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Study of growth condition and characterization of Monothiourea-Cadmium Sulphate Dihydrate single crystals in silica gel

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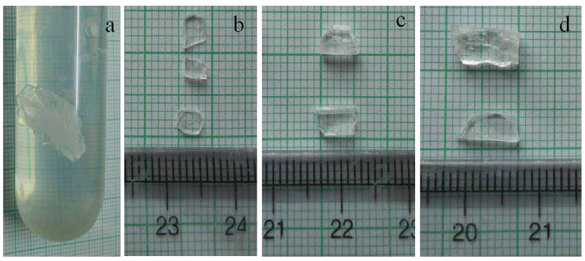
HIGHLIGHTS

- The single crystal was grown by gel growth method.
- The crystal has high transparency from 250 to 1100 nm.
- High stiffness constant indicates strong binding forces between ions.
- Low dielectric constant and dielectric loss at high frequencies.

GRAPHICAL ABSTRACT



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ABSTRACT

Single crystals of Monothiourea-Cadmium Sulphate Dihydrate belonging to Semiorganic material with nonlinear optical properties have been grown in silica gel medium using gel technique. The grown crystals were subjected to single crystal X-ray diffraction (SXRD) and Fourier transform infrared spectroscopy to elucidate their lattice parameters and functional group confirmation. Vickers microhardness measurements reveal that these materials have reverse indentation size effect and belong to the category of soft materials. Further, mechanical characterizations are also asserted from yield strength and elastic stiffness studies. The dielectric studies at different temperatures and frequency applied are measured and their behavior is analyzed. Thermal behavior of the crystal was investigated by thermogravimetric analysis (TGA) and differential thermal analysis.

1. Introduction

In the past three decades, numerous research activities have been in progress on nonlinear optical (NLO) crystals, as they play a key role in frequency conversion, optical image processing and optical communication [1–3]. NLO crystals for visible and ultraviolet (UV) region are of great significance for laser processing and laser spectroscopy [4–9].

The Thiourea molecules are interesting not only due to the structural chemistry but also because of the possibility of formation of organometallic coordination complexes which results in enhanced NLO activity [10,11]. Metal–thiourea coordination compounds have the advantage of both organic and inorganic properties. In the metal thiourea, the small π electron enhances the NLO properties [12]. Thiourea molecule is an attracting inorganic matrix modifier, as it has the potential to form a network of hydrogen bond which is due to the high dipole moment [13,14]. In

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the organometallic complex, the metal part belonging to the group (IIB) (Zn, Hg and Cd) is considered because of their closed d^{10} shell which is responsible for high transparency in the UV region. The physic-chemical behavior and structural analysis of the metal organic materials have also led to the conclusion that the central metal cannot be ignored in calculating the NLO coefficients [15–19]. The capability of Thiourea to form metal complexes through sulphur bonding has been reported [20–25]. Recent investigational reports on metal complexes of thiourea are Thiourea Zinc Chloride (ZTC), Zinc (tris) Thiourea Sulfate (ZTS), Cadmium Thiourea Acetate (CTA), BisThiourea Cadmium Chloride (BTCC), Thiourea Cadmium Iodide, Cadmium Thiourea Sulphate, and TrisThiourea Cadmium Sulfate (TTCS) [26–30]. These complexes are found to exhibit better nonlinear optical properties than potassium dihydrogen phosphate (KDP) [31–33].

Gel growth technique is an alternative technique to solution growth with controlled diffusion, and the growth process is free from convection. The growth of single crystals in gel medium is self-purifying processes, free from thermal strains which is common in crystals grown from melt [34]. Crystals grown by gel technique are superior to those grown by slow evaporation technique and found to have extreme low dislocation densities [35]. The genesis of the compound chosen for research has been crystallized and reported by Cavalca et al. [36].

In the present work, Monothiourea-Cadmium Sulphate Dihydrate crystals were grown by gel technique at room temperature and were characterized through several techniques such as single crystal XRD, spectral, thermal and dielectric measurements.

2. Experimental details

2.1. Synthesis and crystal growth

Single crystals of Monothiourea-Cadmium Sulphate Dihydrate were grown inside silica gel medium, in test tubes by single diffusion method. The stock solution was prepared based on the report given by Henisch [35]. The reaction between cadmium sulphate octahydrate and thiourea is given as

$$CdSO_4 \cdot 8H_2O + CS(NH_2)_2 \rightarrow Cd[CS(NH_2)_2]SO_4 \cdot 2H_2O + 6H_2O \quad (1)$$

To 10 ml of the stock solution (specific gravity 1.03 g/cc) a small quantity of glacial acetic acid was added and the pH was adjusted to 5.5. To this, 25 ml of 2 M thiourea was added and stirred continuously for 4 h using a magnetic stirrer. Then the solution was poured into the test tubes and placed inside constant temperature (40 °C) bath for gellation. After the gel formation, an aqueous solution of 25 ml of 2 M cadmium sulphate octahydrate was pipetted out along the side of the tube. Monothiourea-Cadmium Sulphate Dihydrate crystals of 8 mm length were obtained in 15 days. The experiment was also carried out at different pH (Table 1). The gellation time taken was found to be inversely dependent on the pH. Due to this, the mixing of solution (stock solution with acetic acid) with the inner solution was difficult (aqueous solution of thiourea) for pH greater than 5.5. Besides the above said, Monothiourea-Cadmium Sulphate Dihydrate nuclei was found to decrease as the pH increased. The optimum pH yielding maximum size of transparent title crystal was found to be at 5.5 pH. Photographs, of Monothiourea-Cadmium Sulphate Dihydrate crystal in the gel medium and at different pH are shown in Fig. 1 (a–d) respectively. The size of the crystal increases with the increase in pH as shown in Fig. 1 (b–d). The increase in size of the crystal could be explained due to variation in the gel structure (i.e. by establishing three-dimensional cross-linkages between the molecules). Mover over gel consists of sheet like structure of varying degree of surface roughness and porosity, forming inter-connected cells. The cell walls are thicker for dense cells. The structure of gel depends on the pH during gelation [37] i.e. the pH is below 4, cross-linkage between the polymerization chains is produced and when the pH of the gel is above 4.5 long chain polymerization is produced. Thus it results in the structural change from a box-like network of loosely bound platelets structure with lack of cross linkages which attribute to the increase in crystal size.

2.2. Characterization

The grown crystals of Monothiourea-Cadmium Sulphate Dihydrate was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 diffractometer to elucidate their lattice parameters. The powder X-ray diffraction analysis (XRD) on the Monothiourea-Cadmium Sulphate Dihydrate crystal was also carried out using Brucker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å) over the range 10–60° at a scan rate of 0.02° s^{-1}. The FTIR spectra of title crystals were recorded in the range of 4000–400 cm^{-1} employing a Perkin Elmer spectrometer by KBr pellet method in order to reveal the metal complex coordination. The optical properties of the title crystal were examined between 190 and 1100 nm using Shimadzu UV-1061 UV–vis spectrophotometer. The thermal stability was ascertained from thermogravimetric analysis and differential thermal analysis carried out on the sample using NETZSCH STA 409PC/PG thermal analyzer at a heating rate of 10 °C min^{-1} in nitrogen atmosphere.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The Single crystal X-ray diffraction results reveal that the crystal belongs to the orthorhombic system with space group Pbca. The lattice parameters was determined to be a = 7.783 Å, b = 13.461 Å, c = 15.966 Å, α = γ = β = 90° and its cell volume V = 1692.49 $Å^3$. These results are found to be in good agreement with that of the reported values [36,38].

3.2. Powder X-ray diffraction analysis

Powder X-ray diffraction (PXRD) pattern of the grown crystal is shown in Fig. 2. From the PXRD pattern, we confirm that the grown crystal has high degree of crystallinity which is revealed by the sharp and high-intensity peaks. The peaks were indexed using Powder X software [39] and the indexed peaks were found to match with the JCPDS data [71-2183]. Further, to confirm the

Table 1
Growth parameters of Monothiourea-Cadmium Sulphate Dihydrate.

Density	Inner reagent	pH	Outer reagent	Crystal size	Growth period
1.03	10 ml of stock solution + acetic acid+25 ml of 2 M Thiourea	3.5	25 ml of 2 M cadmium Sulphate (Hydrate)	Crystal of size 2 mm	27 days
1.03	10 ml of stock solution + acetic acid+25 ml of 2 M Thiourea	4.5	25 ml of 2 M cadmium Sulphate (Hydrate)	crystals of size 4–6 mm	21days
1.03	10 ml of stock solution + acetic acid+25 ml of 2 M Thiourea	5.5	25 ml of 2 M cadmium Sulphate (Hydrate)	crystal of size 8–10 mm	15 days

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