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Mechanical Properties of $Zn_xMg_{(1-x)}TS$ Mixed Crystals

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Abstract: *Growing Semi-Organic NLO materials is one of the important fields of research now a days. Mixed crystals are found to be harder than the end member crystals. The tailor made crystals had properties analogous to the end member crystal and some physical properties like microhardness, stability and electrical properties might be enhanced due to mixing. In this view, ZTS and MTS were mixed in the composition ratio $Zn_xMg_{(1-x)}TS$ for various values of x(x = 0 to 1). Vickers's microhardness test was carried out for pure and mixed crystals. The mechanical parameters likeMeyer's work hardening co-efficient, Stiffness constant, Second order elastic constant, Young's modulus, Yield strength, Fracture toughness and Brittleness index were calculated by using available relations. It has been found that all the above parameters vary linearly with load and non-linearly with composition.*

Keywords:*ZMTS mixed crystals, Vicker's microhardness, Stiffness constant, Second order elastic constant, Young's modulus, Yield strength, Fracture toughness, Brittleness index.*

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I. Introduction

Non-linear optical (NLO) materials are receiving great attention and contribute for the substantial progress in development of laser technology, optical data storage and optical information processing. Semi-Organic materials have good mechanical and thermal stability when it is compared to organic NLO materials. Thus, growing Semi-Organic NLO material is one of the fascinating fields of research of today. Several work have been done to grow ZTS single crystal but only limited number of work have been done on pure MTS crystal. Armington et al [1] proposed two methods of hardening (i) solid solution hardening and (ii) by adding divalent impurities. In this view, in the present study, to enhance the mechanical and other properties of MTS and ZTS, mixed crystal of $Zn_xMg_{(1-x)}TS$ for various values of x (x = 0 to 1) were grown by slow evaporation techniquein identical condition. The grown crystals have been examined by Vicker's microhardness indentation test to measure the hardness of the pure and mixed crystals.

Previously Bhuvaneswari Arvind et al [2] and A. Darling Mary et al [3] have grown mixed crystals of ZTS and MTS. A. Darling Mary et al [3] reported that her crystal system was belonging to orthorhombic and soft category materials. She observed that the work hardening coefficient (n) values of the mixed crystals were found to be less than pure ZTS and MTS crystals. M.Sumithra Devi et al [4] have grown magnesium doped ZTS single crystals,she also showed that the crystals was belonged to soft category materials. M.Jeyalekshimi et al [5] have grown $Znso_4$ doped MTS single crystals and sheobserved that, when the dopant concentration increases the hardness of the doped crystals also increases and she also proved that the MTS a soft material category.

II. Materials and Methods

Hardness is an important property of a crystal that is difficult to define as an absolute basis. Microhardness is a structure sensitive property which is affected by several factors like impurities, thermal and mechanical history of the sample used for measurement resulting in variation in values from different sources. The hardness of the crystal is obviously related to the crystal structure of the material or in other words, the pattern in which the atoms are packed and the electronic factors operating to make the structure stable. According to Ashby[6] "hardness is a measure of the resistance to permanent deformation or damage". Earlier microhardness was measured by Mohs scale [7] which is 10 for the diamond (hardest material). Scratch test was also used to test the hardness of the material but it has no values. Metallurgical and other engineers used Brinell hardness test or the Rockwell hardness test to measure the hardness of the material. By using the Scratch test, Brinell hardness test and Rockwell hardness test only relative hardness can be determined. Beyond all the above tests,Vicker's indentation tests have been used by several investigators to study the glide deformations, isotropy or anisotropy,cracks, grain boundary hardening,irradiation effect and environment of dislocation mobility of various crystals [8,9].

In the present study Vicker's microhardness test is carried out for all the grown crystals by using Zwick 3212 hardness tester fitted with Vickers diamond pyramidal indenter. The Vicker's hardness test method consists of indenting the test material with a diamond indenter, in the form of pyramid with a square base and angle of 136º between opposite faces subjected to different loads (here 25g , 50g and 100g loads). The full load is normally applied to 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average is calculated. The area of the sloping surfaces of the indentation is calculated. The Vicker's hardness is the quotient obtained by dividing the kg load by the square mm area of indentation using the relation

$$H_v = 1.8544\ P/d^2\ \text{kgmm}^{-2} \qquad (1)$$

Where, p is the applied load in kg and d is the average diagonal length in mm.

Hardness in Mohs scale (H_M) [10] can be determined from the Vicker's microhardness number (H_v) in kgmm^{-2} by using the relation [11]

$$H_M = 0.675\ (H_v)^{1/3} \qquad (2)$$

It is noted that Mohs scale has no units. The Meyer's work hardening coefficient [12] can be determined by from the Meyer's relation $P= Kd^n$ .Where, k is constant, n is a work hardening coefficient. Plot a curve between log P and log d. By taking log P along x-axis, log d along y-axis. The 1/slope of the line from the best fit of the curve gives the work hardening coefficient (n). Vicker's microhardness number (H_v) can be expressed in GPa by multiplying H_v in kgmm^{-2} by a factor9.806 x 10^{-3} [13].

The elastic stiffness constant (C_{11}) for all the grown crystals have been estimated by using Wooster's empirical formula [14]

$$C_{11} = H_v^{7/4} \qquad (3)$$

And the second order elastic constant (C_{12}) can be determined from the stiffness constant (C_{11}) value by using the relation [13]

$$C_{12} = \frac{3H_v - C_{11}}{2} \qquad (4)$$

Where, H_v is in GPa.

Young's Modulus (E) and the Yield strength(Y) can be determined from the Vicker's microhardness number (H_v) by using the relation [15]

$$E = 81.9635\ H_v \qquad (5)$$

$$Y = \frac{H_v}{3} \qquad (6)$$

Fracture toughness (k_c) and Brittleness index (B_i) is determined by using the formula

$$k_c = \frac{P}{\beta l^{\frac{3}{2}}} \qquad (7)$$

Where, P is the applied load, *l* is the crack length, β is the geometrical constant and β =7 for Vickers diamond indenter

$$B_i = \frac{H_v}{k_c} \qquad (8)$$

III. Results and Discussion

This research work proposes the study of mechanical properties of mixed crystals. The study of mechanical properties is vital especially for real time applications. A diamond shaped morphology crystals have grown as shown in the photograph. All the crystals are less transparent, white in color, hard and stable. The photographs of all the grown crystal are depicted in figure 1.

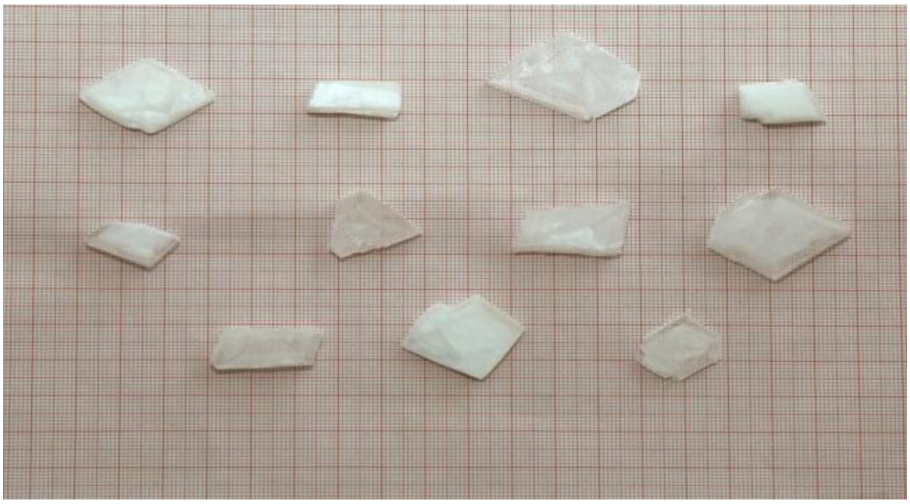

Fig.1 Photograph of all the grown crystals

Top : ZTS, MTS, $Zn_{0.1}Mg_{0.9}TS$, $Zn_{0.2}Mg_{0.8}TS$
Middle : $Zn_{0.3}Mg_{0.7}TS$, $Zn_{0.4}Mg_{0.6}TS$, $Zn_{0.5}Mg_{0.5}TS$, $Zn_{0.6}Mg_{0.4}TS$
Bottom : $Zn_{0.7}Mg_{0.3}TS$, $Zn_{0.8}Mg_{0.2}TS$, $Zn_{0.9}Mg_{0.1}TS$

Vicker's hardness number for different loads in $kgmm^{-2}$, in GPa and in Mhos scale along with work hardening coefficient of all the grown crystals are given in table 1. The literature valueshave provided in the bracket [2].

Table 1. Vicker's microhardness number H_v ($kgmm^{-2}$) ,GPa and Mhos scale and work hardening coefficient(n) of all the grown crystals.

System	Vicker'smicrohardness $H_v(kgmm^{-2})$			Vicker's microhardness H_v(GPa)			Mohs scale (H_M)			Work hardening coefficient (n)
	25g	50g	100g	25g	50g	100g	25g	50g	100g	
ZTS	20.65	22.9	28.65	0.2023	0.2245	0.2809	1.852	1.916	2.065	2.616
MTS	14.8	22	25.45	0.1450	0.2157	0.2495	1.657	1.891	1.985	3.271
$Zn_{0.1}Mg_{0.9}TS$	10.75	15.25	27.9	0.1054	0.1495	0.2735	1.489	1.673	2.047	6.369
$Zn_{0.2}Mg_{0.8}TS$	23.25	29.6	40.1	0.2279	0.2902	0.3932	1.926	2.088	2.310	3.311
$Zn_{0.3}Mg_{0.7}TS$	37.1	53.7	69.95	0.3638	0.5265	0.6859	2.251	2.546	2.781	3.714 [3.8009]
$Zn_{0.4}Mg_{0.6}TS$	6.825	11.65	14.95	0.0669	0.1142	0.1465	1.280	1.530	1.662	4.516
$Zn_{0.5}Mg_{0.5}TS$	16.3	24.55	30.4	0.1598	0.2407	0.2981	1.711	1.961	2.106	3.649 [3.2434]
$Zn_{0.6}Mg_{0.4}TS$	22.55	26.25	36.25	0.2211	0.2574	0.3554	1.907	2.006	2.233	3.041
$Zn_{0.7}Mg_{0.3}TS$	14.85	26.15	34.65	0.1456	0.2564	0.3397	1.659	2.002	2.200	5.1334
$Zn_{0.8}Mg_{0.2}TS$	10.3	14.05	18.7	0.1010	0.1377	0.1833	1.468	1.628	1.791	3.491
$Zn_{0.9}Mg_{0.1}TS$	19.65	27.7	37.55	0.1926	0.2716	0.3682	1.821	2.042	2.260	3.746

The variation of log P versus log d for all the grown crystals is shown in figure 2.

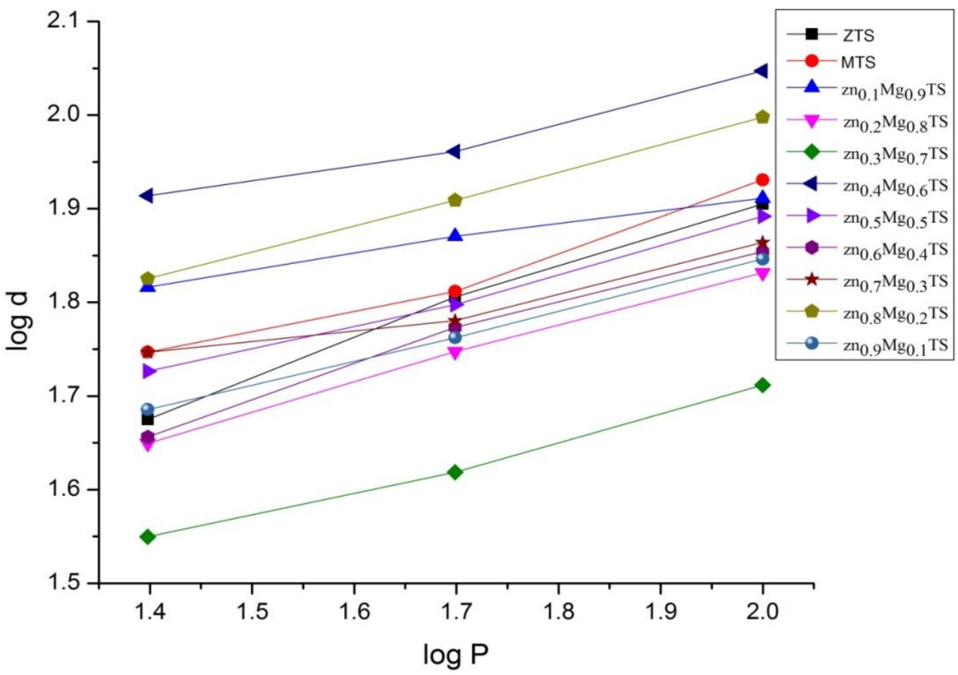

Fig.2 Variation of log P vs log d for all grown Crystals

It is found that the hardness number increases with increase of load and it varies non-linearly with bulk composition as shown in figure2. The non-linear variation of the Vickers hardness number is attributed to the anharmonic vibration of the lattice phonons in the crystal due to mixing. It is more in the case of mixed crystals. Non-linear variation may also be due to the presence of imperfections like vacancies, impurity-vacancy pairs, dislocation, low angle boundaries etc. The origin of low angle boundaries in mixed crystal may be due to the Tiller's eutectic crystallization mechanism [16]. Ananother reason for non-linear composition variation of mechanical parameters in mixed crystals with composition is size effect [17]. Size effect is due to replacement of one atom by another atom. In the present study, replacement of Zn ion and Mg ion are possible. The size ofZn ion (0.74Å) is greater than the size ofMg ion (0.65Å).The work hardening coefficient (n) determine in the present study is found to be greater than 1.6. According to Onitsch and Hanneman [18], crystals having work hardening coefficient is greater than 1.6 belongs to soft category materials. This reveals that the crystals grown in the present study is also belong to soft category materials. The Mhos scale also indicates that the crystals grown in the present study arebelong to soft category materials because it is 1/10 to 1/5 times than the diamond. The Stiffness constant, Second order elastic constant, Young's modulus, Yield strength, Fracture toughness and Brittleness index along with the crack length for the load of 100g are given in the table 2

Table 2.Stiffness constant, Second order elastic constant, Young's modulus, Yield strength, Fracture toughness and Brittleness index along with the crack length for the load of 100g of all the grown crystals.

System	d	Crack length (μm)	H_v (GPa)	E (GPa)	Y (GPa)	C_{11} (GPa)	C_{12}	K_c g/(μm)$^{3/2}$	B_i (μm)$^{-1/2}$
ZTS	80.377	38	0.2809	23.023	0.093	0.108	0.367	0.0609	4.612
MTS	85.280	36.58	0.2495	20.449	0.083	0.088	0.330	0.0645	3.868
$Zn_{0.1}Mg_{0.9}TS$	81.522	68.27	0.2735	22.417	0.0912	0.103	0.358	0.0253	10.810
$Zn_{0.2}Mg_{0.8}TS$	67.842	100.07	0.3932	32.228	0.131	0.195	0.492	0.0142	27.690
$Zn_{0.3}Mg_{0.7}TS$	51.482	79.14	0.6859	56.218	0.228	0.516	0.770	0.0202	33.955
$Zn_{0.4}Mg_{0.6}TS$	111.50	38.12	0.1465	12.007	0.048	0.034	0.202	0.0606	2.417

$Zn_{0.5}Mg_{0.5}TS$	77.992	21.63	0.2981	24.433	0.099	0.120	0.387	0.1420	2.099
$Zn_{0.6}Mg_{0.4}TS$	71.495	35.38	0.3554	29.129	0.118	0.163	0.451	0.0678	5.241
$Zn_{0.7}Mg_{0.3}TS$	73.107	16.90	0.3397	27.843	0.113	0.151	0.434	0.2056	1.652
$Zn_{0.8}Mg_{0.2}TS$	99.517	29.66	0.1833	15.023	0.061	0.051	0.249	0.0884	2.073
$Zn_{0.9}Mg_{0.1}TS$	70.195	32.08	0.3682	30.178	0.122	0.174	0.465	0.0786	4.684

It is observed that all the above parameters determined in the present study increase with increase of load and vary non-linearly with bulk composition of mixed crystals. They are found to be high for the $Zn_{0.3}Mg_{0.7}TS$ crystal, when it is compared to the other mixed crystals, and it is low for $Zn_{0.4}Mg_{0.6}TS$ crystal.

IV. Conclusion

Mixed crystals are found to be harder than the end member crystals and they belong to soft category materials. All the mechanical parameters determined in the present study are also varies non-linearly with bulk composition.

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