Vicker's Microhardness srudies of pure and Cd^{2+} doped ZTS single crystal

M.Sumithra Devi[a], K.Thamizharasan[b], s.Priya[c]
Department of Physics, AIHT, Chennai, India
Department of Physics, Sir Theagaraya college, Chennai, India.
Department of EEE, KLU, Srivilliputhu, india

Abstract: A semi organic crystals of pure and cd^{2+} doped zinc thiourea sulphate has been grown by slow evaporation solution growth technique. Lattice parameters of the grown crystal was confirmed by single X-ray diffraction analysis. Vicker's microhardness indentation tests were carried out with the load ranging 25 – 100 gm mechanical parameters liketoughness (K_c), brittleness index (B_i), Yield strength (σ_y) and stiffness constant (C_{11}) were calculated and reported.

Keywords: Solution growth, X-ray analysis, Vicker's microhardness.

1. Introduction

Semi organic crystals are widely used in device fabrication due to their melting point, high mechanical stability and chemical indenter[1]. The mechanical strength of the material plays an important role in the selecting that materials for device fabrication because it provides information about the structural breakdown under applied stress[2,3], glide, deformation, anisotropy, cracks, grain boundary, hardening state of dispersion of impurity and environment of dislocation mobility[4]. Cd^{2+} doped ZTS single crystal posses good mechanical properties and their second harmonic conversion is high compared to KDP [5]. Therefore attention has been focused to grow Cd^{2+} doped zinc thiourea sulphate crystals for NLO applications. Since the data about load induced Vicker's microhardness properties of as grown Cd^{2+} doped ZTS crystals doesnot exist in the literature for the first time we present our investigations and findings about the as grown Cd^{2+} doped ZTs crystals along with the crystal growth and X-ray analysis(ZTCDS).

2. Experimental

2.1. Growth technique

Analytical reagent (AR) grades Thiourea and Zinc sulphate in the molar ratio 3:1 were dissolved in triply ionized water and it was thoroughly mixed using a magnetic stirrer. To synthesize cadmium sulphate doped ZTS, 1 mol % cadmium sulphate (AR) grade was added to the solution of ZTS separately. The solution was stirred thoroughly to avoid precipitation. Finally Supersaturated Cd^{2+} doped ZTS solution was prepared and filtered solution was poured into petri dishes and kept for slow evaporation at room temperature to get crystalline salt. Optically good quality seed crystals were grown from the solution. Transparent Cd^{2+} doped ZTS crystals with well defined morphology were obtained by spontaneous crystallization.

Cd^{2+} crystals of size (10X4X4 mm^3) were obtained in the growth period of 15- 20 days. The grown Cd^{2+} doped ZTS crystal was shown in the Figure 1.

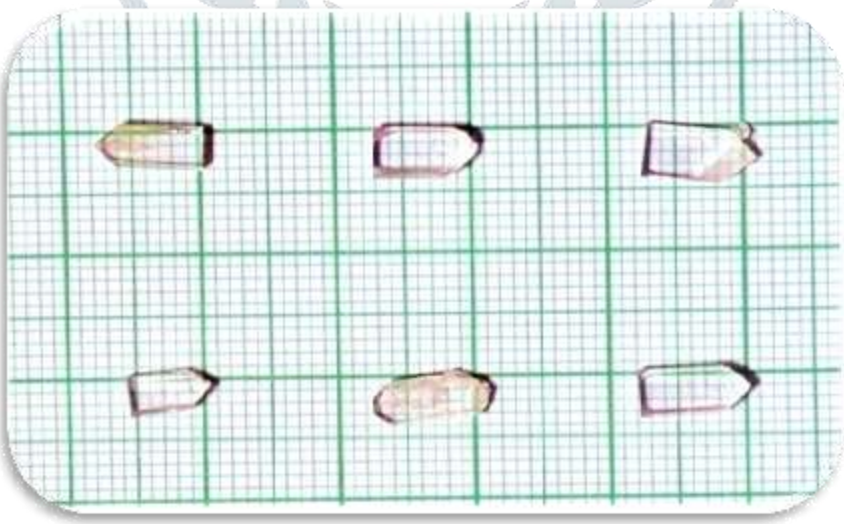


Figure 1. Photograph of As Grown Cd^{2+} Doped ZTS Single Crystal

2.2 Microindentation

High quality defect free surfaces of slow evaporation solution growth of pure and Cd^{2+} dopes ZTS crystal were subjected to static indentation lets at room temperature using Leitz Weltzlar Vicker's microhardness tester fitted with a vicker's diamond pyramidal indentor with microscope. Loads ranging from 25 to 100gm were used for indentation with static indentation time of 10s by keeping the indentor at right angle to the smooth surface of the crystals. At least four indentation were made for each load. The diagonal lengths wer recorded and average diagonal length were taken further calculations. The microhardness value can be calculated using the formula [6].

$$H_v = 1.8544 \times \frac{p}{d^2}\ Kg\text{-}mm^{-2} \quad (1)$$

Where, P is the applied load in Kg and d is the diagonal length of the indentation mark in mm.

3. Results and discussion

3.1 Single crystal X-ray diffraction analysis

Single crystal XRD analysis has been carried out to estimate the lattice parameters, the arrangement and the spacing of atoms in the crystalline material. The data has been collected using Enraf Nonius CAD-4 single crystal X-ray diffractrometer with MoKα (λ = 0.71073 Å) radiation. It were observed from the single crystal XRD data that the grown both crystals of pure and Mg^{2+} doped ZTS possesses orthorhombic crystal system with space group $Pca2_1$. The lattice parameters of pure ZTS is a = 7.78 Å, b = 11.124 Å and c = 15.491 Å, α=β=γ=90̊ and Cd^{2+} doped ZTS is a =7.71 Å, b = 11.250 Å and c = 15.652 Å, Å, α=β=γ=90̊. The volume of the crystal were pure 1341 $Å^3$ and Cd^{2+} doped ZTS 1350 $Å^3$. The single crystal XRD data confirmed that the as grown crystal were pure and Cd^{2+} doped ZTS [7-9].

3.2 Dependence on microhardness on load

Microhardness of the materials are classified as (a) independent of loas[10,11] (b) increase with load[12], (c) complex variation[13] and (d) decrease with load [14,15]. In order to studies the effect of load on pure and Cd2+ doped ZTS single crystals were subjected to theapplied load ranging 25g to 100g and corresponding Hv values were calculated. Figure2 shows the variation of Vicker's microhardness with applied loas (p). It is clear from figure that when the load increases the hardness also increases. Such type of increase in micro hardness with increase in load is known as ISE[16]. The relation between applied load and diagonal length d applied load d of the indentor is given by kick's law[17].

$$P = k_1 d^n \qquad (2)$$

Where n is mayer index

$$\log P = \log K1 + n \log d$$

According to Onitsch n should lies between 1 and 1.6 for hard materials and it should be more than 1.6 for soft materials [18]. Hence, it is concluded that both crystals are soft in nature.

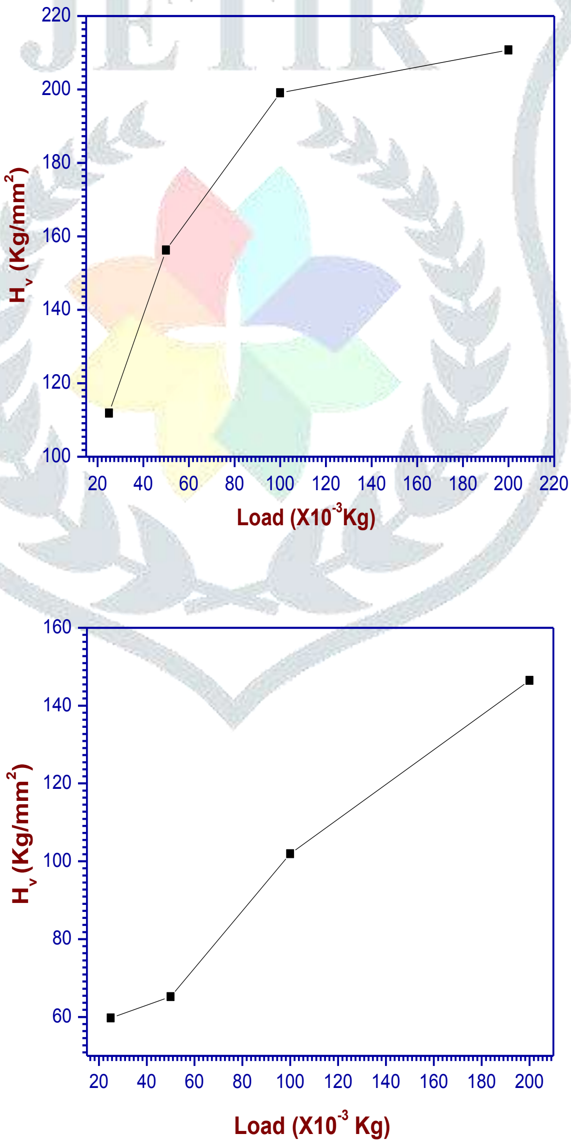
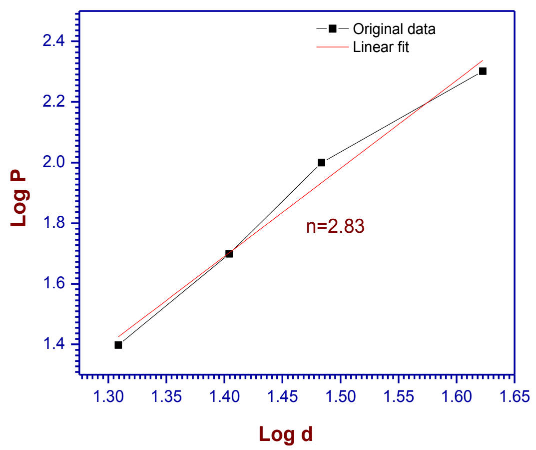


Fig 1. Variation of Vicker's Microhardness with load for pure Cd^{2+} doped ZTS single crystalZTS crystal



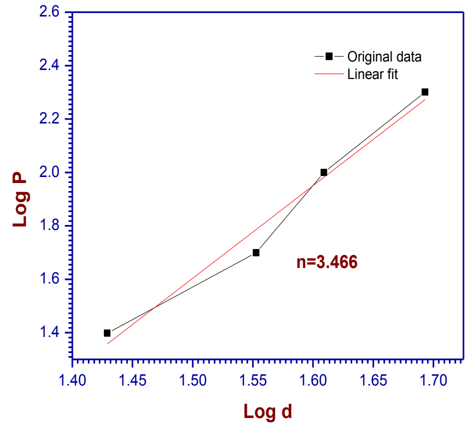


Fig 2. Plot of log f Vs. tanδ of pure and Cd^{2+} doped ZTS single crystal

3.3 Fracture mechanics

Fracture mechanics indicates the toughness of the material and how much stress is required to break the material[19] The fracture toughness of the material was given by the relation[20]

$$K_c = \frac{P}{\beta_0 (C)^{3/2}} \quad (3)$$

Where P is applied load in Kg, C is the crack length measured from the center of ther indentation mark to the end of the crack in micrometer and βo is constant and it is 7 for vicker's microhardness. This equation holds good only for the cracks due to an elastic stress indentation[21]. Pure and Cd^{2+} doped ZTS crystals of K_c values increased for pure 0.197 to 0.297 and Cd^{2+} doped ZTS 0.06 to 0.226.

3.4 Brittleness index

The important property which affect the mechanical behavior of the material is brittleness index[21]. It gives the information about the fracture indeuced in the material under deformation conmdition. The value of brittleness index Can be calculated by the formula [22,23]

$$B_i = \frac{H_v}{K_c} \quad (4)$$

The brittleness insex for pure and Cd^{2+} doped ZTS crystals are calculated and found to vary from pure 10.17 to 7.08 and Cd^{2+} doped ZTS 24.71 to 60.56 ($10^3 mm^{-1/2}$)

The yield strength of the material can be calculated from the hardness value [24]. If Mayer's index n>2

$$\sigma_v = \frac{H_v}{2.9}[1-(2-n)]\left[\frac{12.5(2-n)}{1-(2-n)}\right]^{2-n} \quad (5)$$

The value of yield strength σ_v for pure and doped Cd^{2+} doped crystals varies from pure 200.6 to 77.8 and Cd^{2+} doped 2471 to 6056 Kg/mm^2.
Elastic stiffness constant (**C_{11}**) can be calculated using the relation [20]

$$C_{11} = (H_v)^{\frac{7}{4}} \quad (6)$$

Higher stiffness constant indicates the tightness of the bonding between the neighbouring atoms[21,22]. The value of stiffness constant for pure 3849 to 11655 and Cd^{2+} doped ZTS crystal is 1284.5 to 6166.4.Hence, it is concluded that both crystals are soft in nature.The Yield strength of the material (σ_v), Elastic stiffness constant (C_{11}), Fracture mechanics (K_c), and Brittleness index (B_i) were calculated from hardness value and presented in Table 1 and 2 for pure and Cd^{2+} doped ZTS single crystal.

Table 1 Michrohardness Parameters of pure ZTS crystal

Load $X10^{-3}$Kg	H_v Kg/mm^2	C_{11}	K_c ($Kg/mm^{3/2)}$)	B_i ($mm^{-1/2}$)	σ_v Kg/mm^2
25	111.89	3849	0.10999	10.172	200.63
50	156.284	6970	0.16805	9.299	280.24
100	199.08	10551	0.24038	8.282	356.98
200	210.732	11655	0.29739	7.086	377.88

Table 2 Michrohardness Parameters of Cd^{2+} doped ZTS crystal

Load $X10^{-3}$Kg	H_v Kg/mm^2	C_{11}	K_c ($Kg/mm^{3/2)}$)	B_i ($mm^{-1/2}$)	σ_v Kg/m m^2
25	59.76276	1284.5 58	0.0687 23	24.711 36	2471.1 36

50	65.21921	1496.7 77	0.0872 61	26.967 55	2696.7 55
10 0	101.9353	3270.1 53	0.1450 57	42.149 33	4214.9 33
20 0	146.4653	6166.4 62	0.2266 383	60.562 1	6056.2 1

Conclusion

A semi-organic crystal, pure and Mg^{2+} doped ZTS were grown successfully by slow evaporation solution growth technique. Single crystal X-ray diffraction study that the grown crystal belongs to orthorhombic crystal system. The variation of H_v increases with increase in loads. Vicker's microhardness measurements reveals that both crystals are soft in nature and shows reverse indentation size effect. Various mechanical parameters were calculated and tabulated. Tightness of molecule binding was found from elastic modular and confirms the as grown crystals in a good candidate for non linear optical device fabrications.

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