Study of BaCl doped ZTS Crystals Grown by Gel Method

Kiran T. Rathod[1], I.B. Patel[1,*], Neel Patel[2], Vikram L Bharat[3]

[1] *Department of Physics, Veer Narmad South Gujarat University, Surat, Gujarat-395007, India*
[2] *Shrimad Rajchandra Vidyapeeth, Dharampur, Gujarat-396051, India*
[3] *College of Applied Science and Professional Studies, Chikhli, Gujarat-396521, India*

(Received 10 February 2020; revised manuscript received 15 April 2020; published online 25 April 2020)

Optically good quality doped ZTS crystals with BaCl have grown by silica gel growth method at ambient temperature and their characterization have studied. The presence of functional groups of doped crystals has identified from FTIR spectra. The hardness analysis has performed with using different hardness models. Chemical Etching study has carried out in the present work. The second harmonic generation efficiency has tested from Kurtz-Perry test as the main important finding of this work. The results are reported in the paper.

Keywords: ZTS, BaCl dopant, FTIR, Hardness, Chemical etching, Second harmonic generation efficiency.

DOI: 10.21272/jnep.12(2).02036 PACS numbers: 81.20.Fw, 46.55. + d

1. INTRODUCTION

The non-linear phenomena occur usually by using NLO crystals. So, in recent time, semi organic nonlinear optical crystals have attended more attention from technologist, scientist and researchers due to their significant applications. The NLO material have considerable applications such as optical data storage, printing, spectroscopy inspection, biomedicine, laser tuning experiment, frequency modulation, second harmonic generation, third harmonic generation, Raman spectra shifters etc. Zinc Tris (Thiourea) Sulfate (ZTS) is such an important non-linear optical crystal which gets both organic and inorganic advantages having main application as frequency doubling. ZTS crystal has molecular formula as $Zn(NH_2CSNH_2)_3SO_4$ [1-11].

To grow better crystals, to satisfy technological requirement for numbers of applications, the concept of doping is successfully adopted by researchers. In this research study, ZTS crystal has doped with new chloride dopant as Barium chloride which is grown by Gel growth technique. The doped ZTS crystals are characterized by Fourier Transform Infrared Spectroscopy (FT-IR) analysis, Vickers hardness measurement, Second harmonic generation efficiency test etc. In the present experimental research work, the important study to know the effect of Barium chloride dopant on ZTS crystal has carried out. The growth of ZTS crystal with new chloride dopant such as Barium chloride is discussed

2. EXPERIMENTAL PROCEDURE

In order to prepare gel medium, Silica gel was used as a growth medium during the entire experimental study. This experiment procedure was through at an ambient temperature. AR grade of Zinc Sulfate Heptahydrate and Thiourea were taken in 1:3 molar ratio and 3N solution of Thiourea was prepared using Millipore water and was stirrer with 48 °C temperature to avoid decomposition. The stock solution was acidified either by hydrochloric acid or acetic acid. Thiourea was used as a mother solution and Zinc sulfate heptahydrate was used as a feed solution and vice versa. Barium chloride doped ZTS crystals were obtained with 1N solution of dopant in different atmospheric temperature with required density value. The stirring time of the solution of dopant was one hour and mixed with main solution. The main solution was made up by mixing stock solution with adjusted required density and 3N solution of thiourea the grown doped crystals are shown in Fig. 1 (in test tubes) and in Fig. 2.

3. RESULTS

3.1 FTIR Analysis

The Fourier transform infrared (FTIR) spectra were recorded using Bruker Alpha T FTIR spectrometer by KBr pellet technology with the range of 500-4000 cm^{-1}. The obtained frequencies with their relative intensities of chloride doped ZTS crystals are obtained from FTIR analysis which were recorded in the region 500-4000cm^{-1} by KBr technique. From the FTIR spectra of doped samples; it is clearly shown the minor shifts occurrence due to incorporation of dopant which is shown in Fig. 3.

From the FTIR spectra, the broad band lines of the range 2700 cm^{-1}-3400 cm^{-1} is relate to symmetric and asymmetric vibrations of NH_2 bonds. Absorption around 955 cm^{-1} is due to sulfate ion. The C=S and N-C-N stretching vibrations are shown at around 714 cm^{-1} and 1437 cm^{-1} respectively. The absorption at around 1515 cm^{-1} corresponds to N-C-N stretching vibration. The comparison of pure and doped ZTS crystals shows slight shift in characteristics vibrational frequencies. The additional peaks are also observed which are due to the incorporation of particular dopants in the lattice of ZTS crystal. This observation ascertains the addition of particular dopants in ZTS crystal.

* ibpatel@vnsgu.ac.in

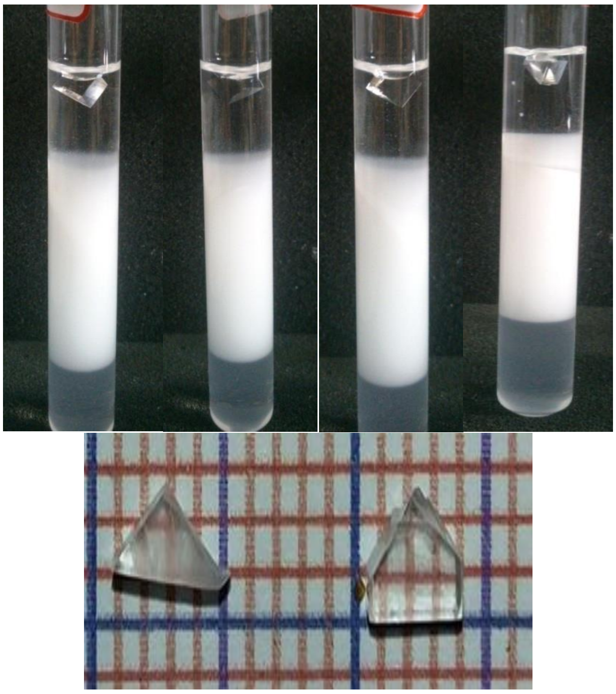

Fig. 1 – Grown Barium chloride doped ZTS crystals in test tubes

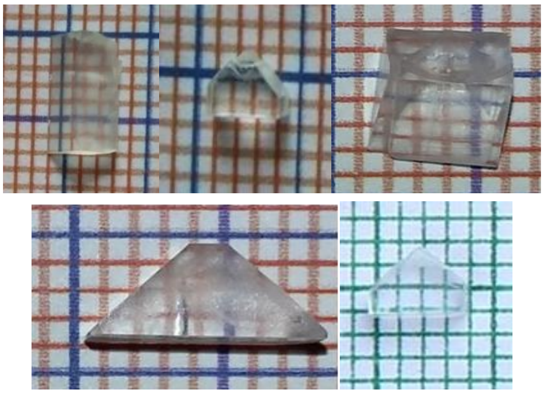

Fig. 2- Barium chloride doped ZTS crystals grown with 1N solution of dopant

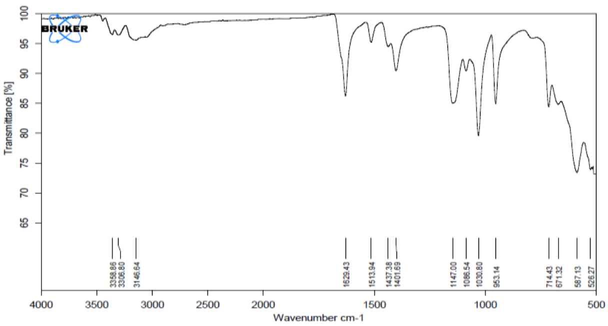

Fig. 3 – FT IR spectrum of Barium chloride doped ZTS crystal

3.2 Vickers Hardness Measurement

The mechanical behavior of doped crystals was tested by using Vaisesikha Vickers micro hardness tester type 7005 equipment. The load range applied crystal was 20 gm-80 gm and fixed time interval as 10

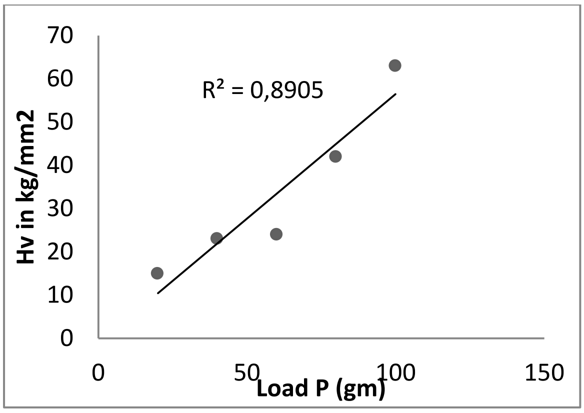

Fig. 4 – Plot of Hardness number (H_v) vs Load P of doped crystals

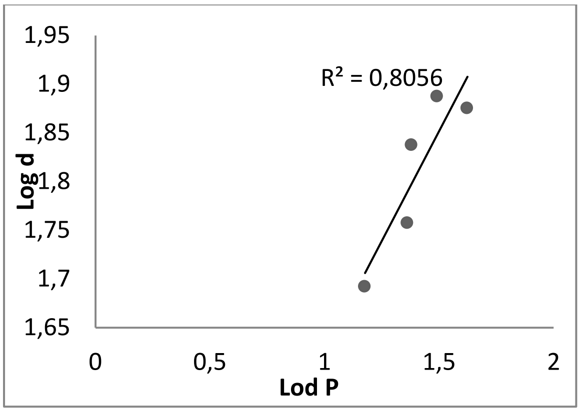

Fig. 5 – Plot of Log d Vs Log P of doped crystals

second was taken. Fig. 4 and Fig. 5 are revealed plots of micro hardness V_s load P and Log d vs Log P of doped crystals. The Vickers hardness number was calculated using the following formula

$$H_v = \frac{1.854P}{d^2} \text{ in kg/mm}^2.$$

Indentation Size Effect (ISE): ISE behavior of material can described by several models with the relationship between applied load and diagonal length are reported [12].

Meyer's Law: A plot of log d vs log P of doped crystals are drown form which Hardening coefficient were calculated. The work hardening coefficient (n) was gave Meyer's Index number (n) by the relation as $P = ad^n$. And it is concluded that Barium chloride doped ZTS crystals are soft crystals $n = 1.8$.

Hays-Kendall's law: Hays-Kendall approach was applied by using the formula $P = W + A_1d^2$. From this approach, the value of H_0 was obtained as 37 gm/mm^2. The values obtained from the graph are drawn in Fig. 6.

PRS Approach: A number of authors [13] have mentioned that ISE behavior of material may be express by the relation as given as $P = ad + bd^2$. From this approach, the value of H_0 was obtained as 50 gm/mm^2. The value of H_0 was calculated by the relation as $H_0 = 1.854b$. The graph is shown in Fig. 7.

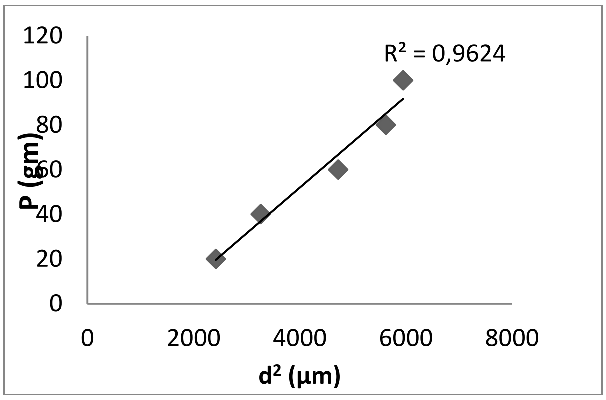

Fig. 6 – Plot of Load *P* vs d^2 of Barium chloride doped ZTS crystals SHG Test

Second Harmonic generating efficiency of the chloride doped crystals were tested using Kurtz-Perry powder technique. Fine powdered samples were filled in the capillaries for the test. The high intensity fundamental wavelength of Nd:YAG laser of 1064 nm with pulse width 10 ns was used. The SHG efficiency of doped crystals is 50 mV which is 1.1 times more than that of pure ZTS crystal.

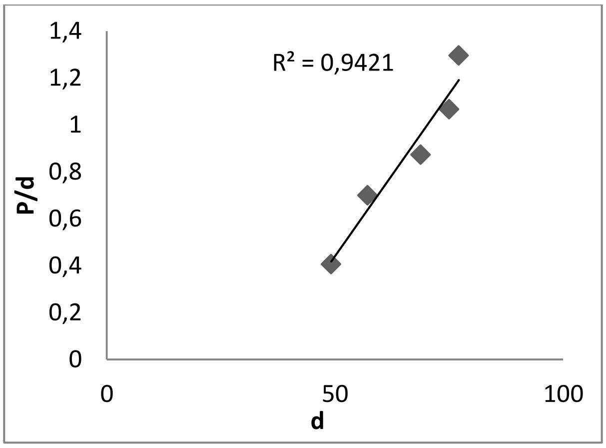

Fig. 7 – Plot of *P*/*d* vs *d* of Barium chloride doped ZTS crystals SHG Test

CONCLUSION

Good quality of Barium sulfate doped ZTS crystals were successfully crystallized by gel growth technique. The changes in Morphology, color, size and in growth rate are observed. According Vickers micro hardness test it is proved that doped ZTS crystals are soft due to the effect of dopant and also concluded that Hays-Kendall approach was more suitable for doped crystals. Enhancement in SHG efficiency was observed in Barium chloride doped ZTS crystal (1.1 times more). Thus it is concluded that Barium chloride doped ZTS crystals are more suitable for NLO device manufacturing.

REFERENCES

1. P.N. Prasad, D.J. Williams, *Introduction to nonlinear optical effects in molecules and polymers* (Wiley: New York: 1991).
2. S.S. Gupte, R.D. Pradhan, C. Desai, N. Melikechi, *J. Appl. Phys.* **89** No 9, 4939 (2001).
3. V. Praveen, N. Vijayan, C. Mahadevan, G. Bhagavannarayana, *Mater. Manuf. Proc.* **23** No 8, 816 (2008).
4. Kiran T. Rathod, I.B. Patel, C.F. Desai, *Int. J. ChemTech Res.* **6** No 3, 1667 (2014).
5. Kiran T. Rathod, I.B. Patel, C.F. Desaiand Y.H. Gandhi, *Int. J. Luminesce Appl.* **5** No 1, 86 (2015).
6. Kiran T. Rathod, I.B. Patel, C.F. Desai, Hozefa Tinwala, *Int. J. Eng. Res. Technol.* **4** No 10, 503 (2015).
7. Kiran T. Rathod, I.B. Patel, C.F. Desai, *Rec. Adv. Eng. Sust.* 29 (2015).
8. Kiran T. Rathod, I.B. Patel, Rajiv P. Shah, *Int. J. Sci. Adv. Res. Technol.* **1** No 10, 197 (2015).
9. Kiran T. Rathod, I.B. Patel, C.F. Desai, Hiren Desai, *National Conf. Mater. Charact.* (2016).
10. Kiran T. Rathod, I.B. Patel, *AIP Conf. Proc.* **1837**, 040057 (2017).
11. Kiran T. Rathod, I.B. Patel, A.M. Shah, *Int. J. Creative Res. Thought* **6** No 2, 593 (2018).
12. D. Tabor, *The Hardness of Metals* (Oxford University Press: Oxford: 1951).
13. K. Singhal, B. Surowska, P. Blaziak, *Mater. Chem. Phys.* **77** No 2, 511 (2002).