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Photoconductivity, spectral and electrical conductivity studies of Zinc boro-d(1-malate) NLO single crystal

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ABSTRACT

A novel nonlinear optical metal-organic Zinc borate - d(1-malate) (ZBdM) single crystal was grown from aqueous solution by slow evaporation technique. The as grown ZBdM single crystal was subjected to solubility, photoconductivity, NLO Test, FTIR, UV-vis-NIR and Impedance studies. The photoconductivity study reveals the positive photo conducting nature of the sample. The various functional groups in the crystalline molecule were identified by FTIR analysis. The cut off wavelength of the crystal was found to be 225 nm from Ultra-Violet-visible-near infrared (UV-vis-NIR) spectral study. The Dc electrical conductivity of the sample was found to be 1.252x10^{-4}mho m^{-1}. Kurtz-Perry test confirms the emission of green radiation from the sample thus exhibiting second harmonic generation (SHG).

Keywords: Solubility, Photoconductivity, NLO, FTIR, UV-vis-NIR, impedance, SHG.

INTRODUCTION

Second order non linear optics (SONLO) is widely used to convert the frequency of coherent laser sources. Application such as laser-based communication, remote sensing and water measure system requires improved non linear optical materials for accomplishing such applications. A strong continuous need is existing for lower cost, more efficient and lighter average power materials for optical parametric amplifier operations and SHG through the blue near UV-spectral region [1-3]. A number of metal organic crystals were grown and characterized. Single crystals of potassium thiourea iodide (PTI), a semi organic nonlinear optical crystal was grown from low temperature solution growth method by a slow evaporation at room temperature. Single crystal X-ray diffraction and FTIR spectral analysis has confirmed the formation of the new crystals [4]. The grown crystals have been subjected to single crystal X-ray diffraction analysis to identify the cell parameters and morphology. Optical transmission spectra revealed the optical properties of the grown crystals [5]. 2-amino-5-nitropyridinium dihydrogen phosphate (2A5NPDP) was synthesized and the molecule structure was elucidated by FTIR, FT-Raman and FT-NMR spectral studies. The proton and carbon configuration of (2A5NPDP) was confirmed through FT-NMR technique. UV-vis-NIR spectrum was recorded and the optical transmittance region was identified as 350 nm. Bulk and powder second harmonic generation (SHG) measurements were carried out using Nd:YAG laser (1064 nm) and its phase matching condition was determined [6]. Thus 2-amino-5-nitropyridinium dihydrogenphosphate/arsenate (2A5NPDP.As) solid solution offers the opportunity to adjust the NLO properties of these hybrid organic-inorganic materials. This continuous solid solution has been structurally characterized by x-ray diffraction. Their good crystalline has been confirmed by synchrotron x-ray diffraction topography [7]. Much recent work has demonstrated that metal organic crystals can have very large nonlinear susceptibilities compared with inorganic transparencies, poor mechanical properties, low laser damage thresholds, and an inability to produce and process large crystals. Metal organic NLO materials typically have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities, because of the lack of extended π-electron delocalization [8]. Examples are zinc thiourea sulphate (ZTS), zinc thiourea chloride (ZTC), Bis (thioure) Cadmium chloride (BTCC) and copper thiourea chloride (CTC). These crystals have better nonlinear optical properties than KDP. BTCC is a promising semiorganic NLO material for second harmonic generation. BTCC crystals have the highest laser induced damage threshold values among the other solution grown NLO crystals. In general, crystals of the type $M[tu]_2 X_2$ where M = Cd, Co, Hg, Pb, Ti and Zn, tu is thiourea and X is a halogen, has been found to exhibit good NLO properties [9]. Bis(thiourea) zinc chloride (BTZC) single crystals have been grown by slow evaporation technique at room temperature. The metal thiocyanate and their Lewis-base adducts are one of the interesting themes of structural chemistry [10]. As SONLO materials, bimetallic thiocyanates: ZnCd(SCN)4, ZnHg(SCN)4, $CdHg(SCN)_4$ and $MnHg(SCN)_4$ (abbreviated as ZCTC, ZMTC, CMTC and MMTC respectively), exhibit efficient SHG at short wavelength. Recently, the high pressure electrical resistivity study have been carried out an zinc tris(thiourea)chloride (ZTS) single crystal [11]. In the complexation of Zn(II), Cd(II) and Hg(II) with thiourea and selenourea, and characterized them by elemental analysis and NMR spectroscopy. A low frequency shift of the C=S resonance of thiones is ^{13}C NMR and high frequency shifts of N-H resonance in ^{1}H and^{15}N NMR are consistent with sulphur or selenium coordination to the metal ions [12]. However, recently grown bulk size of TMTZ crystal by employing ethanol-water mixed solvent. The SHG efficiency of TMTZ is found to be 9.16 times than that of KDP. Fundamental growth parameters such as solubility, metastable sone width and induction period measurements have been estimated [13]. For crystallization of Bis(thiourea) zinc acetate (BTZA) from aqueous solution. It has been reported that, at lower loads there is an increase in the hardness number of the L-threonine, which can be attributed to the electrostatic attraction between zwitter ions present in the molecule. This favours all amino acids for their good mechanical strength [14]. Hence it is believed that exploring the NLO properties of metal organic crystals will be significant for understanding the NLO effect and searching for new NLO materials. Here in we report the synthesis, growth of novel NLO material zinc borate-d(1-malate) (ZBdM). Photoconductivity, spectral and electrical conductivity studies of Zinc boro-d(1-malate) NLO single crystal.

MATERIALS AND METHODS

2.1 Synthesis
0.3 moles of DL-malic acid and 0.15 moles of boric acid are dissolved in 150 ml of water. To this solution, 0.75 moles of zinc carbonate was added. The solution was stirred until all the zinc carbonate has reacted. Salts of zinc boro-d(1-malate) was obtained.

2.2 Solubility
The synthesized salt was used to measure the solubility of (ZBdM) crystals in double distilled water. A 200 ml glass beaker filled with 100ml double distilled water was placed inside a

constant temperature bath. An acrylic sheet with a circular hole at the middle was placed over the beaker through which a spindle from an electric motor was placed on the top of the sheet was introduced into the solution. A Teflon paddle was attached at the end of the rod for stirring the solution. The synthesized salt was added in small amount and stirring was continued till the formation of precipitate, which confirmed the supersaturation of the solution. A 20 ml of the saturated solution was withdrawn by means of a warmed pipette and the same was poured into a clean dry and weighted petri dish. The solution was kept in a heating mantle for slow evaporation till the whole of the solution got evaporated and the mass of 3.5g in 20 ml of solution was determined by weighing the petri dish with the salt. The solubility of ZBdM was determined for different temperatures by adopting the same procedure. The resulting solubility diagram of ZBdM salt is shown in Fig 1. The solubility of ZBdM at room temperature was found to be moderate (25g/150 ml of water).

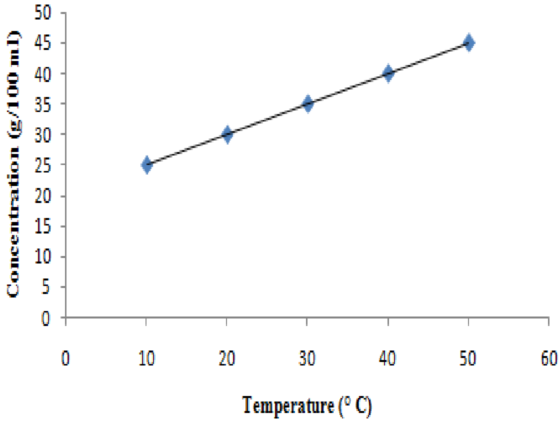

Fig 1.Solubility diagram of as grown ZBdM crystal

2.3 Crystal Growth

The super saturated solution was prepared in accordance with the solubility data. Single crystals of ZBdM were grown from double distilled water using slow solvent evaporation technique. The solvent of the super saturated solution was allowed to evaporate through the perforated lid. Numerous seed crystals were formed at the bottom of the container due to the spontaneous nucleation. Among them, transparent and defect free ones were chosen as seeds for growing bulk crystals. By seeding the super saturated solution and evaporating the solvent, good optical quality crystals of dimensions up to 1x1.5x0.2 mm were harvested in a period of a month. The photograph of as grown crystal of ZBdM is shown in Fig 2.

3. Characterization studies

3.1 Photoconductivity studies

The polished sample of zinc borate-d(1-malate) in a rectangular size was attached to a microscopic slide. Electrical contacts were made in the sample by silver painted copper wire as an electrode. Then the sample was connected in series to a dc power supply with a keithley picoammeter. To measure the photo current, the sample was illuminated with the halogen lamp (100 w) by focussing a spot of light on the sample with the help of a convex lens. The applied voltage was increased from 200 to 240 volt and the corresponding photo current was recorded. The photo current and dark current were plotted as a function of applied voltage is shown in Fig 3. It is observed from the figure that the photo current is always higher than the dark current and both the photo and dark current of zinc borate-d(1-malate) crystals increase linearly with the applied voltage, thus photo current is more than the dark current which may be attributed to the generation of mobile charge carriers caused by the absorption of photon leading to positive photo conductivity.

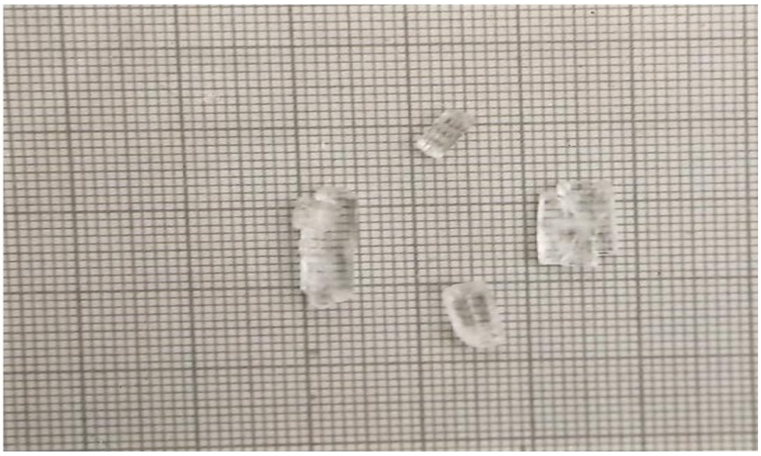

Fig 2. Diagram of as grown ZBdM crystal

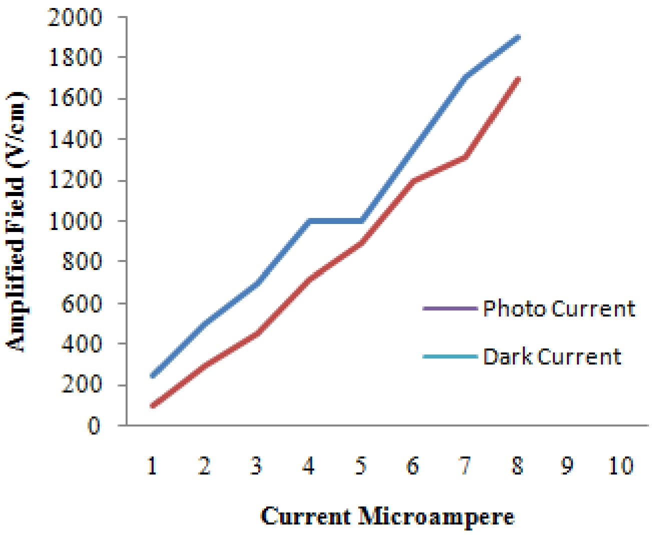

Fig 3. Photoconductivity Studies of ZBdM crystal

3.2 FTIR analysis

The FTIR analysis of zinc boro-d(1-malate) ZBdM single crystals was carried out using the instrument Lamda-35 FTIR spectrometer. The spectrum is shown in Fig 4. A peak at 3407 cm^{-1} is due to the C-H stretching and a peak as 2777 cm^{-1} is attributed to B-H vibration. A peak of 1707 cm^{-1} is assigned to C=O vibrations. There are prominent peaks at 1301.18, 1100 and 538 cm^{-1}. These peaks are assigned to C-C stretching C-O bending and C-H bending respectively. The various frequency assignments pertaining to ZBdM are shown in the spectrum.

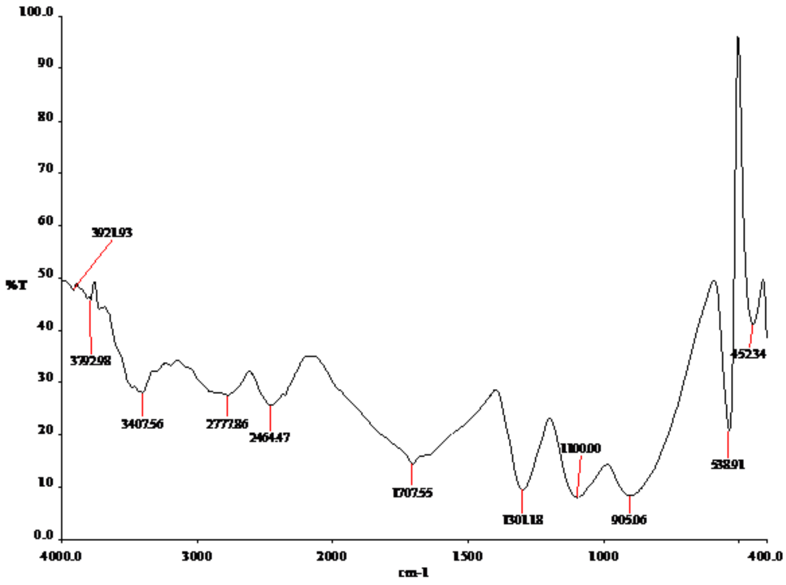

Fig 4. FTIR spectrum of as grown ZBdM crystal

3.3 UV-vis-NIR analysis

The absorption spectrum of ZBdM crystal was recorded in the wavelength range of 190-1100 nm in the entire near ultraviolet visible and near IR region using the instrument Lamda-35 spectrophotometer. Fig 5 shows the spectrum recorded for ZBdM sample. In the near IR region of 700 – 1100 nm, absorbance was not noticed which an essential parameter of NLO crystal. From the spectrum it is evident that ZBdM crystal has a very low cut off wavelength of 225 nm, along with a large transmission window in the entire visible region. Hence it can be utilised for SHG from a laser operating at 1064 nm or other optical application in the blue region.

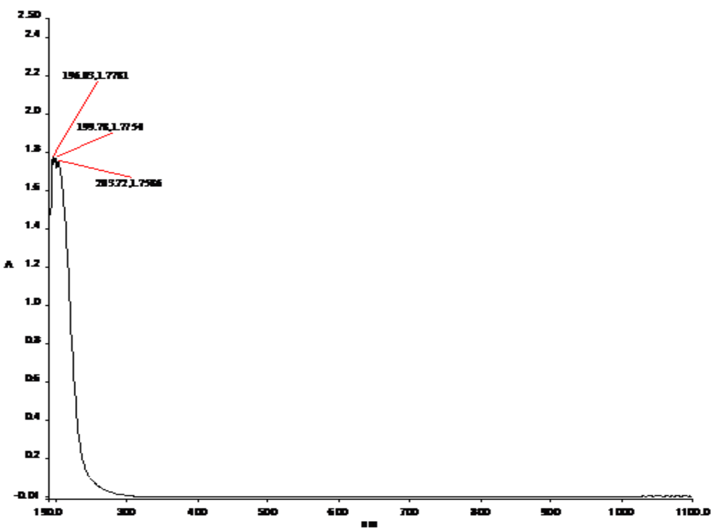

Fig 5. UV-vis-NIR analysis of ZBdM crystals

3.4 NLO Test

The SHG intensity of the crystals using powder technique was developed by Kurtz and Perry. The sample of ZBdM was illuminated using Q-switched mode, locked Nd:YAG laser with the first harmonic output of 1064 nm. The emission of green radiation from the crystal confirmed the second harmonic signal generation.

3.5 Electrical Conductivity

The DC electrical conductivity of ZBdM single crystals was measured using Lamda-35 impedance analyzer. The Dc electrical conductivity was calculated using the equation

$$\sigma_{DC} = \frac{d}{AR_{dc}}$$

where R_{dc} is effective electrical resistance of the sample. The value of R_{dc} was found from the cole-cole plots shown in the Fig 6. In the figure Z"=Zsinθ (imaginary part of impedance) Z'=Zcosθ (real part of impedance). The DC electrical conductivity was found to be 1.252×10^{-4} mho m^{-1} from the cole-cole plot. The low value of electrical conductivity in this crystal is due to the decrease in mobility of the charge carriers by ion size which brings prominent changes in the electronic band structure [15]. The cole-cole plot is very much useful to study the Debye relaxation process in materials. The obtained plot in the form of semicircle finds application in Debye relaxation for materials having large dc conductivity. The magnitude of relaxation time of charge carriers can also be evaluated. If the radius of the semicircle is larger greater will be the relaxation time. Hence at higher frequencies the Debye relaxation time reduces to the enlargement of semicircle [16].

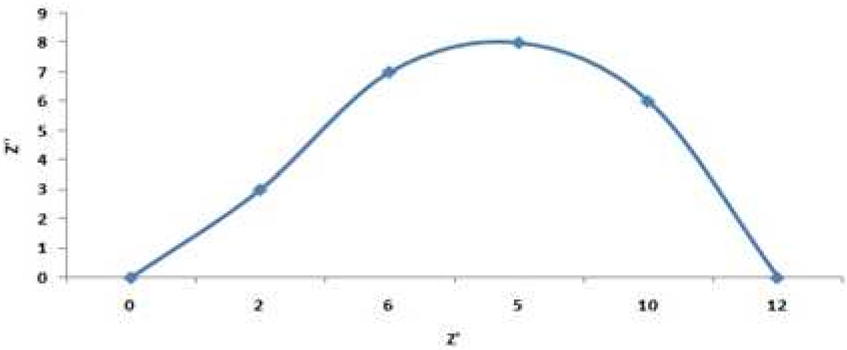

Fig 6. Cole – Cole Plot for ZBdM crystal

CONCLUSION

Single crystals of ZBdM were grown successfully by slow evaporation method. The positive photoconductivity nature of the sample was ascertained by photoconductivity studies. The various functional groups in the molecule were confirmed by FTIR analysis. From the UV-vis-NIR analysis it is evident that ZBdM crystals can be used as SONLO materials. The DC electrical conductivity of ZBdM crystal was estimated to be 1.252×10^{-4} mho m^{-1} from the cole-cole plot.

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