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Structure and Mechanical Properties of Zinc doped Magnesium Thio Urea Chloride Single Crystals

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Abstract: *Second order non linear optics is widely used to convert the frequency of coherent Laser sources. Applications such as Laser based communication, remote sensing and a water measure system require improved non-linear optical materials for accomplishing such applications. MTC is one such promising semi organic material and a limited work has been done. Even though NLO materials have very high SHG efficiency, they have poor physico-chemical stability. In order to overcome these difficulties, researchers grow metallic, semi organic single crystals. So, In the present study, Pure and Zinc doped Magnesium thiourea chloride single crystals have been grown by slow evaporation method in the dopant concentration 1:0.01, 1:0.02, 1:0.03, 1:0.04, and 1:0.05.*

The presence of elements in the grown crystals was identified by EDS measurement. The grown crystals were subjected by SXRD and PXRD techniques to identify the crystal structures and to calculate the lattice parameters. The Vicker's microhardness test was carried out to test the mechanical stability and to determine the hardness parameters.EDS spectrum confirms the incorporation of Zinc atom into the lattice of MTC. SXRD data show that the grown crystals belong to orthorhombic system. The hardness parameters show that the doped crystals are harder than the pure crystals.

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I. Introduction

Efficient nonlinear optical crystals are required for laser devices due to technological importance in the fields of opto electronics, signal processing, instrumentation and optical communication. In the recent years, semi organic NLO crystals are attracting a great deal of attention due to their high NLO efficiency, high damage threshold and high mechanical strength than organic NLO crystals [1].

Armington et al [2] discussed two methods of improving the hardness of alkali halides. (i) solid solution hardening and (ii) impurity hardening. In these view, Zn^{2+} ion has been added to the MTC single crystal to improve the hardness of the crystal. It has been known that divalent cations are much more effective than monovalent ions in raising the strength of alkali halides [3].

The crystal structure of the grown crystals was determined from SXRD taken using Nonius Cad 4/MAC H3 and Bruker Kapper Apex II single crystal diffractometer at Saif,Cochin .The PXRD data were also been collected for all the grown crystals using an automated X-ray powder diffractometer (PAN analytical) with scintillation counter and monochromated CuKα(λ=1.54056Å) radiation. The data were indexed using the available methods.

The dopant concentration was estimated from the EDS spectrum taken for the doped crystals by using FEI Quanta FEG 200 model instrument. No work was done on measurements of microhardness of MTC single crystals but some works have been done on ZTC single crystals [4]. R.Rajasekaran et al [5] have grown ZTC single crystals and measured the hardness. They found that the hardness increases with load.

Hardness is an important solid state property. The hardness of a material is defined [6] as the resistance it offers to the motion of dislocations, deformation or damage under an applied stress. Hardness tests are commonly carried out to determine the mechanical properties such as elastic constants [7] and yield strength [8]. It has been also applied to understand the plasticity of the substance [9].

Mineralogists usually use the so-called Mohs scale in which diamond has a hardness of 10. The hardness of any other mineral is then determined by a scratch test. Metallurgist and other engineers use penetration tests. In these tests, a suitable weighted plunger bears down on the specimen which deforms first elastically and then plastically. The depth or diameter of the indentation produced by a known load is then used as an indication of the hardness of the material. Although it is not possible to calculate what the hardness of the particular crystal should be on purely theoretical grounds, it is generally possible to predict its relative hardness.

Hardness is directly related to the forces that exist between the atoms in the solid. Since these forces are determined by the atoms present and their energy or crystal structure, it is possible to predict not only the relative hardness of a solid but also related properties such as ductility, melting point and others whenever the structure is known.

Many investigators have used the micro hardness, indentation to study glide deformation, anisotropy, cracking, grain-boundary hardening state of dispersions of impurity, quench dislocation mobility. Another method of measuring micro-hardness is Vickers micro-hardness method. In this test a diamond indenter of pyramid shape is used. Of all the above tests, Vicker's microhardness indentation test is commonly used for all types of metals and surface treatments.

II. Experimental Details:

The Vicker's hardness test method consist of indenting the test material with a diamond indenter, in the form of pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a test force of between 1gf and 100gf. The full load is normally applied for 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 Vicker's hardness is the quotient obtained by dividing the kg load by the square mm area indentation. In the present study, Vicker's micro hardness study were carried out for the all the grown crystals.

In the present study, Vicker's microhardness study were carried out for all the six grown crystals using Zwick3212 hardness tester fitted with Vickers diamond pyramidal indenter at St. Joseph College, Trichy for 25, 50,100 and 200gms. The hardness of the crystals was calculated using the relation [10]

$$H_v = 1.8544(P/d^2)\ kg/mm^2$$

where 'P' is the applied load in kg and 'd' is the average diagonal length of the Vicker's impression in millimeter after unloading. The Mayer's work hardening co-efficient 'n' can be determined by plotting log 'p' vs log 'd'. The slope of the best linear fit gives 'n' value. There are several earlier studies on the hardness of alkali halide crystals doped with divalent ions. Dryden et al [11] measured the critical resolved Shear stress (which is related to the hardness) of some materials doped with divalent impurities. They found an increase in hardness proportional to $C^{2/3}$, where C is the molar concentration of the impurity.

Chin et al [12] observed that the increase in hardness (i)is proportional to half power of the Concentration of the divalent impurities($C^{1/2}$) (ii) independent of the host lattice.The hardness of the doped crystals were fitted to the relation,

$$\Delta H_v = kC^m$$

Where ΔH_v is the enhancement in hardness and k and m are constants.

Fleischer [13] 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 the hardening) is proportional to $C^{1/2}$, where C is the concentration of the impurity. Considering the approximations in his model, Fleischer admitted that the values of hardening predicted by his theory can be accurate "to within no better than a factor of two".

Gilman [14] criticized Fleischer's model and proposed a theory in which hardening is associated with the change in electrostatic energy that occurs when a moving dislocation Shears divalent ion-cation vacancy complex. According to this model the hardening is proportional to $BC^{1/2}$ where the hardening co-efficient B, is given by,

$$B = 4.7e^2(\varepsilon\ a^4)^{-1}$$

where 'e' is the electron charge, 'ε' is the static dielectric constant and 'a' the lattice constant of the host crystal. As Gilman's immediate interest was in providing an explanation for the results of Chin et al, he adopted the unusual procedure of assuming average values for the static dielectric constant and the lattice constants of the four alkali halide crystals (NaCl, NaBr, KCl, KBr) and obtained an average value for 'B' which was in fair agreement with the experimental value.

Chin et al have concluded that the impurity hardening observed by them in their study of sodium and potassium halides is independent of the host crystal. However a close look at their diagrams reveals that the data points for each crystals lie on different plots with slightly different slopes which means that the hardening is not altogether independent of the host lattice.

III. Results and Discussion

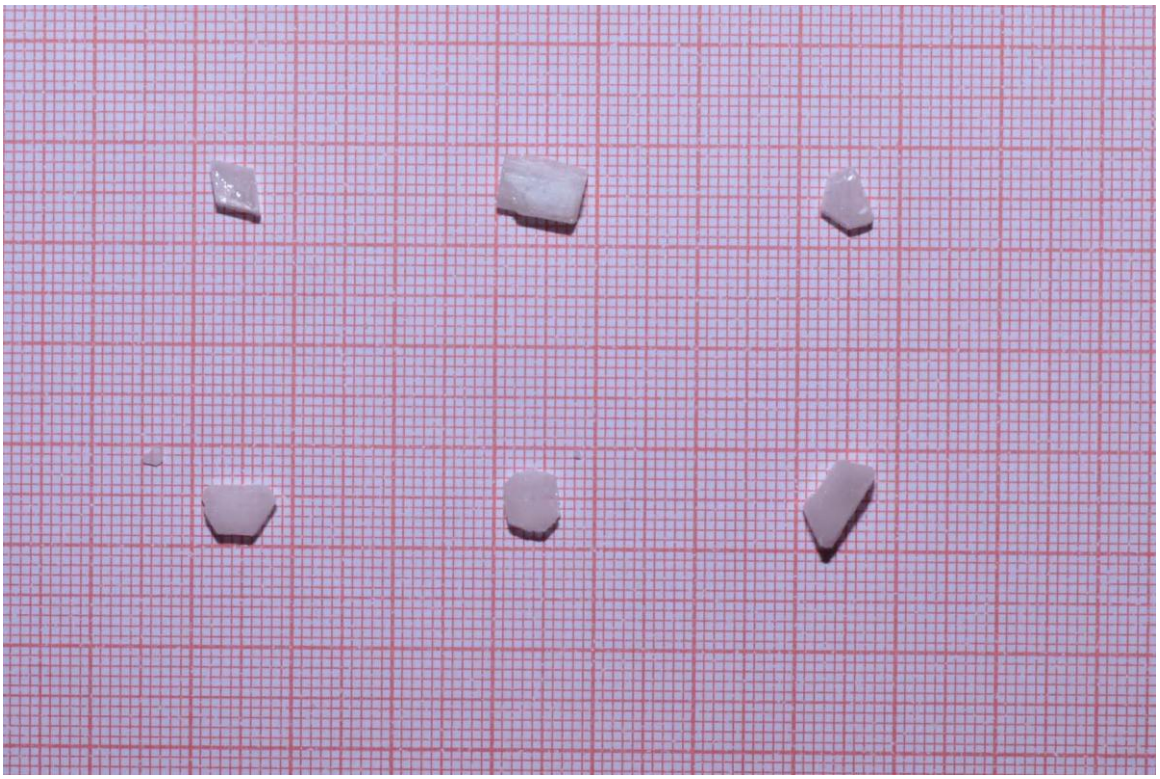

Fig 1: Photograph of grown crystals

Top row : MTC, $Zn_{0.01}$MTC, $Zn_{0.02}$MTC
Bottom row: $Zn_{0.03}$MTC, $Zn_{0.04}$MTC, $Zn_{0.05}$MTC

All the grown crystals were stable and transparent. The lattice parameters were calculated from PXRD data by using the formula $1/d^2=(h^2/a^2+k^2/b^2+l^2/c^2)$

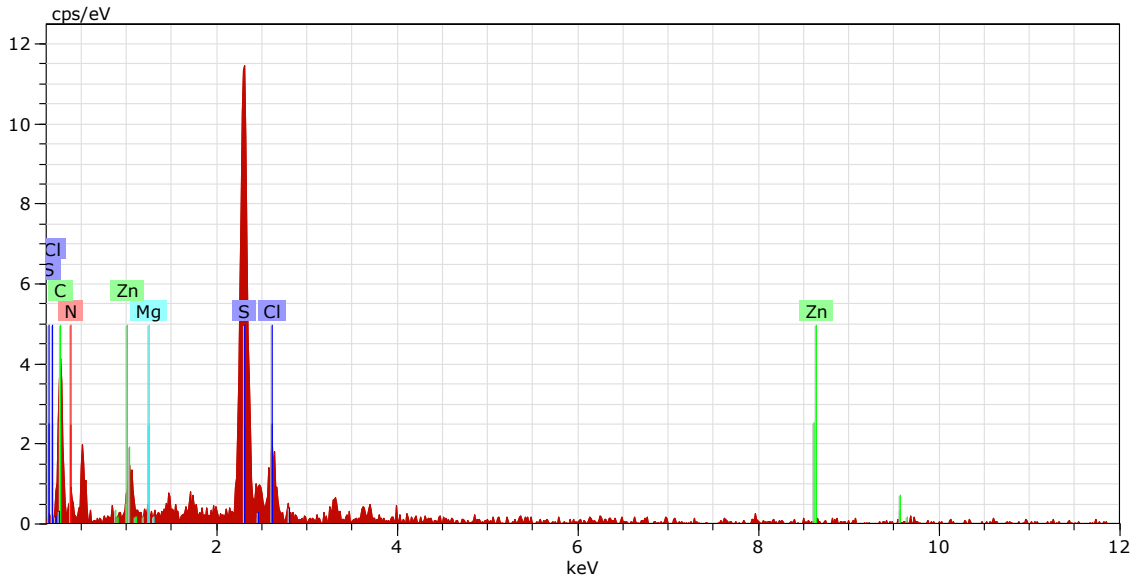

Fig 2: EDS spectrum of Zn0.02 MTC Crystal

EDS spectrum confirms the incorporation of dopant atom into the MTC lattice.

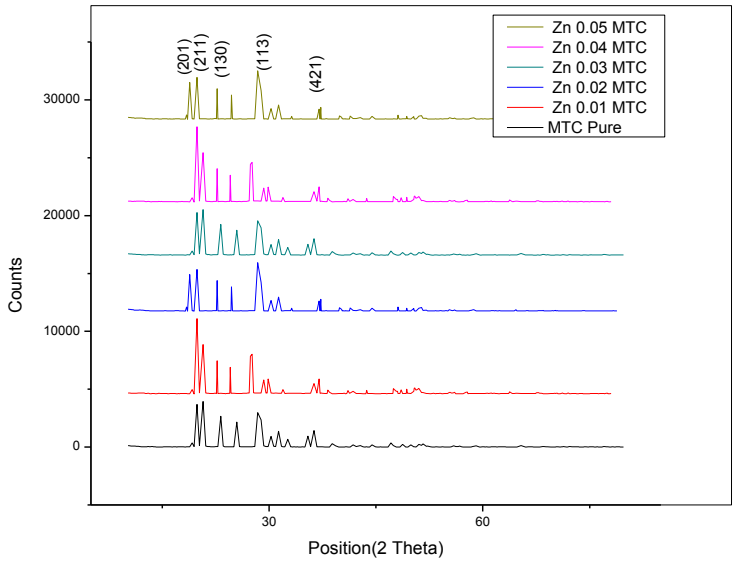

Fig 3: XRD pattern of all the grown crystals

Table 1: Lattice Parameters for all the grown crystals:

System	Single XRD			Powder XRD		
	a(Å)	b(Å)	c(Å)	a(Å)	b(Å)	c(Å)
MTC Pure	5.378	7.682	7.788	5.254	7.672	7.845
$Zn_{0.01}$MTC	5.498	7.680	8.552	5.485	7.743	7.987
$Zn_{0.02}$MTC	5.493	8.523	7.702	5.479	7.987	8.543
$Zn_{0.03}$MTC	5.493	7.684	8.556	5.465	7.654	7.988
$Zn_{0.04}$MTC	5.501	7.680	8.569	5.556	7.689	8.240
$Zn_{0.05}$MTC	5.491	8.569	8.514	5.484	7.998	8.471

The SXRD data shows that the crystals grown in the present study belong to Orthorhombic structure. The lattice parameter calculated from the PXRD data coincides with the SXRD data.

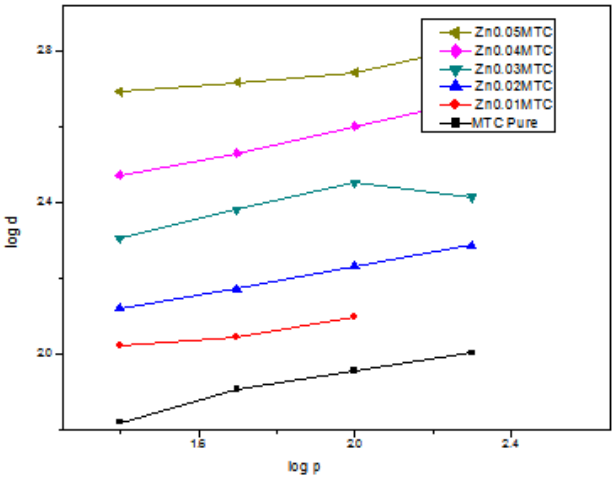

Fig 4: Variation of log P and log d

Table 2: Vicker's micro hardness values and work hardening Coefficient of all the grown crystals:

System	Vickers hardness values (H_v) in GPa				Work hardening Coefficient 'n'	Vickers hardness values (H_M) in Mohs			
	25gms	50gms	100gms	200gms		25 gms	50 gms	100 gms	200 gms
MTC Pure	0.10241	0.11915	0.22213	0.3555	5.076	1.475	1.552	1.909	2.234
$Zn_{0.01}$MTC	0.10829	0.18795	0.29617	0.42881	5.871	1.503	1.806	2.102	2.378
$Zn_{0.02}$MTC	0.13279	0.20987	0.63942	0.98560	5.319	1.609	1.875	2.717	3.138
$Zn_{0.03}$MTC	0.10927	0.15544	0.22409	0.31578	6.667	1.526	1.696	1.915	2.147
$Zn_{0.04}$MTC	0.96824	0.14808	0.21477	0.3099	4.524	1.448	1.668	1.888	2.135
$Zn_{0.05}$MTC	0.66640	0.11817	0.21673	0.61294	5.217	1.279	1.548	1.894	2.679

The Hardness of all the grown crystals increased, when the load was increased and they withstand upto the load of 200gms. The doped crystals are found to be harder than the pure crystals. The Work hardnening coefficient is greater than 1.6 for all the grown crystals. According to Onitch [15], grown crystals in the present study belong to soft category materials.

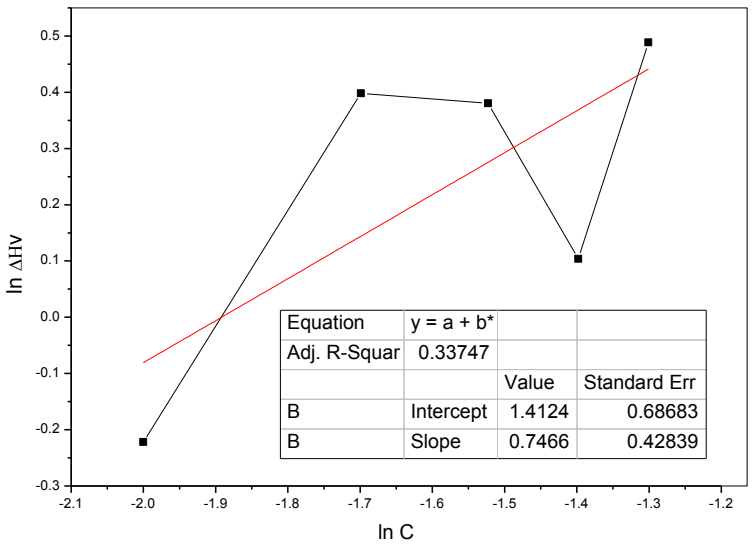

Fig.5: Variation of ln C and ln ΔHv

Table 3: Values of the constants k and m for 25 gms

System	M	k
Zn doped MTC	0.74662	1.41246

In the present study, it is found that, the 'm' value obtained for a load of 25 gm consistent with Gilmen's Theory.

The Young's modulus (E) and Yield strength (Y) of the crystals are calculated from the following equations [16]

E=81.9635Hv and $Y=H_v / 3$, which **increases with increase in load**. The elastic stiffness constant (C11) for various compositions as well as different loads have been estimated using Wooster's empirical formula[17] $C11=(H_v)^{7/4}$. The C11 values are shown in table. These values gives an idea about the tightness of bonding between neighboring atoms.

Table 4: Youngs Modulus, Yield Strength and Elastic Stiffness Constant values of all the grown crystals:

System	Young's modulus values (E) in GPa				Yield Strength (Y) in GPa				Elastic Stiffness Constant (C11) in GPa			
	25gms	50gms	100gms	200gms	25 gms	50 gms	100 gms	200 gms	25 gms	50gms	100gms	200gms
MTC Pure	8.394	9.766	18.207	29.138	0.034	0.039	0.074	0.117	0.0185	0.0242	0.0299	0.1637
$Zn_{0.01}$MTC	8.876	15.405	24.275	35.147	0.036	0.062	0.099	0.143	0.0204	0.0536	0.1189	0.2272
$Zn_{0.02}$MTC	10.884	17.202	52.409	80.783	0.044	0.069	0.214	0.324	0.0292	0.0651	0.4572	0.9749
$Zn_{0.03}$MTC	8.956	12.741	18.367	25.882	0.036	0.052	0.075	0.105	0.0207	0.0385	0.0729	0.1333
$Zn_{0.04}$MTC	79.36	12.137	17.603	25.401	0.323	0.049	0.072	0.103	0.9451	0.0353	0.0677	0.1287
$Zn_{0.05}$MTC	54.62	9.686	17.764	50.239	0.222	0.039	0.072	0.204	0.4915	0.0238	0.0688	0.4246

IV. Conclusion

All the grown Crystals belong to Orthorhombic structure. Lattice Parameter shows that the grown crystals are single crystals. The hardness study shows that the grown crystals belong to soft category. The hardness of the doped crystals obey Gilmen's theory. The non-linear variation of microhardness is due to the presence of imperfections. These imperfections can be vacancies, impurity-vacancy pairs, dislocations, low-angle grain boundaries etc.

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