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Characterization Studies of Magnesium Copper Tartrate Single Crystals Grown in Silica Gel by Nucleation Reduction Strategy at Different Radiations

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Abstract

Magnesium doped copper tartrate (MgCT) single crystals were grown in a gel medium using a single diffusion process at room temperature by exposing light (LASER, CFL) during growth. MgCT crystals were developed in three different growth phase to attain the total nucleation reduction. The optimal conditions were obtained by varying several parameters such as the concentration of the gel, the pH of the gel, the time of setting the gel, and the concentration of the reagents. Crystals having different morphologies were obtained such as blue semi-transparent, star shaped, different shaped crystals. It is found that different light radiations interact and reduce the nucleation and enhances the size and transparency of the crystals. The metallic compositions in the crystals were estimated by Energy-dispersive X-ray analysis (EDX). Thermo gravimetric analysis (TGA) of Magnesium doped Copper Tartrate crystals suggests the possibility of the presence of co-ordinate water molecules and thermal stability of the crystal. The functional groups present in the crystals were identified using Fourier transform infrared (FTIR) spectrophotometer. UV-Vis-NIR transmission spectrum was recorded to study the optical transparency of the grown crystals.

1. Introduction

Single crystals have played an important role within the advancements as technology evolved rapidly during the last century. The crystal growth could be a heterogeneous action within which conversion from one phase to a different phase of a compound is involved. Most of the acids are insoluble in water and decompose before the temperature at air pressure and that an appropriate solvent isn't available, crystals of such material are grown from the gel technique [1-2]. Crystal growth from solution is thought for an extended time, but control of heavy nucleation could be a problem. The gelling process is comparatively simple and inexpensive.

Most of the tartaric acids are insoluble in water with monovalent cations; like cadmium tartrate, sodium tartrate, zinc tartrate, manganese tartrate, and strontium tartrate. The divalent metal ion tartrates are exhibiting nonlinear optical and spectral characteristics and hence are utilized in transducers [3-5]. The metal compounds find many applications in several areas, for dielectric, ferroelectric, thermal, and optical properties of calcium tartrate. Cadmium tartrate is used in the piezoelectric application and lead tartrate in gasoline to stop knocking in motors.

Many of tartrate compounds find several uses in pharmaceutical, medical, and industrial fields. The tartrate compound is incredibly much utilized in the treatment of cognitive disorders related to diabetes, treating cancer with tartrate ions, and using tartrates in herpes. Iron tartrate complexes play a vital role as contrast blocks of renal issues before their dehydration. Also, Iron tartrate is one among the prominent species in fruit crush. Certain compounds find applications in cosmetics as hair conditioner additive and tanning agents for the skin. In the present work, the different light interacts with gel reduces nucleation; hence the number of crystals, size, shape, and colour are different [6-8].

2. Material and Methods

2.1. Crystal Growth of MgCT

Magnesium doped copper tartrate crystals (MgCT) were developed through silica gel using a single tube diffusion process at room temperature and exposure to various light rays (Semiconductor laser (SL) and compact fluorescent lamps (CFL) during growth. Silica gel was developed by adding sodium metasilicate ($Na_2SiO_3.5H_2O$) with a specific gravity of 1.045g.cm^{-3} solution and 1 molar tartaric acid with constant stirring to avoid a large amount of local ion concentration, which can cause early local gelation, and to produce a final solution that is not uniform. The pH of the gel was adjusted to a value of 5. This gel-forming mixture was installed in glass tubes with a size of 200 × 25 mm. The gel started to harden after about 4 days [9]. After the gel hardened, a mixture of an aqueous solution of 1M of copper chloride ($CuCl_2$) and 0.5M of magnesium chloride was pipetted over the hardened gel so that the solution could gradually slide along the walls of the tube to avoid thickened peripheral cracks. These tubes are exposed to different rays of light [10].

All chemicals were used AR grade such as Sodium metasilicate, tartaric acid ($C_4H_6O_6$), Copper chloride ($CuCl_2.2H_2O$), and magnesium chloride ($MgCl_2.6H_2O$). The semiconductor laser (λ=635nm), and 9Watt compact fluorescent lamp (CFL) were used for irradiation. The supernatant solution is dispersed in the gel substrate and reacts with the internal reagent, whereby copper tartrate crystals doped with magnesium are formed. In the growth process we daily observed and reported, it was found that nucleation rate reduces more in the laser medium than other light radiation and without any irradiation medium [11]. Different lights interact with gel reduce the nucleation, and enhance the variation of size, number of the crystal and transparency of the crystals. The grown crystals were collected after one month [12]. Optimized conditions are tabulated in Table 1.

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

Parameters	Optimization Condition
Density of sodium meta silicate	1.045 g.cm^{-3}
Concentration of Tartaric acid	1 M
pH of the mixture	5
Concentration of $CuCl_2$	1 M
Concentration of $MgCl_2$	0.5 M
Room temperature	24ºC
Period of growth	30 days

2.2. Characterization

The crystal morphology and elemental compositions of the grown crystals were determined using CARL ZEISS FESEM attached to the EDS system (Oxford instruments). Powder X-ray diffraction studies of the grown crystal was studied using Bruker AXS D8 advanced model with copper target (CuKα =0.15406nm). Infrared spectra were taken from the IR Presige-21 SHIMADZU Fourier

transform infrared spectrophotometer. The thermal properties of MgCT crystals are studied by TGA using the 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 190-1100nm.

3. Results and discussion

3.1. SEM and EDX Analysis

Scanning electron microscope photographs of magnesium doped copper tartrate single crystals were depicted in Figure 1. Thin and thick layer depositions and plate-like crystal morphology were found in the laser medium. Rock-like morphology shown in CFL irradiated crystal. The individual plates and plane with the sharp boundaries were observed in the crystal surface grown without irradiating at the growth phase [13].

Energy Dispersive Analysis by X-ray (EDX) is a method used for detecting the elemental arrangement of the samples. When a beam of electrons strikes a specimen, a part of the incident electrons excites the atom of the specimen, which then emits X-rays once they return to their state. The concentration by analyzing the energies of X-ray photons emitted as a result of bombardment by a beam [14]. The elemental analysis of the ions can be determined Magnesium doped Copper Tartrate crystals at different radiations are shown in Figure 2. Table 2 gives calculated and observed atomic % weight% of magnesium doped copper tartrate crystals. From Figure 2 and Table 2, it is confirmed that magnesium has present in the lattices of copper tartrate crystals [15].

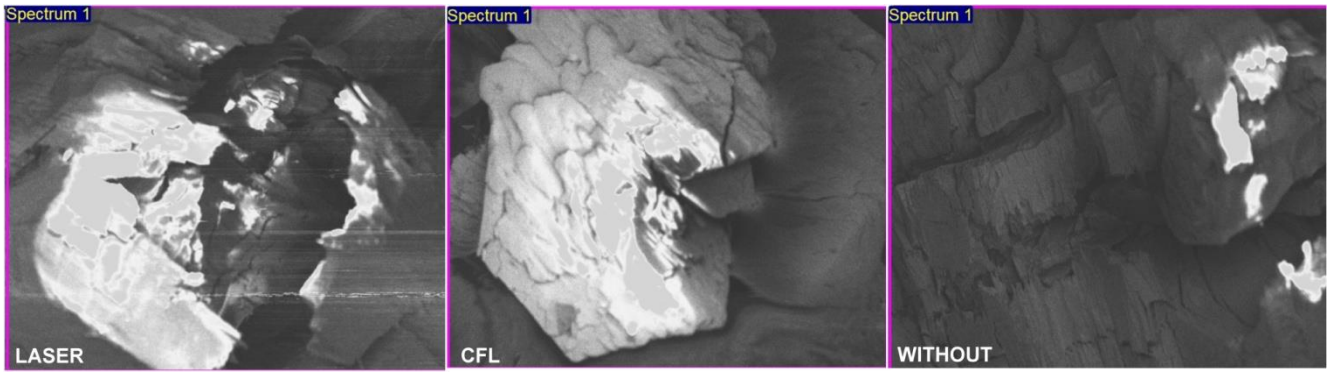

Figure 1. FESEM images of MgCT crystals.

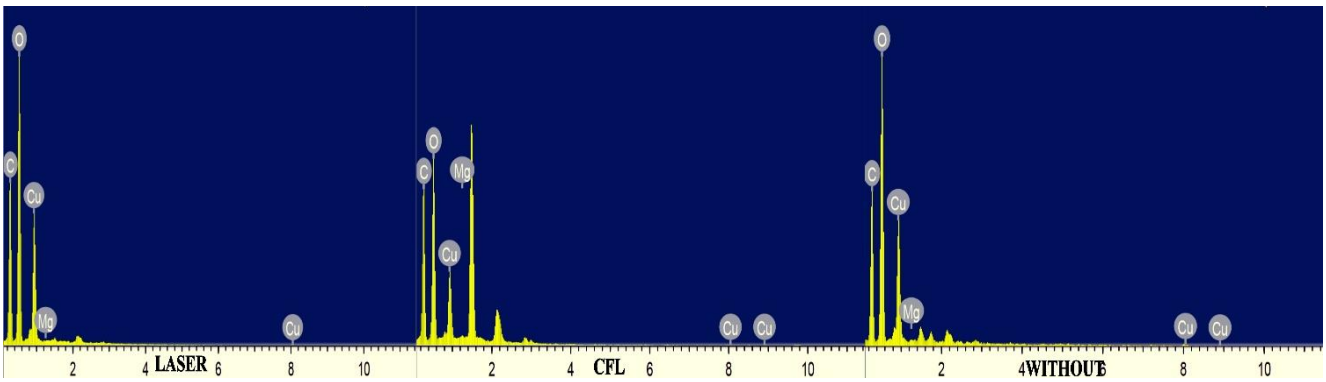

Figure 2. EDX spectrum of different light radiations.

3.2. X-ray diffraction studies

The crystal structure of different radiations grown crystals was studied by powder X-ray diffraction method. The diffraction pattern of the magnesium doped copper tartrate crystals at different growth conditions are shown in Figure 3.

From the powder X-ray pattern observed that, each peak has got a different finite width and different grain size. The grain size is determined by measuring the width of the line with highest intensity peak [15, 16]. The size of the grain can be calculated by using the formula

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where, β is full with of half maxima in radians, D is grain size of the crystal.

The calculated average grain size at different conditions is 0.6444nm (laser), 0.7890nm (CFL), and 0.7092nm (Without). The analysis of different diffraction peaks indicates the high crystallinity of the grown crystals.

Table 2. The atomic and weight percentages of the constituent elements in different growth conditions.

Growth conditions for MgCT	Elements	Atomic%	Weight%
CFL	Cu	9.57	30.58
	Mg	1.10	2.82
	O	60.22	48.40
	C	29.11	18.18
Laser	Cu	10.55	32.66
	Mg	1.02	3.40
	O	58.62	46.49
	C	29.81	17.43
Without radiation	Cu	7.09	24.30
	Mg	1.18	3.04
	O	60.82	52.81
	C	30.91	19.82

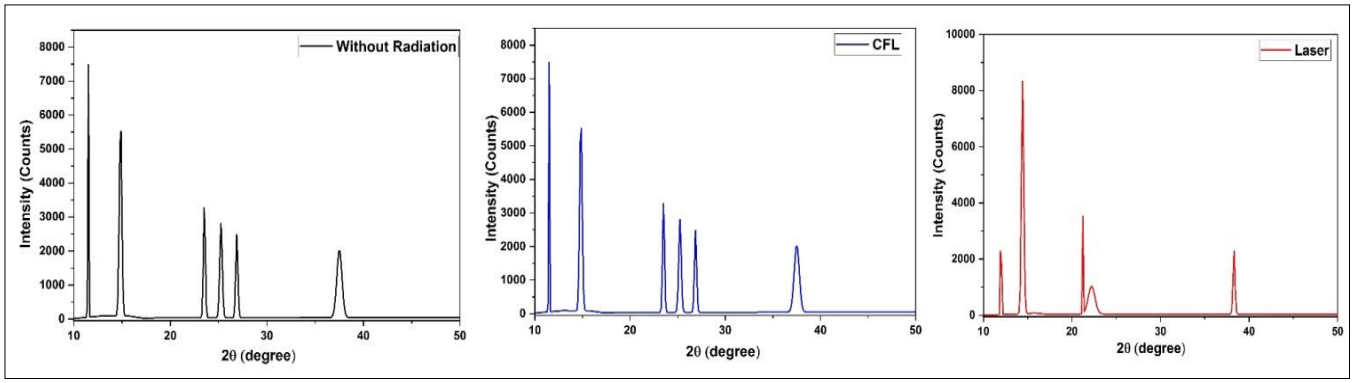

Figure 3. X-ray diffractograms of MgCT crystals.

3.3. FTIR-Analysis

The Fourier transform infrared spectra of magnesium doped copper tartrate single crystals grown at different radiation are shown the Figure 4. The same gel conditions at different radiations during the growth of MgCT single crystals variations of the functional group shown in Figure 4 (d). The different radiations of MgCT crystals observed vibrational frequencies and their assignments are shown in Table 3. It can be observed from the spectra that the band nearly 3168-3182cm^{-1} is due to O-H stretching and water of crystallization [17]. The absorption occurring nearly 2565-2605cm^{-1} is due to asymmetrical C-H stretching [18]. The bands observed at slightly less than 2400cm^{-1} and near 2100 cm^{-1} are due to C=O stretching respectively. The absorption band nearly 1400cm^{-1} and 1100cm^{-1} are due to C-O stretching [19]. The absorptions bands found between near 800-950cm^{-1} are due to C-H bending (out of plane) and O-H bending (out of plane). The absorption bands found between 800 and near 600cm^{-1} are due to C-H

bending and O-H bending [20]. The absorptions bands found between 600cm^{-1} and near 400cm^{-1} are due to metal-oxygen bonding [21-23]. The irradiation at the growth face makes the material to absorb high infrared radiation, hence the crystal become less transparent.

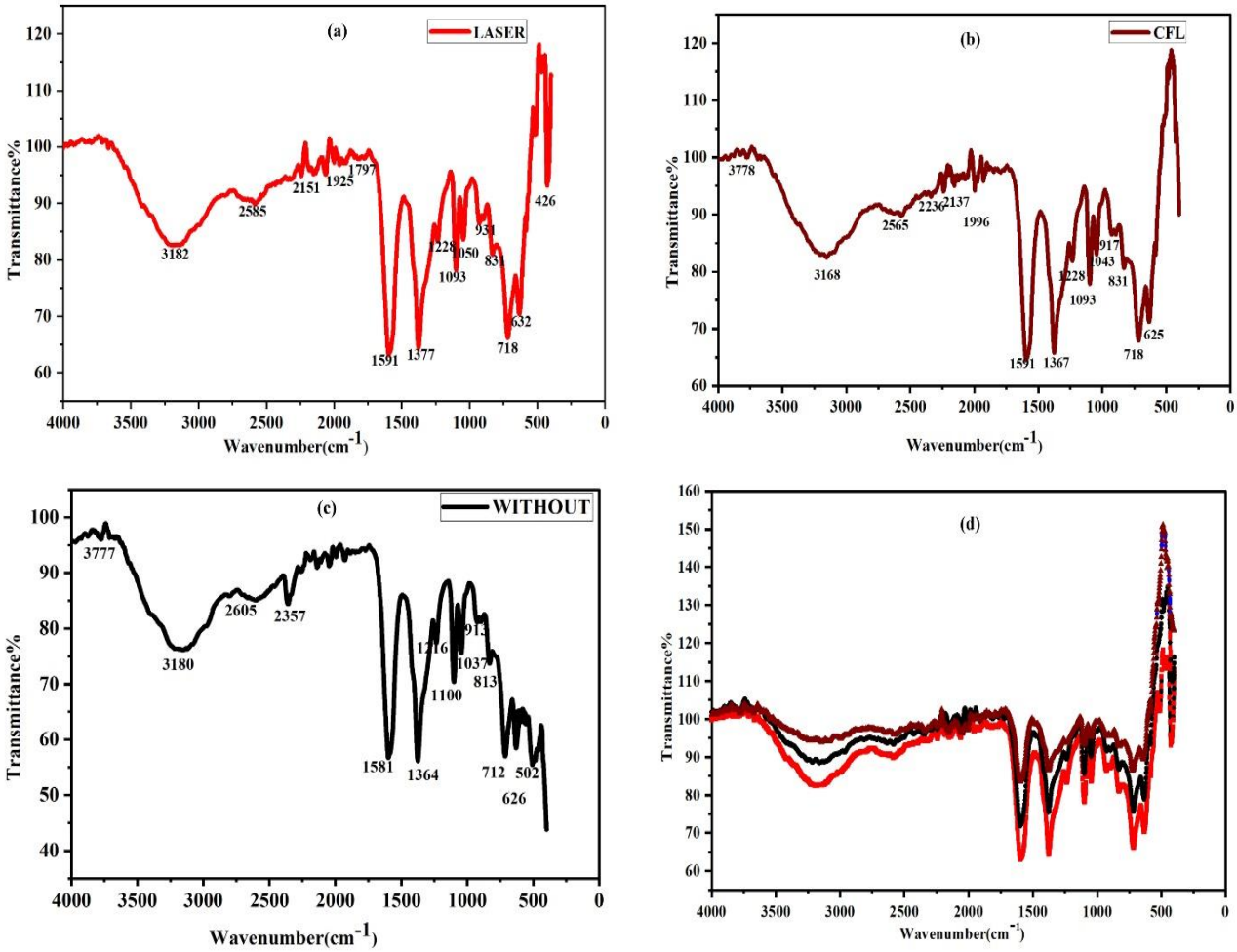

Figure 4. FTIR spectra of MgCT Crystals at (a) Laser, (b) CFL, (c) without radiation. And (d) The overall Changes in functional group.

Table 3. Observed functional group for MgCT Crystals at different growth conditions

Band assignments	Laser	CFL	Without
O-H Strecthing	3182,	3168	3180
C-H Strecthing	2585	2565	2605
C=O	2151	2236,2137	2357
C=C	1591	1591	1581
C-O stretching and OH in plane bending	1377	1367	1364
C-O stretching	1228,1093,1053	1228,1093,1043	1216,1100,1037
C-H bending (out of plane)and O-H bending(out of plane)	931,831	917,831	913,813
C-H bending and O-H bending	718,632	718,625	712,626
Metal oxygen bonding	426	510	502

3.4. Thermal Studies

The TG-DTA plots for the MgCT crystals shown in Figure 5. The thermal decomposition of the crystals grown by inducing different radiations occurs in two stages between 20-500ºC. At the first stage, the crystal loses water molecules and becomes anhydrous in the temperature range from 22 to 106ºC [24]. This results in the formation of anhydrous magnesium copper tartrate. At the temperature ranges

from 215 to 275ºC, the anhydrous MgCT sample decomposed into its oxide form by losing carbon monoxide and carbon dioxide molecules [25]. This result in the formation of magnesium-copper oxide. The weight loss percentages of the crystals were tabulated as shown in Table 4. The transition temperatures at the two stages by endothermic (evaporation of water molecules) and an exothermic (decomposition of carbon monoxide and carbon dioxide molecules) nature from the DTA plots also supports the loss of weight in TG plots.

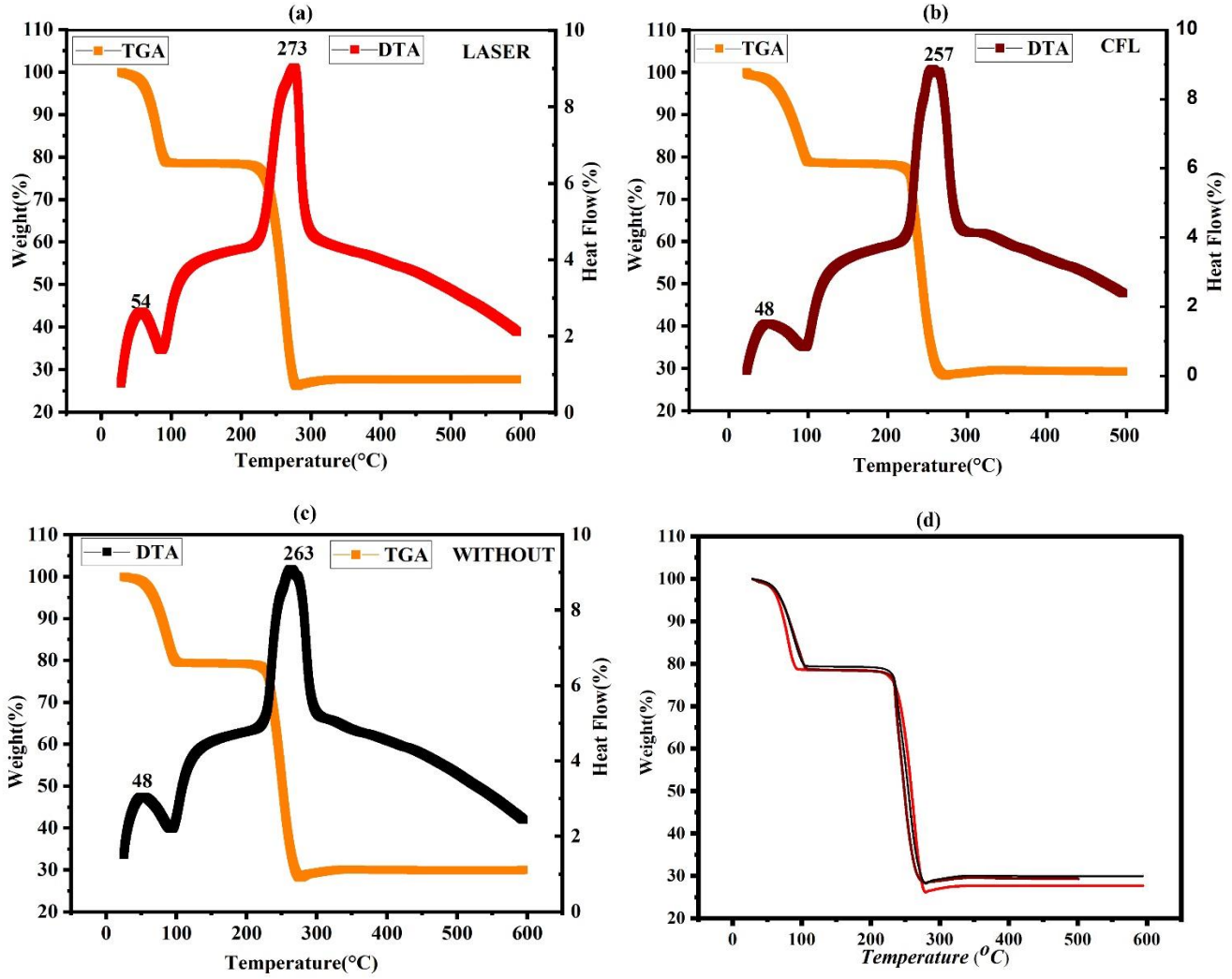

Figure 5. TGA/DTA plots of MgCT Crystals (a) Laser, (b) CFL, (c) without radiations, and (d) The overall changes in different conditions.

Table 4. The weight loss of MgCT crystals at different growth conditions.

Laser		CFL		Without	
Temperature (℃)	**Weight loss (%)**	**Temperature ºC**	**Weight loss (%)**	**Temperature ºC**	**Weight loss (%)**
30.31-92.13	20.05	23.37-101.35	19.97	34.41-105.74	19.23
214.95-278.89	43.45	217.62-275.76	42.13	216.36-274.19	42.15

3.5. UV- Visible NIR Studies

The UV spectrum of MgCT crystals grown at different conditions were presented in the Figure 6. The UV spectrum of different conditions was recorded in the spectral range of 190 - 1100nm. The UV-Visible transmittance spectrum is also shown in the figure. The value of the energy gap was calculated using the UV-Visible absorption spectra. The maximum absorption was observed at 230nm

to 235nm at different radiation. The overall changes of absorption spectrum at different radiation shown in Figure 6(d), and the calculated energy gap can be shown in Table 5.

The energy gap of the material calculated using the formula:

$$E = \frac{hc}{\lambda}$$

Where, E- Energy gap, h- Planck's constant, C- Velocity of light, λ – Wavelength

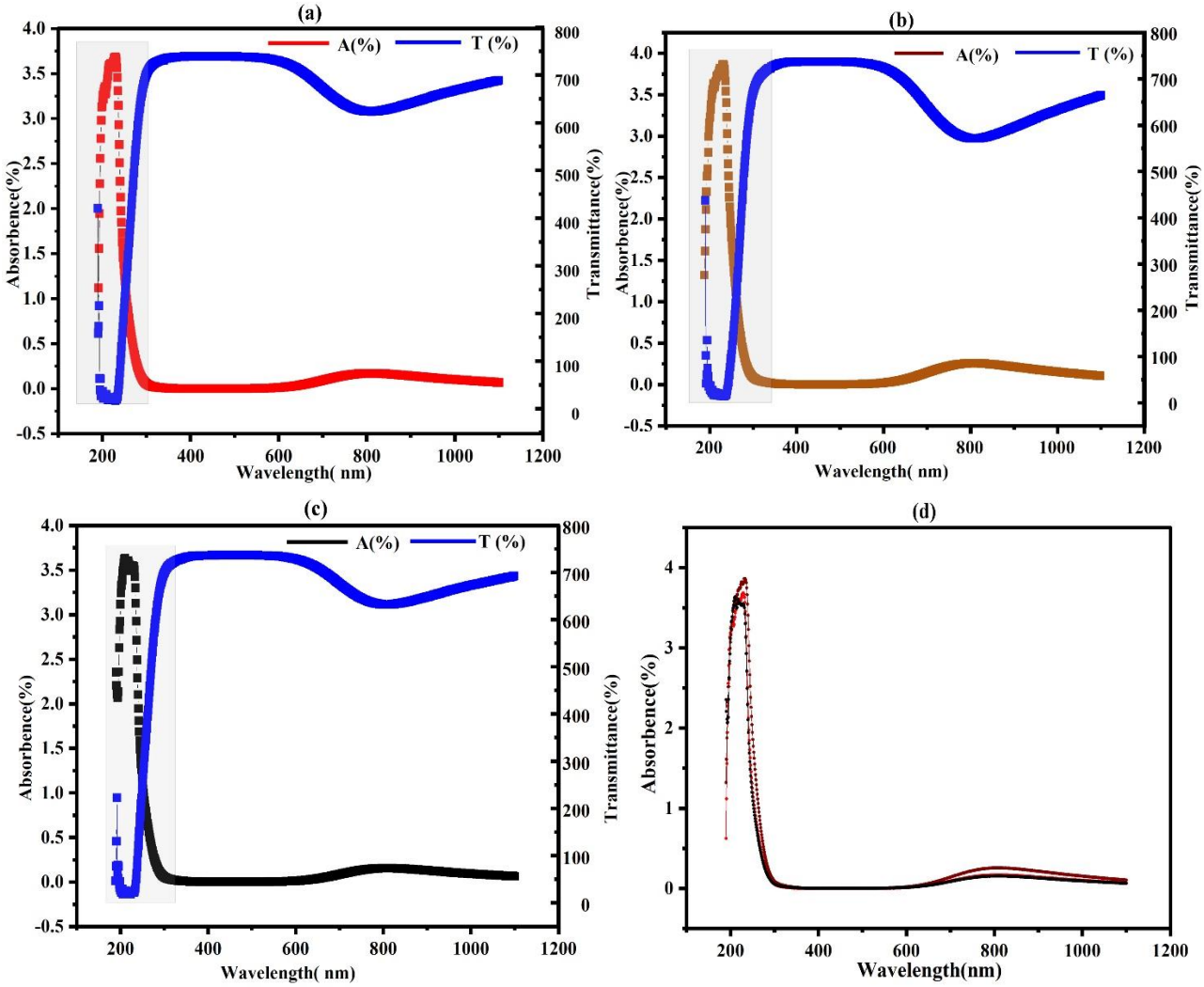

Figure 6. Absorption and transmittance spectrum of (a)Laser ,(b) Compact fluorescent lamp, (c) without radiation and (d) The overall changes in absorbance at different conditions.

Tauc's graph plot between $(\alpha h\omega)^2$ and the photon energy ($h\omega$) is shown in Figure 7. The extrapolation of the linear part of the graph gives the optical band gap energy value [26] as shown in Table 5. The Tauc's plot gives the variation of magnesium doped copper tartrate crystals at different radiations and also exhibits the variation of the energy gap [27-29]. Reddy is given the relation between Refractive index (n) and Energy gap (E_g) and, it can be written as:

$$E_g e^n = 36.3$$

Dispersion is a crucial property for the optical activity of the as grown samples. Further, the Refractive index (n) and Reflectance (R) of the crystals are calculated by the usage of expression [30-34]:

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

The calculated Refractive index (n) and Reflectance (R) as shown in the Table 5.

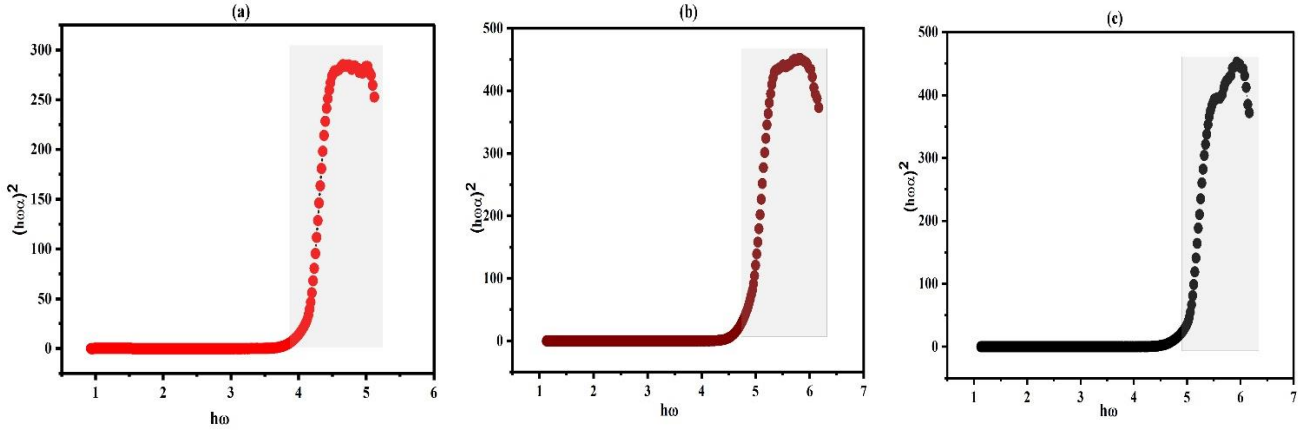

Figure 7. Tauc's graph plot between $(\alpha h\omega)^2$ and the photon energy (hω) of (a)Laser, (b) Compact fluorescent lamp, (c) without radiation.

Table 5. Variation of Energy band gap (E_g), Refractive index (n) and Reflectance (R)

Crystal	Growth Conditions	Band gap Energy (eV)	Refractive index (n)	Reflectance (R)
MgCT	WITHOUT	5.13	1.96	0.105
	LASER	4.00	2.20	0.140
	CFL	4.82	2.02	0.114

Conclusions

Magnesium doped copper tartrate single crystals were successfully grown by the silica gel medium in different light radiation. The optimum conditions were identified by varying different parameters. The MgCT crystals are grown at room temperature by irradiating compact fluorescent lamp (CFL) and semiconductor laser to vary the nucleation. It was found that the MgCT crystal nucleation rate reduces more in the laser medium than other light radiation and without any irradiation medium, different lights interact and reduce the nucleation, and enhance the size, number of the crystal and transparency of the crystals. This is due to the variation of supersaturations. FTIR and EDX spectral studies confirm the presence of Magnesium copper cation and tartrate group bond in these MgCT single crystals. The grown crystals are highly crystalline and thermally stable above 500ºC.

UV-Visible spectroscopic studies confirm that an insulating and transparency behavior of gel grown MgCT single crystals determined by spectral studies to use these materials in the optoelectronic devices.

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