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Optimized Growth, Thermal, Magnetic and Optical Studies of Co^{2+} and Cu^{2+} mixed Cadmium Oxalate Crystals

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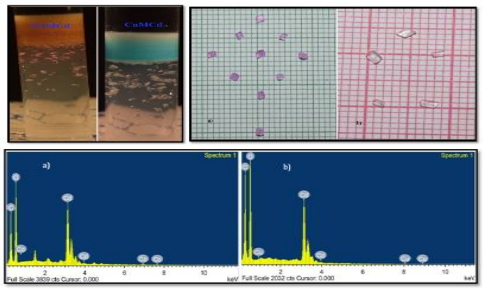
ABSTRACT

Growth of Co^{2+} mixed and Cu^{2+} mixed Cadmium oxalate single crystals were grown by single diffusion method in silica hydro gel at room temperature. Optimum conditions of the as grown crystals were established by varying Specific gravity of Sodium Meta Silicate (SMS), gel setting time, pH of the gel, concentrations of Oxalic acid and concentration of supernatant solutions. Energy dispersive X-ray analysis (EDX) confirmed the presence of major elements such as Co^{2+}, Cu^{2+}, Cd^{2+} ions in the lattice of the grown crystals. Fourier transform infrared (FT-IR) spectral studies of the crystals exhibit water of crystallization, carboxyl group and metal–oxygen bonding. Thermo-gravimetric analysis (TGA) of the crystals elucidated the thermal stability up to 600℃ and the presence of water molecules. Magnetic studies confirm the paramagnetic behavior and UV-Visible spectroscopic analysis measured the energy gap and insulating behavior of the crystals.

Graphical Abstract



Keywords: SMS, EDX, FT-IR, TGA.

INTRODUCTION

Advancements in modern solid-state technology is depend upon the availability of good quality defect less crystalline materials. There are different techniques for growing crystals such as solution growth, vapor phase, melt growth, gel technique etc. Among these, gel technique has become more popular because of its simplicity. It is suitable for crystals having low solubility and it can be used at room

temperature to suppress nucleation centres. Silica hydrogel is commonly used gel for crystal growth due to its better suitability compared with organic gels [**1, 2**]. In this process a gel is chemically inert, which permits the reagents to diffuse into it at a desirable control rate. The mechanical properties of the gel vary widely with the density of sodium metasilicate solution.

MATERIALS AND METHODS

Crystal growth: Copper mixed cadmium oxalate single crystal and Cobalt mixed cadmium oxalate single crystal were grown by single diffusion method. The gel was prepared by adding solution of Sodium Meta Silicate of specific gravity 1.044 to oxalic acid of normality 0.5 N and agitates the mixture gently to ensure homogeneity. The crystallizer was a glass test tubes of length 12 cm and outer diameter 1.7 cm. The gel solution adjusted to a desired pH (4-4.5) was taken in these tubes and kept undistributed for proper setting of the gel. Once gel got set, solution of Copper chloride and Cadmium chloride of 1:1 ratio and Cobalt chloride and Cadmium chloride of 1:1 ratio 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. The optimum conditions for obtaining good quality crystals are recorded in table 1.The growth set up and grown crystals of CoMCd and CuMCd are given in figure 1. Crystals grew within a week and well-shaped crystals were visible in a month. These crystals were removed from gel, washed and dried are shown in figure 2.

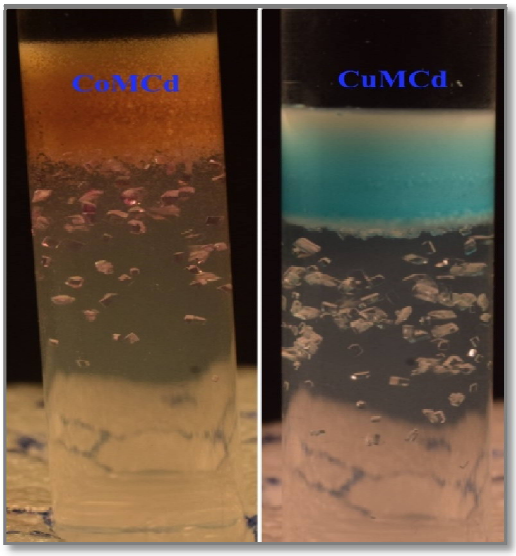


Figure 1. Growth of CoMCd and CuMCd single Crystals.

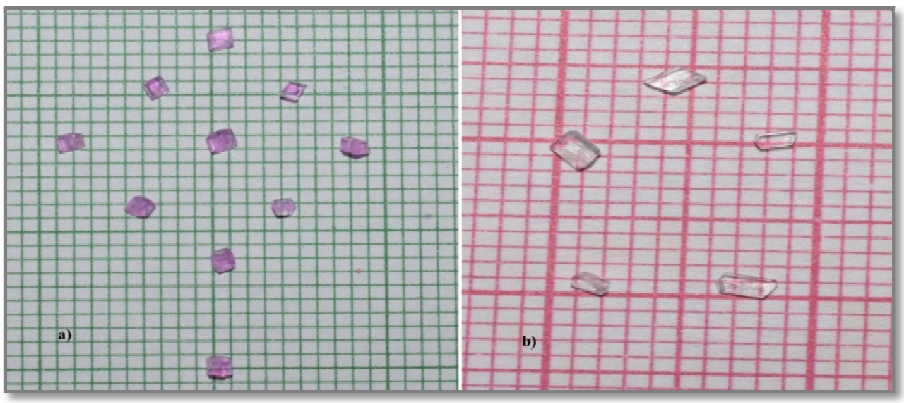


Figure 2. Photograph of grown crystals in graph a) CoMCd b) CuMCd.

Table 1. Optimum condition for growth of CoMCd and CuMCd crystal

Parameters	Optimum Condition CoMCd	Optimum Condition CuMCd
Density of sodium meta silicate	1.044	1.044
pH of gel	4.5	4.8
Concentration of $CdCl_2$ and $CoCl_2$	1N	1N
Gel setting period	4 days	4 days
Gel aging	96 h	96 h
Period of growth	15 days	20 days
Quality	Pink colored	Transparent

Characterization: Elemental composition of the grown crystals ware determined using CARL ZIESS FESEM attached with 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 crystal. Functional groups of crystals are identified using Fourier Transform Infrared Spectrophotometer (IRPrestige-21 SHIMADZU). FTIR analysis (using FTIR spectrophotometer within the wave number range 400-4500 cm^{-1}) is the spectroscopic technique used for analyzing the structural units of samples from their vibrational modes. Thermal properties of CoMCd and CuMCd crystals are studied by TGA using DSC-TGA TA (SDT-Q600) instrument. TGA finds the percentage weight loss 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 190-1200 nm.

RESULTS AND DISCUSSION

SEM/FESEM studies: The very small topographic details on the surface of the grown crystals are visualized using the CARL ZEISS SEM/FESEM attached with EDS system (Oxford instruments). It discloses the information related to structures, shapes, patterns at an ambient temperature of the crystals. Here SEM/FESEM reveals the presence of crystal dislocations of the grown CoMCd and CuMCd crystals. SEM and FESEM images of as grown crystals are shown in figure 3 and figure 4.

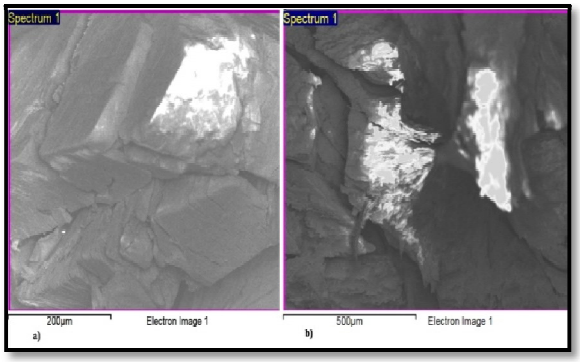


Figure 3. SEM images of (a) CoMCd and (b) CuMCd crystals

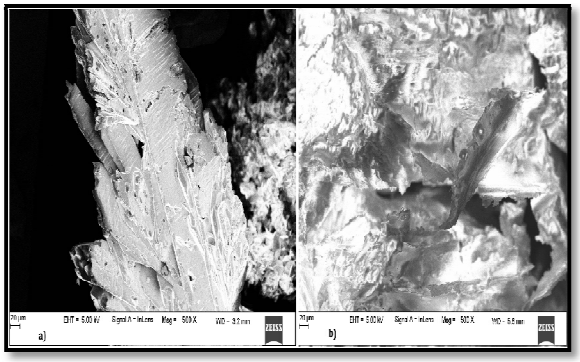


Figure 4. FESEM images of (a) CoMCd and (b) CuMCd crystals.

EDX analysis : The chemical composition of as grown crystals is analyzed by Energy Dispersive X-ray Analysis (EDX).The peaks omitted by the CoMCd sample are 1.490, 2.146, 4.472, 4.834, 11.500 keV and there are no peaks omitted by CuCd. Figure 5 shows the EDX spectrum which confirms the presence of expected elements C, O, Co, Cu, 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 [**3, 4**].

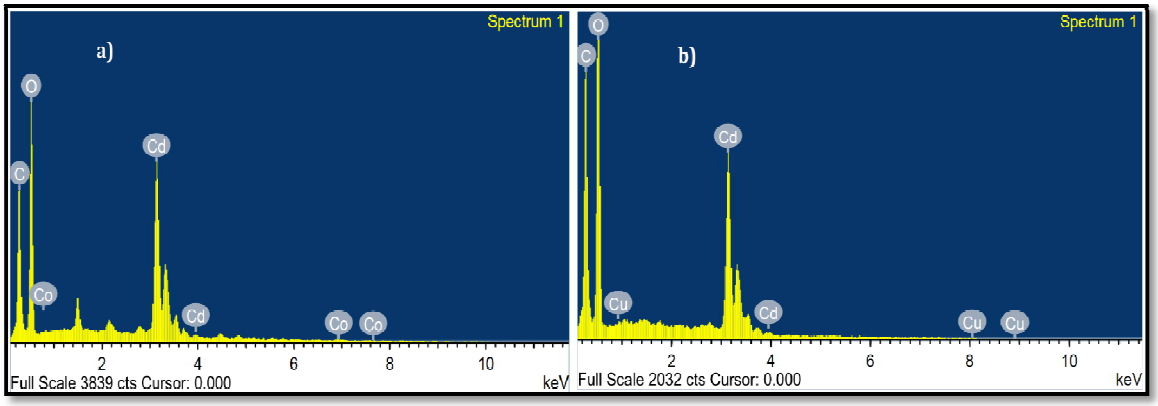


Figure 5. EDAX spectra of CoMCd and CuMCd crystals.

Table 2. Average weight and atomic weight percentage of crystals

Crystals	Elements	Weight %	Atomic %
	O	47.197	62.24
	Co	0.348	0.12
CoMCd	Cd	34.75	6.52
	C	17.71	31.12
	Total	100.00	
	O	52.560	63.48
	Cu	0.147	0.04
CuMCd	Cd	27.570	4.74
	C	19.718	31.74
	Total	100.00	

Thermogravimetry analysis (TGA/DSC): The TGA curve for CoMCd and CuMCd crystal is shown in figure 6. The TG plot of CoMCd revealed that the decomposition occurs in two stages in the temperature range 60-380°C.The first step of thermal decomposition occurs in the temperature range of 50–130°C with measured weight loss of 21.33% (calculated loss: 21.24%) with the loss of three water molecules. The dehydrated CoMCd crystal further decomposed at 255-380°C with a weight loss of 28.77% (calculated loss: 27.34%) loosing CO and CO_2 simultaneously. On heating above 380°C the crystal shows stability until 600°C. In the final stage, the material is reduced to its oxide state (>650°C).

In CuMCd the decomposition occurs in two stages in the temperature range 50-395°C. The first step of thermal decomposition occurs in the temperature range of 50–127°C with measured weight loss of 21.1% (calculated loss: 19.65%) with the loss of three water molecules [**5, 6**]. The second stage of decomposition occurs in the temperature range of 256°C-395°C with a weight loss of 28.54% (calculated loss: 27.45%).

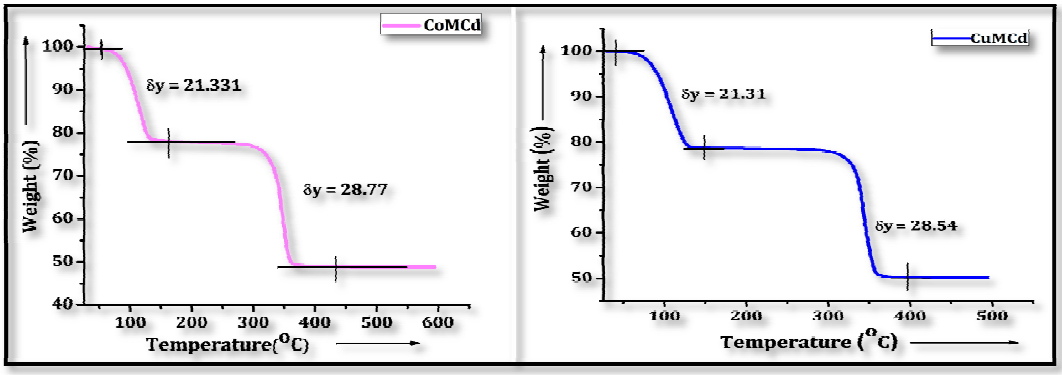


Figure 6. The TGA plot of CoMCd and CuMCd crystal.

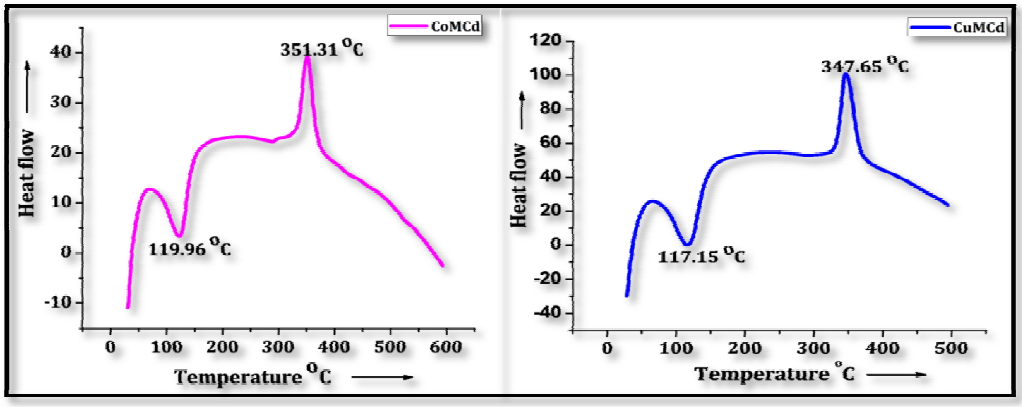


Figure 7. The DSC plot of CoMCd and CuMCd.

The DSC curve for gel grown CoMCd and CuMCd crystals is as shown in the figure 7. DSC shows clearly that endothermic carbonate formation is followed by exothermic disproportionation. On further heating above 900° C (not shown), the cadmium carbonate is decomposed into cadmium oxide by the release of carbon dioxide.

Magnetic susceptibility: The magnetic susceptibility of grown crystals CoMCd and CuMCd have be determined by using Gouy balance. Graphs of variation of Δm with H^2 for CoMCd and CuMCd were given in figure 8. In figure 9 it shows that how magnetizations of grown crystals were varies with magnetic field for CoMCd and CuMCd crystals. The magnetic susceptibilities of CoMCd and CuMCd are given in table 3. The volume susceptibility of grown crystals is a positive value indicating that the grown crystals are paramagnetic in nature.

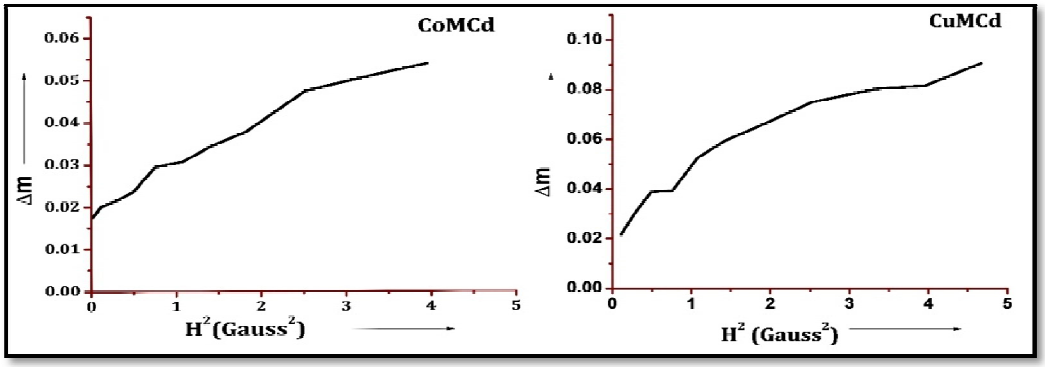


Figure 8. Variation of Δm with H^2.

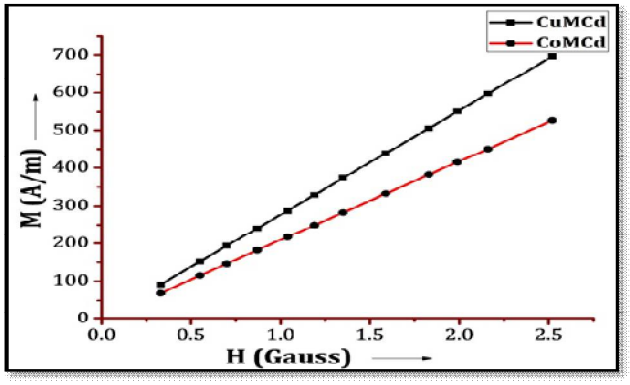


Figure 9. Variation of magnetization with magnetic field.

Table 3. Magnetic susceptibilities of CoMCd and CuMCd oxalate single crystals

Crystal	Volume susceptibility × 10^{-6} emu	Mass susceptibility × 10^{-6} emu
CoMCd	208.97	1.0077
CuMCd	276.46	2.35

FT-IR analysis: FT-IR vibrational spectra of cobalt mixed cadmium oxalate and copper mixed cadmium oxalate crystals are shown in figure 10. The strong absorption peaks in between 3000 cm^{-1} and 3500 cm^{-1} shows the OH stretching and the water bending. The bands around 1600 cm^{-1} were attributed to the C-O and C-C stretching of carbonyl group. The peaks at around 1300 cm^{-1} is assigned to C=O symmetric and O-C=O modes. The absorption peaks at 795 to 780 cm^{-1} indicates the presence of O-H out of plane bending. The absorption bands below 700 cm^{-1} are due to metal-oxygen (M-O) stretching vibrations [7]. Table 4 summarizes the FT-IR results of the grown crystals.

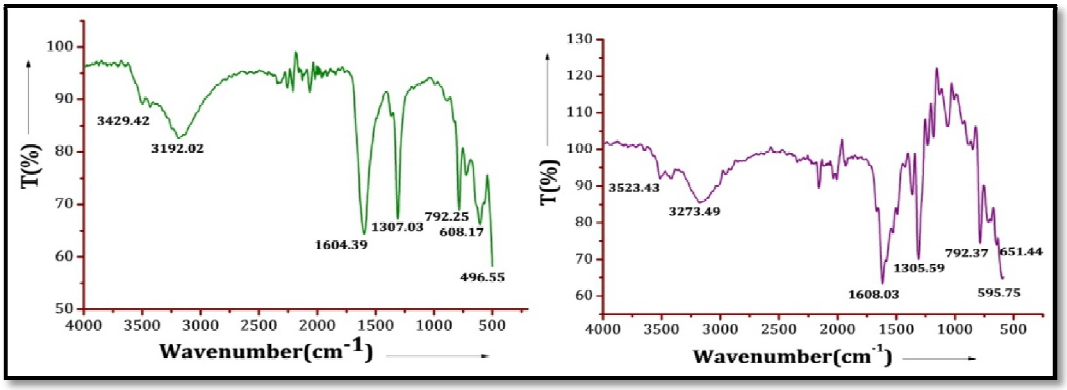


Figure 10. FT-IR spectra of CoMCd and CuMCd crystals.

Table 4. FTIR results of CoMCd and CuMCd crystals.

Wave numbers (cm^{-1})		Peak Assignments
CoMCd	CuMCd	
3429.42, 3192.02	3523.43, 3273.49	Symmetric and asymmetric stretching of OH group and water of crystallization
1604.39	1608.03	C = O stretching, O-H bending
1307.03	1305.59	C-C vibrations, C-O stretching
792.25	792.37	O-H out of plane Bending
608.17, 496.55	651.44, 595.75	O-M stretching

UV-Visible NIR studies: Under UV-visible spectroscopy, the UV cut off wavelength of undoped CoMCd and CuMCd is observed at 340 and 316.52 nm respectively. Figure 11 shows the variation of absorbance of light by the grown crystals as a function of wavelength in the UV-Vis range. The maximum value for the absorbance was found to be 4.05 and 4.15 for CuMCd and CoMCd respectively. The energy dependence of the absorption co-efficient in the high photon energy region is given as

$$A=2.303/t \log (1/T)$$

Where A is the absorbance and t is the thickness of the crystal.

By the linear extrapolation of the $(h\nu\alpha)^2$ v/s energy (hv) axis energy gap (E_g) was calculated which reveals the Band gap value of CuMCd and CoMCd as 4.846eV and 4.314eV respectively as shown in figure 12. The energy of light photon is not enough to overcome the forbidden energy gap

(E_g) of the crystal and crystals are said to become transparent to the visible light since no light photon is absorbed in the visible region [**8**].

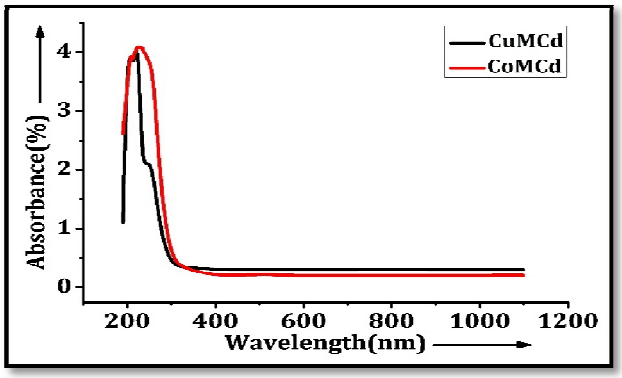


Figure 11. UV-Vis-NIR absorption spectrum of CuMCd and CoMCd.

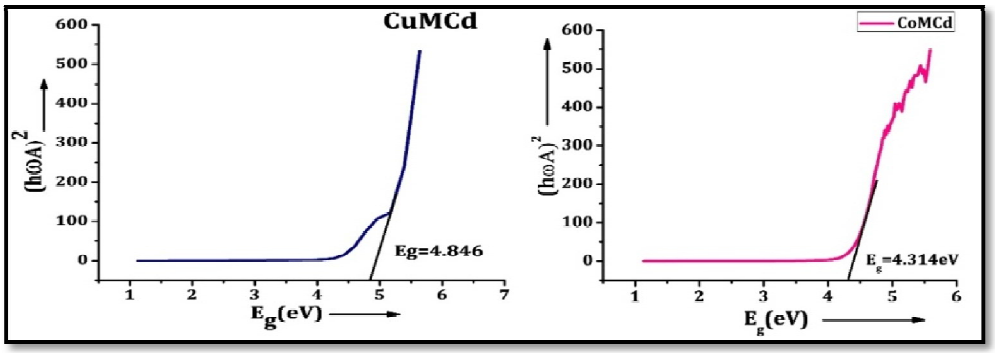


Figure 12. Tauc's Plot of CuMCd and CoMCd crystals.

APPLICATION

Optical transparency of gel grown CoMCd and CuMCd crystals allows them to be used for information control in optical circuit, light valves and optical switching applications where the crystalline perfection and optical transparency is essential. As crystals behave as insulators, they can be used in IC fabrication.

CONCLUSION

Copper mixed cadmium oxalate single crystal and Cobalt mixed cadmium oxalate single crystal were grown by single diffusion method. Size and quantity of grown crystals were changed by varying specific gravity of SMS solution. EDAX spectral studies confirm the presence of expected major elements. FT-IR spectrum of CoMCd and CuMCd crystals confirms the presence of water of crystallization, functional and metal-oxygen bonded groups. The thermal stability was studied by the TGA/DSC supporting its application in the electronic industries. UV visible spectrophotometric studies confirm that the crystal is an insulator.

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