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Growth, Dielectric and Optical Parameters of some TPPO Crystals

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Abstract*— Single crystals of $CdBr_2$ $(TPPO)_2$, $CdCl_2(TPPO)_4$ and $LiCl_2(TPPO)_2$ with good degree of transparency were grown by slow evaporation technique. Single crystal X-ray diffraction analysis has been done to reveal the crystal systems and their space groups. Some fundamental data's such as refractive index, reflectance, susceptibility and electronic polarizability of the grown crystals were calculated. The optical transmission study in the entire visible region and their cut off wave lengths has been found. The optical band gap also has been determined. Dielectric constant and dielectric loss measurements were carried out at different frequencies.

***Index Terms*— crystal growth, energy gap, polarizability, transmission spectra.**

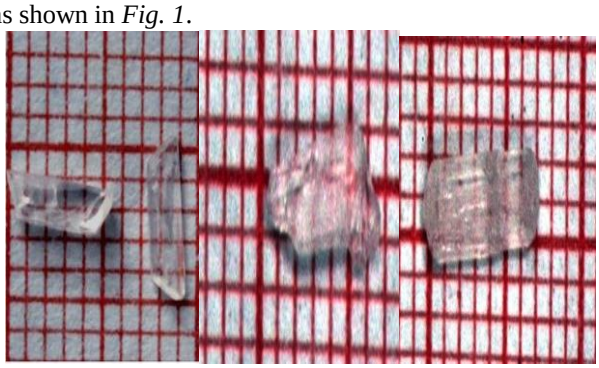
I. INTRODUCTION

Engineering of new non linear optical (NLO) materials, structures, and devices with enhanced figures of merit has developed over the last two decades as a major force to help drive nonlinear optics, from the laboratory experiments to real applications. Because of their potential applications in photonic devices, the NLO properties of molecules and their hyper polarizabilities have become an important area of linear research. The NLO process requires materials that manipulate the amplitude, phase, polarization, and frequency of optical beams [1] –[3].

Materials exhibiting large optical nonlinearity are of great interest for applications in frequency conversion, telecommunication optical computing optical information processing and high optical disk data storage [4]. Metals with d^{10} configuration like *Zinc*, *Cadmium*, *Mercury* readily combine with organic materials resulting in stable compounds with high optical nonlinearity and good physico chemical behavior [5]. Crystals with high conversion efficiencies for second harmonic generation are desirable in various fields with the aim of discovering new useful materials for academics and industrial use, an attempt has been made to synthesize TPPO compounds.

II. GROWTH OF TPPO CRYSTALS

The TPPO crystals were synthesized by dissolving analytical reagent grade cadmium and lithium salts (HIMEDIA) and triphenyl phosphine oxide (TPPO) (Chanshu Yangvan Chemical China) in absolute ethanol in stoichiometric ratios. The temperature of the solution was maintained at about 50°C and precipitate was obtained by the evaporation of the solvent. Purity of the compound was increased by successive recrystallization. The precipitate was taken as raw material. Saturated solutions were prepared at room temperature with ethanol and Dimethyl sulfoxide (DMSO) of 1:1 ratio as solvent. DMSO was added to improve the crystallization. The prepared transparent solution was filtered. The pH of the solution was maintained at 5. The solutions were taken in glass beakers and closed with perforated covers and kept in a dust free atmosphere. The transparent crystals were harvested [6]. The as grown crystals are as shown in *Fig. 1*.



(a) $CdBr_2$ $(TPPO)_2$ (b) $CdCl_2(TPPO)_4$ (c) $LiCl_2(TPPO)_2$
Fig.1. The as grown crystals [6], [7]

III. RESULT AND DISCUSSIONS

Transmission spectra are very important for any NLO material because nonlinear optical material can be of practical use only if it has a wide transparency window. The good transmission property of the crystal in the entire visible region ensures its suitability for second harmonic generation applications. The transparency in the crystals shows their NLO properties. Also, the band gap is sufficiently large so that at room temperature, essentially no carriers are thermally excited across the band gap. This means that there is no free carrier absorption and that interband transitions only become important at relatively high photon energies (above the visible). Thus, insulators frequently are optically transparent. Also, in accordance with the Miller rule [8], the lower value of dielectric constant is a suitable parameter for the enhancement of SHG coefficient. Thus, the low value of dielectric constant at higher frequencies is important for the fabrication of materials towards fabrication of ferroelectric, photonic and electro-optic devices. Figure.2. shows the Tauc plot of determining band gap energy of the grown candidates.

Uniformity of the refractive index throughout an optical element is a prime consideration in selecting materials for high performance lenses, elements for coherent optics, laser

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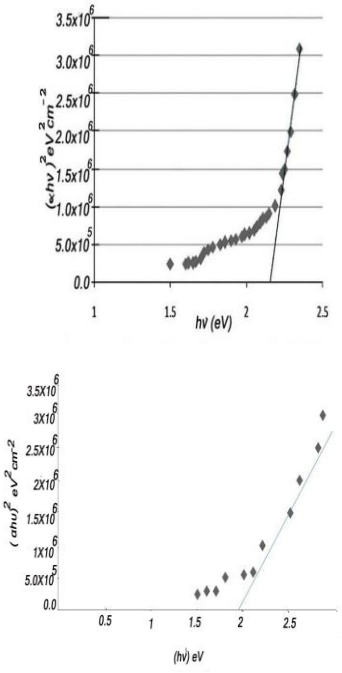
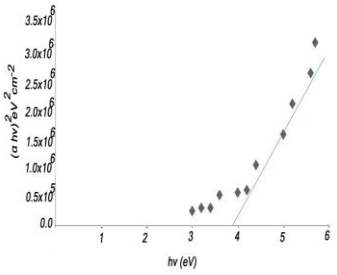
harmonic generation and acousto-optical devices. Intrinsic optical properties of a material are determined by three basic physical processes: electronic transitions, lattice vibrations and free carrier defects. Insulators and semiconductors require the characterization of the lattice vibrations or phonons to fully understand the optical properties. The strength of the free – carrier influence on transmission and absorption depends on the free – carrier concentration; thus free-carrier effects dominate the optical properties of metals in the visible and infrared.



(a) $CdBr_2(TPPO)_2$ **(b) $CdCl_2(TPPO)_4$**



(c) $LiCl_2(TPPO)_2$

Fig.2. (αhν)^2 versus hν curves of TPPO crystals[6], [7]

Free carrier effects can be modeled as an additional contribution to the dielectric constant model. In the transparent region, away from the electronic and vibrational resonances, absorption is governed by impurities and defects. The dielectric constant and refractive index are functions of frequency, hence wavelength. The frequency or wavelength of refractive index is called dispersion. Dispersion is an important property for optical design and in the transmission of information. There are many formulas used for representing the refractive index. The dielectric behavior of a material is an important factor as it has direct influence on the NLO efficiency of the crystals. Further quality of the crystal is an important factor when the crystals are brought into device applications. The relation between refractive index (n) and energy gap (E_g) is given by [9] as

$$E_g e^n = 36.3 \qquad (1)$$

$$R = \left(\frac{n-1}{n+1} \right)^2 \qquad (2)$$

The refractive index and reflectance of the crystals were calculated in the transmission range. The refractive index of the grown crystals had also been experimentally determined for the face (010) using the well known Brewster angle method as done. The calculated theoretical value, are found to be in close agreement with the experimentally determined value. No significant variations were observed in the refractive indices for the other two faces (100) and (001). The high value of refractive index and low value of reflectance reveal that the grown crystals are more transparent to transmit the light from 250 to1200 nm.

The electrical susceptibility (χ_c) was calculated using the following relation,

$$\chi_c = \varepsilon_r - 1 = n^2 - 1 \qquad (3)$$

Hence, since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense. Tables I and 2 gives the estimated values of various optical and dielectric constants.

Table.1 Optical Parameters of the grown TPPO crystals

	Refractive index	Reflectance
$CdBr_2(TPPO)_2$	2.8356	0.2290
$CdCl_2(TPPO)_4$	2.8987	0.2372
$LiCl_2(TPPO)_2$	2.4349	0.1745

Table.2 Dielectric Parameters of the grown TPPO Crystals

	Susceptibility	Polarizability(cm^{-1})
KDP	-	2.14×10^{-23}[8]
$CdBr_2(TPPO)_2$	7.0406	2.726×10^{-23}
$CdCl_2(TPPO)_4$	7.4025	2.23×10^{-23}
$LiCl_2(TPPO)_2$	4.9287	0.521×10^{-23}

As the SHG efficiency depends upon the polarizability, the SHG efficiency is found to be in terms of KDP. The experimental result is thus found to be in good agreement with the theoretically predicted result discussed.

IV. CONCLUSION

TPPO single crystals were successfully grown by slow evaporation technique. XRD data had been used to determine the crystal system.. The band gap, refractive index,

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reflectance, electrical susceptibility and polarizability were calculated to analyze the optical dielectric property. The higher value of polarizability indicates that the second harmonic generation efficiency is more than that of standard material KDP. The theoretical prediction of SHG efficiency was confirmed by Kurtz and Perry powder technique. Thus, the crystals find use in electro-optical applications.

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