dropped wisely into the PEA solution and stirred for 2 hours at 0° C. The solution was dried at 60°C to obtain phenyl ethyl ammonium chloride (PEACl) powder. The powder was recrystallised two times to attain desired purity. The powder is stored in diethyl ether [38, 39]. 1.716g of PEACl and 0.67g of $CuCl_2$ (2:1 ratio) were dissolved in 10 ml DMF and stirred for 4 hours at 80 °C to get $(PEA)_2CuCl_4$ The solution was spin-coated (EZspinA1-spin coater) on FTO glass substrates at 2000 rpm for 40 seconds repeated the process 5 times.

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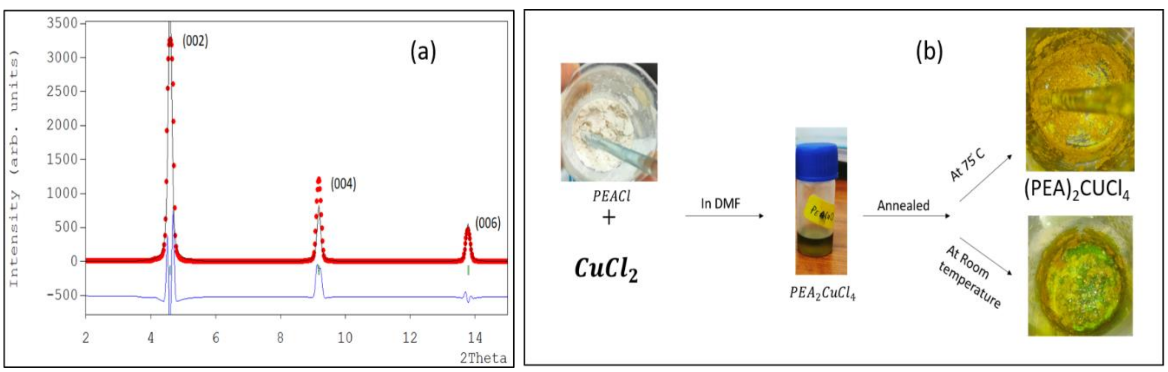
Morphology of the prepared films was checked using Field Emission Scanning Electron Microscope (FE-SEM) (Gemini 300, Zeiss) and structural analysis was done using X-ray diffraction (XRD) facility (Rigaku Goniometer model ultima IV) at COE-AMGT respectively in Amrita Vishwa Vidyapeetham, India. Absorbance in the Ultra Violet (UV)-Visible (VIS) region was analysed using a Thermo Scientific Nicolet iS50 UV-VIS spectrometer at CLIF, University of Kerala, India. The films of $(PEA)_2CuCl_4$ show a colour change from yellow to orange upon heating. This thermochromic behaviour was confirmed via temperature depended optical study done with the help of CARY 100 WIN UV-VIS spectrophotometer version: 4.20 (Agilent Technologies), NIPER Raebareli, India. Electrical characterisations to study photo-induced resistance switching was performed via the semiconductor parameter analyser, Keysight B1500A in IIT Palghat, India.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

Fig. 1(a&b): represents refined XRD pattern of and synthesis process of thermochromic nature of$(PEA)_2CuCl_4$.



Crystallographic Information (CIF file) of $(PEA)_2CuCl_4$ (CCDC No: 892624) was used to refine the powder XRD pattern of synthesised $(PEA)_2CuCl_4$ using The Full proof Suite program [37, 40]. The optimized values of refinement factors obtained such as chi-square, Bragg R-factor, and RF-factor are 14.5, 16.43, and 10.60 respectively. Refinement confirmed that the material belongs to the C m c a (No: 64) space group in the orthorhombic crystal system with unit cell parameter a = 38.58 Å, b = 7.34 Å, c = 7.39 Å, α=β=γ=90. Refined structural characteristics of $(PEA)_2CuCl_4$ is shown in Fig. 1. Planes (002), (004), and (006) are marked in that according to the reflection conditions of C m c a space group.

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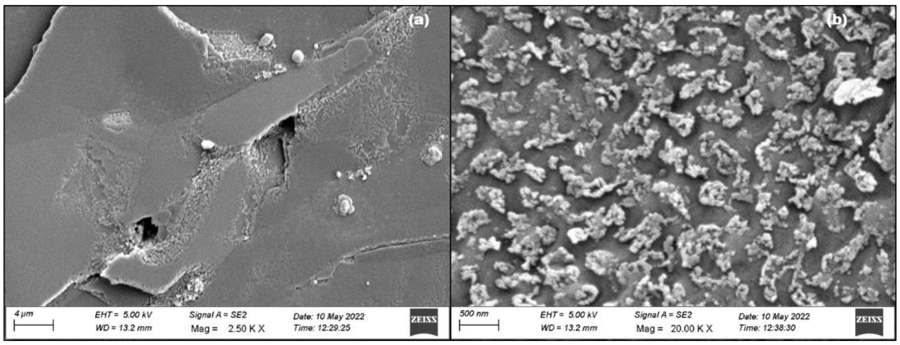
3.2 Morphological Analysis

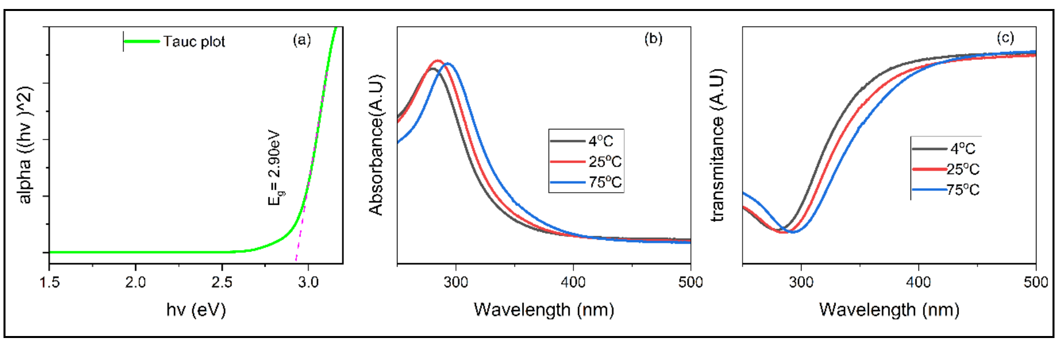
Fig. 2 (a & b): represents FE-SEM micrographs of $(PEA)_2CuCl_4$ at 2.5KX and 20KX magnification respectively



FE-SEM image of $(PEA)_2CuCl_4$ film at a magnification of 2.5KX shown in Fig. 2(a) looks like a smooth and continuous one. Upon increasing the magnification to 20KX the clusters and islands formed on the film became visible as shown in fig. 2(b).

3.3 Optical Analysis

Fig. 3 (a b & c) represents Tauc plot, temperature depended UV-Vis absorbance and transmittance analysis respectively



Thin films of $(PEA)_2CuCl_4$ of thickness 300nm was coated on glass FTO glass substrates and the UV-VIS absorbance spectrum was taken. The obtained data was modified and the Tauc plot was drawn as shown in Fig. 3(a). The nature of the Tauc plot indicates that the synthesized material possesses a direct band gap. The slop drawn at the tailing end touches X-axis at 2.90 eV which is the band gap of the material. During the fabrication of $(PEA)_2CuCl_4$ thin films show a colour change. During the annealing process, the film shows an orange colour at a temperature on and above 75^{o}C. The colour change from yellow to the orange of $(PEA)_2CuCl_4$ was shown in Fig .1(b). Upon cooling, the material's colour changed into pale yellow. On repeating the process of heating and cooling the material shows the same effect indicating the reversible thermochromic behaviour of the material [33]. In Fig. 3(b&c), it is clear that as

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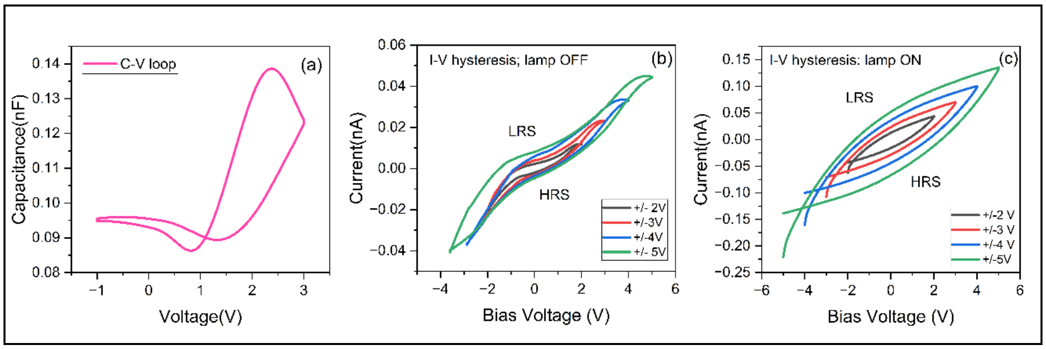
temperature increases absorbance and transmittance of $(PEA)_2CuCl_4$ shows a red shift and confirms its thermochromic nature.

3.4 Electrical Analysis

Fig. 4 (a, b &c) represents variation in capacitance and current in $(PEA)_2CuCl_4$ upon the applied voltage



Electrical properties of $(PEA)_2CuCl_4$was analysed via a semiconducting parametric analyser. It results in capacitance(C) and current upon the applied voltage. Capacitance shows a butterfly-shaped switching indicating non –centrosymmetric nature and the presence of ferroelectricity in $(PEA)_2CuCl_4$. The voltage window was -1 to 3V and the corresponding capacitance produced varied from 0.095nF to 0.135nF with the crossing of the curve at a voltage of 1.1 V at 1KHz frequency. This type of switching in capacitance made the material suitable for non-volatile memory. Voltage-controlled resistance shifts from a high resistance state (HRS) to a low resistance state (LRS) were observable in the I-V characteristics shown in Fig. (b&c). The Resistance switching mechanism present in $(PEA)_2CuCl_4$was studied in two environments such as dark and light. The area of the hysteresis loop varies with voltage change, indicating that the charge storage in this material is non-linear. The I-V characteristics of the material show symmetrical behaviour in different sweep voltages; also, the area covered in the loop increases with an increase in the sweep voltage. According to Fig. 4(b), the current values vary between ±0.04nA when the lamp is OFF. According to Fig. 4(c), the value of current value was ±0.15nA when the lamp was in the ON state. These results confirmed the phot-generated charge carriers support $(PEA)_2CuCl_4$ to increase the current flow and produce a shift in the positions of HRS and LRS and create an improved switching mechanism.

4. CONCLUSION

In summary, $(PEA)_2CuCl_4$ was synthesised by a simple solution-based process and morphological analysis confirmed the uniformity of the formed film. The film showed a change in colour from yellow to orange upon heating evidencing thermochromism. This colour change was reversible in nature. Temperature depended on optical analysis shows a red shift in pattern raised upon heating confirming thermochromism. Rietveld

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refinement $(PEA)_2CuCl_4$ is in good accordance with the known crystallographic data. The material is belonged to C m c a space group and possesses a non-centrosymmetric crystal structure and ferroelectric properties. The electrical characteristics indicated that the material is suitable for non-volatile memory applications. Switching between high and low resistance states is visible in current versus voltage characteristics. The same characteristics upon light environment output enhanced the resistance switching behaviour presented in$(PEA)_2CuCl_4$.

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