International Journal of Luminescence and Applications (ISSN: 2277-6362)
Vol. 5, No. 1, February 2015. Article ID: 060. pp.86-88.

Photo-Luminescence Studies of Pure and Doped ZTS Single Crystals Grown by Single Diffusion Technique

Kiran T. Rathod[1], I.B. Patel[1], C.F. Desai[2] and Y.H. Gandhi[3]

[1]*Department of Physics, Veer Narmad South Gujarat University, Surat, Gujarat-395007*
[2]*Department of Physics, Faculty of Science, The M. S. University of Baroda, Gujarat*
[3]*Department of Applied Physics, Faculty of Tech. and Eng.The M. S. University of Baroda, Gujarat*

Abstract— *Zinc Tris (Thiourea) Sulfate, a metal organic nonlinear optical single crystal is grown by single diffusion Gel Technique which is new to grow it. In order to get gel medium stock solution which is prepared by Sodium Metasilicate (SMS) is used throughout present experimental research work. Widely transparent crystal is successfully harvested with adjusting nucleation rate by controlling various growth parameters such as various densities of stock solution, molar ratio of inner solution as well as outer solution, pH, temperature, etc. Chemical identification is verified by Energy Dispersive Analysis by X- ray (EDAX) test. X-ray powder diffraction is carried out to confirm orthorhombic structure of the crystal which is confirmed. With adding dopants, the crystals are investigated by photo-Luminescence study. According to the photo luminescence study the luminescence intensity is increased with increasing dopant. Results are discussed in present paper.*

Keywords— *ZTS crystal, Single diffusion technique, Growth parameters, dopants, Photoluminescence study.*

1. INTRODUCTION

Non Linear Optical materials have become pivotal and active research in photonics and optical science. Zinc tris (Thiourea) Sulfate (ZTS), Zn $[CS(NH_2)_2]_3$ SO_4 is an essential metal organic nonlinear optical crystal having applications in frequency doubling devices and electro-optic area. ZTS crystal has 1.2 times more nonlinear efficiency than Potassium Dihydrogen Orthophosphate (KDP) [1]. Therefore, ZTS crystals are better in frequency doubling and laser tuning experiments than KDP crystals. Wide transparency and high damage threshold make it good candidate for nonlinear optical applications. ZTS crystal is consist of orthorhombic system with space group Pca_{21} (point group mm2) and lattice parameters a= 11.126 Å, b = 7.773 Å and c= 15.491 Å [2].

Some of the researchers have reported considerable results on PL studies of pure and doped ZTS crystals [3,4]. The present work aim to compare photo – luminescence of pure and of doped ZTS crystals with different dopants. In the present experimental research, an effort has been made to investigate the effect of some dopants such as potassium bromide, potassium sulfate, manganese sulfate, and oxalic acid. The results obtained are reported here.

2. EXPERIMENTAL

In order to grow pure and doped ZTS crystals, the test tube single diffusion technique of gel method was used. AR grade thiourea and zinc sulfate heptahydrate were taken in molar ratio of 3:1. Sodium metasilicate (SMS) was used as a gel medium. The appropriate specific gravity range was attained by addition of millipore water in the stock solution (SMS) while the desired pH range (3.5-5) was obtained by adding acetic acid to this solution. Thiourea was added in this solution and the solution was continuously stirred for half an hour. Then after to get doped ZTS crystals, one normality solution of dopant was added to this solution and put it stirred for about 5-7 hours. After that, the prepared solutions were transferred to test tubes and open ends of the test tubes were closed with cotton to avoid unwanted impurities and evaporation of the solution. After gel setting, outer solution was poured into the test tubes. Thiourea was used as the inner solution and zinc sulfate heptahydrate was used as the outer solution. The test tubes were kept at a safe place undisturbed to avoid unwanted interruptions at room temperature. Gel setting time was about 7-10 days and crystal forming duration was from 2 to 4 weeks depending on the dopants and various parameters such as pH, density, concentration ratios in solutions, weather, etc. Good quality crystals, ranging in size of about 9 mm x 5 mm x3 mm, were harvested.

3. XRD ANALYSIS

X-ray powder diffraction was carried out to confirm crystal structure and to determine lattice parameters of as grown ZTS crystal.

PXRD was recorded in the 2θ range of 20° to 80° at room temperature using wavelength of 1.54060 A° as shown in fig. 1.

* *Corresponding Author Email: patelishverb@yahoo.com*

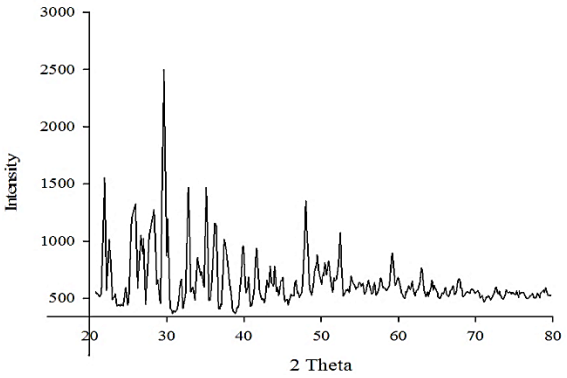

Fig. 1: XRD pattern for pure ZTS crystal

According to PXRD, unit cell parameters obtained are a= 11.13Å, b=7.76 Å, c= 15.56 Å and $\alpha = \beta = \gamma = 90^{o}$, fairly agreeing with the reported parameters [JCPDS No. 76-0778], a=11.12 (Å), b= (Å) 7.773, c=15.49(Å) with space group Pca_{21}[2]. There was no apparent variation of lattice parameters observed for the doped crystals and the results above are the averages of lattice parameters determines for all doped crystals.

4. PHOTOLUMINESCENCE ANALYSIS

The PL spectra of pure and doped ZTS crystals are shown in Figure 2 to 5.

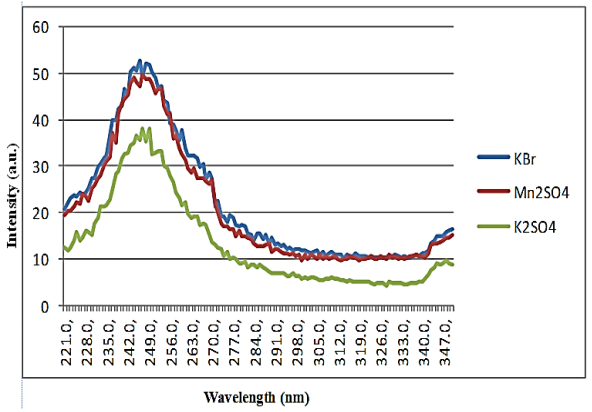

Fig. 2: PL Excitation Spectra

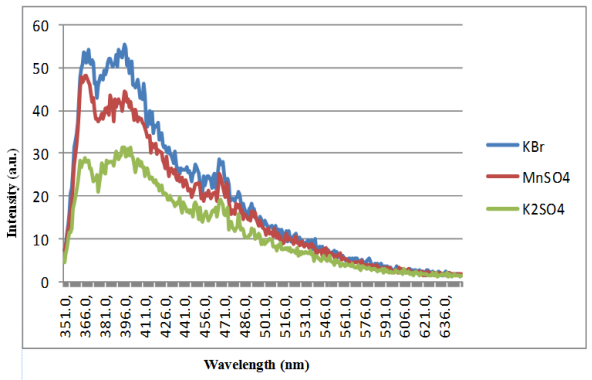

Fig. 3: PL Emission Spectra

The excitation spectra were obtained in the range from220 nm to 350 nm while the emission spectra were obtained in the range from 350 nm to 650 nm.

For doped ZTS crystals, the excitation peaks were observed at 246 nm, 247 nm, 249 nm and 250 nm while the emission peaks were observed at 396nm, 367nm, 395nm and 366nm for potassium bromide, manganese sulfate, potassium sulfate and oxalic acid, respectively.

Whereas, for pure ZTS crystals, the excitation peak was observed at 248 nm and the emission peak at 369 nm.

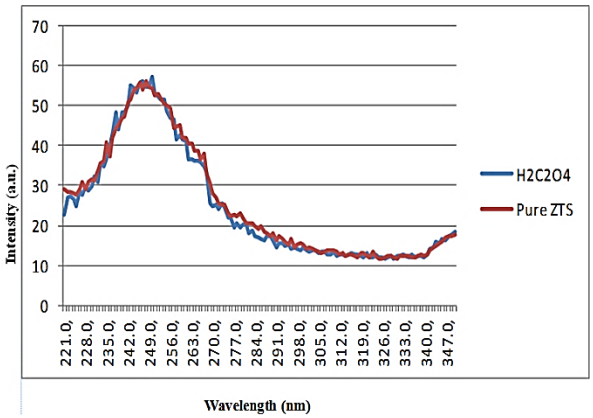

Fig. 4: PL Excitation Spectra

Energy band gap of pure and doped ZTS crystals were calculated using formula E=hc/ λ, where λ is the wavelength of the band gap luminescence [3,5].

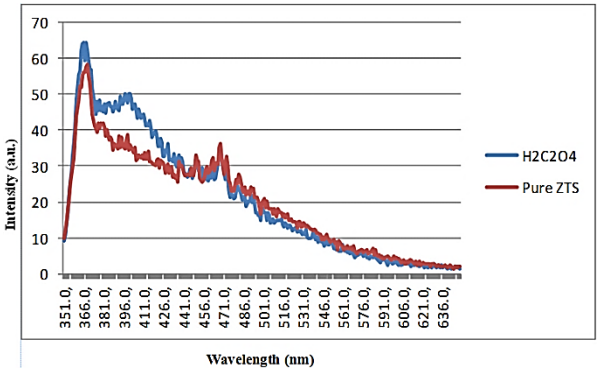

Fig. 5: PL Emission Spectra

According to the formula, energy band gap of doped ZTS crystals were calculated to be 3.1eV, 3.4eV, 3,1eV and 3.4eV for potassium bromide, manganese sulfate, potassium sulfate and oxalic acid, respectively. Whereas, for pure ZTS crystal, the band gap was found to be 3.4 eV. Usually, the energy band gap of an insulator lies above 3 eV. The PL study confirms the insulating nature of pure and doped ZTS crystals.

5. CONCLUSION

Transparent & colourless pure and doped ZTS crystals can be successfully grown by single diffusion gel technique. Orthorhombic crystalline structure of ZTS crystal was confirmed by X–ray powder diffraction technique. According to PL studies, it is confirmed that pure and doped ZTS crystals have insulating nature.

ACKNOWLEDGEMENT

Authors are very thankful to Dr. KVR Murthy for providing facilities for photo luminescence spectra.

REFERENCES

[1] T. C.Sabari Girisun, S.Dhanuskodi, Cryst.Res.Technol.44, No.12 (2009), 1297-1302.

[2] S. DInakaran, S.Verma, S. Jerome Das, G. Bhagavannarayan, S. Kar, K.S. Bartwal, Appl.Phy B(2011), 1103: 345-349.

[3] K.Senthil kannan, S. Gunasekaran, Seethalakshmi KA, Bhrigunathn Prasad, International J. of Scientific and Engineering Research Volume 4, Issue 2, 2013, 1-4.

[4] P.M. Wankhede, S.A. Gundale, M.N. Rode, G.G. Muley, International J. of Basicand Applied Research Special Issue 2012, 290-292.

[5] S. Ariponnammal, S. Chandrasekaran, C. Sanjeeviraja, Digest J. of Nanomaterials and Biostructures, Vol.7, No. 3(2012), 947-957.