Growth, FTIR And Mechanical Studies Of Gel Grown Magnesium Chloride Doped Tris Thiourea Zinc Sulfate (ZTS) NLO Crystal

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Abstract

NLO semi-organic ZTS crystals are doped using gel technique with sodium metasilicate gel. Magnesium chloride is taken as a dopant. Doped ZTS crystals are grown with different morphologies. As per FTIR analysis, the functional groups are identified. Different approaches like H-K, PRS and EPD are applied to the doped crystal. The measurements are performed on (100) plane of the doped crystal with load range from 20-80 gm. It is found that crystal hardness is increasing with increasing the applied load. So Reverse Indentation Size Effect presents. Other mechanical properties are calculated as discussed in the paper.

Keywords: ZTS Crystal, Gel Method, FTIR, Mechanical Studies

Introduction

Nonlinear optical (NLO) materials have significant applications in nonlinear optics particularly in the field of information technology and in industry. The significant enhancement of the understanding of the nonlinear polarization and its relation with structural characterization has been revealed by researchers in few years. The new technical expansion for the growth and device fabrication of artificial materials has spectacularly furnished to this evaluation. In the current past, the new approach of the combination of high NLO coefficient of the organic molecules with good physical properties of inorganic has found to be the immense success. Thiourea is centrosymmetric however provides and characterizes good noncentrosymmetric approach. [1].Usually, thiourea is the semi-organic material which includes both organic as well as inorganic advantages. Several researchers have been grown a variety of crystals of this class such as Glycine doped cadmium thiourea sulfate [2], Bis thiourea zinc chloride doped potassium dihydrogen phosphate[3] and Zinc tris thiourea sulfate (ZTS) [4-7] are reported. Zinc thiourea tris sulfate (ZTS) is a potential semi-organic NLO material, which exhibits type-II second harmonic generation (SHG) [8–10]. In the present study, ZTS crystal was doped with magnesium chloride dopant and characterized.

Experimental Procedure

AR grade of Zinc sulfate heptahydrate, thiourea and magnesium chloride along with Millipore water were used to grow the doped crystals. The used glass wares were made by borosilicate. Density was adjusted to 1.05 gm/ cc using Millipore water with the stock solution and the solution was acidified with acetic acid and required pH value between 4-5pH was obtained. The 2N solution of dopant was made separately and stirred for one and half an hour and was mixed with the main solution and stirred it for at least 15 hours at 800rpm. Finally, the final solution was transferred to the test tube set with the fixed amount, without giving any chance to the formation of air bubbles. Usually, the gel was found out to be set in 15 days depending mostly on pH, density, concentration and volume of solutions and atmospheric temperature. After setting gel, the 1Normal aqueous solution of Zinc sulfate heptahydrate was poured gently over the set gel without cracking gel surface. Then after, the set of test tubes was allowed to stand until crystal growth can take place. The crystals were harvested within 5 weeks which are shown in fig 1.

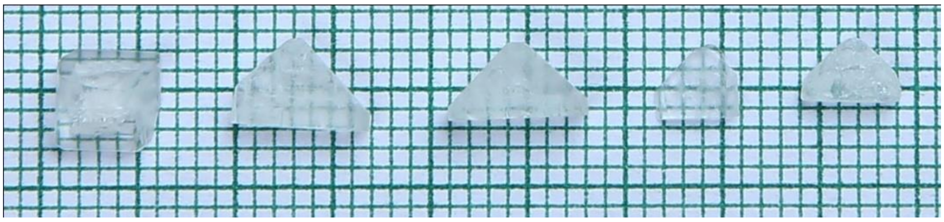


Figure 1: Grown magnesium chloride doped ZTS crystals

RESULT & DISCUSSION (for CHARACTERIZATIONS)

The grown Magnesium chloride doped ZTS crystals were subjected to characterization techniques. The Fourier transform infrared (FTIR) spectra were recorded using Bruker Alpha T FTIR spectrometer by KBr pellet technology with the range of 500-4000cm^{-1}. The Vickers hardness measurement was made of the crystals using Vaisesikha Vickers microhardness tester type 7005 equipment.

FTIR Analysis

The obtained frequencies with their relative intensities of doped ZTS crystal are obtained from FTIR analysis which was recorded in the region 500-4000cm^{-1}by KBr technique. From the FT IR spectra of the doped sample; it is clearly shown the minor shifts occurrence due to the incorporation of dopant which is shown in fig 2. The functional group assignments form FT IR analysis of crystals are given in table 1. The comparison of pure and doped ZTS crystals shows the slight shift in characteristics of vibrational frequencies. The additional peaks are also observed which are due to the incorporation of dopant in the lattice of ZTS crystal. These observations ascertain the addition of dopant in ZTS crystal.

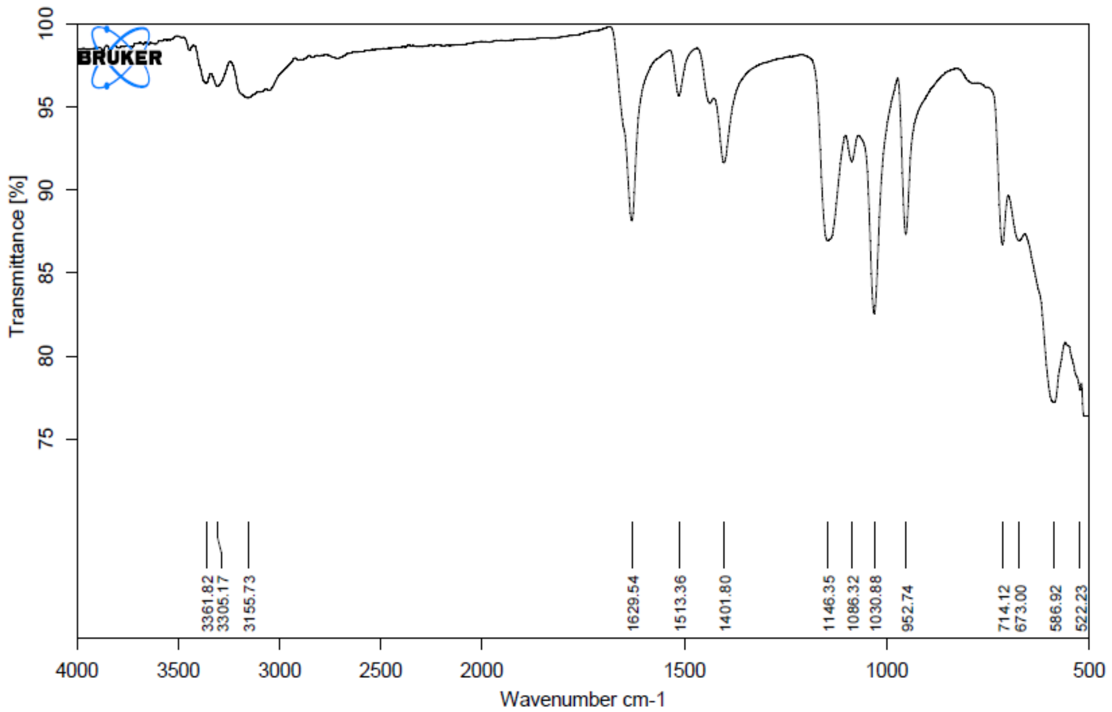


Figure 2: FT IR spectrum of Magnesium chloride doped ZTS crystal

Table 1: Frequency assignments of pure and chloride doped ZTS crystals

ZTS crystal (wave no. in cm^{-1})	Magnesium chloride doped ZTS crystal	Assignments
668.37	673.00	vas (N-C-S)
716.90	714.12	vs (C=S)
955.92	952.74	δ (=C-H)
1032.94	1013.88	v (C-N)
1088.12	1086.32	v (C-N)
1153.45	1146.35	vs (C-N)
1403.78	1401.80	vas (C=S)
1516.15	1513.36	v (N-C-N)
1644.29	1629.54	δ (N-H)
-	3155.73	vs ($N-H_2$)
3317.24	3305.17	vs ($N-H_2$)
3376.07	3361.82	vs ($N-H_2$)

δ = bending, v= stretching, s= symmetric, as = asymmetric

Mechanical Study

Vickers microhardness was performed on the smooth surface and (100) plane of the doped crystal. The smooth surface of the doped crystal with different loads such as 20gm, 60gm and 80 gm were applied to test. Hardness number (H_V) of doped ZTS crystal is evaluated using given a relation

$$Hv = 1.854\ P/d^2\ \ Kg/mm \qquad (1)$$

where P is the load applied in Kg and d is a diagonal length of the indentation impression in mm.
The plot of Vickers hardness number against applied load is shown in fig 3(a). The plot shows that the hardness number of the crystal is increased with increasing load and which is agreed with Reverse Indentation Size Effect (RISE) [11-14].

The relation between load (P) and a diagonal length of indentation (d) is given by Mayer's law[15]
The work hardening coefficient n was obtained by Meyer's Law as given formula

$$P=k_1d^n \qquad (2)$$

P is applied load in gm and n is hardening coefficient. The Hardening coefficient n was calculated from the slope of the plot of Log P vs Log d (fig.3(b))which is 2.7. As per Onitsch (1947) and Hanneman (1941), hardening coefficient (n) is to be 1 and 1·6 for hard materials, while it is above 1·6 for soft material. So, the doped crystal has belonged to the soft material category.

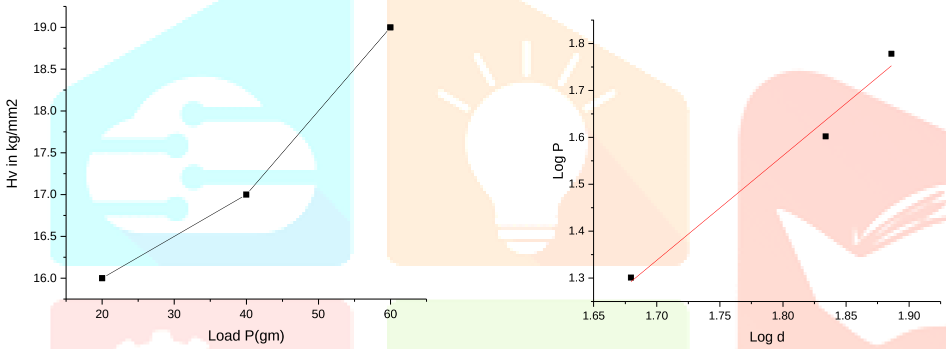


Figure 3 : (a) Plots of Hv versus Load P and (b) Log P versus Log d

Hays - Kendall's (H-K) Model

Hays and Kendall [16] has proposed micro - hardness which is load dependence can write using a relation as given

$$P = W + A_1d^2 \qquad (5)$$

Where, W = minimum load required to begin plastic (permanent) deformation and A_1 = load-independent constant.

$$H_0 = 1.8544 \times (P-W)/d^2 \qquad (6)$$

$$H_0 = 1.854\ A_1 \qquad (7)$$

Minimum load W is required to begin plastic deformation and the case of below the value of W, plastic deformation does not begin, however, only elastic deformations take place. The values of W and A_1 are calculated from the plot of the graph of P versus d which is shown in fig. 4(a). The H_0 was calculated from the formula as given as 7. The values of W, A_1, and H_0 are given in table 2. The positive value of W indicates that load is plenty to start both plastic and elastic deformation.

PRS Approach

Li and Bradt [17] have explained ISE using Proportional Specimen Resistance (PSR) approach. PRS approach is given in the formula as

$$P = ad + bd^2 \qquad (8)$$

Where a is responsible for the dependence of hardness on load, b is the part of load independent.
The plot of P/d vs d shows the straight line. H_0 was calculated by the relation as

$$H_0 = 1.854b \qquad (9)$$

The measured values of a, b and Hardness H_0 are listed in table 2. The plot of P/d vs d is drawn in fig. 4(b).

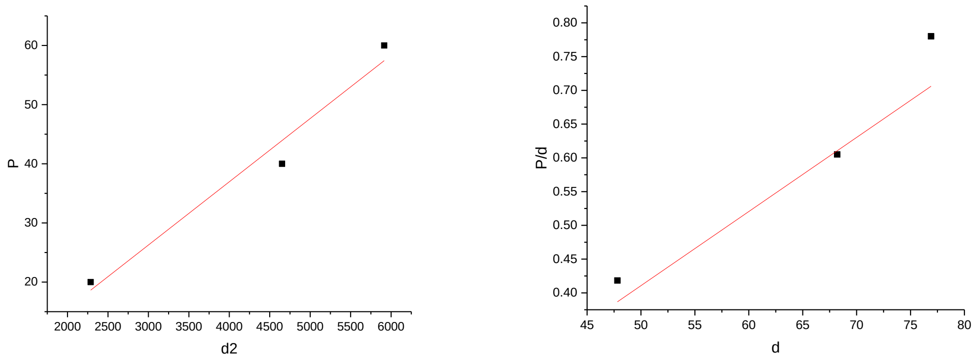


Figure 4 : (a) Plots of P versus d^2 and (b) P/d versus d

Elastic/Plastic Deformation (EPD) model

Bull *et al.* [18] have introduced Elastic/Plastic Deformation (EPD) model which relates the indentation size and applied load as

$$P = A2\ (d + d_0)^2 \qquad (10)$$

where A2 is constant, d_0 is associated to the plastic deformation.

The plot of √P versus d (fig. 5(a)) gives the values of A2 and d_0 which are calculated. The value of Ho is calculated from the formula

$$Ho = 1.854 A_2 \qquad (11)$$

The values of microhardness were calculated using this model for the sample is listed in table 2. It is concluded from all above observations that EPD model is well explained for doped ZTS crystal.

Table 2: The values of different approaches of doped ZTS crystal

H-K model			PRS approach			EPD model		
A_1	W	H_{H-K}	b	a	H_{PRS}	A_2	d_0	H_{EPD}
0.313	51.59	58.03	0.011	-0.138	2.40	0.108	-0.806	20.27

Table 3: The mechanical values of doped ZTS crystal

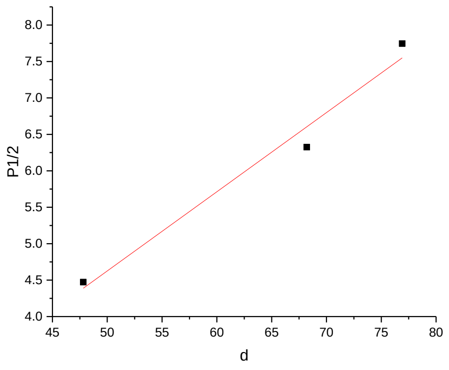
Load P (gm)	Elastic Stiffness Constant (C11) MPa	Yield Strength σ_y Mpa	Elastic Modulus E
20	20.69	40.9044	1311.416
40	21.08	43.8697	1393.38
60	21.97	49.8003	1557.307

Elastic stiffness constant (C_{11})

As per Wooster's empirical formula, elastic stiffness constant (C11) was obtained using formula as given

$$C_{11} = (Hv)^{7/4} \qquad (12)$$

Elastic stiffness constant can give information of tightness of bonding which exhibits between neighboring atoms. The elastic stiffness constant were calculated and listed in table 4. A plot of elastic stiffness versus d is shown in fig 5 (b). The values indicate that the force between the ions is quite strong.



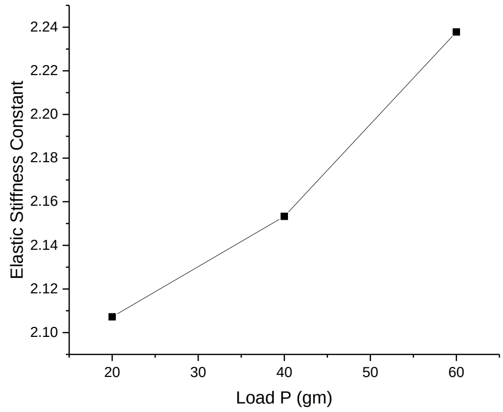


Figure 5 : (a) Plots of $P^{1/2}$versus d and (b) Elastic stiffness constant versus Load P

Fracture toughness (Kc)

The Fracture toughness (Kc) occurs in indentation process which gives the formula for producing crack that extends under center loading conditions. Fracture toughness (Kc) is a significant parameter to select for device applications where the load goes beyond the limit or yield point [19]. The resistance of fracture reveals the toughness of a material and the fracture toughness Kc from which it decides that how much fracture stress is applied under uniform loading is given by a formula as [20-22]

$$Kc=P/\beta_0 C^{3/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

β_0= Constant which depends on the indentation geometry and for Vickers indenter β_0 is =7. P=applied load, C= crack length which is measured from the center of the indentation impression to the crack tip. The estimation of the brittle materials is obtained from fracture toughness. The values of Kc are calculated and listed in table 4. In the case of $c/a \leq 2.5$, the cracks were formed during indentations which were palmqvist cracks.

$$Kc=kP/al^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

Where l=c-a; length of the palmqvist crack

The fracture toughness of the specimen reveals to resistance to fracture which increases with dopant as shown in figure 6.

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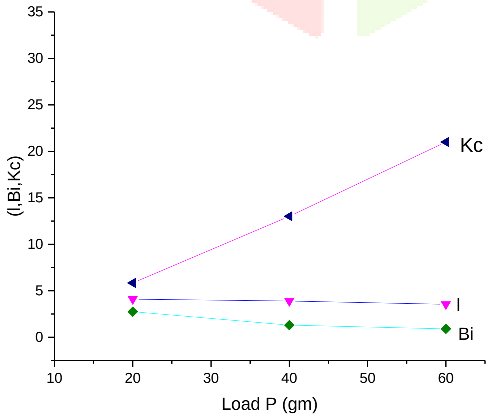

Figure 6 : (a) Plots of Kc versus Load P, (b) l versus Load P and (c)Bi versus Load P

Brittleness index (Bi)

Brittleness is a significant property which affects the mechanical behavior and determines the fracture without any appreciable deformation of the material. It is estimated using formula as given below which is already reported [23-26].

$B_i = Hv/K_c$……………………………(15)

The brittleness index Bi of the doped crystal is written in table 4.

Yield Strength (σ_v)

The Yield strength of the doped crystal was evaluated using given formula as

$$\sigma_v = Hv/2.9[1-(n-2)] \ \{12.5 (n-2)/1-(n-2)\}^{n-2} \ldots\ldots(16)$$

The value of Yield strength and yield point are obtained as written in table 4.

According to Unwin (1918), the tensile strength (T) and yield point (Y) of the doped crystal were calculated using linear mathematical formulas as given below

$$T=0.2Hv + 6 \ldots\ldots(17)$$

Table 4: The mechanical calculations of doped ZTS crystal

Load (gm)	Hv in MPa	B_i ($m^{-1/2}$)	K_c ($kg\ m^{-3/2}$)	Tensile strength (T)(MPa)
20	156.91	2.741615	64.49422	90.22
40	166.71	1.306101	118.1596	92.18
60	186.33	0.904687	172.4935	96.10

Conclusion

Good quality of magnesium sulfate doped ZTS crystals were successfully crystallized by gel growth technique. The changes in morphology, color, size and in growth rate are observed. The functional groups are identified using FTIR analysis. According to Vickers microhardness test, it is proved that magnesium chloride doped ZTS crystal is soft material. The hardness was increased with increased applied load. The work hardening index number is 2.7 which indicate reverse indentation size effect of doped crystal. Heys-Kendall, PRS, and EPD approaches for doped crystal are studied. As per studied these approaches, it seems that EPD model is more suitable for doped crystal. The elastic stiffness constant (C11), Brittle index (B_i), yield strength (σ_y), Elastic Modulus (E), fracture toughness (Kc), tensile strength (T) and yield point (Y) are calculated. The stiffness of doped crystal was increased with increased the applied load. As per Heys-Kendal approach, the positive value of W concluded that applied loads are sufficient to start both plastic as well as elastic deformation in the doped crystal.

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