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Studies on Thermal and Spectroscopic Properties of Magnesium Doped Single Crystal

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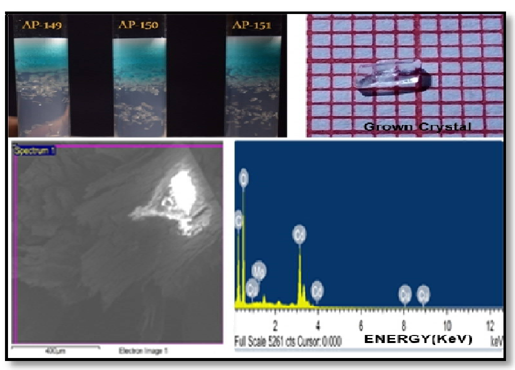
ABSTRACT

Solid state spectroscopy provides important information about solids, particularly on their band structures. Lot of work has been done in the recent years on the study of behavior of impurity particles in crystals with respect to their influence on lattice structure and optical absorption. Magnesium (Mg^{2+}) Doped Copper Cadmium Oxalate (MDCCO) single crystals were grown by single diffusion reaction method using silica gel at ambient conditions. Thermo Gravimetric Analysis /Differential thermal analysis (TGA/DTA).UV- Visible absorption and transmittance spectra of the grown crystals were obtained. The results were discussed and reported.

Graphical Abstract



Keywords: Impurity, Magnesium, MDCCO, TGA/DTA

INTRODUCTION

Crystal growth was found to be an advancing field because of its important applications in scientific research as well as commercial field. There are many techniques to grow single crystals in which crystal growth in gels is an efficient and most simple technique to grow water insoluble single crystals at ambient temperatures. Gel method developed at the end of the 19th century. Number of researchers have been utilized the technique in various manners to grow single crystal of different materials.

The crystal growth was a heterogeneous chemical process in which conversion from one phase to another phase of a compound is involved. For the compounds of high melting point and insoluble in aqueous solutions, crystals can be grown from the melt at elevated temperatures. For the materials, which decompose before melting point at atmospheric pressure and for which a suitable solvent is not available, crystals of such material can be grown from gel technique.

The TGA/DTA and optical characteristics of oxalates explained their thermal stability and band gap energy found applications in optoelectronic industries. [1-5]. A known property of oxalates was their insolubility in water, which is useful in separating the transition elements from the mineral as oxalates precipitate. Therefore, to obtain good quality of single crystals of oxalates, no evaporation and high-temperature methods can be used to grow oxalates as they decompose before melting [6-7]. But the insolubility of oxalates in water was an advantage in growing these crystals by silica gel method, and also, the gel grown transition metal oxalate materials have attracted many solid state physicists to study their thermal properties and their potential applications in the field of organic semiconductors, analytical chemistry, and in electronic industries [8-9]. However, the principal aim of the present study is mainly focused to study the 1) growth of magnesium doped copper cadmium oxalate (MDCCO) crystals in single diffusion technique, 2) Thermal and Optical properties.

MATERIALS AND METHODS

Preparation of Single Crystals: The growth of Magnesium (Mg^{2+}) Doped copper Cadmium Oxalate (MDCCO) crystals was carried out in silica gel media by adopting the single-diffusion technique. The high-purity elements such as cadmium chloride, magnesium chloride, oxalic acid, and sodium meta silicate with AR grade were used as the starting materials in the single-diffusion method at a temperature of 25°C. in order to obtain the best experimental conditions for the growth of good quality crystals, the growth experiments can repeated by varying gel density, gel pH, gel ageing, concentration of oxalic acid, concentration of the feed solution and its molar ratio.

Crystal Growth of MDCCO: The optimized growth of gel grown crystals is accomplished by controlled diffusion process. This control of nucleation growth is greatly influenced by single diffusion reaction technique. A test tube (height, 15 cm; diameter, 1.5 cm) was selected as a container for growing the crystals in single-diffusion method. Silica gel was prepared by adding sodium meta silicate solution with a specific gravity of 1.03 to oxalic acid (0.75 M), drop by drop with continuous stirring to avoid excessive local ion concentration which may cause premature local gelling and make the final solution inhomogeneous. This solution was set with a desired pH range of 4.45 and poured into different test tubes for setting the gel. The gel setting period was exactly 8 days and then in order to avoid the surface damage and breakage of the gel in the test tube the supernatant solutions [magnesium chloride (0.5M) and cadmium chloride (1 M)] was poured over the set gel with the help of a pipette. The expected and the desired quality of crystals larger in size, transparent, and prismatic shape were grown in the gel within in the period of 10-15 days. Typical growth conditions and photographs of as-grown crystals are displayed in table 1 and figure 1(a) and 1(b).

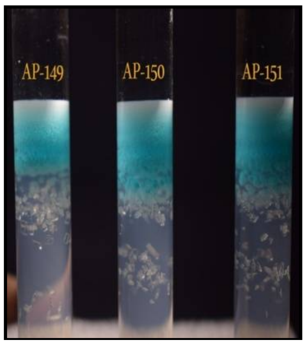
When sodium meta silicate goes into a solution, mono silicic acid is expected to be produced [10-12] according to the following reaction.

$$Na_2SiO_3 + 3H_2O \rightarrow H_4SiO_4 + 2NaOHR$$

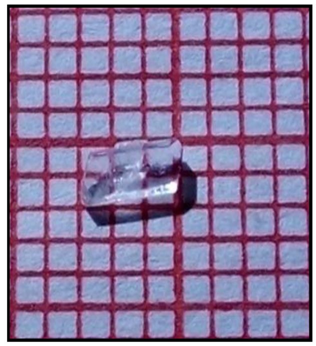
This sodium hydroxide is expected to react with oxalic acid, diffusing in a gel from the supernatant solution and forming magnesium doped copper cadmium oxalate (MDCCO) crystals.

Table 1. Optimum condition for growth of MDCCO crystal

Various Parameters	Optimum Condition MDCCO
Density of sodium meta silicate	1.03
pH of gel	4.45
Concentration of $CdCl_2$ and $CuCl_2$	1M
Concentration of $MgCl_2$	0.5M
Gel setting period	8 days
Gel aging	48 h
Period of growth	15 days
Quality	Transparent



(a)



(b)

Figure 1. Growth of MDCCO single Crystals: (a) formation in silica gel (b) Photograph of as-grown MDCCO crystal.

Characterization: FTIR absorption spectrum of as grown crystal was recorded using IR Prestige-21 SHIMADZU FTIR spectrometer in the region 400 - 4000 cm^{-1}. SEM-EDAX spectrum of as grown crystals were analyzed using CARL ZIESS FESEM attached with EDS system (Oxford instruments) at the scanning image range is 2.73 kx to analyze the observation defects. TGA and DTA of grown crystals were carried out using the DSC-TGA TA (SDT-Q600) system in the argon gas atmosphere to study the thermal stability and the decomposition stages of as grown MDCCO crystals. UV-VIS-NIR Absorption spectrum was recorded in the UV-Visible–NIR spectrophotometer (UV-1800 SCHIMADZU) with a scanning speed of 480 nm min^{-1} between the wave length ranges of 200 nm and 700 nm to determine the band gap energy.

RESULTS AND DISCUSSION

Functional Group Identification Using FTIR Spectrum: FT-IR vibrational spectra of MDCCO (Fig. 2) crystals grown in silica gel exhibits strong absorption peaks in between 3400 and 3500 cm^{-1}, which is due to OH stretching vibrations of water [13]. On adding magnesium as dopant, the shift in the band from its usual position to the lower wave number side was observed, which may be due to the OH bond weakness caused by the interaction of the additionally added metal ion Mg^{2+} in the crystal lattice. The bands at approximately 1600 cm^{-1} were attributed to the C=O stretch of the carbonyl group and the peaks at around 1300 cm^{-1} was assigned to C=O symmetric and O–C=O modes [14-15]. The bands below 800 cm^{-1} were due to metal–oxygen bonds [16]. As seen, magnesium-doped CCO has more number of absorption bands in the lower wave number region (<800 cm^{-1}), which reveals the incorporation of magnesium ions in the crystal lattice forming additional metal–oxygen (Mg–O) bonding. Table 2 summarizes the FT-IR results of the magnesium doped copper cadmium oxalate crystals.

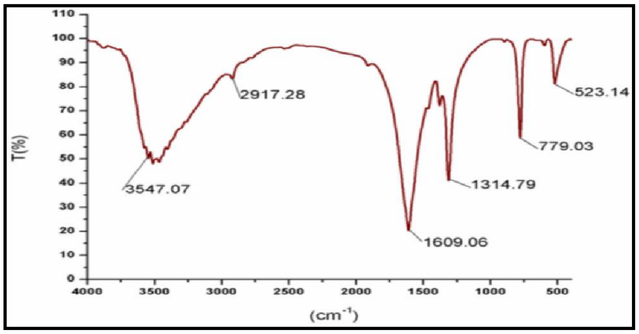
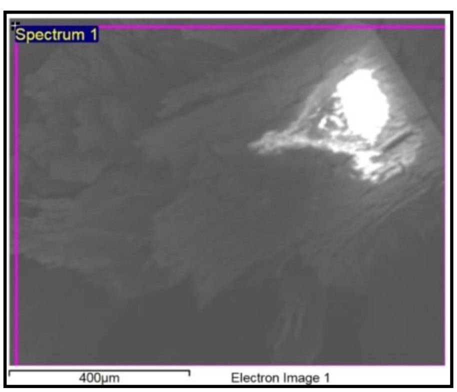


Figure 2. FTIR spectrum of the gel grown crystals.

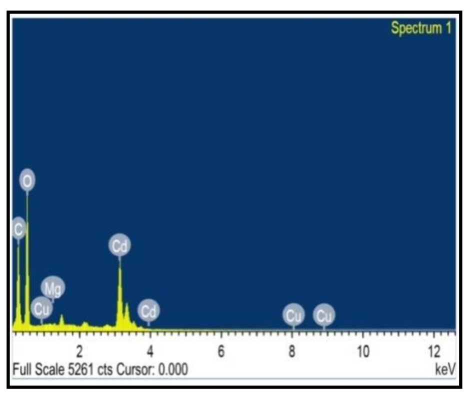
Table 2. FTIR spectrum for functional groups identification of **CCO** versus **MDCCO** crystals.

Wave number of MDCCO (cm^{-1})	Band assignment
1609.06	C-O with C-C
1314.79	C=O
779.03 and 523.14	M-O
3547.07 and 2917.8	O-H

SEM-EDAX Measurements: The increasing demand for crystals of better perfection for use in the fabrication of electronic devices and in the understanding of the plastic deformation leads to analyze the defects in crystal. The SEM micrograph is shown in figure 3(a). The micro morphology [17] is photographed and analyzed under the optical microscope. The surfaces contain few rock and valley shaped dislocations due to plastic deformation caused by thermal stresses. Thus the results of SEM are consistent with XRD analysis. The changes in the EDAX measurements are made at different points on the surface of crystals were given in figure 3(b) and the presence of required atoms of average weight and atomic percentage values obtained was shown in table 3. The spectrum confirms the presence of expected major elements like cadmium, copper, magnesium, carbon and oxygen of the title compound.



(a)



(b)

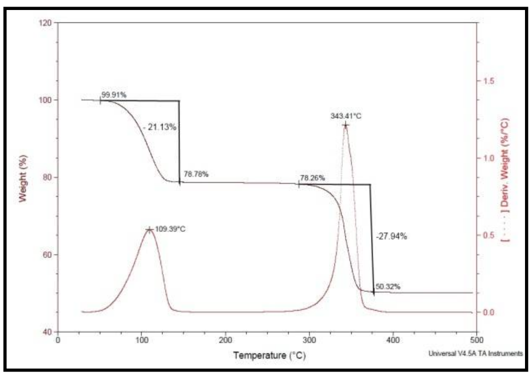
Figure 3. a) Morphology of MDCCO crystals; b) EDAX spectrum of MDCCO crystals.

TGA/DTA Thermal analysis: The study of thermal analysis was significant for knowing the different phases and a stage of the stability of the compound.TGA thermo-gram from fig. 4 shows two distinct steps. The first step of dehydration starts at 40°C and ends at 150°C, which shows the formation of anhydrous MDCCO crystal from magnesium doped copper cadmium oxalate dihydrate crystal, resulting in the weight loss of 21.13%. The second step represents the decomposition of magnesium doped copper cadmium oxalate crystal into magnesium doped copper cadmium oxide in the temperature range of 260°C and 400°C with 27.94% weight loss, which shows the release of CO_2 and CO molecules as gases. This variation in the 1^{st} and 2^{nd} stages of mass losses explained that the process is non-spontaneous [18].

Table 3. Atomic and weight percentages of MDCCO crystal.

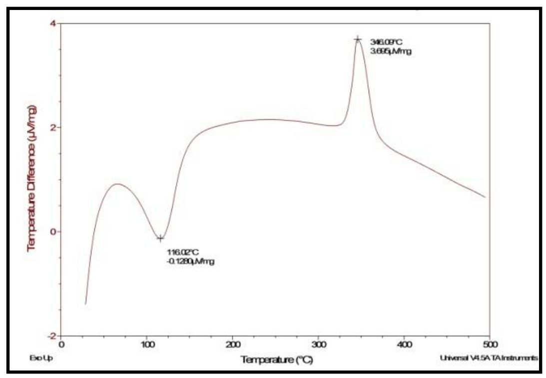
Element	Weight %	Atomic %
C	52.97	60.18
O	28.14	30.09
Mg	0.11	0.08
Cd	12.62	9.51
Cu	6.16	0.15
Total	100	

On the DTA curve, there was one endothermic peak at 116.02°C due to the decomposition of MDCCO dihydrate into anhydrous MDCCO crystal. The exothermic peak at 346.09°C confirms the decomposition of magnesium doped copper cadmium oxalate crystal into magnesium doped copper cadmium oxide. In the differential thermal analysis, temperature changes in the sample were due to the reactions caused by phase changes, decomposition, oxidation, reduction, or other chemical reactions [19-20].



(a)

Figure 4. TGA of MDCCO single crystals.



(b)

Figure 5. DTA of MDCCO single crystals.

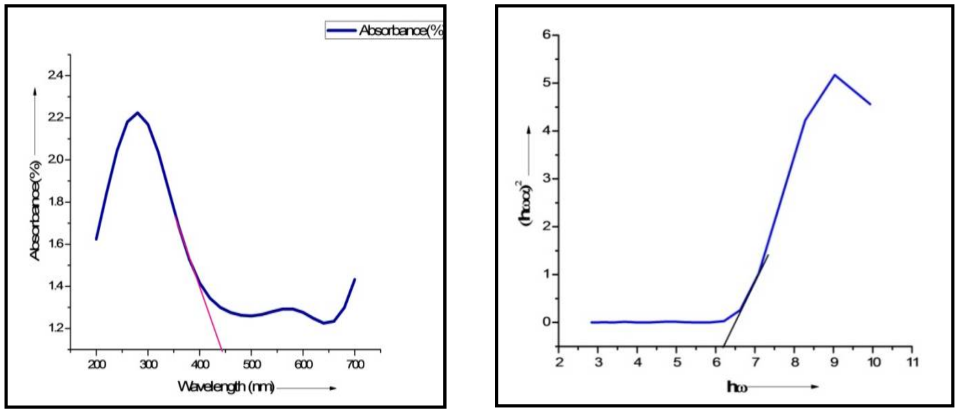
UV Absorption Spectrum: UV-VIS spectrum of MDCCO crystals were found to be active in the Visible and UV region having a significant absorption in the lowest cut off wavelength of 445 nm were shown in figure 6a. In the high photon energy region, the energy dependence of absorption coefficient

$$\alpha = \frac{2.303}{t}\log\frac{1}{T} \qquad (1)$$

where '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 (hυ) [21],

$$(\alpha \dot{h}\upsilon)^2 = A(Eg - h\upsilon) \qquad (2)$$

where 'α' is the absorption coefficient, 'h' is the Plank's constant, 'A' is a constant 'υ' is the frequency of the incident photon and 'Eg' is the optical band gap. The Tauc's graph [22] plot between $(\alpha \dot{h}\omega)^2$ and the photon energy ($\dot{h}\omega$) is shown in figure 6b The extrapolation of the linear part of the graph gives the optical band gap energy value to be 6.2074 eV, this wide band gap of MDCCO crystals confirms the transparency in the visible range.



(a) (b)

Figure 6. a) UV-Vis-NIR Absorption spectrum and b) $h\grave{\omega}$ vs $(\alpha h\grave{\omega})^2$ of MDCCO crystal.

APPLICATION

MDCCO crystals are transparent to visible light. This allows them to be used for window applications where the crystalline perfection and optical transparency is essential. As crystals behave as insulators, they can be used to develop copper clad laminates in PCBs.

CONCLUSIONS

Magnesium doped Copper Cadmium Oxalate single crystals were grown by the gel method. The optimum conditions were identified by varying different parameters. FTIR and EDAX spectral studies confirm the presence of expected functional and metal-oxygen bonded groups of as-grown crystal. The SEM micrograph shows the good perfection and few defects on the surface of the grown crystals. The band gap energy, wide transparent nature indicates that the MDCCO crystals were insulators and suitable for the fabrication of materials for opto-electronic devices. The thermal stability was studied by the TGA/DTA supporting its application in the electronic industries.

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