ZINC SULPHATE DOPED CADMIUM THIOUREA SULPHATE CRYSTALS BY SLOW EVAPORATION TECHNIQUE: OPTICAL AND HARDNESS PROPERTIES

S.Minisha[a*], J.Johnson[a], A.Darlin Mary[a], R.Kalaivani[a]

[a]Research Scholar, (Register Number :19213012132032)Department of physics and Research Center,Annai Velankani College,*
Tholayavattam-629157,Tamil Nadu, INDIA.

Abstract

Cadmium and its derivatives are found in many applications such as electrodes, batteries etc. The pure and zinc sulphate doped cadmium thiourea sulphate was grown by slow evaporation technique. Powder X-ray diffraction pattern is used to analyze the crystal structure which confirms that the grown crystal belongs to the orthorhombic system. The functional groups of the crystal are confirmed by FTIR analysis. Mecanical behaviour of the grown crystals has been studied by Vickers microhardness test. The hardness value is greater than 1.6 and so the grown crystal is soft material.

Keywords: CZTS ; XRD; FTIR; Microhardness

1. Introduction

Today, the metal complexes of thiourea, allylthiourea and thiocyanate explorea strong second order nonlinear optical properties for laser application. The properties such as non-linearity, low cut off and their ability to grow bulk crystals make these materials as interesting. [1-2]. These materials possess huge property of combining high optical non-linearity and chemical flexibility of organic compounds with the mechanical properties and chemical inactivity of inorganic materials. Thiourea molecule is capable to form widespread network of hydrogen bonds. When the thiourea molecules merge with inorganic salts the centro symmetric nature of it becomes non-linear optical properties [3-4]. Due to this instinctive attitude, changing the asymmetric conjugated organic molecules into inorganic distorted polyhedral, several thiourea complexes were synthesized and screened for their powder efficiencies and tris-thiourea cadmium sulphate was identified as one of the promising materials. Slow evaporation solution growth is widely used technique to grow crystals of CZTS family. When the starting materials are unstable at high temperatures [5] they undergo phase transformations below the melting point [6]. Hence the present work focuses to prepare the zinc sulphate doped cadmium thiourea sulphate crystals and study their optical and hardness values.

2. Experimental procedure

2.1 Preparation of CZTS Single Crystal

Single crystals of pure and zinc sulphate doped Cadmium Thiourea Sulphate(CTS) were grown from aqueous solution by slow evaporation technique. Thiourea and Cadmium Sulphate were dissolved in distilled water in the ratio 1:1 to get a saturated solution. The above solution was stirred for 2 hours to obtain the homogeneous solution. The supersaturated solution for the formation of $ZnSO_4$ doped CTS crystal was prepared by dissolving required amount of zinc sulphate along with the CTS. The prepared saturated solution were stirred for 2 hours and filtered using filter paper. The solution was transferred to porously sealed beakers and kept in undisturbed place. Slow evaporation took place and nucleation started within 6-7 days. Crystals were harvested within 15-20 days. The grown crystals were shown in Fig.1

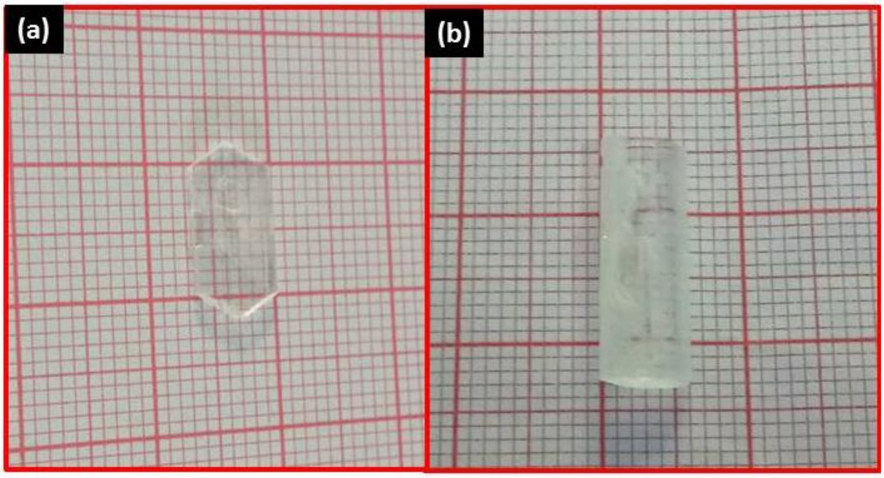


Fig. 1. Photography of grown a) CTS b) CZTS crystals

Finally the prepared crystals were subjected to different characterization techniques such as XRD, FTIR,UV-Vis- NIR and Vickers microhardness studies.

3. Results and Discussion

3.1. X-ray diffraction analysis

Powder X-ray diffraction pattern of grown CZTS Single crystal was shown in Fig.2. The diffraction peaks are matched with the standard JCPDS (PDF....) file. It is found that the grown crystal belongs to the orthorhombic primitive system with lattice parameters a=13.461Å, b=7.783Å, c=15.967Å and cell volume 1672.81A^3.

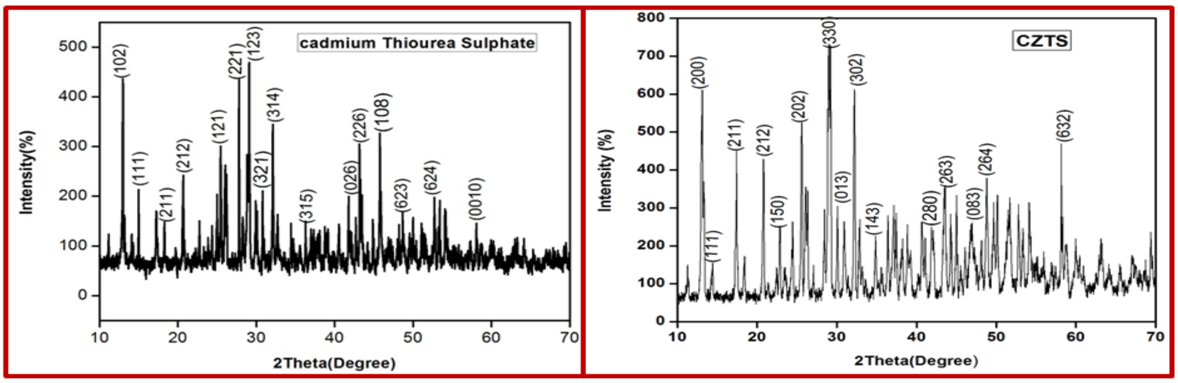


Fig. 2. XRD pattern of the CTS and CZTS Crystals

3.2. FT-IR analysis

To record FT-IR spectra of CZTS crystal, Perkin Elmer spectrometer was used in the range 400-4000cm^{-1} which was in the form of solid dispersed KBr pellet. The recorded spectra was used to identity various functional groups present in the Fig.3. In the FTIR spectrum of CTS, the intensity 3543.30 cm^{-1} is due to N-H stretching vibration of the NH_2 group of thiourea. The C=S stretching vibrations occurs at 1622.57cm^{-1}. The peaks at 1438.80 cm^{-1} is due to NH_2 bending vibration. C-N is observed at 1167.9 cm^{-1}.

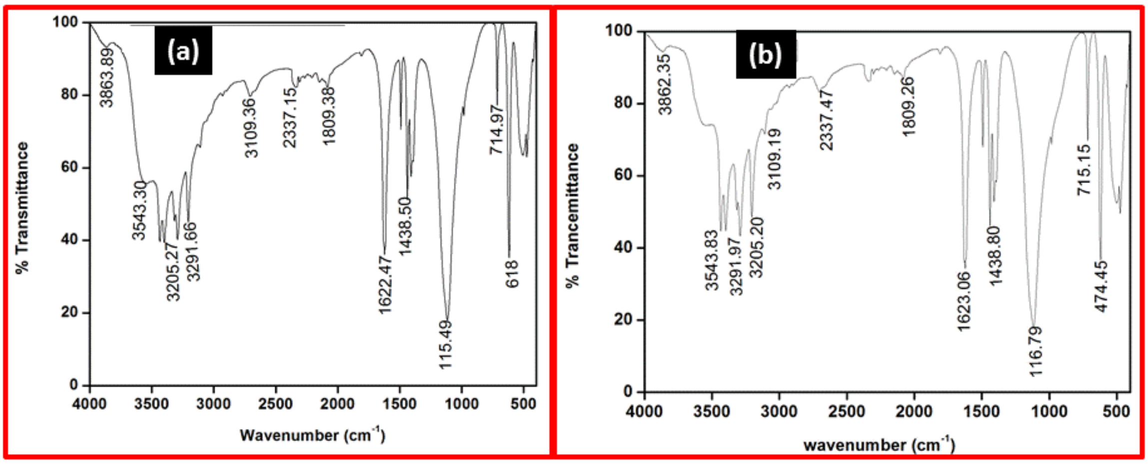
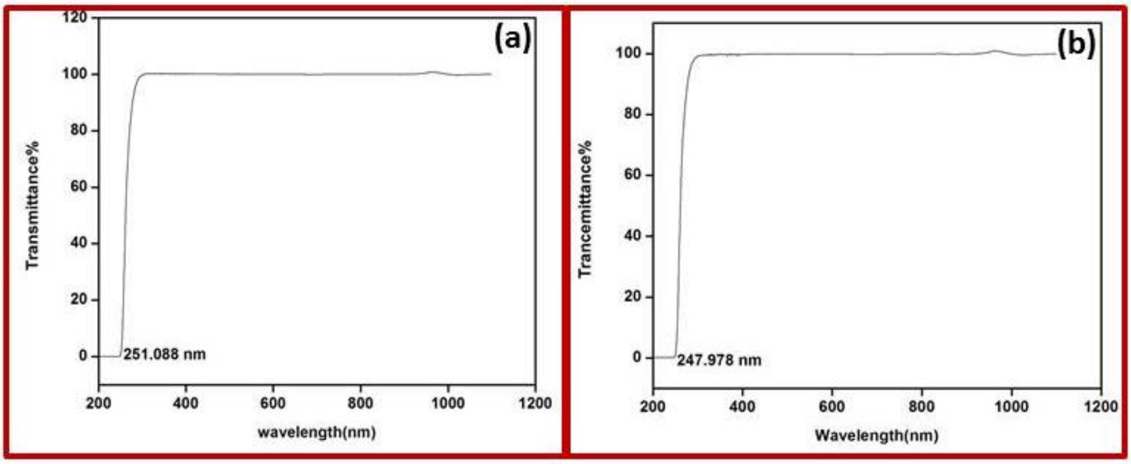


Fig. 3. FTIR spectra of a) CTS b) CZTS

3.3 UV-vis-NIR studies

Highly transparent material with wide range of wavelength could offer effective output for optical device. The optical transmission spectrum recorded in the range 190-1100 nm is shown in Fig.4. From the spectrum, it is observed that the transmission of the crystal is considerably high in the wavelength region 190-1100 nm. The UV cut off wavelength for the grown crystal is found to be 251.088 nm for pure CTS and 247. 978 nm and this absorption wavelength will make CZTS as potential material for optical device fabrication.



3.4. Vickers microhardness Test

Mechanical strength of the materials plays a key role in device fabrication. Microhardness of a crystal is of its capacity to resist indentation. That is, hardness is a measure of its resistance to local deformation. Micro hardness measurements were carried out by Vickers hardness test at room temperature. The hardness measurments were taken for applied load varying from 25, 50 and 100gm. The vickers hardness number(Hv) was calculated using the relation [7]

$$H_v = \frac{1.8544P}{d^2}\frac{Kg}{mm^2}$$

Where, P is the applied load and d is the diagonal length of the indentation impression.

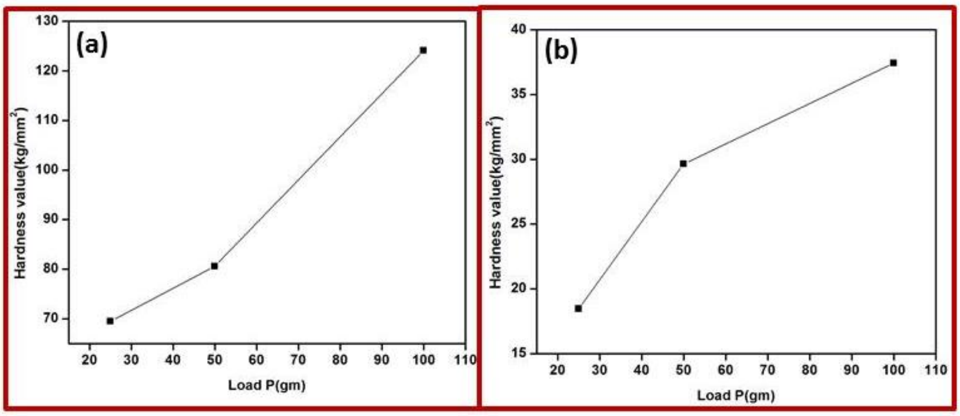


Fig. 4. Plot between H_v vs Applied load of a) CTS b) CZTS

The variation of H_v with the applied load is shown in Fig.4. It is evident from that the hardness number of the grown crystal increase with the applied load. The work hardening coefficient for both crystals is measured to be 4.207 and 4 respectively. The hardness value indicates that the grown crystals are belongs to soft material.

4. Conclusion

Single crystals of CZTS were successfully grown using slow evaporation technique. Crystalline nature and structure of the grown crystals was verified with PXRD analysis. FTIR analysis confirms the presence of functional groups present in the grown crystal. Hardness of the crystals is studied by Vickers Hardness analysis which indicates that the grown crystal is a soft material.

References

[1] Eaton DF, *Nonlinear optical materials. Science.* 253(1991)281-7.

[2] Rajasekaran R, Ushasree PM, Jayavel R, Ramasamy p. *Influence of PH on the growth and characterization of nonlinear optical Zinc Thiourea Chloride (ZTS) Single crystal.J Crystal Growth*. 252(2003)317-27.

[3] Marcy HO, Warren LF, Webb MS, Ebbers CA, Velsko SP, Kennedy GC, Catella GC, *Second-harmonic generation in Zinc tris (thiourea) sulphate. Applied Opts.*31(1992) 5051-60.

[4] Venkatramanan V, Maheswaran S, Sherwood JN, Bhat HL. *Crystal growth and physical characterization of semiorganicbis (thiourea) cadmium chloride. J Crystal growth.*;179(1997)605-10.

[5] BR Pamplin Crystal growth (Pergamon Press,New York,1980)

[6]RM Hooper, RS Naranes, BJ Hearole, JN Sherwood, Crystal growth second edition (Ed) B.R Pamplin (pergamon Press, New York,1980)

[7] S.Suresh and D. Arivuoli, *J.Minerals & Materials characterization & Engineering*, 12(2011)1131-1139.