

Elucidation of structural and Optical Studies on mixed metal coordination complexes of ligand Crystal; A potential Material for Opto-Electronic device Fabrication .

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Abstract:

A new inorganic good optical material $\text{CdNa}_2 \cdot 2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was synthesized and characterized by single crystal X-Ray diffraction method. Monoclinic structure of the cadmium sodium oxalate hydrate crystal (CSO) was confirmed by the Single Crystal XRD patterns. Absorption spectra showed the low UV cutoff of wavelength at 224.64 nm and found the better transmittance in the entire visible region enabling the suitability of as grown crystal for Electronic and opto-electronic device fabrication material.

Keywords: Crystal growth; crystal structure; optical material.

1. Introduction

Metal oxalates with monoclinic cells and well defined oxalate anions surrounded by metallic cations form a group of compounds which are useful to create new semiconducting materials for nanopowder technology undergoing thermal decomposition process. Oxalate as a bidentate ligand has been of great interest in coordination chemistry for many years because of its analytical, catalytic and biomedical applications [1-3]. Many bis(oxalato)diaqua compounds of iron(III) and iron(II), chromium(III), indium(III), or manganese(III) have been reported [4-6]. Cadmium oxalate crystals grown from gel technique have been investigated by X-ray methods from which lattice constants and space group were determined [7]. Since in these cadmium oxalate crystals Na^+ are present in a very small proportion (0.2% of the total volume), these impurities are expected to affect the structural properties of as grown crystal in general is exhibited monoclinic structure with two water molecules system instead of the reported triclinic structure of pure cadmium oxalate crystal [8]. Present study is mainly focused the structural, spectral and mechanical properties of the newly synthesized cadmium sodium oxalate dehydrate crystal plays a key role to fabricate new optoelectronic materials.

2. Experimental

2.1. Synthesis of $\text{Na}_2[\text{Cd}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$

All substrate compounds are commercially available and were purchased from Sigma-Aldrich. The complex was prepared according to a modified procedure [9]. Cadmium (II) chloride hexahydrate (4.0 g, 16 mmol) was dissolved in 15 mL of distilled water (A). The mixture was stirred at 40°C for about 30 minutes. 0.5 g of activated charcoal was added to a solution of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, 6g, 32 mmol) in 10 mL of warm water (B). The solutions (A) and (B) were mixed together and air was bubbled through the mixture for 16 hours. The activated charcoal was removed and the red-purple filtrate was evaporated under an air stream on a steam bath to a volume of 10 mL. The solution was cooled on ice. The colourless crystals of $\text{Na}_2[\text{Cd}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$ (1.8 g) were collected.

3. Results and Discussion

3.1 Single crystal XRD

Single crystal X-ray diffraction analysis was done for the determination of unit cell parameters, crystal system and space group using single crystal diffractometer with its main parts of (i) D8 X-ray generator, (ii) Goniometer (Kappa cradle), (iii) Detector and (iv) Cryoflex (Model Tr-60). The Refinement method Full-matrix least-squares on F^2 adopted is used for the crystal structure solution of the title compound. The calculated values of lattice parameters were $a=12.8566 \text{ \AA}$, $b=11.4338 \text{ \AA}$, $c=14.1144 \text{ \AA}$, $\alpha=90^\circ$, $\beta=113.072^\circ$, $\gamma=90^\circ$ and $V=1908.86(\text{ \AA}^3)$. Calculated a, b and c values showed the structure of the crystal belongs to monoclinic system with space group $p2_1/n$. Coordination environment of the complex with atom numbering scheme is shown in Fig.1. The central Ca atom is surrounded by six oxygen atoms symmetrically. Two coordinated oxalate oxygen atoms O (2) are from bidentate chelating oxalate ring and two from the water molecules is shown in Fig.2.

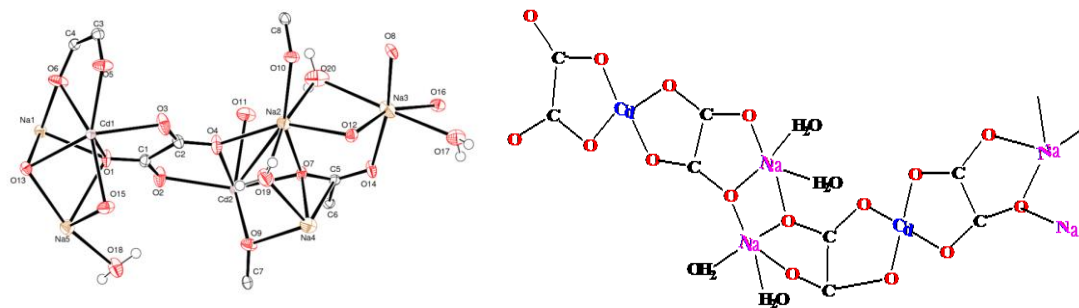


Fig.1. Molecular structure of CSO Crystal. **Fig.2.** polymeric representation of CSO crystal.

For chelating bidentate carboxyl oxygen Cd-O and Na-O distances in the range 2.3075(3)-2.4516(3) Å and Na-O-Cd-O angles in the range 179.22°-173.19° [(Na-O-Cd-O)_{av} = 176.20°] revealed the as grown crystal belongs to monoclinic and the structural refinement parameters of CSO crystals are given in **table.1**. Four oxygen atoms designated as O (5), O (6), O (13), and O(15) are coordinated to Cd corresponds to tetradentate edge of oxalate group. In the same way each Na atom is coordinated to six oxygen atoms represented O(6), O(16), O(12), O(14), O(17) and O(20) symmetrically. Each oxalate group is coordinated to two independent Cd (1), Cd (2) and Na (2), Na (3) atoms form two six membered chelate rings sharing a common edge C(1)-C(2) and C(5)-C(6). This shows that the chelating oxalate ligand is bonding in an asymmetric manner. The O-C-O angle of carboxyl group of oxalate ligand namely O(1)-C(1)-C(2)-O(4) is 177.84° greater than the 120° expected for a sp² hybridized RCO₂⁻ moiety. The distance of chelating tetra dentate carboxyl oxygen Cd (1)-O (5) and Na (3)-O (14) are 2.3075 Å and 2.3556 Å. Intermolecular hydrogen bonds O(1)...O(2), O(1)...O(3), O(8)...O(15) are stabilized the crystal structure by forming them between the water molecules and oxygen atoms of oxalate group. This results are moderately agreed with the previously reported results [10].

Table.1. structural parameters of CSO crystal

Compound name	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/mm ³	Z	Size/mm ³
Na ₄ Cd ₂ ·(C ₂ O ₄) ₄ ·8H ₂ O	12.83	11.43	14.11	90	113.0	90	1908.8	8	0.30x0.25x0.20

3.2. UV Absorption spectrum.

UV-Vis transmission spectrum of CSO crystal sample was recorded in the range of 190-1100nm using a polished crystal sample of 2mm thickness.

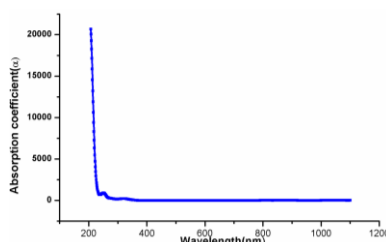
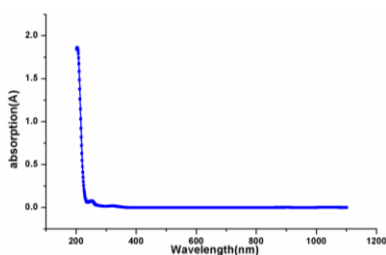


Fig.3. plot of absorption (A) Vs. wavelength **Fig.4.** plot of absorption coefficient (α) Vs. wavelength

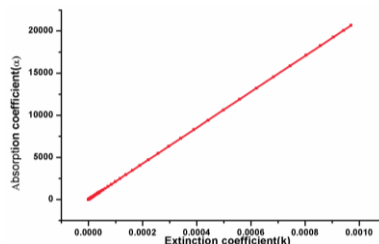
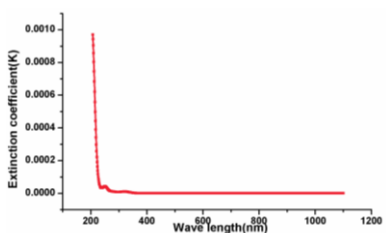


Fig.5.plot of Extinction coefficient(K) Vs.Wavelength Fig.7.plot of α Vs.K

Table.4.optical parameters of CSO crystals.

Wavelength(nm)	Energy gap(eV)	Reflectance(R)	Refractive index(n)	Optical conductivity(σ)	Electrical susceptibility(χ)
250	4.96	0.163	2.35	2.25E+11	3.36

Optical studies on pure cadmium oxalate crystals were exhibited both direct and indirect transitions to the band gap energy values: E_g (direct) = 4.4eV and E_g (indirect) = 4.2 eV under an absorption edge between 270-280nm in the spectral range of 180-500nm has already been reported [11]. The recorded optical spectrum of the title compound is found to be active in the UV region having a significant absorption in the lowest cut off wavelength of 250.97nm is shown in Fig.3. In the high photon energy region, the energy dependence of absorption coefficient

$$\alpha = \frac{2.303}{t} \log \left(\frac{1}{A} \right) \tag{1}$$

where A is the Absorbance and t is the thickness of the crystal sample. Absorption coefficient α suggests the occurrence of direct band gap of the crystal obeying the following equation for high photon energies (h ν) [12]

$$(\alpha h\nu)^2 = A(E_g - h\nu) \tag{2}$$

Where α is the absorption coefficient, h is the Plank’s constant, A is a constant is the frequency of the incident photon and E_g is the optical band gap. The optical band gap energy value to be **4.9eV** at the lowest absorption cutoff wavelength at **250.97nm** and this wide band gap of CSO crystal confirms the opto-electronic activity of as grown crystal in the opto electronic industries. The absorbance spectrum shows a sharp increase in absorption at wavelength near to the absorption edge of the threshold wavelength for onset of absorption, the energy corresponding to this determines the band gap of the semiconductor material. The CSO crystal shows absorption coefficient (α) of about $4.04 \times 10^{-6} m^{-1}$ near the absorption edge of wavelength 250.97 nm reveals that the grown crystals have a direct band gap material. Plotting the graph between $(\alpha h\nu)^2$ versus photon energy gives the value of direct band gap. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ gives the value of band gap. From the optical absorption studies, the absorption coefficient and extinction coefficient decrease with increase in wavelength are shown in Fig.5.&Fig.6.indicates the maximum transmittance of as grown crystal.The optical conductance of as grown crystal is obtained by using the relation,

$$\sigma = \frac{\alpha n c}{4\pi} \tag{3}$$

Where σ is the optical conductance, c is the velocity of the radiation in the space; n is the refractive index and α is the absorption coefficient.The relation between refractive index (n) and the energy gap (E_g) is given by Reddy *et al* [13] through some modified form of T.M.Moss [14]

$$E_g e^n = 36.3 \tag{4}$$

This relation holds true for energy gaps greater than 0 eV. So it was proposed to overcome some of the drawbacks of the Moss relation by Reddy and Ahammed [15] is given by

$$n^4 (E_g - 0.365) = 154 \tag{5}$$

However, it is not valid when the energy gap is not less than 0.36 eV nor does it hold for infrared materials such as lead salts and In Sb. But for cadmium complexes, band gap energies are more than 0.36 eV has been proved [16].The frequency or wavelength of refractive index is called dispersion. Dispersion is an important property for optical design and in the transmission of information. There are many formulas used for representing the refractive index. Further studies on the refractive index (n) and reflectance (R) of the crystals were calculated by using the expression,

$$R = \left(\frac{n-1}{n+1} \right)^2 \tag{6}$$

The high value of refractive index and low value of reflectance reveal that the grown crystal is more transparent to transmit the light from 250 to 1100nm. The extinction coefficient can be determined by using the relation,

$$K = \frac{\alpha \lambda}{4\pi} \quad (7)$$

where n is the refractive index λ (5893Å) is the wavelength corresponding to the absorption edge. **Fig.7.** shows the plot of absorbance coefficient (α) versus extinction coefficient (k).The linear relationship between the extinction coefficient and the absorbance coefficient of CSO crystals reveal their SHG efficiency. Therefore electrical susceptibility (χ_c) in terms of dielectric constant with respect to refractive indices was calculated at the lowest absorption edge 250nm of UV Absorption spectrum of CSO crystals using the following relation,

$$\chi_c = \epsilon_r - 1 \quad (8)$$

Since

$$\epsilon_r = n^2 \quad (9)$$

$$\chi_c = n^2 - 1 \quad (10)$$

Table. 4. gives the estimated values of optical parameters of CSO crystals at the lowest absorption edge 250nm of UV Absorption spectrum. Hence $\chi_c = 3.36$, since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense. The dielectric behavior of a material is an important factor as it has direct influence on the NLO efficiency of the crystals. Further quality of the crystal is an important factor when the crystals are brought into device applications.

4. Conclusion

The cadmium sodium oxalate dehydrate crystals of prismatic and rectangular in shapes are synthesized well at 40°C temperature using advanced technique. The single crystal XRD confirms the structure of the crystal is monoclinic and the structural coordination atoms are well defined with appropriate bond angles and bond lengths. UV spectral studies of band gap energy 4.9eV are proved the potential applications of CSO crystals are best suited for preparing opto electronic materials.

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