Investigation Of The Effect Of Cd^{2+} Doping On The Mechanical Properties Of Tetrakis(Thiourea) Barium Chloride Nonlinear Optical Crystal

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Abstract : From aqueous solution, by slow solvent evaporation technique, good quality single crystals of cadmium chloride doped tetrakis(thiourea) barium chloride (CTTBC) have been grown and successfully harvested. In an effort to shed light on the mechanical behaviour of the title crystal and to assess its mechanical strength, Vickers micro hardness study has been performed. The hardness study has been done on the crack free crystal surface using loads of 25 to 100 g in steps of 25 g increment and the indentation time of 8 s has been used in all trials. The hardness measurements have suggested a reverse indentation size effect (RISE) pattern of the CTTBC crystal where hardness number has been found to be linearly increasing with the applied load. As an extension of this study, the RISE pattern has been validated by making used of the theoretical models proposed by Meyer and Hays – Kendall. In addition, the mechanical robustness of the crystal has been authenticated by deducing the appropriate mechanical parameters such as elastic modulus, fracture toughness, yield strength, brittleness constant, corrected hardness and elastic stiffness constant.

IndexTerms - **Vicker's micro hardness; RISE; Meyer's law; mechanical parameters**

1. Introduction

The applications of non linear optical (NLO) materials in the fields of optical data storage, optical signal processing, switching and frequency generation, image storage and optical communication have been proved undoubtedly (Sumithradevi et al 2014, Zhou et al 2002). In a special reference to the semi- organic NLO materials, thiourea metal complexes, complexes of thiourea, both in their pure and doped forms, have gained a remarkable attention from the researchers in the crystal growth field owing to the fact that they can be efficiently employed as the better alternatives for potassium dihydrogen phosphate (KDP) crystals in optoelectronics, optical modulators, photonics, optical parametric oscillator devices , laser fusion experiments and frequency doubling process (Lopes et al 2004, Mohd Anis et al 2016, Perumal and Moorthybabu 2007). It has also been reported that the metal complexes of thiourea have exhibited distinct low values of UV cut-off wavelength, good crystallinity, high thermal stability and better second harmonic generation properties (Venkataramanan et al 1997, Mercy et al 1992, Vijayan et al 2004, Mohankumar et al 2005).Thiourea is essentially a centro-symmetric molecule. But it is noteworthy that when metal ions are co-ordinated with the centrosymmetric thiourea, the nature of centrosymmetry vanishes and the complex becomes non-centro symmteric, which is a salient prerequisite of a NLO crystal. Furthermore, thiourea has been strongly recommended as a model organic material with large dipole moment and found to be capable of forming metal – ligand through wide and strong hydrogen bonding network (Shahil Kirupavathy et al 2007).

In this context, tris thiourea zinc sulphate, bis-thiourea strontium chloride ,tertrakis thiourea nickel chloride , bis thiourea lead chloride , tris thiourea zinc selenate , tetrakis(thiourea) palladium chloride and bis thiourea antimony tribromide (Bhaskaran et al 2007, Rajagopalan et al 2016, Muthu et al 2015, Rajagopalan et al 2017) crystals have been synthesized and found to have appreciable mechanical strength and favourable NLO properties. Doping studies have been carried out on the thiourea complexes using alkali, alkaline earth metal and transition metals (Muthu et al 2013, Kanagasabapathy et al 2013). In this direction, this study investigates about the effect of cadmium doping on the mechanical parameters of tetrakis(thiourea) barium chloride (TTBC).

2. Experimental

Tetrakis(thiourea) barium chloride (TTBC) has been synthesised by reacting the thiourea with barium chloride, in a stoichiometric ratio of 4:1. To overcome the problem of co-precipitation of multiple phases, a constant stirring of the reactant mixture has been adopted by employing a motorized magnetic stirrer. The stirring has been carried out for 4 h. For the process of crystal growth, slow solvent evaporation technique has been practiced. During the crystallization process, doping of 10 mol% cadmium in the form of cadmium chloride was done. In this manner, Cadmium doped TTBC crystals have been harvested after a time span of 35 days. To examine the mechanical properties of the crystal and to verify the suitability of the material for devices, Vickers micro hardness tests have been carried out. The grown crystals have been tested for their micro hardness property using Shimadzu HMV Vicker's tester fitted with a diamond indenter. The crystal which was free from defects with a flat and smooth surface has been mounted carefully on the base of the microscope. Then the sample crystal has been indented gently by the loads between 25 to 100 g, in steps of 25 g, using Vickers diamond pyramid indenter. The dwell period has been constantly maintained as 8 s. The Vickers indented impressions have been found to be nearly square in shape. The length of the two diagonals has been measured by a calibrated micrometer attached to the eye-piece of the microscope and their average has been calculated. For a particular load four well defined indentations have been carried out and the average of all the diagonals has been taken for further calculations.

3. Results and Discussion

3.1 Finding the hardness number (Hv)

The resistance shown by a crystal towards any deformation, structural damages and lattice destruction can be regarded as its hardness. It is possible to relate the hardness of a crystal with its molecular binding, yield strength and elastic constants. It also carried certain vital information about the pattern in which the atoms are packed and describes the factors that are operating to make the structure stable (Subadhra et al 2000). For an applied load of P and the indentation length of d, the hardness number, Hv has been deduced by the expression,

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

When a graph has been plotted between the H_v values and the respective loads, as given in Fig. 1, it has been noted that the H_v values are increased with increasing applied load. This trend is in accordance with Reverse Indentation Size effect (RISE) (Gupta et al 2011).

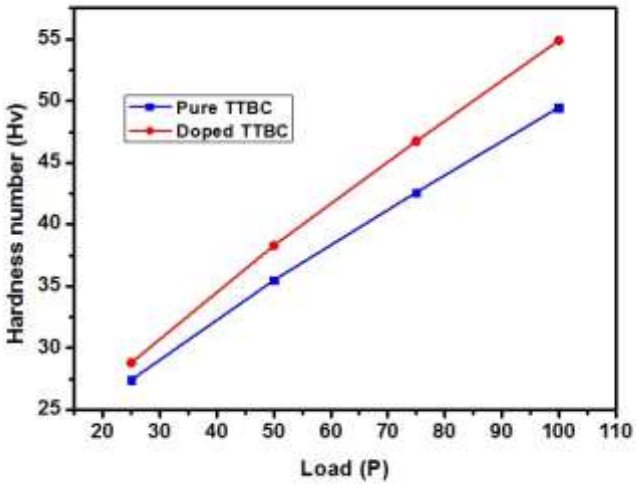

Fig. 1 Plot of hardness Vs load

The calculated H_v values for various applied loads have been tabulated in Table -1 for pure TTBC and in Table -2 for cadmium doped TTBC. It has been noted from the Tables 1 & 2 and from the Fig.1 that for all the cases of applied load, the cadmium doped TTBC crystal has found to exhibit higher hardness values than that of the pure TTBC.

3.2 Verification of RISE pattern by Meyer's rule

As per the Meyer's rule, the materials having the Meyer's index value (or) Meyer's work hardening co-efficient (n) between 1 and 1.6 are considered as hard material category. Meyer law suggested that the materials which are showing the n value greater than 1.6 will follow RISE pattern.The Meyer's index can be calculated by following equation:

$$\log P = \log k_1 + n \log d \quad \text{---(2)}$$

Where P is the load, d is the diagonal crack length and k_1 is the load independent constant.

The equation (2) is in the form of a straight line equation. So, when a graph is plotted between log P Vs log d (Fig. 2 for pure TTBC and Fig. 3 for doped TTBC) and after subjecting it to linear fitting, their slope value gives the value of Meyer's index while the intercept gives the value of the constant k_1. From the graphs, the value of n for pure TTBC has been found to be 3.44 and for doped TTBC it is 3.69.

As per Onitsch rule if the Meyer's index (n) value for a material is greater than 1 but less than 1.6 , it can be considered to be falling in hard material category whereas the materials whose Meyer's index value higher than 1.6 will be grouped under soft material category.

As these values are greater than 2, it can be concluded that both the pure and doped TTBC crystals belong to soft material category and follow RISE pattern.

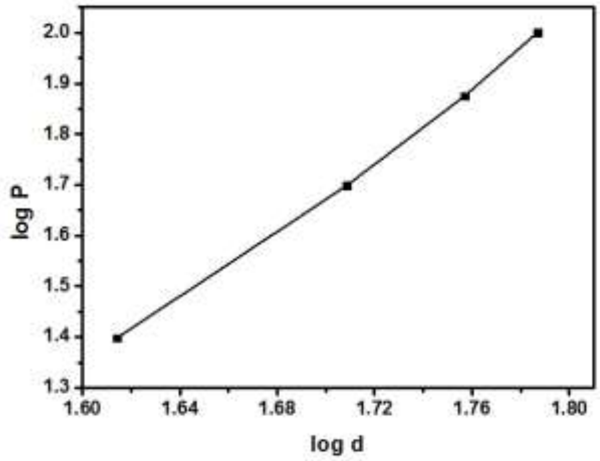

Fig. 2 Plot of log P Vs log d for pure TTBC

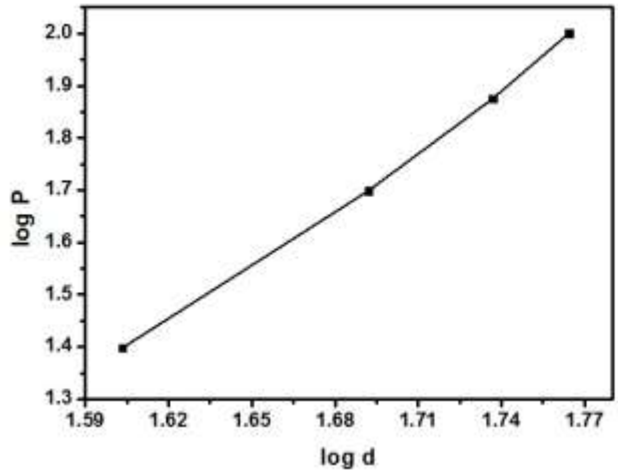

Fig. 3 Plot of log P Vs log d for cadmium doped TTBC

3.3 Verification of RISE pattern by Hays-Kendall rule

Hays and Kendall, through their theory of resistance pressure, defined the resistance pressure as a minimum level of indentation load (W) below which there is no plastic deformation occurs. They also found out that the negative value of minimum level of indentation load (or) Newtonian resultant pressure (W) will be suggesting a possibility of RISE pattern (Gupta et al 2005). As per the theory, the relationship between load (P), Newtonian resultant pressure (W) and the indentation crack length (d) is given by the expression,

$$P = W + k_2 d^2 \qquad \text{---(3)}$$

Where k_2 is load dependent constant. When a plot is drawn between P and d^2 (as given in Fig. 4 and 5 for pure and doped TTBC respectively) and the resultant lines are subjected to linear fitting technique, their intercept will be giving the value of Newtonian pressure and the slope will result in the value of k_2 . Hays-Kendall also suggested that the negative intercept of the plot is an indication of RISE pattern. From the Fig.4 and Fig.5, which resulted in negative intercepts, the feasibility of RISE pattern in the pure and doped TTBC crystal has been authenticated.

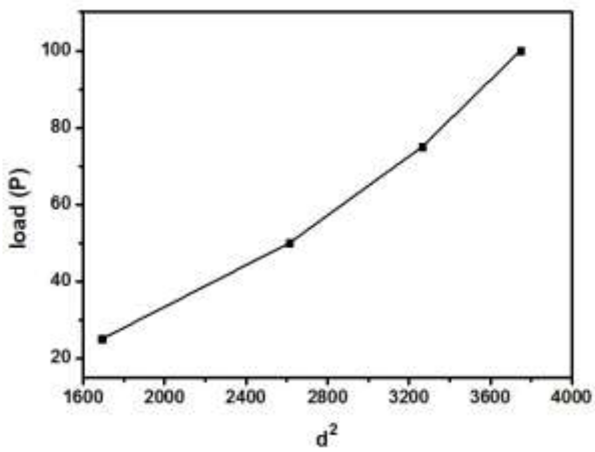

Fig. 4 Plot of load Vs d^2 for pure TTBC

From the Fig. 4, the Newtonian pressure value for pure TTBC has been found to be

39.03 g whereas the Fig. 5 indicated that the doped TTBC exhibited a value of 45.59 g of Newtonian pressure. The load dependent constants k_2 have been calculated as 0.03589 and 0.04164 for pure and doped TTBC crystals respectively.

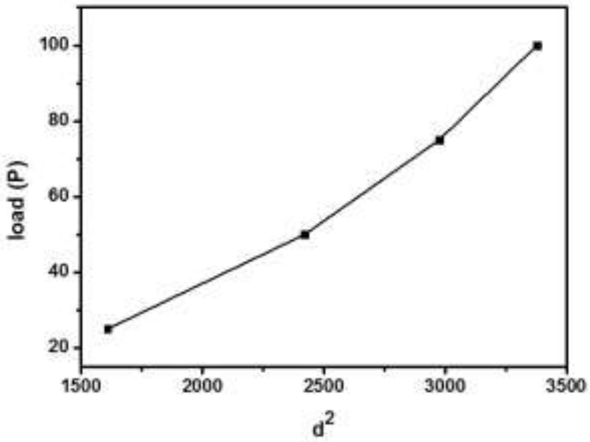

Fig. 5 Plot of load Vs d^2 for cadmium doped TTBC

3.4 Determination of important mechanical parameters

Estimation of various significant mechanical parameters to estimate the mechanical stability of the sample crystal has been done through a series of inter-related formulae (Lawn and Fuller, 1975) which are explained as follows:

The k_2 value determined in the last step is used to calculate the corrected hardness (H_o) value from the equation,

$H_o = 1854\ k_2$

The corrected hardness values have been computed as 66.54006 and 77.20056 for pure and doped crystals respectively.

Wooster formula is used to find out the elastic stiffness constant (C_{11}) of the material. It states that,

$$C_{11} = (H_v)^{7/4} \quad \text{--- (4)}$$

The rigidity and the tightness of inter-atomic crystalline bonding have been visualized by the trend of increasing elastic stiffness value with increasing load (Table -1).

The hardness number values are also used to deduce the yield strengths (Vesta et al 2007) by the formula,

$$\sigma_V = \{H_V / 2.9\} \times \{(1 – (n\text{-}2)] \times [12.5\ (n\text{-}2) / 1\text{-}(n\text{-}2)]^{\ n-2}\} \quad \text{--- (5)}$$

The Moh's hardness number is calculated from the values of Vicker's hardness number by the following equation

$$H_M = 0.675 \times (H_v)^{1/3} \quad \text{--- (6)}$$

The materials whose Moh's number (H_M) is less than 4 are known as soft materials. The calculated values also supported the soft material nature of pure and doped TTBC crystals.

The elastic modulus is derived from the formula,

$$E = 81.9635\ \sigma_V \quad \text{--- (7)}$$

The fracture toughness for a crystal is given by

$$K_C = [(1/7)\ \times P \times (d/2)] / (c\text{-}a)^{1/2} \quad \text{--- (8)}$$

Where c is the crack length in micrometer. Once, the fracture toughenss is calculated, it can be related to yet another mechanical parameter Brittleness index (B_i) as,

$$B_i = H_V / K_C \quad \text{--- (9)}$$

The calculated mechanical parameters for pure TTBC and cadmium doped TTBC have been tabulated in Table -1 and Table – 2 respectively. The optimal values of mechanical parameters of the title crystals have attested the suitability of the materials for constructive device applications. On comparing the tables, it is inferred that the doping of cadmium to TTBC crystals has increased the mechanical parameter values of the parent crystal.

Table -1

Mechanical parameters of pure TTBC

Load, P (gm)	Hardness number, H_v (Kg/mm^2)	Elastic stiffness constant, C_{11} (GPa)	Yield strength σ_V (Gpa)	Fracture toughness (K_C) ($g/\mu m^{1/2}$)	Brittleness index (B_i) ($10^3\ \mu m^{-1/2}$)	Elastic Modulus (E)	Moh's hardness number (H_M)
25	27.41	3.22	0.85	11.06	2.47	70.00	2.01
50	35.48	5.05	1.11	15.21	2.33	90.59	2.19
75	42.59	6.96	1.32	22.03	1.93	108.76	2.33
100	49.48	9.04	1.54	28.29	1.75	126.33	2.45

Table -2
Mechanical parameters of Cadmium doped TTBC

Load, P (gm)	Hardness number, H_v (Kg/mm^2)	Elastic stiffness constant, C_{11} (GPa)	Yield strength σ_V (Gpa)	Fracture toughness (K_C) (g/µm$^{1/2}$)	Brittleness index (B_i) (10^3 µm$^{-1/2}$)	Elastic Modulus (E)	Moh's hardness number (H_M)
5	28.80	3.51	2.18	11.47	2.51	178.70	2.05
50	38.29	5.78	2.89	18.58	2.06	237.57	2.25
75	46.74	8.19	3.53	22.92	2.03	290.00	2.40
100	54.89	10.85	4.16	28.38	1.93	340.63	2.53

4. Conclusion

By employing slow solvent evaporation method, single crystals of pure and Cd^{2+} doped tetrakis(thiourea) barium chloride (TTBC) have been grown at room temperature. The micro hardness studies revealed the existence of RISE pattern for both the crystals. The Meyer's index value of 3.44 (for pure) and 3.69 (for doped) suggested that the crystals belong to soft material category. The values have also supported the possibility of RISE pattern. The Hays-Kendall theory inferred that the minimum load need to initiate the plastic deformation in the surface (W) was 39.03g for pure and 45.59 g for doped TTBC crystals. In the process of computing the mechanical parameters for the crystals such as hardness number, elastic stiffness constant, yield strength and elastic modulus, higher values have been obtained for the doped crystals than the parent crystals. At the same time, the cadmium doping has also decreased the brittleness index of the pure TTBC which in turn further attested the enhanced mechanical stability of the crystal. Based on the observations, it is possible for us to arrive at the conclusion that the mechanical strength of the pure TTBC crystal has been considerably increased upon cadmium doping. Hence, in view of mechanical strength aspect, it can be concluded that cadmium doped TTBC crystal can be considered as an effective material to be utilized in device fabrication.

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