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RESEARCH ARTICLE

GROWTH AND CHARACTERIZATION OF CALCIUM DOPED BARIUM TARTRATE CRYSTAL FROM SILICA GEL

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ABSTRACT

In the present investigation, single crystals of Barium calcium tartrate were grown by gel technique using diffusion method. The growth conditions were optimized by varying the parameters such as concentration of the gel, setting time of the gel and concentration of the reactance. The test tubes were used as crystallization vessels while silica gel as a growth media. The grown crystals were characterized by using X-ray diffraction, Scanning electron microscopy, Ultra-Violet visible spectroscopy, Photoluminescence and FTIR analysis. From Scanning electron microscopy, Barium calcium tartrate crystal revealed a regular morphology.PL shows a ultra violet emission at 360nm, 385nm, Blue-green emission at 495 nm and green emission at 530nm.The grown crystals have an excellent transparency in the region above the cut of wavelength, which is an essential parameter for optical applications.

INTRODUCTION

In recent years crystals growth in gel medium has attracted the attention of many investigators (Henisch *et al*., 1965; Henisch, 1970; Dharma Prakash and Mohan Rao Bull, 1986; Shedam and Venkateswara Rao Bull, 1993 and Garud and Saraf Bull, 2008). The principle relies on the slow migration of crystal constituents (ions) through silica gel so that a very slow reaction occurs with the formation of a sparingly soluble compound. When the concentration of this compound exceeds the solubility limits, crystals will be formed, the main function of the gel being to control the flow of reacting ions.

Mixed crystals growth has scarcely been studied by employing the gel technique (Joshi *et al*., 1980 and Dharma Prakash and Mohan Rao, 1986) and the field is in an early stage of development with many opportunities to create new species. Most of the tartrate compounds are in soluble in water and decompose before melting. Hence single crystals of such type of compounds cannot be grown by either slow evaporation or melt technique. In this situation gel method is the appropriate one for their growth. It was thought work while to undertake investigation on growth of crystals of barium calcium tartrate and their characterization by different methods. Optimum conditions were established by varying various parameters such as concentration gel solution, setting time of the gel solution and concentration of the reactance. These crystals were characterized by using X-ray diffraction Scanning electron microscopy, Ultra-Violet visible spectroscopy, and Photoluminescence and FTIR analysis.

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MATERIALS AND METHODS

Crystal growth in gel media is very effective and has attracted much attention in recent years, due to its unique characteristic of suppression of nucleation centres. Crystals grown at ambient temperature have lower concentration of non-equilibrium defects than grown at elevated temperature. The barium calcium tartrate crystals were grown by gel technique using single diffusion method at room temperature. Gel was prepared by mixing the solutions 1M tartaric acid ($C_4H_6O_6$), 1M sodium meta silicate (Na2SiO3). After setting the gel, it was left for aging. Over the set gel, 0.7 molar Barium Chloride solution, 0.3M calcium nitrate solution were mixed and gently poured with the help of a pipette, so as to allow the solution to fall steadily along the walls of the tube without disturbing the gel surface. The mouth of tube is covered by cotton plug and kept for the setting. The solution was faint milky and transparent, initially, but with lapse of time its color slightly change. The test tubes were kept undisturbed at room temperature. The supernatant ions (Ca++ and Ba++) slowly diffuse into the gel medium where it reacts with inner reactant. Tiny nuclei were seen at the interface of the diffusion layer in

two to three days. After twenty days the crystal was taken out from the test tube for the further characterization.

RESULTS AND DISCUSSION

X-ray diffraction

X-ray diffractogram of gel grown Barium Calcium tartrate crystal was recorded using powder rotation photograph method on 'XPERT PRO' X-ray diffractometer at department of Physics, Alagappa University, Karaikudi. CuKα-radiation (wavelength λ=1.5406 A^0) was used. The appearance of sharp and strong peaks confirms the good crystallinity of the growth of tartrate crystal. The characteristic 100% peak of Barium calcium tartrate has appeared at around 38.4226.The crystalline perfection of the crystals is extremely good without having any internal structural grain boundaries. XRD has the potential ability to identify the active ingredient. A compound can be easily distinguished form other members by examining X-ray data, comparing the XRD pattern; the incorporation of the dopants in Calcium Nitrate lattice is confirmed. The present study is compared with preview literature (Suryanarayana and Dharmaprakash, 2000). The result well agrees with reported value these is observed shift in the peak position in 2θ.This shift in the peak position may be due to addition of Calcium Nitrate in barium Chloride. The intensity of last peak indicates the calcium nitrate (Pradyumnan and Shini, 2009).

Determination of Grain size from XRD spectra

From the XRD pattern, it is observed that, each peak has got a finite width. The grain size is determined by measuring the width of the line with highest intensity peak. The grain size can be calculated by using the formula (Kose *et al*., 2009):

Grain size $D = 0.9 \lambda / \beta \cos\theta$

Where, β is full width of half maxima in radian and D is grain size of the crystal.

$D = 0.9 \times 1.54056Å / 0.0025761 \times \cos(19.2113)^\circ$
$= 56.998$ nm.

The values of 2θ, d values, intensity ratio and their corresponding h, k and l plane were shown in the Table (1). The observed d-values, 2θ values and h, k and l plane were compared 23with standard data of 2002 JCPDS v. 2.3, 26-0192 and JCPDS 7440-393, (Suresh Keda Bachhav *et al*., 2010).

Table 1. Shows XRD data of Barium Calcium tartrate crystals

2 Theta Deg.		d-spacing A^0		Intensity	hkl
Observed	From JCPDS	Observed	From the literature & JCPDS		
12.4561	11.464	7.10623	7.0934	77.49	101
15.8429	16.202	5.59399	5.2949	32.41	002
20.2769	19.894	4.37965	4.2303	11.54	021
24.2630	23.061	3.66840	3.9850	21.39	-211
25.9010	25.774	3.44000	3.3117	18.53	310
29.1682	28.273	3.0617	3.0795	17.25	-301
31.7363	30.608	2.81956	2.8195	7.10	222
36.0442	36.796	2.49184	2.5582	13.02	420
38.4226	38.630	2.34290	2.3140	100	332
41.2413	42.152	2.18905	2.1330	24.74	360
51.6028	51.524	1.77124	1.7710	66.04	193

The three highest intensity and lowest intensity peaks grain size and dislocation density were calculated. These values were shown in the give Table (2).

Table 2. Shows grain size and dislocation density

Grain size (nm)	Lattice strain ($x10^{-4}$ m)	Dislocation density ($x10^{15}$ m)	Intensity (%)
56.998	6.08152	0.307808	100
54.1477	6.3648	0.34106	77.49
29.891	11.5963	1.11922	66.04
6.99446	49.55849	20.4405	7.10
24.69652	14.03577	1.63956	6.69
8.5565	40.51122	13.65866	2.16

FT-IR spectral analysis

FT-IR is used for structural analysis. In the present study IR spectrum of Barium Calcium tartrate and citrate sample was recorded using Thermo Nicolet X-ray diffractogram at St. Joseph's college Trichy.

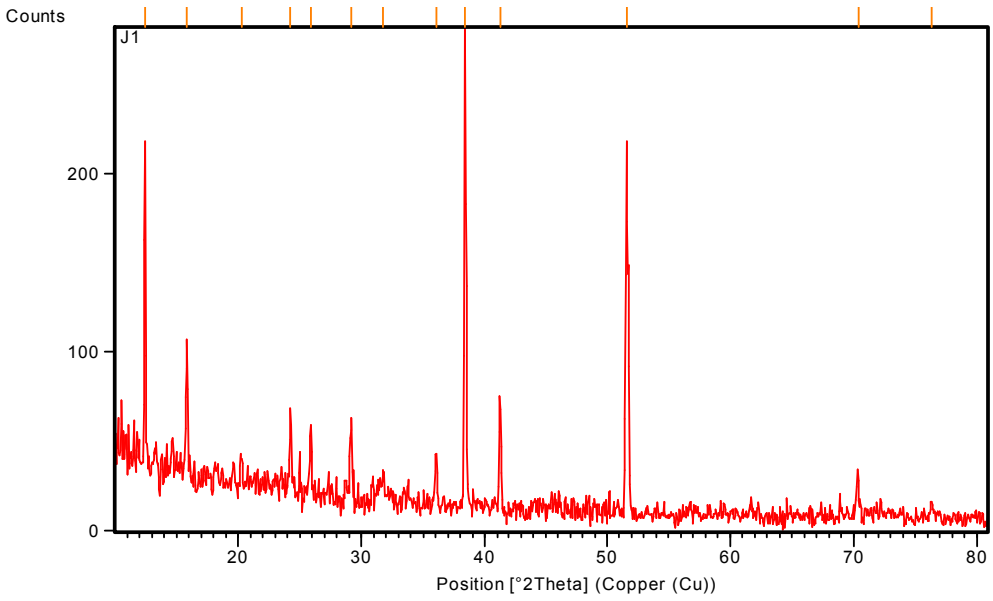


Fig. 1. X-ray diffractogram of gel grown Barium Calcium tartrate

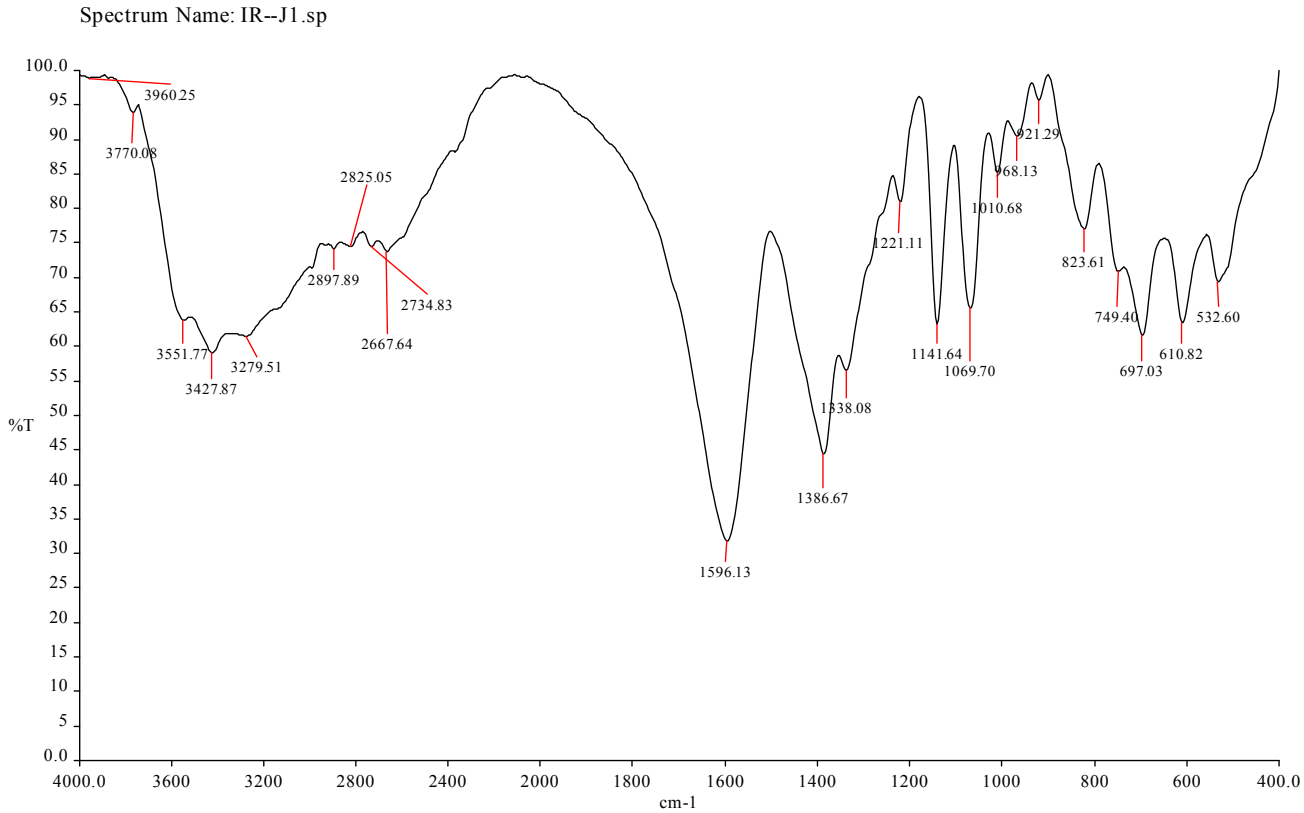


Fig. 2. Barium Calcium Tartrate Crystal

Fig (2) shows FT-IR Spectrum of Barium Calcium tartrate crystal. The IR spectra of these grown crystal was recorded in the wave number range 500cm^{-1}- 4000cm^{-1}. The band at 3427.87cm^{-1}, 3557.77cm^{-1}are due to O-H stretching and water of crystallization and the bands at 2825.05, 2897.89cm^{-1} are assigned to H-C-H stretching vibrations. The bands at 2734.51, 2667.64 cm^{-1} Hydrogen bonded O-H stretching vibration. The bands at 1596.13cm^{-1} is attributed due to C=O stretching in Carboxylate ion. The bands at1338.08cm^{-1}, 1386.67 cm^{-1} are due to C=O weaker symmetric stretching in Carboxylate ion and at 1221.11cm^{-1}are due to O-H in plane bending. The bands at 1141.64cm^{-1}, 1069.70 cm^{-1}, 1010.68cm^{-1} are due to C-O stretching mode. The absorption bands are found at 968.13cm^{-1},921.29cm^{-1}, 823.61cm^{-1} are due to the metal oxygen bonding. It is confirmed that Water of crystallization and metal oxygen bonding is present in the grown crystal (Pradyumnan and Shini, 2009).

SEM Analysis

In the present work powdered sample of Calcium Barium tartrate crystals was examined by using SEM technique at the Gandhigram Rural institute. The study of the surface of the crystal gives valuable information about its internal structure. Figure illustrates SEM photographs of single crystals of Barium Calcium tartrate crystal. The high depth of field of the SEM images make it's especially suitable for the study of the fractured surfaces and complex microstructure such as those found in composite material. These crystals are grown by gel method. Thick and thin layers are seen in Fig (3a,3a & 3c). The fig (3a) shows the regular arrangement of honeycomb like structure with the sharp edges was observed. Fig (3b&c) shows the appearance of embedded crystal lattice (Sawant *et al*., 2011).

Photoluminescence (PL) Analysis

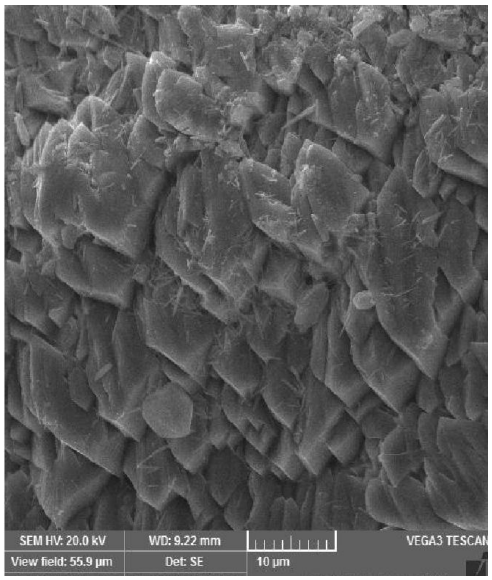
The photoluminescence spectroscopy is one of the non-destructive tools in analysing the crystalline defects present in the sample. Fig (4) shows the room temperature photoluminescence emission spectrum of Barium calcium tartrate crystal which is excited at a wavelength of 280 nm. The peaks obtained at 360 nm, 385 nm 495 nm and 530 nm were attributed to the crystalline defects such as interstitials (or) vacancies present in the samples. The intensity of the band edge emission peaks which denotes the better crystalline nature of Barium calcium tartrate crystal. Of these, the Ultra violet emission at 360nm, 385nm, Blue-green emission at 495 nm and green emission at 530nm (Sawant *et al*., 2011).

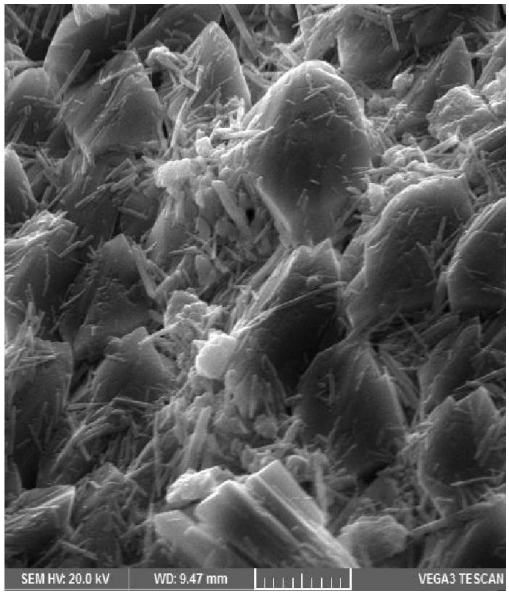
UV-visible spectral analysis

In a crystalline material, the region of transparency to electromagnetic radiation defines the intrinsic loss mechanism and also theoretical transmittance achievable within the region. The transmission range of Barium Calcium Tartrate crystals were determined by recording optical transmission spectra in the wavelength region 190-1100 nm using UV - Lamda-35 spectrometer. The % of transmittance verses wavelength (nm) is shown in Fig (5). From the graph, it is evident that the optical transparency of the grown crystals shows an excellent transparency window above the cut of value 225nm (Sawant *et al*., 2011).

Determination of optical band GAP

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons.





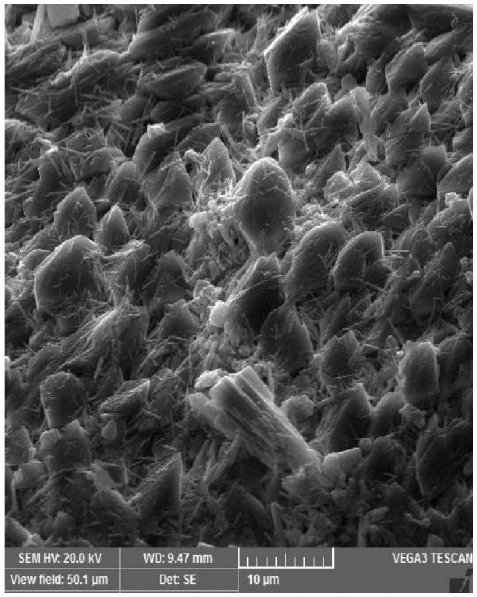


Fig. 3a. Honeycomb structure; Fig. 3b&c. Embedded crystal lattice

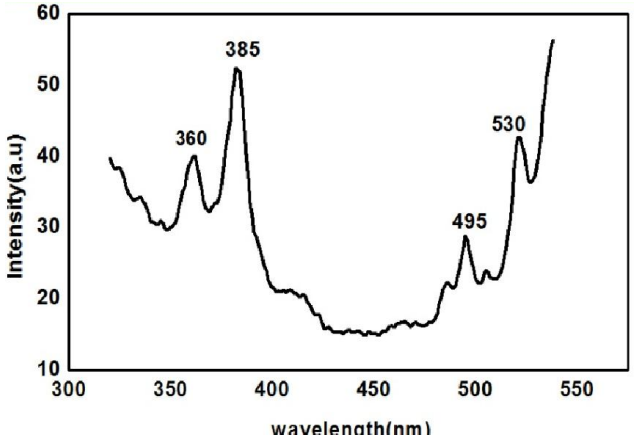


Fig. 4. Emission spectrum of Barium calcium tartrate crystal

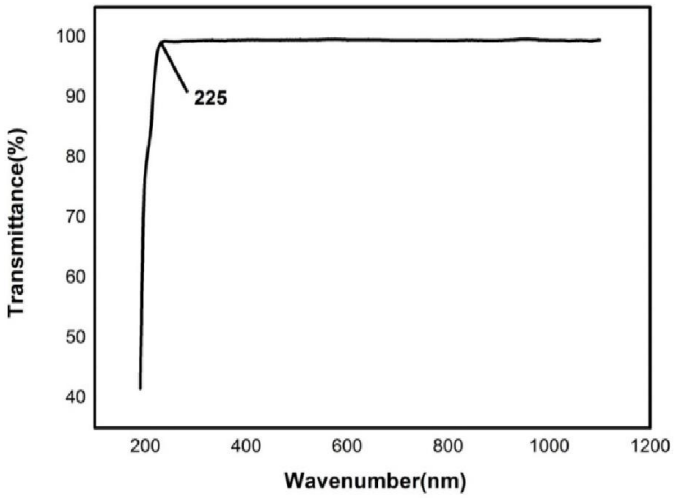


Fig. 5. UV- Transmittance Spectra of Barium Calcium Tartrate Crystal

The absorption coefficient (α) were determined using Beer's law

$\alpha = 1/d \log (1/T)$

where T is the transmittance and d is the thickness of the cell. As the indirect band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (Rajaram *et al*., 2013),

$$\alpha = \frac{A(h\vartheta - Eg)}{h\theta}$$

where Eg is optical band gap of the crystal and A is a constant. The plot of variation of Photon energy (E) in eV and $(\alpha h\upsilon)^2$ is shown in figures. The linear region of the curve was extrapolated to find the X – intercept which gives the Band gap of the grown crystal.

From the Fig (6) shows the band gap energy of Barium Calcium Tartrate crystal . The band gap was found to be 5.2eV.

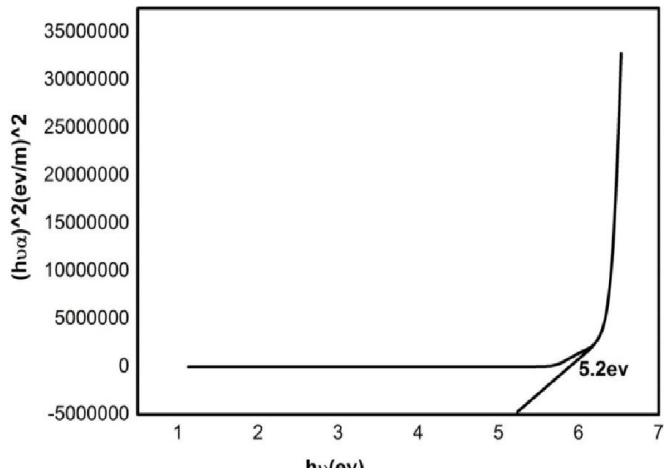


Fig. 6. Bandgap curve of Barium Calcium Tartrate crystal

Determination of extinction coefficient

The optical properties of a crystal can be evolved mainly from its optical transparency, band gap, extinction coefficient and the refractive index. The optical properties of the crystals are governed by the interaction between the crystal and the electric and magnetic fields of the electromagnetic wave. Extinction coefficient is the fraction of light lost due to scattering and absorption per unit distance in a participating medium. In electromagnetic terms, the extinction coefficient can be explained as the decay or damping of the amplitude of the incident electric and magnetic fields. The extinction coefficient can be calculated from the following relation,

$$k = \frac{\lambda \alpha}{4\pi}$$

From the graph it is clear that the extinction coefficients (k) varies with wavelength and hence depend on the photon energy. The internal efficiency also depends on the photon energy. Hence by tailoring the photon energy, one can achieve the desired material for the device fabrication.

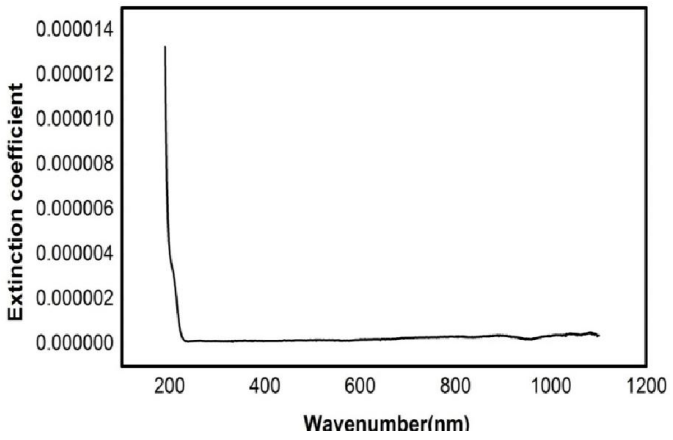


Fig. 7. Extinction coefficient curve of Barium Calcium Tartrate crystal

Conclusion

- The growth of Barium Calcium tartrate crystals in the system $Bacl_2$ -$Ca(No_3)_2$ — Na_2Sio_3 – $C_4H_6O_6$ were grown by single diffusion technique in gel method.
- The crystalline nature and phase purity of the grown crystals barium calcium tartrate crystal are confirmed by powder XRD pattern.
- The fundamental groups present in ba-ca have been confirmed by FTIR spectral analysis.
- Scanning electron microscopy is used to determine the sample morphology. Barium calcium tartrate crystal revealed a regular arrangement of honeycomb like structure with the sharp edges.
- Crystalline defects of barium calcium tartrate crystal were studied by photoluminescence spectroscopy.
- The optical property of barium calcium tartratecrystal are studied by taking the optical absorption and transmission spectrum in the range of 190 -1100nm using UV spectrometer.
- In UV Spectroscopy, the grown crystals have an excellent transparency in the region above the cut of wavelength, which is an essential parameter for optical applications. The cut of wavelength is 225 nm. The band gap was found to be 5.2 eV.

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