

MICROHARDNESS STUDIES OF CESIUM MERCURIC IODIDE (Cs₂Hg₃I₈) _ A NON LINEAR OPTICAL CRYSTAL

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Abstract

Cesium mercuric iodide (Cs₂Hg₃I₈) single crystal has been grown by slow evaporation technique. The grown crystal was characterized by powder X-Ray diffraction analysis. It belongs to monoclinic structure with a non centrosymmetric space group. The UV- absorption spectrum was performed for the grown crystals. It shows excellent transparency in the range of 0.5-25 μm in the region 190-1100 nm. Fourier transform infrared (FTIR) spectrum confirms the presence of various functional groups. The Vicker's hardness studies carried out on Cesium mercuric iodide (Cs₂Hg₃I₈) revealed that the grown crystal is soft in nature.

1. Introduction

Non-linear optical (NLO) material is important in the field of Laser frequency conversion, optical parameter oscillator (OPO) and signal communication. This results in the development of many NLO crystals for application in UV and Visible regions. On the other hand development of NLO crystals such as GaSe[1], AgGaS₂[1,2], AgGaSe₂[3], ZnGeP₂[4], Ag₃AsS₃[5], Tl₃AsSe₃[6] for applications in IR application was found to be difficult as they are difficult to grow and having low optical damage threshold. To overcome these limitations crystals of halides groups such as CsGeX₃ (X=Cl, Br, I) [7-10], Tl₃PbBr₅[11], Tl₄HgI₆[12], CsCdBr [13] and Cs₂Hg₃I₈ [14] have been developed. In the present work we report the growth of Cs₂Hg₃I₈ by slow evaporation technique. The grown crystals were subjected to various characterization studies.

2. Experimental procedure

2.1 Synthesis of Cesium mercuric iodide

Raw material for the growth of Cesium mercuric iodide was synthesized by mixing the solutions of cesium iodide and mercuric iodide in the ratio 1:1.5 in Acetone. The solubility of CsI and HgI₂ in various solvent is given in table 1

Table 1 solubility of Cesium mercuric iodide

	Solubility in water	Solubility in Acetone	Solubility in Ethanol	Solubility in Ether
CsI	94	0.27	Nil	Nil
HgI ₂	0.006	2.4	2.0	0.35

The above said three different organic solvents were tested and acetone was finally chosen as the solvent because both cesium iodide and mercuric iodide are uniformly soluble in Acetone. The advantage of organic solvent among aqueous solution is that the reaction is faster and can proceed in room temperature. The chemical reaction for the synthesis is



Before starting the synthesis process, the commercially available raw materials namely mercuric iodide and Cesium iodide were subjected to repeated recrystallization processes to get purified initial compounds.

2.2. Growth of Cs₂Hg₃I₈

The synthesis of Cs₂Hg₃I₈ was first reported by Fedorov et al. in aqueous solution [15]. In the present work all the synthesis and growth processes were carried out in acetone. The Cs₂Hg₃I₈ was grown by the slow evaporation technique. The calculated amount of Cesium iodide and Mercuric iodide were

dissolved 100 ml of Acetone. The saturated solution of $Cs_2Hg_3I_8$ was obtained by dissolving the recrystallized material with continuous stirring of the solution using a magnetic stirrer. On reaching saturation, the equilibrium concentration of the solute was determined gravimetrically. The mixture of the reactants was stirred well to avoid co precipitation of multiple phases. The product was purified by successive recrystallization. The saturated solution was further purified by filtering through the whatman filter paper provided with fine pores of 1-micrometer porosity. The filtered solution was tightly closed with thick filter paper so that the rate of evaporation could be minimized. The grown crystal of suitable size were carefully taken and washed with acetone. The optical quality single crystal of size $10 \times 7 \times 3 \text{ mm}^3$ (Figure1) was grown by slow evaporation method after 15 days.

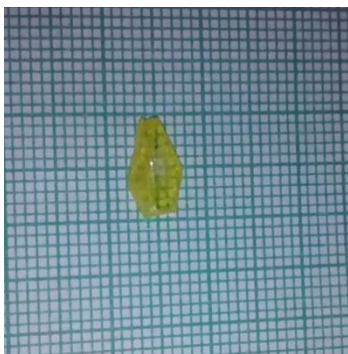


Figure 1 Photograph of grown $Cs_2Hg_3I_8$ crystal.

3. Characterization

3.1. XRD Analysis

Powder X-ray diffraction analysis of the grown $Cs_2Hg_3I_8$ crystal was carried out using PANalytical-X-ray diffractometer in the range $10 - 70^\circ$ to confirm the structure and phase. The $K\alpha$ radiations from a copper target ($\lambda = 1.5406 \text{ \AA}$) was used. The Powder-XRD spectrum of grown crystal is shown in Figure 3. The grown crystal belongs to monoclinic structure with a non centrosymmetric space group C_m . The X-ray diffraction peak were indexed for the lattice parameter and the prominent peaks obtained from powder X-ray diffraction confirm the structure of the grown crystal. The cell parameters of $Cs_2Hg_3I_8$ are $a= 7.4415 \text{ \AA}$, $b=21.6629 \text{ \AA}$, $c=7.6726 \text{ \AA}$, $\alpha=90^\circ$, $\beta=108.050^\circ$, $\gamma=90^\circ$.

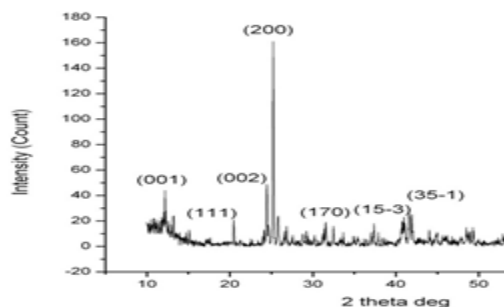


Fig. 2 Powder XRD spectrum of $Cs_2Hg_3I_8$ crystal

3.2. FTIR Analysis

The FTIR spectrum of the title compound was recorded in the range $450 - 4000 \text{ cm}^{-1}$ by using Perkin Elmer Spectrum two FT-IR/ ATR Spectrometer as shown in figure 3. The peak at 1591.42 cm^{-1} is assigned to the C=O stretch. The absorption bands in the region of 3557.13 cm^{-1} and 3491 cm^{-1} are due to C-H symmetric stretching vibration. Stretching at 650 cm^{-1} is the evidence for the existence of Hg-I group.. The observed band at 837.90 cm^{-1} in IR is assigned to C-H out of plane bending mode of vibration.

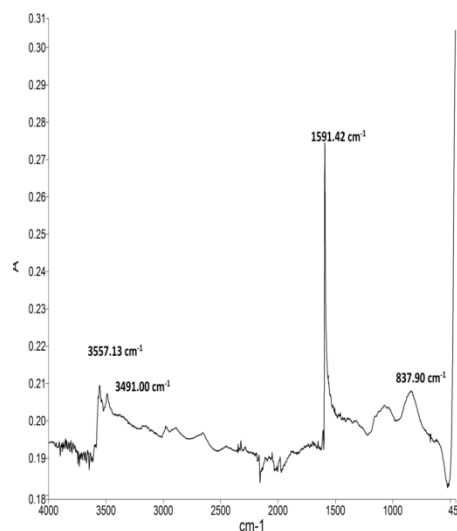


Fig. 3 FTIR- Spectrum of $Cs_2Hg_3I_8$

3.3. U-V Visible analysis

The U-V visible absorption spectrum of $Cs_2Hg_3I_8$ crystal was recorded using Lambda 35 UV

Winlab Spectrometer. The UV spectrum was recorded between 400 to 1100 nm. The recorded absorption spectra of Cs₂Hg₃I₈ crystal is shown in Figure 4. The lower cut off wave length was observed at 352 nm. . From the UV-spectrum it is clearly seen that the crystal is found to be transparent in the region of 400-1100 nm . The calculated band gap value for the grown crystal was found to be 2.56 eV.

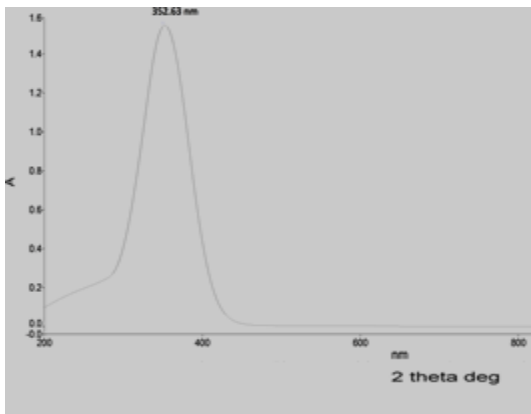


Fig. 4 UV-vis spectrum of Cs₂Hg₃I₈ crystal

3.4. Second harmonic generation

NLO Efficiency of the grown Cs₂Hg₃I₈ crystalline sample was measured by the Kurtz and Perry technique. A Q-Switched Nd : YAG laser was used as light source. A laser beam of fundamental wave length 1064 nm, 8 ns pulse width, with 10 Hz pulse rate was made to fall normally on the sample cell. KDP crystalline sample was used as a reference material in the SHG measurement. The input laser energy incident on the powdered sample was chosen to be 5mJ/pulse. The second harmonic generation efficiency of Cs₂Hg₃I₈ was found to be 2.37 times of the standard KDP crystal.

3.5. Vicker’s micro hardness studies

In the present investigation, the microhardness of the grown crystal was determined using the static indentation test with Vicker’s diamond pyramid indenter at room temperature. The load was varied as 10, 25, 50,100 grams. The Fig.5 shows the variations of Hv with the applied load p. the hardness number was estimated using the following relation

$$H_v = 1.8544 * W/d^2 \text{ kg/mm}^2$$

Where, Hv = Vickers microhardnessnumber ,W = applied load, d = Diagonal length of the indentation impression in meter. The hardness of the grown crystal found to increase with increase of load. At lower loads hardness is relatively low and it increases for higher loads and remain constant up to 50 g. Above 50g load, significant cracking occurs due to the release of internal stress generated locally by indentation.

The hardness number for the sample is found to decrease with the applied load. Fig.6 shows that the plot between log p vs log d is a straight line. Meyer’s index number was calculated from Meyer’s law [15], which relates the load and indentation diagonal length as

$$P = kd^n,$$

$$\log P = \log k + n \log d,$$

The above relation indicates that Hv should increase with P, if n >2 and decrease with P when n <2. This is well satisfied as shown by figure 5. In order to find the value of ‘n’, a graph is plotted for log P against log d (figure 6), which gives a straight line. From the slope line, Meyer’s index number ‘n’ was calculated and was found to be 2.96. According to Hanneman [16], the values of n were 1–1.6 for hard materials and more than 1.6 for soft ones. Thus, Cs₂Hg₃I₈ crystal belongs to soft material category.

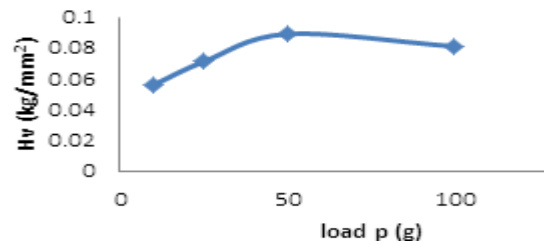


Fig. 5 Variation of Hv with load

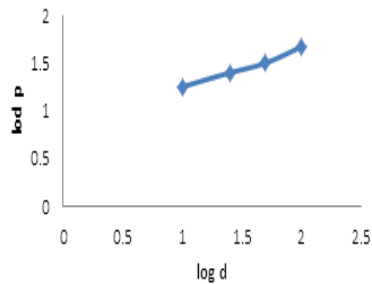


Fig. 6 Plot between log p and log d

4. Conclusion

The synthesis of $Cs_2Hg_3I_8$ has been carried out in organic solvent instead of aqueous solution. The advantage organic solvent is that the reaction is faster and can be proceeded in room temperature. Pale yellow coloured Cesium mercuric iodide ($Cs_2Hg_3I_8$) single crystal of size of $10 \times 7 \times 3 \text{ mm}^3$ has been grown by slow evaporation in acetone at room constant temperature. The intensity of second harmonic generation effect is similar to that of KTP and the effect is phase matchable. The compound is transparent in the range of $0.5\text{-}25\mu\text{m}$. Its band gap is calculated to be about 2.56 eV. The hardness of the material is studied by Vicker's Hardness test. From the hardness study Meyer's index number 'n' was calculated and was found to be 2.96. This clearly indicates that $Cs_2Hg_3I_8$ crystal belongs to soft material category.

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