

Studies on the Mechanical Properties of Pure and Cadmium Chloride doped Zinc - (tris)Thiourea Sulphate (CCZTS) Single Crystals

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ABSTRACT: The microhardness study reveals the mechanical strength of the grown crystal. The Vicker's hardness study was performed to understand the mechanical behavior of the pure and cadmium chloride doped zinc (tris)thioureasulphate (CCZTS) crystals. The Vicker's hardness number (H_V) for the crystal was found for different loads. It is found that these numbers increase with an increase in the load. The Mayer's index (n) was found to be greater than 1.6 predicting a soft-material nature. The fracture toughness value (K_{IC}), was determined from the measurements of the crack length. The brittleness indices (B_i) were found for the grown crystals. Using Wooster's empirical relation, the elastic stiffness constant (C_{11}) was calculated from the Vicker's hardness values at different loads.

KEYWORDS: Microhardness number, Mayer's index, brittleness indices, elastic stiffness constant.

I. INTRODUCTION

In recent years several studies dealing with organic, inorganic and semi organic molecules and materials called nonlinear optics (NLO) are being reported due to the increasing need for photonics applications. The nonlinear (NLO) responses induced in various molecules in solution and solids are of great interest in many fields of research [1]. Inorganic and semi organic nonlinear optical (NLO) materials have higher optical quality, larger nonlinearity, good mechanical hardness and low angular sensitivity when compared to organic NLO materials [2]. Zinc (tris)Thiourea Sulphate is a good nonlinear optical semi organic material for second harmonic generation. Special features of this material are that it has a high laser damage threshold; a low UV cut off and 1.2 times higher second harmonic generation (SHG) efficiency than potassium dihydrogen orthophosphate (KDP) [3]. Also, ZTS has excellent mechanical properties when compared to other semiorganic nonlinear optical crystals [4].

The microhardness method is widely used for studying the individual structural constituent elements of metallic alloys, minerals, glasses, enamels and artificial abrasives. Microhardness test is one of the best methods to understand the mechanical properties of materials [5]. Hardness is an important factor in the choice of ceramics for abrasives, bearings, tool bits, wear resistance coatings etc. Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage. Measurement of hardness is a destructive testing method to determine the mechanical behaviour of the materials [6]. The term hardness is having different meanings to different people depending upon their areas of interest. For example, it is the resistance to penetration to a metallurgist, the resistance to cutting to a machinist, the resistance to wear and tear to a lubrication engineer and a measure of flow of stress to a design engineer. All these actions are related to the plastic stress of the material. Also, the hardness of the crystal is dependent on the type of chemical bonding, which may differ along the crystallographic directions. Hardness is generally taken as a ratio of the applied load to the area of indentation. The measurement of hardness is very important, as far as the fabrication of devices is concerned.

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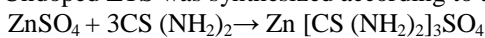
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In the present investigation, attention is focused on the mechanical properties of the pure and cadmium chloride doped zinc- (tris)thioureasulphate single crystals such as Meyer's index number, brittle index and fracture toughness calculated from Vicker's microhardness number (H_v).

II. EXPERIMENTAL PROCEDURES

Undoped ZTS was synthesized according to the reaction,



Analytical Reagent (AR) grades thiourea and zinc sulphate in the molar ratio 3:1 were dissolved in deionised water and it was thoroughly mixed using a magnetic stirrer and the mixture was heated at 50°C till a white crystalline salt of ZTS was obtained. Temperature was maintained at 50°C to avoid decomposition. To synthesize CCZTS crystal the composition of $x=1.0$ and $x=0.5$ mol% of cadmium chloride (AR grade) were added to the solution of ZTS separately. To prepare the supersaturated solutions the amount of solute (m) in grams may be obtained by using the following formula,

$$m = \frac{M \times X \times V}{1000} \text{ (in gram units)}$$

Where,

M → is the molecular weight of the solute,

X → is the supersaturated concentration in molar units and

V → is the required volume of the solution

Using the above relation the required amounts of the synthesized substances were taken and dissolved in distilled water and the saturated solution was prepared. The filtered solution was poured into beakers and kept for evaporation at room temperature. A few days later, tiny crystals were seen in the beaker and reach optimum size in 20 days. The grown crystals are shown in Figures(2.1). Large size single crystals were obtained due to collection of monomers at the seed crystal sites from the mother solution. The mechanical characterization of the grown crystals was made by Vickers microhardness test. The grown crystal with flat and smooth faces and free from any defects was chosen for the static indentation tests. Now the selected face was indented gently by varying the loads for a dwell period of 5 s using Vickers indenter.

The mechanical characterization of pure and CCZTS crystals were made by Vickers microhardness test.

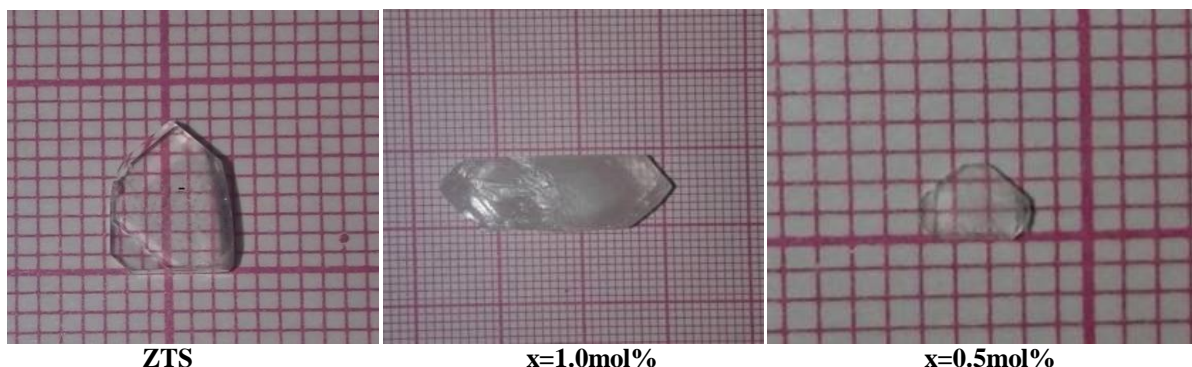


Figure (2.1):(a) Photograph of the grown pure and doped ZTS crystals

III. VICKER'S TEST

Vicker's test is said to be a more reliable method of hardness measurement. In order to get a similar geometrical impression under varying loads, Smith and Sandland [7] have suggested that a pyramid be substituted for a ball. The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a right

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pyramid with a square base and an angle of 136° between opposite faces and subjected to a load of 1 to 100 kg (Figure 3). The base of the Vickers pyramid is a square and the depth of indentation corresponds to $1/7^{\text{th}}$ of the indentation diagonal. The longitudinal and transverse diagonals will be in the ratio of 7:1. The full load was normally applied for 10 to 15 s. The two diagonals of the indentation left in the surface of the material after the removal of the load were measured using a microscope, and their average was calculated. The area of the sloping surface of the indentation was calculated.

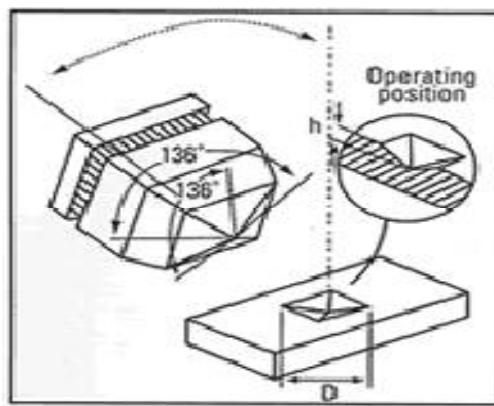


Figure 3 : Vickers hardness test.

The Vicker's hardness is the quotient obtained by dividing the kg load by the square mm area of indentation.

$$H_v = \frac{2P \sin(136/2)}{d^2}$$

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

Where H_v = Vickers hardness number, P = load in kg, d = arithmetic mean of the two diagonals.

When the mean diagonal of the indentation has been determined, the Vicker's hardness number can be calculated from the above formula. Several different loading settings give practically identical hardness numbers on uniform material, which is much better than the arbitrary changing of scale with the other hardness testing methods. The advantages of the Vicker's hardness test are that extremely accurate readings can be taken, and just one type of indenter is used for all types of metals and surface treatments.

IV. RESULTS AND DISCUSSION

(i) Vicker's microhardness test:

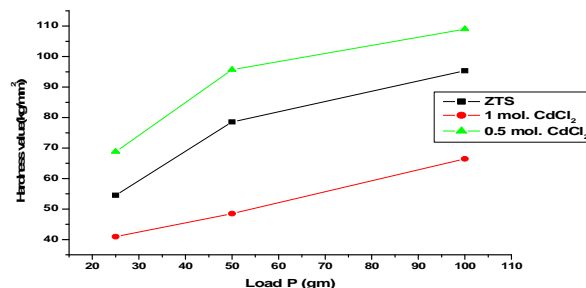


Figure 4(a) : Variation of hardness Vs load for the pure and CCZTS crystals

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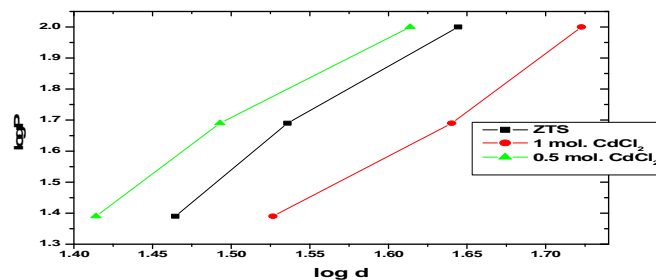


Figure 4(b) :Plots of log P Vs log d for the pure and CCZTS crystals

Figure 4(a) shows the variation of H_v as a function of applied loads, ranging from 25 to 100 g. According to the normal indentation size effect (ISE), microhardness of crystals decreases with increasing load and in reverse indentation size effect (RISE), the hardness value increases with increasing load. In grown crystals, H_v increases with increase in load up to 100 gm, hence exhibiting reverse ISE effect [8]. The traditional Meyer's law, which gives relationship between load P and size d^n is

$$P = Ad^n$$

Where, the exponent n is the Meyer's number and A is a constant. For normal ISE behaviour the exponent $n < 2$, when $n > 2$ there is reverse ISE behaviour and when $n = 2$ the hardness is independent of applied load. The value of n is determined from log d versus log P plot. It is shown in Figure 4(b).

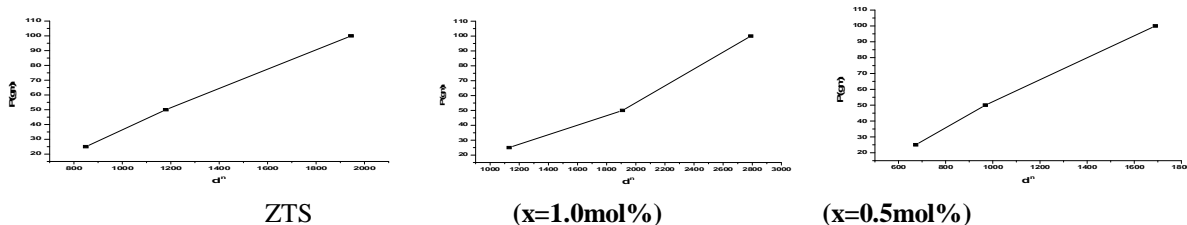


Figure 4.1(a) : Plot of d^n versus P for grown pure and CCZTS crystals

The straight line in the graph shows its agreement Mayer's law. The slope of the graph ($x = 1.0 \text{ mol\%}$ & $x = 0.5 \text{ mol\%}$) gives n and it is determined. According to Onitsch [9,10], n should be between 1 and 1.6 for hard materials and above 1.6 for softer material category.

According to Hays-Kendall's approach load dependent hardness may be expressed by

$$P = W + A_1 d^n$$

Where W is the minimum load to initiate plastic deformation. A_1 is the load independent constant and the exponent $n = 2$ [11]. The value of W and A_1 can be calculated by plotting the experimental P against d^n plot. These two values have been estimated from the plot drawn between P and d^n shown in Figures 4.1(a). The corrected hardness H_v has been estimated using the relation.

$$H_v = 1.8544 \times A_1$$

The calculated hardness parameters are given in Tables 4.2(a),(b)&(c). The elastic stiffness constant (C_{11}) for different loads are calculated using Wooster's empirical formula $C_{11} = H_v^{7/4}$, and it is shown in Table (4.3). The stiffness constant gives an idea about the tightness of bonding with the neighboring atoms. In the case of the grown pure and CCZTS crystals the stiffness constant is found to increase with the applied load.

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Table 4.1: Mayer's index number(n) for grown crystals

Crystals	Mayer's index number (n)
ZTS	3.428
CCZTS (x=1.0 mol%)	2.545
CCZTS (x=0.5 mol%)	3.75

Table 4.2(a): Hardness parameters for pure ZTS

W=15		W=16	
A1	H _v (kg/mm ²)	A1	H _v (kg/mm ²)
0.01177	21.82	0.01059	19.63
0.02967	55.02	0.02882	53.44
0.0437	81.05	0.04319	80.09

The crack length is measured from the centre of indentation mark to the crack end. Here, the crack length (l) is the average of two crack lengths for each indentation. Resistance to fracture indicates the toughness of material [12].

Table 4.2(b): Hardness parameters for CCZTS crystals

W=15		W=16	
A1	H _v (kg/mm ²)	A1	H _v (kg/mm ²)
0.0088	16.39	0.00795	14.75
0.01833	33.99	0.01781	33.03
0.03046	56.48	0.03011	55.83

W=15		W=16	
A1	H _v (kg/mm ²)	A1	H _v (kg/mm ²)
0.01484	27.51	0.013364	24.78
0.03614	67.01	0.03510	65.08
0.05030	93.27	0.0497	92.16

x=1.0 mol% x=0.5 mol%

Table 4.3: The elastic stiffness constant for pure ZTS and CCZTS crystals

Load P (g)	H _v (kg/mm ²) for			C ₁₁ ×10 ¹⁴ Pa for		
	Pure ZTS	CCZTS (x=1.0 Mol%)	CCZTS (x=0.5 Mol%)	Pure ZTS	CCZTS (x=1.0 Mol%)	CCZTS (x=0.5 Mol%)
25	54.55	40.95	68.8	10.94	6.62	16.43
50	78.55	48.5	95.2	20.72	8.91	29.01
100	95.35	66.45	109	29.09	15.46	36.77

The calculation of the stiffness constant (C₁₁) reveals that the binding force between the ions is quite strong. [6]. The fracture mechanics of the indentation process gives an equilibrium relation for a well-developed crack extending under the centre loading condition

$$K_c = \frac{P}{\beta_0 l^{3/2}}, \quad l \geq \frac{d}{2}$$

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where β_0 is the indenter constant, equal to 7 for the Vicker's diamond pyramid indenter [13] and other symbols have their usual meanings. The B_i and K_c values are tabulated in Table (4.4) and (4.5). Brittleness is another property, which affects the mechanical behaviour of a material, and is expressed in terms of the brittleness index (B_i) as,

$$B_i = H_v / K_c$$

Table(4.4) Brittleness for various loads

Crystals	$B_i(10^4 \text{ m}^{-1/2})$		
	Load		
	25 (g)	50 (g)	100 (g)
Pure ZTS	8.50	8.39	7.12
CCZTS(x=1.0mol%)	8.75	7.49	6.16
CCZTS(x=0.5mol%)	10.09	9.39	7.87

Table (4.5): Crack length for various loads

Crystals	Crack length K_c ($10^4 \text{ kg m}^{-3/2}$) For		
	Load		
	25 (gm)	50 (gm)	100 (gm)
Pure ZTS	6.14	9.35	13.38
CCZTS(x=1.0 mol%)	4.67	6.47	10.77
CCZTS(x=0.5 mol%)	6.81	10.19	13.84

V. CONCLUSION

The Vicker's microhardness study was carried out on the grown pure and cadmium chloride doped ZTS (CCZTS) single crystals. The Vickers hardness numbers were calculated for the grown crystals, by the application of load and the hardness numbers were found to increase with an increase in the load, which confirms the reverse indentation size effects of the crystal. The value of the Mayer's index number is found, which proves that the grown crystals falls in the soft-material category, which shows that the mechanical strength is high so that it can be used for device fabrication. The calculation of the stiffness constant (C_{11}) reveals that the binding force between the ions is quite strong.

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