Growth, Optical and Thermal properties of Co$^{2+}$ doped copper tartrate single crystals at different environmental conditions.

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Abstract Cobalt doped Copper Tartrate (CoCT) crystals were grown in silica gel medium using single diffusion methods at room temperature, passing semiconductor laser and passing various UV visible radiation. The optimum conditions were obtained by varying parameters such as gel concentration, pH of gel, gel setting time, the concentration of reactant. The presence of cobalt, copper, carbon, and oxygen is confirmed by the Energy dispersive X-ray spectroscopy (EDX). The crystals obtained, are regular or elongated shaped depending on the growth and environmental conditions. The grown crystals are characterized by FTIR and PXRD. TGA studies explain the thermal behavior of the grown CoCT crystal. UV-Vis-NIR transmission spectroscopic analysis measured the energy gap and, to study the optical transparency of the grown crystals.

1. Introduction

Single crystals have played a fundamental preference in the advancements as technological know-how evolved swiftly at some stage in the final century. Most of the tartrate composites not dissolve in water and molder earlier than melting. Hence single crystals can't be grown by using either slow evaporation or melt technique. In this situation, the gel method is a splendid one for their growth. Such types of tartaric acid numerous purposes in science and technology [1-2]. The spectrum of the applications of the single crystals is huge beginning from the single crystal silicon used in microelectronics to the nonlinear crystals used in lasers and optics. The present technological build-depend extraordinarily on the scope of single crystals, whether it is for optical devices, lasers, superconductors, magnetic devices, telecommunication, semiconductors, etc. Several of tartrate composites including pure and mixed tartrate deserve superior attention due to its industrial, medical, and pharmaceutical application, eg -Injections of Na-Cr tartrate increase the susceptibility of the transplanted sarcoma to the effects of X-rays, calciphylaxis response of various ferrous tartrate compounds to prevent anemia in animals, ferrous tartrate to tan skin, the use of manganese tartrate crystals in manufacture of champagne, tanning action of ferrous tartrate to tan skin, tan use of manganese tartrate crystals in chemical temperature indicators, strontium tartrate used in ammunition units, Zinc tartrate with other compounds from bright coating and used as protecting powder for metals, etc [3-4] Hence today’s demand for developing massive single crystals. An alternation of pure, combined and doped crystals have been grown via many researchers to pick out new single crystals for industrial and practical functions.
2. Experimental

2.1. Crystal Growth

All chemicals used such as tartaric acid, Sodium Meta Silicate (SMS), copper chloride and cobalt chloride were of AR grade to keep away from impurity growths. Cobalt doped copper tartrate crystals had been grown from a free solution of tartaric acid, copper chloride, and cobalt chloride. Silica gel had been prepared by way of adding tartaric acid (1M) combination to sodium metasilicate solution of unique gravity 1.045gm/cm$^3$ drop through drop until the pH of the gel adjusted to 5. Continuous stirring avoids excessive neighborhood ion concentration, which might also purpose untimely local gelling and make the ultimate answer inhomogeneous. The solution with the desired value of pH is transferred to a numeral of glass test tubes. The gel observed to set in 30min to 24 hours, relying upon its pH and the environmental temperature. Once gelled, feed solution of aqueous 1M copper chloride and 0.5 M cobalt chloride used to be cautiously placed with the help of a pipette over the set gel to keep the away different conditions from the floor injury and breakage of the gel. The Co$^{2+}$ and Cu$^{2+}$ ions diffuse slowly through slim pores of the gel to react with the tartrate ions, giving rise to the formation of single crystals[5-6].

Table 1. The optimum condition for the growth of CoCT crystals

| Parameters                   | Optimum Condition          |
|------------------------------|-----------------------------|
| Density of sodium meta silicate | 1.045 gm/cm$^3$            |
| Concentration of Tartaric acid | 1 M                        |
| pH of the mixture            | 5                           |
| Concentration of CuCl$_2$  | 1 M                        |
| Concentration of CoCl$_2$  | 0.5 M                      |
| Room temperature          | 24 ℃                       |
| Period of growth           | 4 weeks                    |

Figure 1. Growth condition in test tube

Figure 2. Harvested crystals on different condition

3. Results and discussion

3.1. Energy Dispersive X-ray Analysis

The elemental analysis of cobalt doped copper tartrate crystals at different condition are shown in figure 3. Table 2 gives the observed and calculated atomic/weight% of cobalt doped copper tartrate crystals. From figure 3 and table 2, it is confirmed that cobalt has entered into the lattices of copper tartrate crystals [7-8].
3.2. **Scanning electron microscope**

Scanning electron microscope photographs of single crystals of Cobalt doped copper tartrate crystal. An enlarged Scanning electron microscope at different condition image is shown in Figure 4. It shows plate-like crystal morphology. These crystals are grown by layer deposition. Thick and thin layers are seen in the figure. The individual plates of samples are plane and the plates with the sharp boundaries were observed. On some plates, further plate-like growth was observed. [9-10]

![Figure 4. Scanning electron microscope spectra of CoCT crystals in different conditions.](image)

3.3. **Thermal analysis.**

Thermal decomposition stages of CoCT single crystals were investigated by thermogravimetric analysis. The thermal behavior of the grown crystal was studied by using TGA technique. The thermal decomposition of the crystals in different environmental conditions was shown in figure 5(a),(b),(c). The thermal decomposition occurs in two stages between 20-600°C. Decomposition of the...
sample at 35 °C and terminates at 277 °C. There are two stages of decompositions. At the first stage the crystal loss water and become anhydrous in the temperature range of 34 to 111 °C. Then it decomposes into carbonate at the temperature range of 204 - 277 °C. The weight loss of cobalt doped copper tartrate with various radiations was tabulated in Table.3.[11]

![Graphs showing thermal decomposition](image1)

**Figure 5.** (a),(b),(c) shows the thermal decomposition of different conditions.

**Table 3.** The weight loss of cobalt doped copper tartrate with various conditions.

| Laser Radiation | Temperature (°C) | Weight loss (%) | CFL Light Radiation | Temperature (°C) | Weight loss (%) | Without radiation | Temperature (°C) | Weight loss (%) |
|-----------------|------------------|-----------------|---------------------|------------------|-----------------|--------------------|-----------------|-----------------|
|                 | 38.45 - 79.53    | 20.56           |                     | 37.8 - 102.54    | 20.06           |                    | 34.56 - 110.23   | 19              |
|                 | 204.01 - 275.62  | 51.30           |                     | 204.99 - 271.66  | 51.06           |                    | 205.96 - 276.18  | 48.07           |

3.4. UV-Visible-NIR studies

The optical properties of as-grown CoCT single crystals were studied using a UV-Vis-NIR spectrophotometer in the range of 185 nm to 320 nm. The absorption spectrum of the as-grown CoCT single crystals is shown in Figure 6. The energy bandgap of the CoCT crystal was determined using Tauc’s plot varies from 4.8 eV to 5 eV due to the change of growth condition, it is shown in Fig. 7. Hence, this high bandgap of CoCT crystals confirms that the newly grown material behaves as an insulator. The energy bandgap variation in CoCT single crystal at the different conditions as shown in Table.

![UV-Vis-NIR absorption spectrum](image2)

**Figure 6.** UV-Vis-NIR absorption spectrum of CoCT crystals.

![Tauc's Plots of CoCT crystals](image3)

**Figure 7.** Tauc’s Plots of CoCT crystals.
3.5. X–ray diffraction analysis.
The crystal structure of a sample compound was studied by powder X-ray diffraction method. The X-ray diffraction was recorded Bruker AXS D8 Advance model with Cu radiation of wavelength $\lambda=1.54056\text{Å}$. The recorded diffraction pattern of the cobalt doped copper tartrate crystals at different conditions is shown in figure 8.

| Condition | $\beta$ | $\theta$ | D (Å) |
|-----------|---------|---------|-------|
| Laser     | 3.8416  | 11.508  | 7.7356|
| CFL       | 2.9807  | 14.849  | 7.1210|
| Without   | 3.8464  | 11.484  | 7.6820|

The calculated average grain size is 0.77356nm, 0.71210nm, and 0.76820 nm. The analysis of different diffraction peaks indicates the formation of the system. The diffraction peaks at 20 values were measured very carefully and converted into d value using Bragg’s equation putting n=1. The size of the crystal is very small compared to the other Tartrate Single Crystals [12].

4. Conclusion
The Cobalt doped Copper Tartrate single crystals are grown at room temperature and exposed to different light like compact florescent light and laser medium. It was found that CoCT single crystal nucleation rate is reduced more in the laser medium than other lights-exposed medium and room.
temperature, which is due to variation of supersaturation. These results are recorded and compared with the reported values. This revealed the effect of grown crystal at different environments. SEM analysis also done and it reveals the surface morphology of CoCT single crystal. The decomposition temperature and percentage of weight loss of the grown crystal are recorded by TGA analysis. CoCT lattice parameters and structure of the unit cell are calculated by PXRD.

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