Effect of Strontium doping on Thermal and Optical properties of Gel grown Copper cadmium and Cobalt cadmium oxalate crystals

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Abstract : In the present paper, the Sr²⁺ doped Copper cadmium oxalate (CuCO) and Cobalt cadmium oxalate (CoCO) crystals were grown by the single diffusion method in silica hydrogel at room temperature. Optimum conditions of the as-grown crystals were established by varying different growth parameters. Energy-dispersive X-ray analysis (EDX) confirmed the presence of major elements such as Sr²⁺, Co²⁺, Cu²⁺, Cd²⁺ ions in the lattice of the grown crystals. The percentage weight loss, molecular weight and thermal stability of the grown crystals were studied using Thermogravimetric analysis (TGA). The Energy gap, refractive index, reflectance and electrical polarizability of the crystals were calculated by using UV-Visible spectroscopy. Direct and Indirect band gaps are calculated using Tauc’s plot.

Keywords : CuCO, CoCO, X-Ray Diffraction, UV-Visible Spectroscopy.

Introduction

Crystal growth in gels at ambient temperature is one of the simple inexpensive techniques to get good quality crystals. Gel technique is suitable to grow crystals which are water-insoluble and decompose before melting [1]. The physical and chemical properties of the parent crystal can be modified by introducing dopants at the time of growth. Many researchers have been reported the growth of oxalate crystals in gel [2-4]. On reviewing the past crystal growth studies it is found that very little investigations were done on alkaline earth elements ions doped oxalate crystals [5]. Inorganic oxalate crystals show special physical and chemical properties that enable them to behave as catalysts, a solid electrolyte for batteries, linear and nonlinear optical components, nutritional supplements, etc [6]. In the present investigation Sr²⁺ doped Copper cadmium oxalate (CuCO) and Cobalt cadmium oxalate (CoCO) crystals were grown by a single test tube gel diffusion method using silica hydrogel as media of growth. The grown crystals were characterized and their thermal, optical properties were measured. The results obtained for Sr²⁺ doped [SCuCO and SCoCO] crystals were compared with the intrinsic CuCO and CoCO crystals.
Experimental

Pure and Sr$^{2+}$ doped CuCO and CoCO crystals were grown by a single diffusion method using silica hydrogel at room temperature. Sodium metasilicate solution (SMS) was prepared by dissolving 22 g of Na$_2$SiO$_3$ into 250 ml of distilled water with constant stirring and kept in dark and cool place. The SMS solution was diluted to attain specific gravity of nearly 1.042 [7, 8]. 0.5 m oxalic acid was prepared by dissolving 15.76 g in 250 ml of double-distilled water. SMS solution of specific gravity 1.042 was mixed with 0.5 m oxalic acid in a beaker by adding SMS solution drop by drop with constant stirring in the ratio 5:4. The pH of the gel was adjusted to 4.20. Mixed solutions (9 ml) were collected in test tubes and allowed to set. Once the gel set in the test tubes, solution of Cobalt chloride and Cadmium chloride of 1:1 ratio (for CoCO) and Copper chloride and Cadmium chloride (CuCO) were poured to gel carefully through the walls of crystallizer to avoid gel breakage [9, 10]. The openings of the test tubes were tightly covered to prevent contamination of the gel surface by atmospheric impurities. Crystals grew within a week and well-shaped crystals were visible in 3 weeks. The same procedure is repeated to grow the Strontium doped CuCO and CuCO crystals. The optimum condition of growth for SCuCO and SCoCO crystal is shown in Table 1 and grown crystals are shown in Figure 1. The following general chemical reaction was employed for the growth of the title crystals:

$$\text{CdCl}_2 \cdot \text{H}_2\text{O} + \text{Cu}^{2+} + \text{Sr}^{2+} + (\text{COOH})_2 \cdot 1.5 \text{H}_2\text{O} \rightarrow \text{Sr: [Cu: Cd]}\text{C}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O} + 2\text{HCl}$$

$$\text{CdCl}_2 \cdot \text{H}_2\text{O} + \text{Co}^{2+} + \text{Sr}^{2+} + (\text{COOH})_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Sr: [Co: Cd]}\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O} + 2\text{HCl}$$

![FIGURE 1. Growth of SCuCO and SCuCO Crystals](image)

| Parameters                      | Optimum Condition |
|---------------------------------|-------------------|
| **SCuCO**                      | **SCoCO**         |
| Density of sodium metasilicate  | 1.042             | 1.042             |
| pH of gel                       | 4.20              | 4.20              |
| Concentration of CdCl$_2$ and CoCl$_2$ | 1N               | 1N               |
| SMS: Oxalic acid                | 5:4               | 5:4               |
| Concentration of SrCl$_2$       | 0.5N              | 0.5N              |
| Period of growth                | 3 weeks           | 3 weeks           |
| Physical appearance             | Transparent       | Pink colored     |
The elemental compositions of the grown crystals were determined using CARL ZEISS FESEM attached with the EDS system (Oxford instruments). EDX analysis is used for chemical characterization of materials to detect chemical elements present in nanometers depth from the surface of the crystal. Thermal properties of CuCO, SCuCO CoCO, and SCuCO crystals are studied by TGA using DSC-TGA TA (SDT-Q600) instrument. TGA finds the percentage weight loss, molecular weight of a sample for the increase of temperature. Optical absorption studies are carried out using UV-Visible Spectrophotometer (UV-1800 SHIMADZU) in the spectral range of 190-1100 nm.

Results and Discussion

1. Surface Morphology

The FESEM images of as-grown crystals are given in figure 2. CuCO crystal structure has an irregular shaped flat surface revealed at 20μm as in figure 2 (a). Due to the doping of Sr\(^{2+}\) there exists an aggregation of irregularly shaped well-interconnected grains, flakes at 20μm as in figure 2(b).

As similarly, CoCO crystal morphology contains a long irregular structure with crevices at 20μm is shown in figure 2(c). Sr\(^{2+}\) doping creates agglutination of many irregular shaped granule structure is in figure 2(d).

![FIGURE 2. FESEM images of CuCO, SCuCO, CoCO, and SCuCO crystals.](image)

2. EDX Analysis

The chemical composition of as-grown crystals is analyzed by Energy Dispersive X-ray Analysis (EDX). Figure. 3 shows the EDX spectrum which confirms the presence of expected elements C, O, Cu, Co, Cu, Sr, and Cd. The presence of required atoms of average weight and atomic percentage values obtained are shown in Table 2. The stoichiometric composition was computed using experimental and theoretical results of EDX [11].
FIGURE 3. EDAX spectra of SCuCO and SCuCO crystals.

Table 2. Average weight and atomic weight percentage of crystals

| Crystals | Elements | Weight % | Atomic % |
|----------|---------|----------|----------|
| SCuCO    | O       | 48.57    | 62.20    |
|          | Cu      | 20.98    | 3.80     |
|          | Cd      | 11.96    | 2.84     |
|          | Sr      | 0.25     | 0.08     |
|          | C       | 18.24    | 31.10    |
|          | Total   | 100.00   |          |
| SCoCO    | O       | 52.98    | 63.55    |
|          | Co      | 0.233    | 0.07     |
|          | Cd      | 26.61    | 4.54     |
|          | Sr      | 0.287    | 0.06     |
|          | C       | 19.89    | 31.77    |
|          | Total   | 100.00   |          |

3. Thermal Studies

Thermogravimetric analysis (TGA) is carried out to investigate the thermal performance, quantitative measurement of the mass change in materials associated with transitions and thermal degradation. Figure 4 shows the TGA thermograms of Pure and Strontium doped crystals.

In figure 4 a) the first step of dehydration starts at 40°C and ends at 150°C, which shows the formation of anhydrous CuCO and SCuCO crystal from pure and strontium doped copper cadmium oxalate trihydrate crystal. The second step represents the decomposition of pure and strontium doped copper cadmium oxalate crystal into pure and strontium doped copper cadmium oxide in the temperature range of 260°C and 400°C, which shows the release of CO₂ and CO molecules as gases[12].

In figure 4 b) the first step of dehydration starts at 40°C and ends at 150°C, which shows the formation of anhydrous CoCO and SCoCO crystal from pure and strontium doped cobalt cadmium oxalate trihydrate crystal. The second step represents the decomposition of pure and strontium doped cobalt cadmium oxalate crystal into pure and strontium doped cobalt cadmium oxide in the temperature range of 260°C and 360°C, which shows the release of CO₂ and CO molecules as gases. On heating above 400 °C, the crystals show stability until 700 °C.

The Sr²⁺ doped crystals exhibits more thermal stability compare to pure CuCO and CoCO crystals. The observed and calculated weight losses of the as-grown crystals are summarized in Table 3.
Figure 4. TGA plot of a) CuCO and SCuCO crystal, b) CoCO and SCoCO crystal.

TABLE 3. TGA results of the gel grown crystals

| Sample | Weight loss (Calculated) % | Weight loss (observed) % | Molecule decomposed | Molecular weight |
|--------|---------------------------|-------------------------|---------------------|-----------------|
| CuCO   | 21.260                    | 21.738                  | 3H$_2$O CO & CO$_2$ | 254.023         |
|        | 28.351                    | 28.585                  |                     |                 |
| SCuCO  | 20.690                    | 19.874                  | 2.5H$_2$O CO & CO$_2$ | 217.560         |
|        | 33.110                    | 31.324                  |                     |                 |
| CoCO   | 21.310                    | 22.040                  | 3H$_2$O CO & CO$_2$ | 253.461         |
|        | 28.401                    | 29.117                  |                     |                 |
| SCoCO  | 21.320                    | 20.726                  | 3H$_2$O CO & CO$_2$ | 253.320         |
|        | 28.429                    | 27.679                  |                     |                 |

4. UV-Visible NIR Studies

The UV-Visible spectroscopy was carried out to investigate the optical properties of Sr$^{2+}$ doped copper cadmium oxalate (CuCO) and cobalt cadmium oxalate (CoCO) crystals. UV-VIS-NIR absorption spectrum was recorded in the wavelength range between 190 nm and 1100 nm (Figure 5). From the absorption spectrum, the lower cut-off wavelength is found to be 236.76 nm, 224.09nm, 284.99nm and 221.93nm for CuCO, SCuCO, CoCO, and SCoCO respectively. It is found that the absorbance is lowered and the absorbance curve shifts towards a low wavelength side due to the addition of Sr$^{2+}$ ions in both the crystals. The lower percentage absorption indicates that the crystal readily allows the transmission of the light radiation in the range between 230 nm and 1100 nm. It shows that the grown crystal has good transparency in UV, visible and near IR region indicating that it can be used for NLO applications. Hence it is concluded that the grown crystal can be used for optoelectronic applications.
FIGURE 5. UV-Vis-NIR absorbance spectrum.

The direct energy bandgap ($E_D$) was calculated from the Tauc’s plot [13] of $h \nu$ ($h =$ Planck’s constant, and, $\nu$ = frequency of light) versus $(\alpha h \nu)^{2}$ ($\alpha =$ absorption coefficient of material) shown in Figure 6.

The relation between refractive index ($n$) and energy gap ($E_g$) is given by Reddy et al. [14, 15] as,

$$E_g n^2 = 36.3$$

This relation is suitable for the material with the energy gap greater than 0 eV. Dispersion is an important property for the optical activity of the as-grown samples. Further, the Refractive index ($n$) and Reflectance (R) of the crystals are calculated by using the expression,

$$R = \frac{(n-1)^2}{(n+1)^2}$$

The electrical susceptibility ($\chi_e$) of the materials [16] was calculated using the following relation,

$$\chi_e = \epsilon_r - 1$$
$$\chi_e = n^2 - 1 \quad \text{ (Since, } \epsilon_r = n^2)$$

FIGURE 6. Tauc’s Plot for the determination of the direct bandgap.

The indirect energy bandgap ($E_{in}$) was calculated from the Tauc’s plot of $h \nu$ ($h =$ Planck’s constant, and, $\nu =$ frequency of light) versus $(\alpha h \nu)^{1/2}$ ($\alpha =$ absorption coefficient of material) shown in Figure 7.

The calculated data of direct energy bandgap ($E_D$), Indirect energy bandgap ($E_{in}$), Refractive index ($n$), Reflectance (R) of the crystals are tabulated in table 4.
FIGURE 7. Tauc’s Plot for the determination of the Indirect bandgap.

TABLE 4. Calculated optical parameters of as-grown crystals

| Sample | Bandgap energy (Direct) $E_D$ (eV) | Bandgap energy (Indirect) $E_{I_n}$ (eV) | Ref. Index (n) | Reflectance (R) | Electrical susceptibility ($\chi_e$) |
|--------|-----------------------------------|------------------------------------------|----------------|-----------------|-------------------------------|
| CuCO   | 5.240                             | 4.580                                    | 1.935          | 0.101           | 2.746                         |
| SCuCO  | 5.536                             | 5.088                                    | 1.879          | 0.093           | 2.534                         |
| CoCO   | 4.353                             | 3.738                                    | 2.130          | 0.130           | 3.540                         |
| SCoCO  | 5.590                             | 5.052                                    | 1.870          | 0.092           | 2.500                         |

Conclusions

$\text{Sr}^{2+}$ doped Copper Cadmium oxalate (SCuCO) and $\text{Sr}^{2+}$ doped Cobalt Cadmium oxalate (SCoCO) single crystal were grown by the single diffusion method. By varying the specific gravity of SMS solution, gel age, gel pH and the concentration of upper and lower reactants leads to the change in Size and quantity of grown crystals. EDX spectral studies confirm the presence of expected major elements. Thermal stability, changes in mass due to dehydration, decomposition, and oxidation of grown crystals with time and temperature were determined by thermal studies. Spectroscopic study revealed that Strontium doping led to an increase in the bandgap and shifting of absorption edge to the lower wavelength. Also, confirm that the crystal is an insulator suitable material for the fabrication of optoelectronic devices. The high value of electrical susceptibility of the as-grown crystals shows that when the incident light is more intense, the crystals can be easily polarized.

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