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OPTICAL PROPERTIES OF GEL GROWN CA^{2+} DOPED COPPER CADMIUM OXALATE SINGLE CRYSTALS

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Abstract

Growth of Ca^{2+} doped copper cadmium oxalate (CCuCO) single crystals were grown by the single diffusion method in silica hydrogel at room temperature. Energy-dispersive X-ray analysis (EDX) confirmed the presence of major elements such as Ca^{2+}, Cu^{2+}, Cd^{2+} ions in the lattice of the grown crystals. Powder X-ray diffraction (XRD) studies show the triclinic nature of the crystals. Fourier transform infrared (FT-IR) spectrum exhibits the presence of OH, carboxyl group and metal-oxygen bonding. UV-Visible spectroscopic analysis measured the energy gap and insulating behavior of the crystals.

Keywords :CCuCO, EDX, XRD, FT-IR, UV.

Introduction

A periodic or recurring array of atoms arranged in a three-dimensional structure with equally repeated distance in a given direction is a single crystal. Crystal growth is an important field of materials science, which involves controlled phase transformation. Raise in the standard of living is desirable for modern society, which requires modifications in the existing ones. Crystals are proven to be the pillars of modern technology [1, 2, 3, 4]. Quartz, calcite, and diamond are the natural crystals that are extensively used in various technological applications that involve applications in optical instruments, electronic devices, laser, medicine semiconductor, solid-state laser, non-linear materials and detectors [5, 6, and 7]. The material in the form of single crystals are required by many fields and the supply of these single crystals are limited in nature. Hence under these circumstances, the synthesis of single crystals is very essential. In the present investigation Ca^{2+} doped nickel-cadmium oxalate crystals were grown by single test tube gel diffusion method using silica hydro-gel as media of growth. The grown crystals were characterized and their optical properties were measured.

Materials And Methods

A Single diffusion gel technique was employed to grow CCuCO crystals at ambient temperature. Chemicals used for growing CCuCO crystals were Sodium Meta Silicate (SMS-$Na_2SiO_3.9H_2O$), Oxalic acid $(COOH)_2$, Copper Chloride ($CuCl_2$), Cadmium Chloride ($CdCl_2.2H_2O$) and Calcium Chloride($CaCl_2$) of AR grade.

Silica hydrogel was prepared by mixing 0.5 N Oxalic acid with SMS solution. To control damage and premature gelling, Oxalic acid was added drop by drop to SMS with constant stirring. The pH of the gel was adjusted between a value of 3.5 and 5 by mixing the oxalic acid and sodium metasilicate in various proportions by volume. The resulted solution (5:4) was transferred to test tubes with 9 mL each and allowed to set for gelling [8]. After setting the gel, 0.5 M $MgCl_2$,1M

$CuCl_2$ and 1M $CdCl_2$ solutions (0.2 : 2: 2) were poured over the gel surface along the sides of the test tube, without disturbing the gel. Cd^{2+} and Cu^{2+} ions diffuse slowly through the narrow pores of the gel to react with oxalate ions, giving rise to the formation of single crystals of Ca[Cu: Cd](C_2O_4)**.** $3H_2O$.

The growth process of CCuCO crystals was completed in about 3 weeks. The growth process was optimized and nucleation centres were controlled by varying gel parameters and concentrations of reactant mixtures [9,10].

After harvesting the fully grown crystals, structural characterization was performed using X-ray powder diffraction technique. XRD patterns were obtained using Minflex 600 Rigakuwith Cu Kα (λ=1.54A^0) radiation at a scan speed of 1˚ $minute^{-1}$. Chemical constituents of the CCuCO crystals were estimated using CARL ZEISS FESEM attached with the EDS system (Oxford instruments). Bruker (Alpha) KBr Fourier Transform Infrared Spectrophotometer (FTIR) was used to identify the functional groups associated with the crystals. The spectrum was recorded for the wavenumber range 400-4500 cm^{-1}. Absorbance, transmittance and bandgap of intrinsic and doped crystals were analyzed with the aid of UV-Visible spectrophotometer (UV-1800 Schimadzu) in the spectral range 200-1200 nm.

Results And Discussion

Growth of crystal

The following chemical reaction was expected in the growth of Calcium doped copper cadmium oxalate (CCuCO) crystals.

$$0.5CaCl_2 + 0.5CuCl_2 + CdCl_2 + 2H_2C_2O_4 \rightarrow Ca_{0:5}\,[Cu_{0.5} : Cd\,](C_2O_4)_2 + 4HCl$$

Table 1 displays a detailed summary of the optimized growth parameters of CCuCO crystals and grown crystals are shown in figure 1.

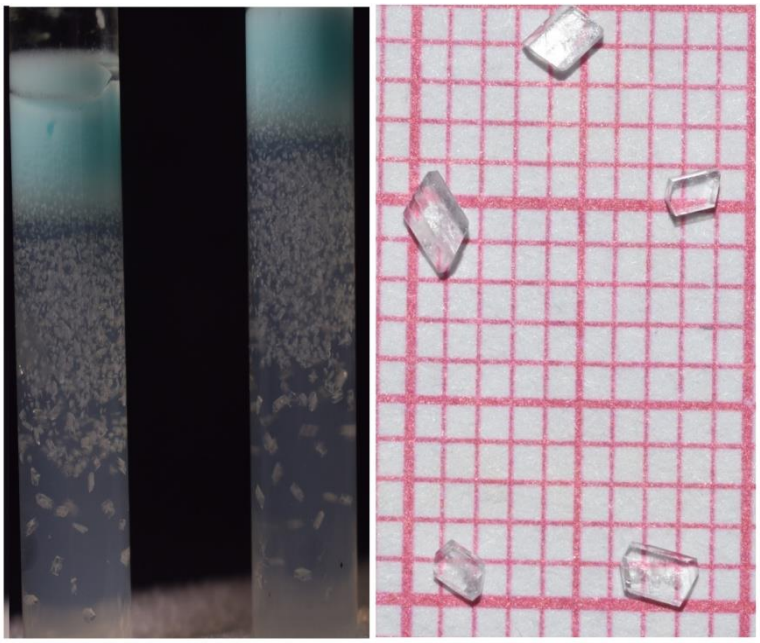

Figure 1.Photograph showing the grown CCuCO crystals.

Table 1.Optimized growth parameters of CCuCO crystals

Parameters	**Optimum Condition**
Specific gravity	1.038
pH of gel	4.25
Concentration of $CdCl_2$ and $NiCl_2$	1N
SMS: Oxalic acid Gel setting period	5:4 95 h
Concentration of $MgCl_2$	0.5N
Period of growth	3 weeks
Physical appearance Lattice type	Transparent Triclinic

FESEM and EDX Studies

Morphology and chemical composition of as grown crystals of grown crystals were shown in figure 2. EDX spectrum which confirms the presence of expected elements C, O, Ca, Cu, and Cd.

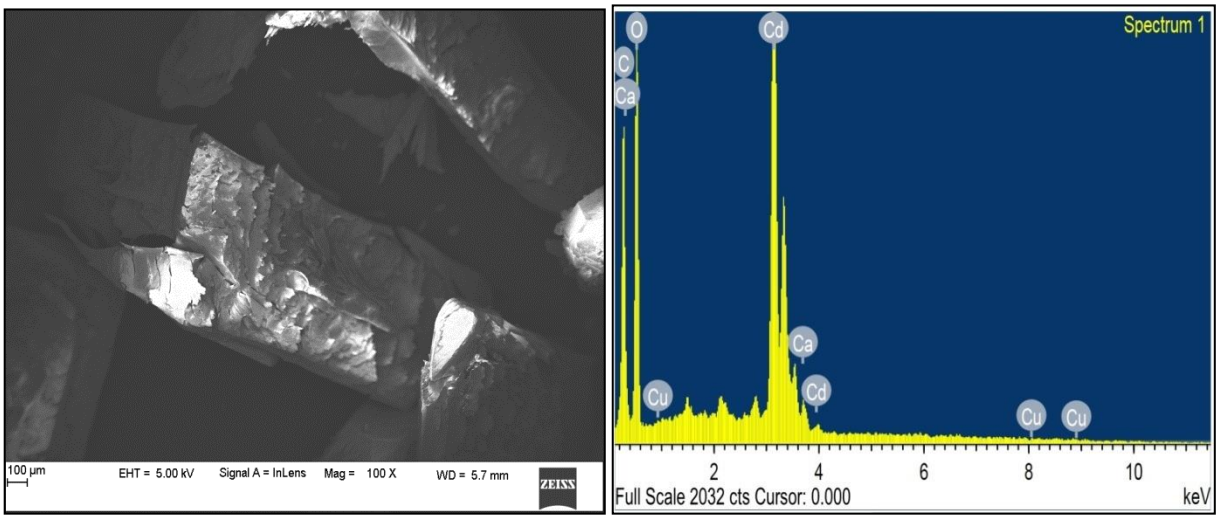

Figure 2.FESEM and EDX images of CCuCO crystals.

Powder X-Ray Diffraction

The powder XRD diffractogram of Ca^{2+} doped [Cu: Cd](C_2O_4)**.** $3H_2O$ single crystals were shown in figure 3. The occurrence of highly resolved intense peaks at specific Bragg angles 2θ indicates the high crystallinity of the grown material. Grown crystal exhibit triclinic structure with unit cell dimensions a= 5.989Å, *b* = 6.633Å, *c* = 8.451Å, α =74.92°, β =74.22° and γ=81.01°.

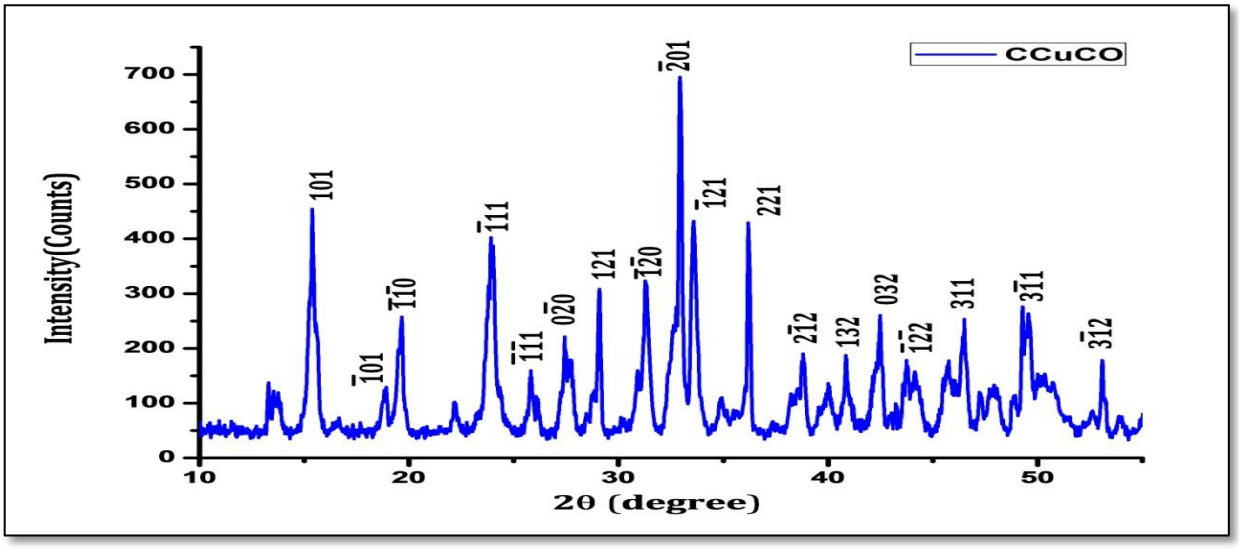

Figure 3.Powder X-ray Diffractogram of CCuCO crystals.

Fourier transform infrared spectrum

The FT-IR spectrum of Ca^{2+}doped [Cu: Cd](C_2O_4)**.** $3H_2O$crystals grown in silica gel were shown in figure 4. The spectrum in the range of 400 to 4000 cm^{-1}shows a strong band centered at about 3415.79 and 3184.72 cm^{-1} attributed to the water OH stretching and the water bending. The bands at approximately 1600 cm^{-1} are attributed to the C=O stretch of the carbonyl group and the peaks at around 1300 cm^{-1}corresponds to the asymmetric stretching mode of C-O bond. The absence of bands in between 1300 to 800 reveals the purity of the grown oxalate crystals without any C–H bonding. The absorbed IR bands below 800 cm^{-1} are due to the metal oxide M-O bond. The infrared spectral studies confirm the presence of water of crystallization and the oxalate group in the grown crystals. Detailed band assignment of some selected absorption bands observed in the FT-IR spectrum of Ca^{2+}doped [Cu: Cd](C_2O_4)**.** $3H_2O$is shown in Table 2.

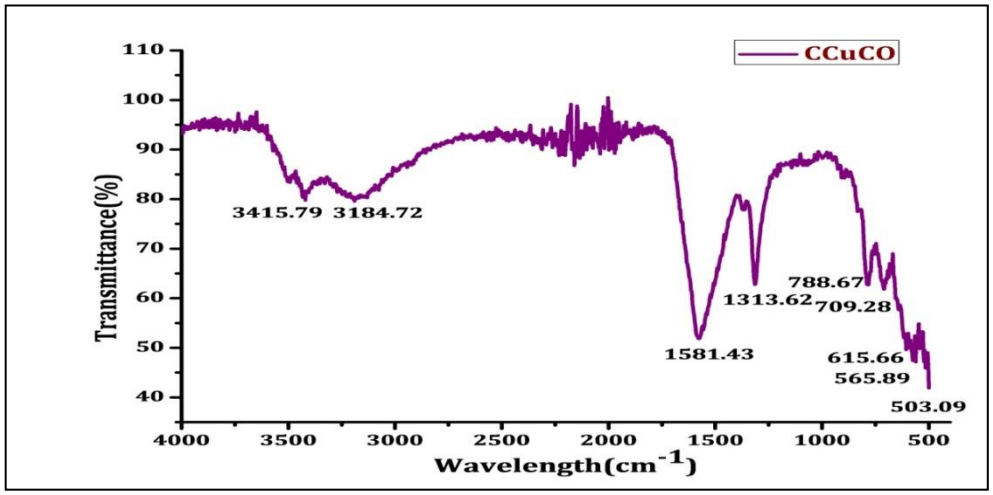

Figure 4.FT-IR spectra of CCuCO crystal.

Table 2. Vibrational modes, in wavelength (cm^{-1}), observed in the infrared spectra for the CCuCO crystal.

Wave number (cm^{-1})	**Band assignments**
3415.79 & 3184.72	Water γ(OH)
1581.43	γ(CO) + (CC)
1313.62	γ(CO) + δ(O–C=O)
788.67	δ (OC=O) + γ(M-O)
565.89 & 503. 09	γ (MO)

UV-Visible Absorption studies

From the UV absorption spectrum, the lower cut off wavelength for CCuCO crystals was found to be 233.6 nm were shown in figure 5.The bandgap of CCuCO crystal was estimated by plotting $(\alpha h\nu)^2$ versus hν as shown in the inset of figure 5 and extrapolating the linear portion near the onset of absorption edge to the energy axis. From this figure, the value of bandgap was found to be 5.29eV. The wide bandgap of the title crystals confirms the less absorbance (large transmittance) in the visible region. Figure 6 shows the transmittance spectrum of as-grown crystal.

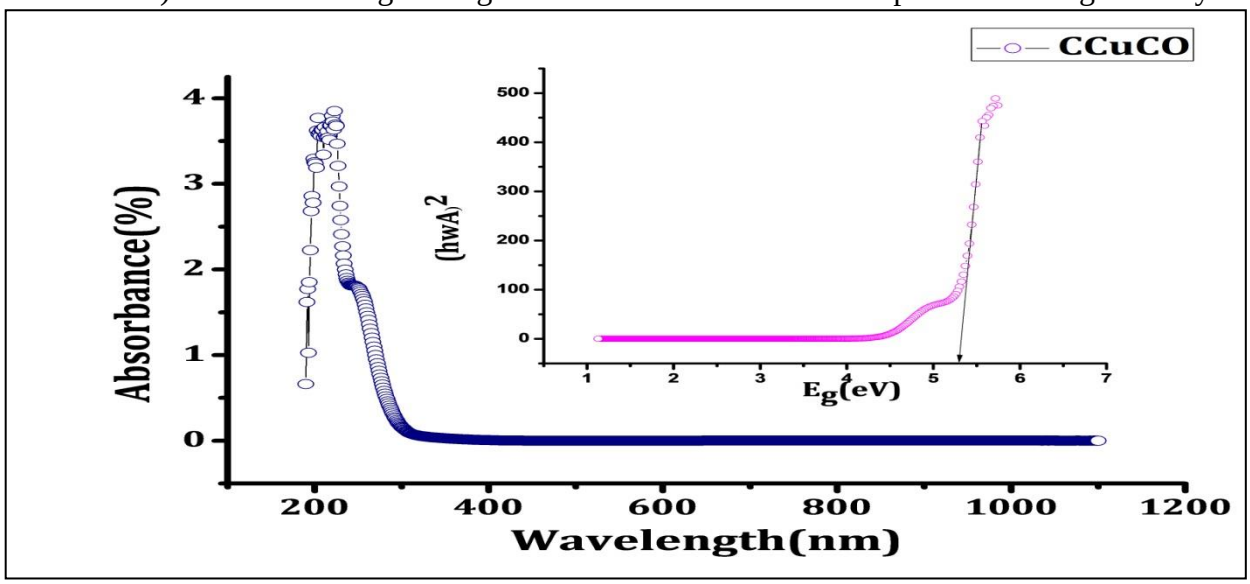

Figure 5.Absorption spectrum and Tauc's Plot ofCCuCO crystals

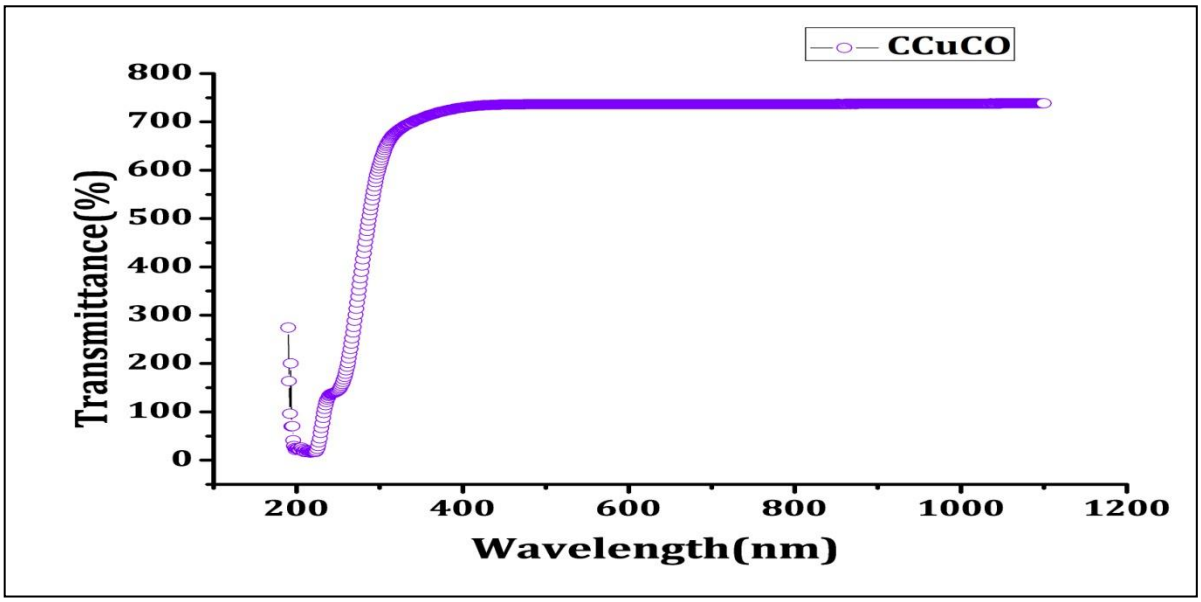

Figure 6.Transmittance spectrum ofCCuCO crystals

Conclusion

Ca^{2+} doped Copper Cadmium oxalate (CCuCO) single crystal was grown by the single diffusion method. Size and quantity of grown crystals were changed by varying specific gravity of SMS solution, gel age, gel pH and the concentration of upper and lower reactants. EDX spectral studies confirm the presence of expected major elements. FT-IR spectrum shows the presence of water of crystallization, functional and metal-oxygen bonded groups. UV visible spectrophotometric studies confirm that the crystal is an insulator, suitable material for the linear and nonlinear optical devices.

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