Quantifying Mechanical properties on L-Threonine doped Tris Thio Urea Zinc Sulphate crystals

N. Bhuvaneswari[1], S. Nalini Jayanthi[2]

Assistant Professor, Department of Physics

KCG College of Technology, Karappakam, Chennai-600097, India

Abstract:- This Investigation is mainly focused on the Quantifying Mechanical properties of L-Threonine doped ZTS crystal. As ZTS crystal proved its significance in many fields especially in opto-electronic devices and LASER applications, the growth of 1 mole percent inclusion of LTH in ZTS crystals is carried out in 23 days and a short discussion about the growth is explained. An exclusive in-depth mechanical analysis is done by various techniques to describe the endurance strength of the grown crystal. A complete analysis of mechanical stability is illustrated by different methods like Vickers hardness test, Meyer power law method, Hays-Kendall's method (HK method), Li and Bradt method (PSR method) and Elastic/ Plastic deformation method (EPD method). Every method ascertains the strong inclination towards RISE nature of the crystal. The EPD model validated that it is best technique in helping to describe the quantifying mechanical properties of the grown crystal.

Keywords: *Single Crystal,Slow evaporation method, Mechanical studies.*

1. Introduction

Ever since the Opto-electronic field has emerged, materials with NLO properties have attained a center of attraction due to their versatile usage in the field of optic devices such as electro optic devices, optical switches etc., For the past few decades many number of thiourea - metal coordination compounds have been grown and explored because of the unique property of thiourea molecule when combined with metal-organic coordination compound results in enantiomorphic properties. Zinc tris thiourea sulphate (ZTS) is an excellent metal-organic material for second harmonic generation (SHG) device application and laser tuned experiments [1]. Inspired by these above materials, a sincere trial has been made to synthesize zinc tris thiourea sulphate (ZTS) [2]and it is then doped with L-threonine of 1mole percent as it is well known that all the basic essential properties can be improved through doping.

ZincTris thiourea sulphate (ZTS) [3] is an assuring metal-organic NLO material for second harmonic generation from metal complexes of thiourea. ZTS is 1.2 times more nonlinear than KDP [4]. ZTS possesses an orthorhombic structure with space group Pca21[5].

L-Threonine shows a dipolar ionic nature in powder form as well as in solution form. Hence L-Threonine is an excellent candidate which exhibits greater SHG efficiency than other amino acids. In the present report, pure ZTS and L-threonine doped ZTS [6] were grown and an exclusive endurance strength analysis is carried out by using various techniques.

.Experimental Procedure

2.4 Growth of ZTS and 1% LTH doped ZTS

Pure crystals of Zinc tris thiourea sulphate (ZTS) were produced by taking 1:3 ratio of zinc sulphate and thiourea and dissolved thoroughly in doubly deionized water at room temperature. In order to get a homogenous proportion of the above mixed solution, it was continuously stirred by using magnetic stirrer for 5-6 continuous hours. The transparent pure ZTS crystal of size 15x12x8 mm^3 was obtained.

To the above produced salt, of ZTS, 1 mole% L-Threonine was added in doubly deionized water. The quality of the grown crystal can be improved by repeated recrystallization process [7]. Pure ZTS was obtained in a size of 15x12x8 mm^3 and L-TH doped ZTS was obtained in a size of 18X10X10mm^3.

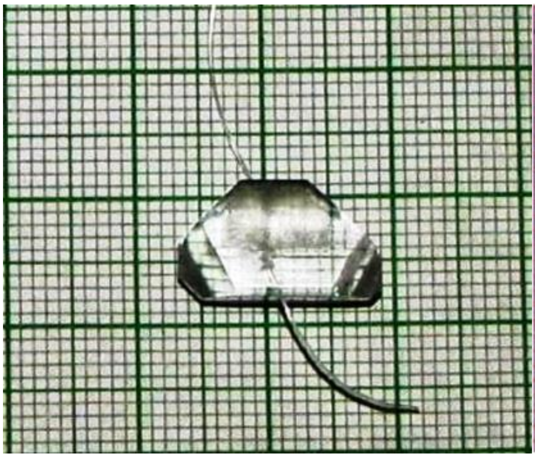

Fig. 1: Pure ZTS Crystal as grown

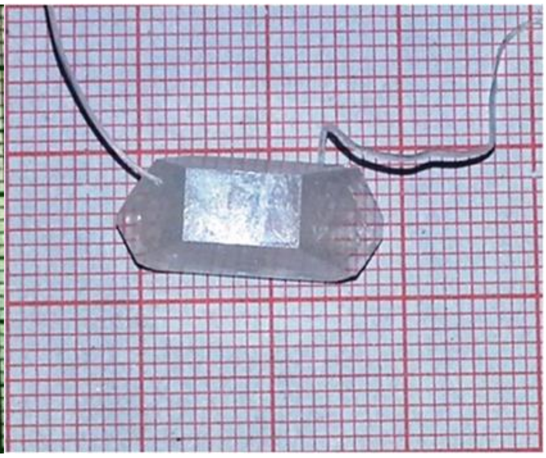

Fig. 2: L-TH doped ZTS as grown

2.5 Basic Characterisations

The as grown crystals were exposed to Enraf-Nonius CAD 4-MV31 Singly crystal X-ray diffractometer to reveal the crystal parameters like crystal structure and lattice constant. They belong to orthorhombic crystal system [8] with space group pca21.

Also, to know upto what temperature the grown crystal is stable enough, it is then continued to carried out Thermal analysis tests like DTA and TGA. Pure ZTS crystal was stable up to 300^0C and the LTH doped ZTS was stable up to 311.9^0C. LTh Inclusion into the ZTS revealed increased stability towards their thermal characteristics.

Second harmonic generation studies were performed on the grown crystals. LTH doped ZTS crystals have greater NLO efficiency than pure ZTS. One mole percent of LTH increases the SHG efficiency. Hence this quality can be termed as very defining character that L-threonine doped ZTS are very important materials for frequency conversion and other Opto-electronic applications.[9]

1. Results

1.1. Micro Hardness Testing Method

The mechanical stability and crystals nonlinear optical usability can be determined by subjecting the material to undergo Vicker's micro hardness testing. The surface of the crystal was compressed by a hardness tester with a diamond pyramidal indenter coupled to a metallurgical microscope [10].

Both Pure and LTH doped ZTS are exposed to various testing process and their results are discussed in detail. The grown crystals with appropriate sizes were selected for micro hardness investigation. The sample was gradually subjected to load in the order of 3g, 5g, 10g ,25 g, 50 g and 100 g. For every load the duration period is chosen to be 10s.

2.2 Effect of load on Vicker's Pyramid Number (Hv)

Vickers Pyramid Number (Hv) can be calculated using the following formula [4] and measured in terms of Pascal from known applied force (F) and diagonal length of the diamond pyramid indenter(d).

$$H_V = \frac{(2\sin 68^0)F}{d^2} \text{ pa} \quad (1)$$

Or

$$HV = \frac{1854.4F}{d^2} \text{ pa} \quad (2)$$

The errors which occur during hardness measurement are bound to happen. The hardness value was calculated using the following formula

$$HV = 1854.4\ [(\frac{\Delta F}{Y})^2 + (\frac{F}{\Delta Y})^2]\ \text{GPa} \quad (3)$$

Here $Y = d^2$, $\Delta Y = 2d\ \Delta d$.

ΔY, ΔF and Δd are the random errors on the calculation of variations of Y, F and d. A graph is plotted for Hardness value versus Load for both pure and doped ZTS crystals (Fig. 3). The graph shows that Hv increases linearly with the applied force (Table 1,2), which is indicated as the Reverse Indentation Size Effect (RISE). [11]. Initially when the applied force is less, the indenter slightly affects the top layer alone, leads to less active parallel glide planes. As the applied force increases, more glide planes are produced [12]. This produces a non-linear behaviour of the crystal and eventually the material is becoming independent of the applied force. Hence, it is almost impossible to determine the material's true ultimate tensile strength with high precision. In order to explain this ISE behaviour various techniques have been carried out.[13].

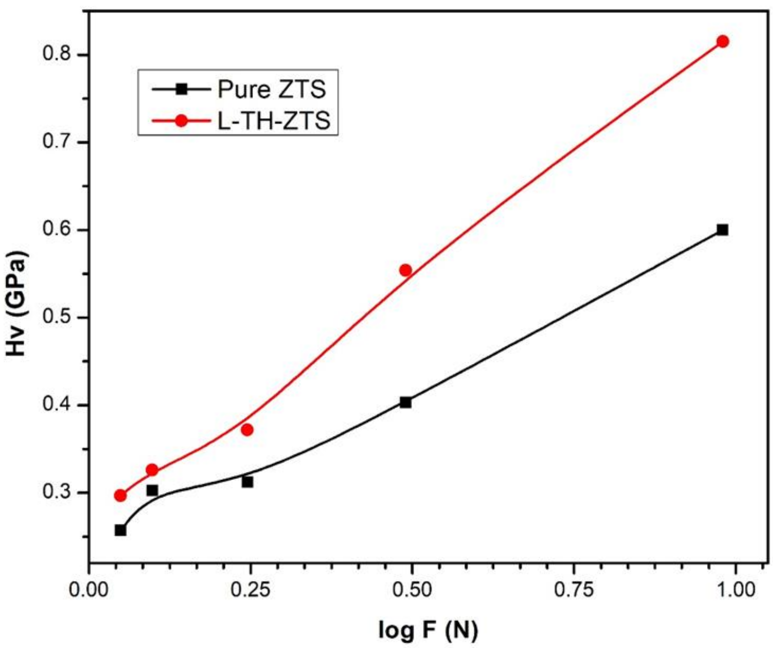

Fig. 3: Hv v/s log F

2.3 Meyer's Hardness Method

This method explains how the applied force affects the surface of the crystal.

Meyer's law for pyramid indenter is [8],

$$F = k_1 dn \qquad (4)$$

And

$$\ln F = \ln k_1 + n \ln d \qquad (5)$$

where n is Meyer's index or work hardening coefficient, k_1 is the standard hardness for a particular material. Firstly, the graph is drawn for logarithmic value of diagonal length of the crystal versus logarithmic value of applied force (Fig. 4) to determine the nature of the material. A straight line is obtained which ultimately arrives a good agreement with the Meyer's law. From the slope of Fig.5, The work hardening coefficient was calculated as 2.64 (pure) and 2.91 (1 mol% doping).

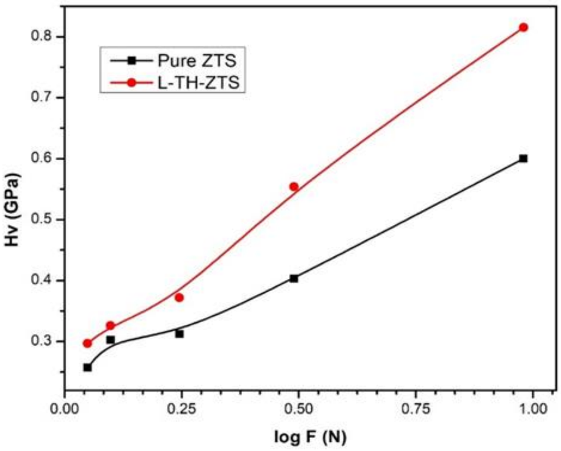

Fig. 4: log F v/s Hv (GPa)

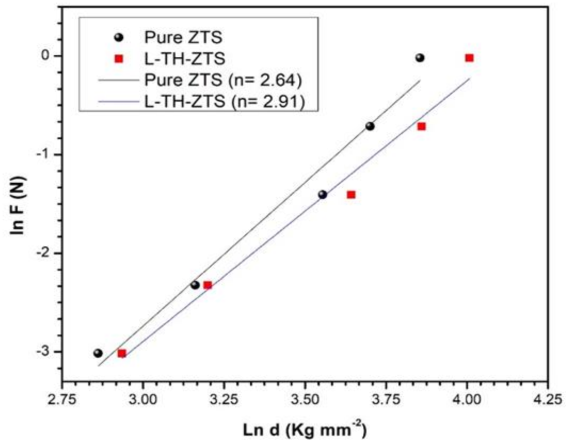

Fig. 5: ln d v/s ln F

Table 1: Microhardness measurement of Pure ZTS

Load (F)	Hv (GPa)	C_{11}(Kg/mm^2)	E (GPa)	Y (GPa)	K_{ic} Pa/m^3
0.05	0.257	302.96	21	0.0855	
0.098	0.303	404.25	24.8	0.101	
0.245	0.312	425.53	25.5	0.104	
0.49	0.403	668.48	33.1	0.134	
0.98	0.6	1339.62	49.2	0.2	$1.29X10^3$

Table 2: Microhardness measurement of LTH doped ZTS

Load (F)	Hv (GPa)	C_{11}(Kg/mm^2)	E (GPa)	Y (GPa)	K_{ic} Pa/m^3
0.05	0.297	391.94	24.4	0.0991	
0.098	0.303	461.49	26.7	0.109	
0.245	0.312	579.76	30.5	0.124	
0.49	0.403	1166.87	45.5	0.185	
0.98	$6.00X10^{11}$	2292.12	66.8	0.272	$1.5X10^3$

From the graphs and the interpretations obtained, the pure and LTH doped ZTS crystals are hence described as soft materials, in turn proves the RISE behaviour. Elastic modulus(E) is called as the inherent property of the grown crystal which describes the bonding between the atoms. It can be calculated using the following relation [14],

$$E = 83.20231HV \text{ GPa} \quad (6)$$

Table 2 reveals the LTH inclusion in ZTS, where the Elastic modulus value increases with the increase in applied load. Also, it is necessary to see the nature of bonds among the atoms. It can be assessed by utilizing Wooster's empirical relation [15],

$$C_{11} = (HV)^{7/4} \quad (7)$$

It is evident from Table 2 that the addition of LTH increases the stiffness of pure ZTS crystal, indicating that this is a desirable material for device fabrication. The following relationship can be used to determine the intensity of fracture stress which is developed in the material with a uniform applied force [16]

$$K_{IC} = 0.016[\frac{E}{HV}]0.5[\frac{F}{C_{1.5}}] \frac{Pa}{m^3} \quad (8)$$

Pure ZTS crystal shows fracture toughness (K_{IC}) of 1.29 × 10^3 Pa/m^3, and 1 mol %LTH doped crystals show 1.5 × 10^3 Pa/m^3, respectively. Comparing the table 1 and table 2 the inclusion of LTH in ZTS increases the value of fracture toughness. The opposing stress that a crystal experiences when it reaches its elastic limit can be evaluated using [17],

$$Y = \frac{HV}{3} \text{ GPa} \quad (9)$$

The formula above is applicable to materials that express RISE behaviour when an external force is applied. Table 2 shows that there was a marginal variation in elastic limit due to the inclusion of LTH in ZTS.

2.6 Hays-Kendall's Method (HK Method)

Another form of finding Load independent mechanical properties of the grown crystal is called Hays-Kendall's law. According to this law, the resistance offered by the crystal due to applied force which in due course responsible for permanent deformation. In order to express this, the ratio of the applied force to the surface area of the crystal is obstructed by the cavity.

According to Hays-Kendall's law [17],

$$F = WHK + A_1 d^2 \quad (10)$$

$$\text{and } HHK = 1854 \text{ X } A_1 \quad (11)$$

Table 3 lists the slope of the graph (A_1) between applied force and the square of the indentation length "d" the minimum load (W_{HK}) necessary to start deformation, and the crystal's hardness as determined using Hays-Kendall's Method (Fig. 6). The inclusion of LTH in ZTS crystal does not show any considerable change because of these observations indicated by the minimal stress which is required to start the ultimate tensile stress or deformation.

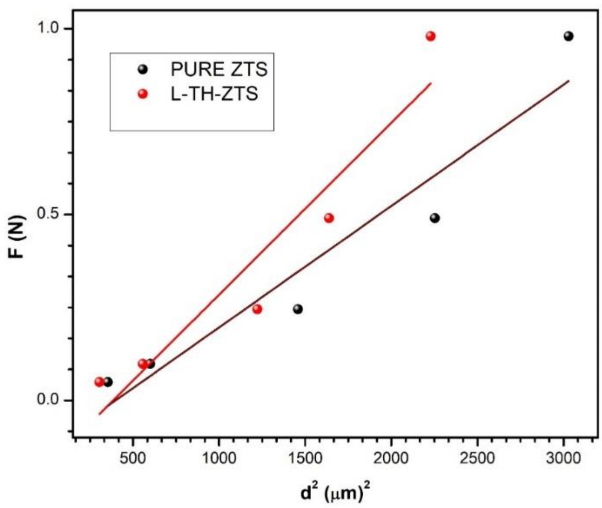

Fig. 6: d^2 v/s F

HK – ZTS			HK-LTH-ZTS		
Factors	Value	Unit	Factors	Value	Unit
A_1	0.0003266	$N^{1/2}/\mu m^2$	A_1	0.0004624	$N^{1/2}/\mu m^2$
H_{hk}	0.605647	Gpa	H_{hk}	0.8574746	Gpa

W_{Hk}	-0.13038	N	W_{Hk}	-0.17811	N

Table 3: Crystal Hardness using Hays-Kendall's Approach

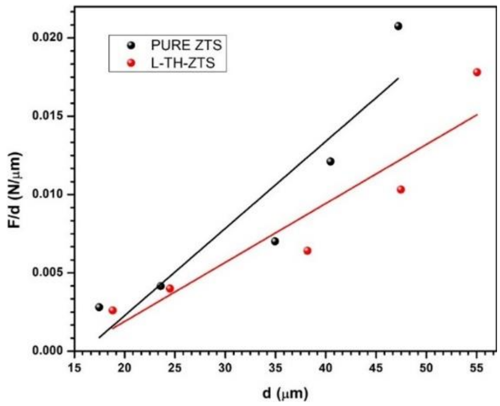

Fig.7: d v/s F/d

2.7 Li-Bradt Technique - Proportional Specimen Resistance method (PSR method)

Usually, Microhardness is affected by two parameters namely elastic resistance of the crystal sample and the force exerted by the indenter on the sample.

According to the PSR method, a force that affects the surface of the crystal is [18],

$$F = \alpha d + \left(\frac{F_c}{d0^2}\right)d^2 \quad (12)$$

$$\frac{F}{d} = \alpha + \beta d \quad (13)$$

Where α arises due to the specimen's surface energy, and the sign of α designates whether a compressive or tensile force exists on the surface. The pure ZTS and the inclusion of LTH in ZTS are exposed to this PSR method first.

The graph is taken for F/d versus d of the above crystals. It is noted that a straight line is obtained for both which reveals linear variation (Fig. 7). From the graph obtained, the slope and the intercept value are calculated for both pure LTH doped ZTS. The negative intercept value indicates there is a presence of tensile stress acting on both the surfaces of the crystals and hence reverse ISE is confirmed [19].

According to Table 4, the calculated value of α for LTH doped ZTS is minimally changed when compared with Pure ZTS.

Table 4: Crystal Hardness using PSR process

PSR Process - ZTS			PSR Process -LTH-ZTS		
Factors	Value	Unit	Factors	Value	Unit
β	0.00886	N	β	0.003767	N
Hpsr	16.429984	GPa	Hpsr	0.6985525	GPa
Y_o	5.4766613	Gpa	Y_o	0.2328508	Gpa
E_0	1346.659	Gpa	E_0	57.255806	Gpa
α = -0,00886			α = -0,00564		

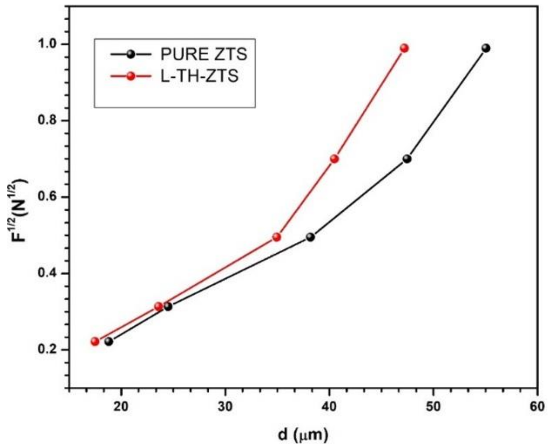

Fig.8: $F^{1/2}$ v/s d

2.8 Analysis according to Elastic/Plastic Deformation Technique (EPD Technique)

EPD technique explains how the crystal's microhardness is independent of load and also explains about the fixed load which is required for the elastic strain. When a strain was formed on the surface of the crystal, workability was noted and hence a reduced size in indentation was observed. The Formula for indentation force, elastic and plastic strain can be expressed as

$$F = A_2 [d_p + d_e]^2 \qquad (14)$$

Where d_p is plastic strain, d_e is elastic strain and A_2 is constant.

A graph is plotted against $F^{1/2}$ vs d Fig. 8). And from the graph A_2 and d_e values are obtained. It is observed that both pure and LTH doped crystal attained negative intercepts (Table 5). A negative intercept implies that the crystal shows RISE behaviour [20].

The appropriate load independent microhardness values can be obtained using the formulae tabulated in Table 5.

$$HEPD = 1854 \text{ X } A_2 \text{ GPa} \qquad (15)$$

Table 5. Crystal Hardness using EPD model

EPD Model- ZTS			EPD Model- ZTS		
Factors	Value	Unit	Factors	Value	Unit
A_2	0.01991	N/ µm	A_2	0.041	N/ µm
H_{EPD}	36.921104	GPa	H_{EPD}	76.0304	GPa
d_e	-0.1888	N	d_e	-0.26493	N

3. Conclusion

The above calculated results of different methods of Hardness techniques ascertain that the inclusion of LTH in ZTS does not affect the mechanical stability of the material, However the doping of LTH minimally alters the softness of the crystal.

The Fracture stress, Yield stress, Elastic stiffness and the Young's modulus of the grown material were compared for both pure and LTH doped ZTS. Both are showcasing outstanding mechanical stability. Hence LTH doped ZTS is a suitable material for the application of second harmonic generation than pure ZTS from the perspective of increased non linearity property and unaltered mechanical stability of the crystal.

Refrences

[1] Oussaid M, Becker P, KemicheMand Carabatos-Nedelec C1998 Low temperature phase transitions in zinc tris (thiourea) sulphate (ZTS) determined by raman scattering Phys. Stat. Sol. B 207 103–10

[2] Ushasree PM, Muralidharan R, Jayavel R and Ramasamy P 2000 Metastable zone width, induction period and interfacial energy of zinc tris (thiourea) sulphate J. Cryst. Growth 210 741–5

[3] Venkataramanan V, Dhanaraj G, WadhawanVK, Sherwood JNand BhatHL 1995 Crystal growth and defects characterization of zinc tris (thiourea) sulphate: a novel metal organic nonlinear optical crystal J. Cryst. Growth 154 92–7

[4] Arunmozhi G, Gomes E, DeMand Ganesamoorthy S 2004 Growth kinetics of zinc (tris) thiourea sulphate (ZTS) crystals Cryst. Res.Technol. 39 408–13

[5] Meenakshisundaram S, Parthiban S, Sarathi N, Kalavathy R and BhagavannarayanaG2006 Effect of organic dopants on ZTS single crystals J. Cryst. Growth 293 376–81

[6] DeviMS, Arthi A P, Sagayaraj P and Thamizharasan K 2013 Growth, optical, theoretical and dielectric studies on ZTS single crystalsArch. Phy. Res. 4 67–73

[7]P.M. Ushashsree, R. Jayavel, C. Subramanian, P. Ramasamy, J. Cryst. Growth 197 (1999) 216–220.

[8] H.O. Marcy, L.F. Warren, M.S. Webb, C.A. Ebbers, S.P. Velsko, G.C. Kennedy, G. C. Catella, Appl. Opt. 31 (1992) 5051.

[9] R.P. Ravender Tickoo, K.K. Tandon, P.N.K. Bamzai, Mater. Sci. Eng. B 110 (2004) 177–184. [4] J. Rictoe, L. Pardo, B. Jimenez, J. Mater. Sci. 29 (1994) 3248.

[10] B. Lal, K.K. Bamzai, P.N. Kotru, Mater. Chem. Phys. 78 (2002) 202.

[11] B. Basu, N.K. Mukhopadhyay, J. Manisha, Eur. Ceram. Soc. 29 (2009) 801. [7] P.N. Kotru, S. Bhat, K.K. Raina, J. Mater. Sci. Lett. 8 (1989) 587.

[12] F. Kick, Das Gesetzder Proportionalen Winderstande and Science Anwendung, Felix, Leipzig, 1885.

[13] E.M. Onitsch, Mikroskopie 2 (1947) 131. [10] M. Hanneman, Metall. Manchu. 23 (1941) 135. [14] S. Safran, E. Asikuzun, E.S. Kilicarslan, A. Kilic, O. Ozturk, A. Gencer, J. Mater. Sci. Mater. Electron. 25 (2014) 2737–2747.

[15] O. Ozturk, H.A. Cetinkara, E. Asikuzun, M. Akdogan, M. Yilmazlar, C. Terzioglu, J. Mater. Sci. Mater. Electron. 22 (2011) 1501–1508.

[16] H. Wyatt, Metals, Ceramics and Polymers, Cambridge University Press, London (1974), Chap. 5 and 6.

[17] K. Sangwal, A. Klos, Cryst. Res. Technol. 40 (2005) 429.

[18] F. Frohlich, P. Grau, W. Grellmann, Phys. Stat. Sol. 42 (1977) 79. [16] Q. Ma, D.R. Clarke, J. Mater. Res. 10 (1995) 853.

[19] A.B. Keshav kumar, N. Bhuvaneswari, S. Nalini Jayanthi, Materials Today: Proceedings. 2022; 62: 2873-2877.

[20] S. Nalini Jayanthi, N. Bhuvaneswari, Mater. Today:Proc. 55 (2021) 250–252.

.