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Growth and Structural Properties of *MTS* Single crystal doped with $ZnSO_4$

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Abstract: Nonlinear optical materials are used in laser technology, such in new NLO materials is the fascinating research today. Several authors try to grow new inorganic, organic and semi organic NLO materials have many advantages over both inorganic and organic NLO materials. In this view, in the present investigation ZnSO4 doped Magnesium ThioUrea Sulphate(MTS) single crystals were grown by slow evaporation technique using rain water as solvent. The grown crystals were characterized by SXRD and PXRD measurements. The density of the crystals was determined by conventional floatation technique. The mechanical strength of the grown crystals was examined by Vicker's Microhardness test. The SXRD and PXRD data show that the grown crystal belongs to tetragonal system. The Work hardening co-efficient determined by hardness number shows that, the crystal belongs to soft category materials.

Index Terms — Crystal growth, SXRD, Microhardness.

INTRODUCTION

Nonlinear optics plays an important role in the emerging photonic and opto-electronic technologies, Non-linear optical materials find wide applications in the area of Laser technology, optical communication [1,2] and the data storage technology. Semi organic nonlinear optical (NLO) materials are reputed candidate for device fabrication technology, owing to their large nonlinear coefficient, high laser damage threshold and exceptional mechanical and thermal stability.

In this present study, Magnesium Thiourea Sulphate (MTS) doped with Zinc Sulphate, semi organic NLO material was grown by slow evaporation technique and characterized by X-ray Diffraction Data and Vicker's Microhardness measurement.

2. EXPERIMENTAL PROCEDURE

2.1: Synthesis of MTS

MTS salt was synthesized by dissolving AR grade Thiourea and Magnesium Hepta Hydrate in the ratio 3:1 in Rain Water. The mixture was stirred using Magnetic stirrer for about half an hour. The precipitate was filtered and the solution was allowed to evaporate. The MTS was synthesized as per the following reaction.

$$3[CS(NH_2)_2] + MgSO_4\ 7H_2O \qquad Mg\,[CS(NH_2)_2]_3.SO_4.7H_2O$$

2.2: Growth of Sample Crystal

To grow doped MTS crystals Zinc Sulphate was added in the dopent ratio 1: 0.002, 1: 0.004, 1: 0.006, 1: 0.008, 1: 0.01, 1: 0.02, 1: 0.04, 1: 0.06 and 1: 0.08 by slow evaporation technique. Big size crystals were obtained and were harvested after one month. Totally 10 crystals were grown (1 - Pure MTS & 9 - doped)

The density of all the grown crystals in the present study was determined by the conventional flotation technique. Carbon tetra chloride of density 1.59 (g/cc) and Bromoform of density 2.89 (g/cc) were used as low density and high density liquids respectively.

The Pure MTS crystal was characterized by SXRD using Bruker Kappa Apex (II) diffractometer with $\lambda = 0.71073$ Å radiation at room temperature. The crystal belongs to tetragonal system. The ZnSO4 doped MTS crystals were subjected to PXRD using XPERT-PRO diffractometer with Cu K alpha of (λ=1.5406 Å)

The Vicker's Microhardness measurement was carried out for all the 10 crystals using SHIMADZU Model-HMV-2T for the load of 25gm, 50gm and 100 gm and the Work-hardening coefficient was also determined.

The microhardness is calculated using the expression,

$$H_v=1.8544\ P/d^2\ kgmm^{-2}$$

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

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3. RESULTS AND DISCUSSION

The photograph of all the 10 crystals grown in the present study is shown in Fig.1. S1→Pure MTS, S2→1:0.002Zn, S3→1:0.004Zn, S4→1:0.006Zn, S5→1:0.008Zn S6→1:0.01Zn, S7→1:0.02Zn, S8→1:0.04Zn, S9→1:0.06Zn, S10→1:0.08Zn. The crystal grown in the present study are transparent, hard and stable. The maximum size of the crystal obtained is 5 cm x 2 cm x 1 cm for 1: 0.02 and 1: 0.04 dopent concentration. This indicated that we can obtain big size crystal when we use Rain water as solvent instead of distilled water.

Figure 1.Photograph of grown crystals

The SXRD taken from the pure MTS single crystal shows that the crystal belongs to tetragonal system. a = 11.918(4) Å, c = 6.8485(14) Å. Meena et al [3] also shows that, the MTS crystal grown by them also belongs to tetragonal system, a = 11.905 Å, c = 6.773 Å. The lattice parameters determined from PXRD data are given in the table below. The XRD pattern of Pure MTS is shown in Fig.2. The lattice parameters determined for the doped crystals in the present study vary non-linearity with dopent concentration. The dopent concentration has no significant influence on the lattice parameter.

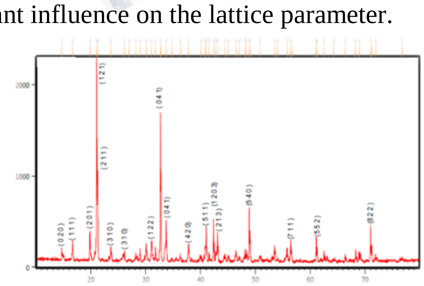

Figure 2.Indexed pattern of Pure MTS crystals

Table -1.Values of Lattice parameters(Å),Lattice Volume(Å) and Density of all grown crystals

System	Lattice Parameters		Lattice Volume Å^3	Density	
	a(Å)	c(Å)		By flotation technique g/cc	By calculation g/cc
Pure MTS	11.9214 11.905[3]	6.85236 6.773[3]	973.7815	1.60873	1.61
1: 0.002Zn	11.9553	6.84273	977.9924	1.60674	1.61243
1: 0.004Zn	12.0135	6.8852	993.687	1.58732	1.58697
1: 0.006Zn	11.8143	6.98085	974.12802	1.61253	1.61883
1: 0.008Zn	11.9116	6.87729	975.71874	1.6151	1.61619
1: 0.01Zn	11.9219	6.84314	975.598	1.6155	1.61639
1: 0.02Zn	11.939	6.8471	975.90837	1.616	1.61588
1: 0.04Zn	11.9338	6.85191	975.79595	1.6079	1.61606
1: 0.06Zn	11.9254	6.77021	962.76577	1.6277	1.63793
1: 0.08Zn	11.9053	6.86646	973.17993	1.62	1.6204

The density was calculated from the Single crystal XRD data using the relation ρ = (M.Z)/(N.V), where M is the molecular weight of the MTS crystal, Z is the number of molecules per unit cell, N is Avogadro's number, and V is the volume of the unit cell. The density measured by floatation technique and calculated from the lattice volume are found to agree with each other. The values are given in table 2. The density of the doped crystals also varies non-linearly with Zinc Sulphate concentration.

Table-2.Values of Vicker's microhardness and work hardening co-efficient of grown crystals

System	Vickers Hardness number, H_V			Work Hardening Coefficient n
	Load			
	25g	50g	100g	
PURE MTS	39.950	49.200	65.600	3.118
1 : 0.002 Zn	24.650	46.450	61.153	3.177
1 : 0.004 Zn	27.6	35.35	55.8	4.565
1 : 0.006 Zn	36	44.9	58.9	3.091
1 : 0.008 Zn	34.2	36.3	44.8	2.805
1 : 0.010 Zn	40.9	50.6	88.7	4.247
1 : 0.020 Zn	44.35	61.3	85.65	3.784

1 : 0.040 Zn	45.95	56.95	72.900	2.994
1 : 0.060 Zn	56.735	68.267	75.524	2.515
1 : 0.080 Zn	58	70	80	2.616

Vicker's Microhardness values for Pure and ZnSO4 doped MTS crystals are given in Table 2. The plot drawn between the corresponding loads and hardness values of the Pure and doped MTS crystals is shown in Fig. 3. It indicates that the hardness number increases with increase in load. The microhardness shows non-linear variation with dopent concentration. The hardness of the doped crystals of low dopant concentrations less than that of pure and for higher dopant concentrations greater than that of pure. This reveals that the hardness increases with increase in dopant concentration. The Meyer's work hardening co-efficient can be calculated from the Meyer's law [4,5] which relates the load and indentation diagonal length

$$P = kd^{n},$$
$$\text{Log } P = \text{Log } k + n \text{ Log } d$$

Where P is load in kg, d is the diameter of recovered indentation in mm, k is constant and n is the work hardening coefficient. The Plot log d Vs log P gives in the figure 3. The slope of the best linear fit graph gives 'n' value.

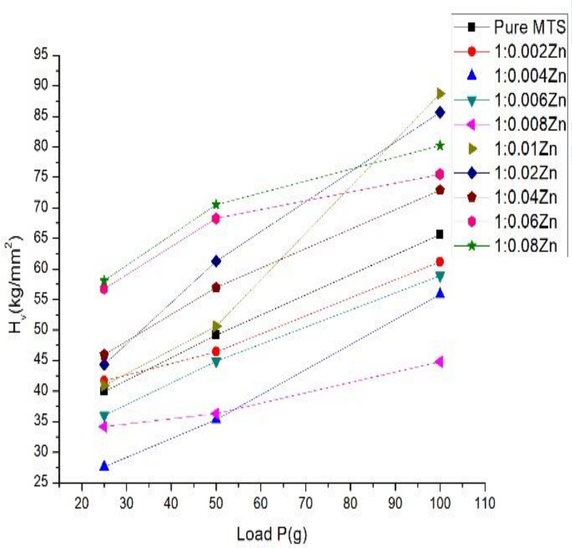

Figure 3. Variation of Vickers Microhardness number Vs load for grown crystals

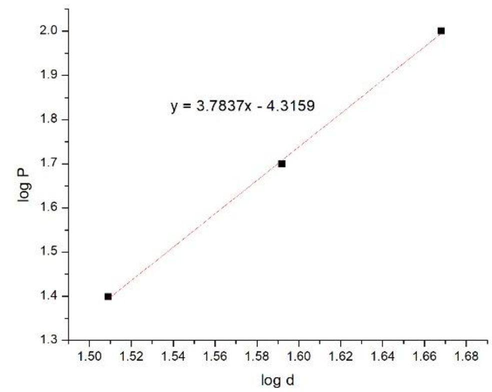

Figure 4. Variation of log d Vs log P for 1:0.02Zn Crystal

Chin et al (1973) [6] on the hardness of Sodium and potassium halides, it is noted that the observed value of m (0.6) is close to the value of 0.5 obtained by Chin et al (1973)

Fleischer (1962) [7] developed a model to account for the hardening of alkali halides by divalent impurities. The divalent impurities are strongly attracted by positive ion vacancies resulting in large tetragonal distortions. A moving dislocation experiences a force due to the distortion. The resulting expression for the flow stress (which is a measure of hardening) is proportional to C1/2 ,where C is the concentration of the impurity.

The hardening co-efficient determined from the dopent concentration is found to be 0.602(≈0.5) and it agrees with the value obtained by Chin et al [6] and Fleischer[7] and it obeys the law

$$\Delta H_v = kC^{1/2}$$

Table-3.Variation of concentration and difference in Vicker's microhardness number

concentration	ΔH_v	Hardening co-efficient,m
0.002	-6.5	0.602
0.004	4.6	
0.006	-4.95	
0.008	3.65	
0.010	-10.65	
0.020	-21.35	
0.040	-17	
0.060	-28.317	
0.080	-40.25	

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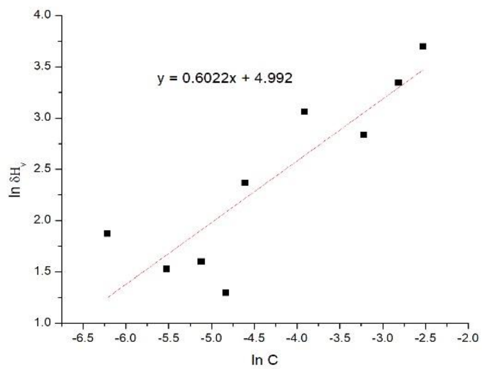

Figure 5. Variation of ΔHv with dopant concentration for the Load of 50g

The Mayer's work hardening co-efficient determined for Pure and doped crystals which is given in table 2, is found that the values are greater than 2. According to Onitsch [8] and Hanneman [9] the 'n' value below 1.6 for hard materials and more than 1.6 for soft materials. This implies that the crystals grown in the present study belong to soft category materials.

CONCLUSION

Pure and $ZnSO_4$ doped MTS crystals were grown by slow evaporation technique. All the crystals grown in the present study belong to tetragonal system. The hardness of the doped crystals of low dopant concentrations less than that of pure and for higher dopant concentrations greater than that of pure. The grown crystals in the present study belong to soft category materials.

REFERENCES

[1] Monaco, S.B., Denis L.E., Velsk S.P., Wang F. T. Eimeral D., J.Cryst.Growth 85(1987)252

[2] Marcy H.O., Rosker M.J., Warren L.F., Cunningham P.H., Thomas C.A., Delvach L.A., Velsko S.P., Ebbers C.A., Liao J.H., Kanatzidis M.G., Opt.Lett.20(1995)252

[3] G.Meena,N.Neelakanda Pillai,IJLTMAS,September 2017,Volume VI,Issue IX ISSN 2278-2540

[4] G. Anand et al Adv. Appl. Sci. Res., 2011, 2 (3):550-557

[5] Mayer E., Verein Z., Deut. Ing. 52 (1908) 645.

[6] Chin G Y, Van Uitert L G,Green M L,Zydzik G J and Kometani T Y 1973 J.Am.Ceram.Soc.56 369

[7] Fleischer R L 1962 J.Appl.Phys.45 508

[8] Onitsch E.M. (1956), 'The present status of testing the hardness of materials', Mikroskopie,Vol.95, pp.12-14.

[9] Hanneman M., Metall. Manchu 23, (1941) 135