Dielectric, Magnetic and Spectral studies of gel grown Mg$^{2+}$ Doped Copper Cadmium Oxalate Single Crystals

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Abstract Mg$^{2+}$ doped Copper Cadmium oxalate (MCuCO) single crystals were grown by a single diffusion method in silica hydrogel at room temperature. Powder X-ray diffraction (XRD) studies show the triclinic nature of the crystals. The dielectric constant, ac resistivity and ac conductivity have been measured as a function of frequency. The dielectric constant of MCuCO crystal decreases as the frequency of applied field increases; at the end it gives the diminishing value of dielectric constant. AC conductivity increases with the increase of frequency. Absorbance, transmittance, reflectance, refractive index, and energy gap of MCuCO crystal were determined by UV-Visible spectroscopy. A high bandgap corresponds to the dielectric behavior of the crystal.

Keywords: MCuCO, XRD, UV-Visible.

1. Introduction

Extensive researches have been carried out over the years on the growth of defect free single crystals due to their wide applications in the field of optoelectronics, linear and non linear mechanics and solid state lasers. The crystal growth is a heterogeneous chemical process in which one phase of a compound is converted into another phase [1, 2]. Crystal growth from aqueous solution is known from long time, but control of large nucleation is a problem. Gel method is relatively simple and inexpensive. In the present investigation Mg$^{2+}$ doped copper cadmium oxalate (MCuCO) crystals were grown by single test tube gel diffusion method using silica hydrogel as media of growth. The grown crystals were characterized and their crystalline, optical, dielectric and magnetic properties were measured.

2. Experimental

2.1. Crystal Growth

Mg$^{2+}$ doped copper cadmium oxalate crystals were grown by single diffusion method using silica hydro gel at room temperature. Sodium Meta Silicate 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 [3, 4]. The SMS solution was diluted to attain specific gravity nearly 1.042. 0.5 m oxalic acid was prepared by dissolving 15.76 g in 250 ml of double distilled water [5-8]. 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. 9 ml of mixed solutions were collected in test tubes and allowed to set for four days. Once the gel set in the test tubes, solution of Magnesium chloride, Copper chloride and Cadmium chloride of 0.5:2:2 were poured to gel carefully through the walls of crystallizer to avoid gel breakage. The openings of the test tubes were tightly covered to prevent contamination of gel surface...
by atmospheric impurities. Crystals grew within a week and well-shaped crystals were visible in 3 weeks. The optimum condition of growth for each crystal is shown in Table 1 and grown crystals are shown in the Figure 1.

Table 1. Optimized growth parameters of MCuCO crystals

| Parameters                     | Optimum Condition |
|--------------------------------|-------------------|
| Specific gravity               | 1.042             |
| pH of gel                      | 4.25              |
| Concentration of CdCl₂ and CuCl₂ | 1N                |
| SMS: Oxalic acid               | 5:4               |
| Gel setting period             | 95 h              |
| Concentration of MgCl₂         | 0.5N              |
| Period of growth               | 3 weeks           |
| Physical appearance            | Transparent       |

Figure 1. Photograph showing the grown MCuCO crystals.

2.2. Characterization techniques
Structural characterization was performed using X-ray powder diffraction technique. XRD patterns were obtained using Miniflex 600 Rigaku with Cu Kα (λ=1.54Å) radiation at a scan speed of 1° minute⁻¹. The Dielectric and conductivity measurements were done using a Wayne Kerr 6500B precision impedance analyzer in the frequency range 10 Hz to 5 KHz at room temperature. The Magnetic susceptibility of grown crystals MCuCO has been determined by using Gouy balance. 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.

3. Results and discussion
3.1. XRD Analysis
Powder X-ray Diffractogram Mg²⁺ doped Copper Cadmium oxalate (MCuCO) crystal is shown in Figure 2. The well defined peak at specific 2θ values showed high crystalline nature of the grown crystal. Observed XRD pattern of the crystals were indexed using N-TREOR09 program. Obtained d-spacing and the Miller indices are in agreement with the standard values (JCPDS data). Cell parameters of grown crystals are given in Table 2.
Table 2. Cell parameters of MCuCO crystal

| Cell parameters | MCuCO         |
|-----------------|---------------|
| a               | 5.976 Å       |
| b               | 6.650 Å       |
| c               | 8.463 Å       |
| α               | 74.67°        |
| β               | 74.17°        |
| γ               | 80.88°        |
| Volume          | 310.7 Å³      |
| Space group     | P1            |
| Crystal system  | Triclinic     |
| Grain Size      | 308.9293 Å    |

3.2. Dielectric study

The capacitance and dissipation factor of the sample were measured for various frequencies, in the range 10Hz to 5 KHz. Dielectric constant ($\varepsilon_r$), dielectric loss (tan\(\delta\)) were calculated using the relations

$$\varepsilon_r = \frac{C_d}{\varepsilon_0 A}$$

And, $$\tan \delta = \varepsilon_r \omega$$

and shown in Figure 3. It is observed that the $\varepsilon_r$ and tan\(\delta\) values are found to decrease with the increase in frequency. The ac conductivity ($\sigma_{ac}$) has been calculated for the MCuCO crystal from the following formula

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$

where $\varepsilon_0$ is the vacuum dielectric constant ($8.85 \times 10^{-12}$ farad/m), $\varepsilon_r$ is the relative dielectric constant and $\omega$ is the angular frequency ($\omega = 2\pi\nu$) of the applied field. Figure 4 shows the variation of ac conductivity and ac resistivity with various frequencies. It is seen that the value of ac conductivity increases with increase in frequency, ac resistivity decreases with increase in frequency.
3.3. Magnetic study

The magnetic susceptibility of grown crystals MCuCO has been determined by using Gouy balance. The magnetic susceptibilities of MCuCO crystal were given in Table 3. The volume susceptibility of grown crystals is a negative value indicating that the grown crystals are diamagnetic in nature.

| Materials | $\Delta w$ (gm) | $\chi_v \times 10^6$ (e.m.u) | $\chi_m \times 10^6$ (e.m.u) | Magnetic moment |
|-----------|----------------|-----------------------------|-----------------------------|----------------|
| MCuCO     | -0.0003        | -2.3203473                 | -587.400796                 | -2.252613748   |

3.4. UV-Visible NIR Studies

UV-VIS-NIR absorption spectrum and transmittance spectrum were recorded in the wavelength range between 200 nm and 1200 nm shown in Figure 5. From the absorption spectrum, the lower cut-off wavelength is found to be 248.84 nm and the lower percentage absorption indicates that the crystal readily allows the transmission of the laser beam in the range between 250 nm and 1200 nm. It shows that the grown crystal has a 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.

The term “band gap” refers to the energy difference between the top of the valence band to the bottom of the conduction band; electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition. The band gap energy ($E_g$) was calculated as 4.99 eV from the Tauc’s plot 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 refractive index is one of fundamental properties of a material because it is closely related to the electronic polarizability of ions and the local field inside the material. The relation between the refractive index ($n$) and the energy gap ($E_g$) were given by the expression \[ E_g e^0 = 36.3 \] This relation is suitable for the energy gap greater than 0 eV. Dispersion is an important property for optical activity of the as-grown samples.

Reflectance ($R$) is the amount of light reflected by a crystal surface, normalized by the amount of light incident on it. Transmittance is the amount of light transmitted by a surface, normalized by the amount of light incident on it. Any light not reflected or transmitted is absorbed ($\alpha$).
Further studies on 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 refractive index and reflectance of the crystal were calculated as 1.984 and 0.109 respectively in the transmission range.

The electrical susceptibility (\(\chi_e\)) was calculated using the following relation,

\[ \chi_e = \varepsilon_r - 1 \]
\[ \chi_e = n^2 - 1 \quad \text{(Since, } \varepsilon_r = n^2) \]

Hence, \(\chi_e = 2.9363\)

Since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense.

**Figure 5.** UV-Vis-NIR absorbance and transmittance spectrum of MCuCO crystal

**Figure 6.** Tauc’s Plot of MCuCO crystal

### 4. Conclusion

Mg\(^{2+}\) doped Copper Cadmium oxalate (MCuCO) single crystal were grown by 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. Grown crystals are triclinic in nature. Dielectric loss, resistivity and conductivity studies confirm the response of the newly grown material with the variation of frequency. The grown crystals exhibit diamagnetic behaviour. UV visible spectrophotometric studies confirm that the crystal is an insulator suitable material for the fabrication of optoelectronic devices.
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