Structural Studies of $Zn_XMg_{(1-X)}TS$ Mixed Crystals

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Abstract **– Search of New NLO material is a fascinating field of research today. In this view, in the present study mixed crystals of $Zn_XMg_{(1-X)}TS$ for various values of x viz 0, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9 and 1 were grown by slow evaporation techniques. The density of the grown crystals were determined by floatation technique and composition was estimated from the measured density. The grown crystals were characterized by SXRD and PXRD. The lattice constants also been determined. The grown crystals are single crystals and they crystallize in to different structures like orthorhombic, tetragonal and hexagonal.**

Key words -- ZMTS, Crystal growth, Density, Lattice parameter.

I. INTRODUCTION

Non-linear optical (NLO) materials have become a focus of current research in view of their potential applications in various photonic technologies [1-3]. Materials with NLO activity find use as electro-optic switching elements for telecommunication and optical information processing. Variety of materials including inorganic, organometallic, organic and polymeric have been studied for their NLO activity, but it is the organometallic materials which have been receiving the maximum attention due to its high mechanical strength and high SHG efficiency. Mixed crystals generally have enhanced properties than the pure crystals. In this view, in the present investigation mixed crystals of $Zn_xMg_{(1-x)}TS$ (ZMTS) were grown and characterized by measuring density and XRD pattern.

II. MATERIALS AND METHODS

The ZMTS salt was synthesized by the stoichiometric mixing of AR grade Zinc SulphateHeptahydrate, Magnesium SulphateHeptahydrate, and Thiourea in the molar ratio 1:3. The component salts were well dissolved in deionized water which was thoroughly mixed using a Magnetic stirrer and the mixture was heated at 50℃. ZMTS salt was synthesized according to the reaction.

$$Zn_xMg_{(1-x)}SO_4.7H_2O + 3CS(NH_2)_2 \rightarrow Zn_xMg_{(1-x)}[(CS(NH_2)_2)_3]SO_4$$

Where$x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9\ and\ 1$

Single crystals of ZMTS was grown by slow evaporation technique at room temperature. Totally 8 crystals were grown. All the grown crystals were subjected to single crystal XRD analysis using Nonius CAD4/MAC H3 and BrukerKapper Apex II single crystal diffactometer to determine the unit cell dimensions (saif / Cochin).

Powder X-ray diffraction patterns were obtained using powder X-raydiffractometer with scintillation counter andmonochromated$CuK_\alpha(\lambda = 1.54056Å)$ radiation at a temperature of $25 + 1$℃. The density of the crystals were determined by floatation technique using bromofome $(2.894g/cc)$ and ethanol $(0.78g/cc)$ as higher and lower density liquids respectively. EDS spectrum of all the mixed crystal were recorded using FEI Quanta FEG 200 model scanning electron microscope. The bulk composition of the mixed crystals were estimated from both the density and EDS data. The lattice parameters were determined from the procedure followed by Lipson and Steeble[4]. The composition dependence of lattice constants in a mixed crystal series can be expressed by a general relation of the type.

$$a^n = xa_1^n + (1-x)a_2^n$$

Different values have been proposed for the exponent n, when n=1 equation 1 becomes

$$a = xa_1 + (1-x)a_2$$

This equation, which predicts a linear composition dependence, was suggested empirically by Vegard[5] and is known as Vegard's law. If the volumes are assume to be in additive, we get

$$a^3 = xa_1^3 + (1-x)a_2^3$$

This equation is known as Retger's rule and represent an ideal mixed crystal.

III. RESULTS AND DISCUSSIONS

The photograph of all the grown crystals are shown in fig 1. The Morphology of the crystals grown in the present studies are diamond shape of 2mm thickness and they are transparent. The measured density and weight percentage from EDS data are given in table 1. The EDS spectrum of $Zn_{0.2}Mg_{0.8}TS$ crystal is shown in fig 2. The estimated bulk composition from density and EDS are provided in table 2.

Fig 1. Photograph of grown crystals

Top row :$ZTS, MTS, Zn_{0.1}Mg_{0.9}TS, Zn_{0.2}Mg_{0.8}TS$

Bottom row: $Zn_{0.4}Mg_{0.6}TS, Zn_{0.6}Mg_{0.4}TS,$

$Zn_{0.8}Mg_{0.2}TS,\ Zn_{0.9}Mg_{0.1}TS$

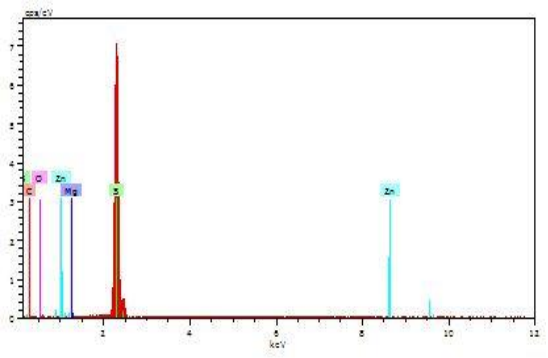

Fig 2. EDS spectrum of $Zn_{0.2}Mg_{0.8}TS$ crystal

Table: 1 Density and Weight Percentage

System	Density	Atomic Weight percentage	
		Zn	Mg
$Zn_{0.1}$ $Mg_{0.9}$ TS	1.57	0.12	0.49
$Zn_{0.2}$ $Mg_{0.8}$ TS	1.58	0.16	0.30
$Zn_{0.4}$ $Mg_{0.6}$ TS	1.65	0.31	0.19
$Zn_{0.6}$ $Mg_{0.4}$ TS	1.69	1.59	0.33
$Zn_{0.8}$ $Mg_{0.2}$ TS	1.71	20.08	1.37
$Zn_{0.9}$ $Mg_{0.1}$ TS	1.72	16.16	1.01

Table:2 Estimated composition of grown crystals

System	Actual Composition		Estimated Composition from			
			Edax		Density	
$Zn_{0.1}$ $Mg_{0.9}$ TS	$Zn_{0.1}$	$Mg_{0.9}$	$Zn_{0.083}$	$Mg_{0.916}$	$Zn_{0.102}$	$Mg_{0.897}$
$Zn_{0.2}$ $Mg_{0.8}$ TS	$Zn_{0.2}$	$Mg_{0.8}$	$Zn_{0.165}$	$Mg_{0.834}$	$Zn_{0.181}$	$Mg_{0.818}$
$Zn_{0.4}$ $Mg_{0.6}$ TS	$Zn_{0.4}$	$Mg_{0.6}$	$Zn_{0.377}$	$Mg_{0.622}$	$Zn_{0.370}$	$Mg_{0.629}$
$Zn_{0.6}$ $Mg_{0.4}$ TS	$Zn_{0.6}$	$Mg_{0.4}$	$Zn_{0.641}$	$Mg_{0.358}$	$Zn_{0.622}$	$Mg_{0.378}$
$Zn_{0.8}$ $Mg_{0.2}$ TS	$Zn_{0.8}$	$Mg_{0.2}$	$Zn_{0.844}$	$Mg_{0.155}$	$Zn_{0.898}$	$Mg_{0.101}$
$Zn_{0.9}$ $Mg_{0.1}$ TS	$Zn_{0.9}$	$Mg_{0.1}$	$Zn_{0.856}$	$Mg_{0.143}$	$Zn_{0.937}$	$Mg_{0.063}$

The density measured for mixed crystals vary linearly with bulk composition. It increases with increase in the mole percentage of ZTS. The bulk composition determined from the density and EDS were well matched with the actual composition taken. The SXRD data shows the mixed crystals crystallize in different crystal structure as given in Table 3.

Table :3 Lattice Parameter determination from SXRD& PXRD

System	Crystal structure	Single XRD			Powder XRD		
		a(Å)	b(Å)	c(Å)	a(Å)	b(Å)	c(Å)
ZTS	Orthorhombic	11.799	12.008	6.804	11.729 [11.158]	12.138 [15.497]	7.014 [7.780]
MTS	Tetragonal	11.905	11.905	6.773	11.893	11.893	6.788
$Zn_{0.1}$ $Mg_{0.9}$ TS	Orthorhombic	11.864	11.998	6.840	11.744	12.110	7.053
$Zn_{0.2}$ $Mg_{0.8}$ TS	Tetragonal	11.933	11.933	6.897	11.852	11.850	6.942
$Zn_{0.4}$ $Mg_{0.6}$ TS	Tetragonal	11.955	11.955	6.833	12.262	12.262	6.670
$Zn_{0.6}$ $Mg_{0.4}$ TS	Hexagonal	13.687	13.687	11.989	13.469	13.469	11.823
$Zn_{0.8}$ $Mg_{0.2}$ TS	Orthorhombic	11.166	15.503	7.783	11.917	12.254	6.769
$Zn_{0.9}$ $Mg_{0.1}$ TS	Tetragonal	11.897	11.897	6.812	11.939	11.939	6.734

The reported values[6] are given in parenthesis for reference.The powder XRD data were indexed with the respective crystal structure given in table 3. The powder XRD pattern of $Zn_{0.4}Mg_{0.6}$TScrystals are shown in Fig. 3.The lattice constant determined from SXRD and PXRD coincide with each other. The lattice constant calculated from Vegard's and Retger's rule for the mixed crystals are given in table 4.

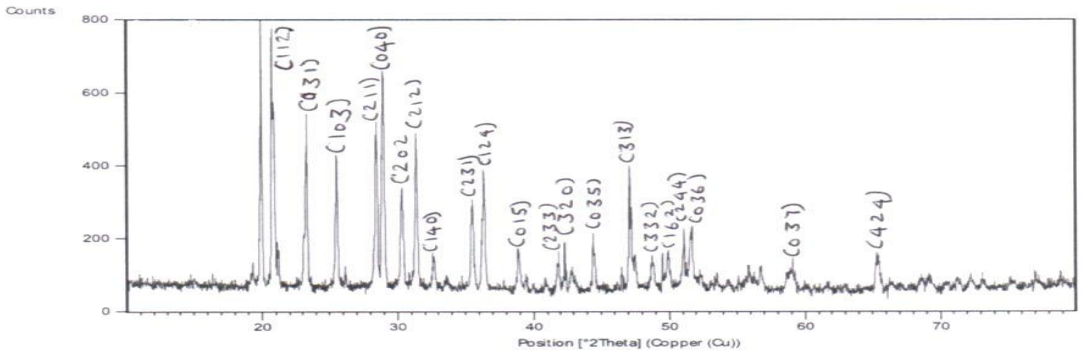

Fig 3. XRD pattern of $Zn_{0.4}Mg_{0.6}TS$ crystals

Table :4 Calculated Lattice parameters

System	Vegards law			Retgers law		
	a(Å)	***b***(Å)	***c***(Å)	***a***(Å)	***b***(Å)	***c***(Å)
$Zn_{0.1}$ $Mg_{0.9}$ TS	11.868	11.900	6.801	11.878	12.236	6.806
$Zn_{0.2}$ $Mg_{0.8}$ TS	11.860	11.977	6.820	11.864	11.932	6.825
$Zn_{0.4}$ $Mg_{0.6}$ TS	11.839	11.971	6.860	11.840	13.124	6.862
$Zn_{0.6}$ $Mg_{0.4}$ TS	13.784	12.046	6.931	11.789	12.051	6.934
$Zn_{0.8}$ $Mg_{0.2}$ TS	11.750	12.100	6.980	11.754	12.102	6.981
$Zn_{0.9}$ $Mg_{0.1}$ TS	11.736	12.125	6.999	11.737	12.127	7.004

The lattice constant calculated from the Vegards and Retgerdsrule for the mixed crystals (estimated composition from EDS is used) well agreed with the lattice constant determined from PXRD. This reveals that the components of mixed crystals properly mixed. The single lattice constant assigned for the mixed crystals prove that the mixed crystals are single crystals.

REFERENCES

[1]. Prasad, Paras N., and David J. Williams (1991). Introduction to nonlinear optical effects in molecules and polymers. Vol. 1. New York, Wiley.

[2]. Eaton, David F. (1991) Nonlinear Optical Materials: The Great and Near Great. 128-156.

[3]. D.S.Chemla, J.Zyss, (1987).Introduction to Non-linear optical properties of organic molecules and crystals, Vol. 1 and 2, Academic press Orlando

[4]. Lipson, Henry, and Harry Steeple. (1970).Interpretation of X-ray powder diffraction patterns. Macmillan.

[5]. Vegard, L. (1921).The constitution of mixed crystals and the space occupied by atoms. Z. Phys 5.17 17-26.

[6]. Ravi, Sandhya, and S. Chenthamarai. (2014). Growth and Characterization of Single Crystals of Thiourea based compounds. Indian J. Sci. Res 9.1 051-057.