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SEM, PL, and UV Properties of Mixed Crystals of Ca-Ba tartrate in silica Gel

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ABSTRACT

Calcium Barium tartrate single crystals were grown in silica gel at ambient temperature. Effect of various parameters like gel pH, and gel aging, gel density and concentration of reactants on the growth of these crystals were studies. Crystals having different morphologies and habits were obtained. Whitish semitransparent, pale yellow, rhombohedra shaped, needle shaped crystals of Calcium-Barium tartrate were obtained. Some of them were transparent diamond shaped, some are twined. The crystals grown were characterized by PL, SEM, and UV. XRD studies reveal that the crystal lattice of the Calcium Barium tartrate is orthorhombic and crystalline perfection of the crystals is extremely good. Photoluminescence spectrum shows Cyan, green, orange, and red emissions. SEM image showed plate like morphology and further plate like growth was observed on some plates.

Keywords*:* Gel technique, Calcium Barium tartrate, SEM, UV, and PL.

INTRODUCTION

In recent years crystals growth in gel medium has attracted the attention of many investigators [1-5].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 [6-7] 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. The growth of single crystals oh Calcium tartrate was reported [1] and single crystals of strontium tartrate was reported [8].thermal studies on tartrate crystals grown by gel method were reported by many investigators [9-11]. Tartrate crystals are of considerable interest, particularly for basic studies of some of their interesting physical properties. Some crystals of this family are ferroelectric [12-14], some others are piezoelectric [15] and quite a few of them have been used for controlling laser emission [16]. As tartrates are sparingly soluble in water and decompose before melting, the gel method is found to be more promising than the high temperature crystal growth methods.
Many tartrates salts with monovalent cations; such as rubidium hydrogen tartrate [17], sodium tartrate [18], and ammonium tartrate [19] and divalent cations; such as calcium tartrate [20], cadmium tartrate [21], manganese tartrate [22], zinc tartrate [23] and strontium tartrate [24-25] have been studied for their dielectric and thermal properties.

Mixed crystal of tartrate have several applications in medicine, optics etc. and hence; it was thought work while to undertake investigation on growth of crystals of mixed tartrate and their characterization by different methods. The purpose of the present paper is to report for the first time (to the best of our knowledge) the growth of mixed single crystals of Calcium Barium tartrate in silica gel at ambient temperature.

MATERIALS AND METHODS

Experimental

Good crystal can be grown in gels in a variety of ways; the single diffusion method was employed in the present work for the growth of Calcium Barium tartrate crystals. The growth process involves the diffusion of mixed Calcium Chloride-Barium Chloride solution in to a gel in which tartaric acid is impregnated beforehand. The silica gel was used as a growth media. The chemicals used for growth mixed tartrate were $C_4H_6O_6$, $CaCl_2$, $BaCl_2$ and Na_2SiO_3 all chemicals were of AR grade. The crystallization apparatus consist of borosilicate glass test tubes of length 20 cm and diameter 2.5 cm placed vertically on wooden stands. Tartaric acid, Calcium Chloride and Barium Chloride solution were prepared by dissolving these compounds in an appropriate amount of distilled water to give the required molarities. Gels of required specific gravity were prepared by adding to the solution of sodium Meta silicate, a calculated amount of redistilled water and a stock solution was kept ready for doing further experiments. Tartaric acid solution of particular strength was taken in a 100ml beaker and sodium Meta silicate solution of a suitable gravity was added drop wise using a tephlon cock burette, constantly stirring the solution in a beaker by magnetic stirrer. Stirring is done to avoid the excessive local ion concentration which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. Here tartaric acid acted as a lower reactant. The systronic digital pH meter model number 335 was used to measure the pH. The solution after noting pH values, being allowed to fall along the side of a test tube without giving chance for the formation of the bubbles. Test tubes were then closed with rubber corks or cotton to prevent evaporation and contamination of the exposed surface of the gel by dust particles of the atmosphere. The solution was found to be strongly

depends on pH. High pH value gel takes lower time to set than low pH value, depending on the environmental temperature. After ensuring firm gel setting, the saturated mixed solution of Calcium Chloride and Barium Chloride (supernatant) of particular strength was poured over the set gel with the help of a pipette. The solution being allowed to fall along the wall of the test tube to prevents the gel surface from cracking. The supernatant ions (Ca^{++} and Ba^{++}) slowly diffused in to the gel medium where it reacts with inner reactant.

The following reaction is expected to take place in the formation of Calcium Barium tartrate crystals.

$2C_4H_6O_6 + x\ CaCl_2 + (1-x)BaCl_2 \rightarrow Ca_xCd_{(1-x)}\ (C_4H_4O_6)_2.xH_2O + 4HCl.$

The systematic growth experiments were performed by adding $CaCl_2$,$BaCl_2$, as feed solution of strength varing from 0.2m to 1.2m over the set gel of pH range 4 to 4.5 the gel density range 1.02gm/cm^3 to 1.05 gm/cm^3.

RESULT AND DISCUSSION

The various optimum conditions for the growing crystals were found and are given in table 1.

Table 1: Optimum conditions for growth of Calcium Barium tartrate.

Conditions	Calcium Barium tartrate
Density of sodium meta silicate solution	1.04 gm/cm^3
Concentration of tartaric acid	1M
Volume of tartaric acid	7ml
Volume of sodium meta silicate solution	16ml
pH of the gel	4.2
Concentration of $Cacl_2$	1M
Concentration of $Cacd_2$	1M
Temperature	Room temperature

Figure1. (a) Whitish prismatic semi transparent, some are Pale yellowish crystals of Calcium Barium tartrate.

Figure 1(b) Semitransparent, needle shape crystals of Calcium Barium tartrate.

Figure 1.(c) Transparent crystal of Calcium Barium tartrate.

Figure 1(a), (b), (c). Optical photographs illustrating varied morphology of Calcium Barium tartrate crystals grown under different growth conditions.

Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel aging time, etc have considerable effect on growth rate. Figure 1(a), (b), (c) illustrates different morphologies of pure Calcium Barium tartrate crystals grown under different conditions of growth. The crystals grown are Whitish semitransparent, pale yellow, rhombohedra shaped, needle shaped crystals of Calcium-Barium tartrate were obtained. Some of them were transparent diamond shaped, due to fast growth rate twined crystals are obtained; faces are well developed and polished.

Characterization

Calcium Barium tartrate crystals were characterized by UV, PL, SEM.

4.1UV Absorption spectroscopy:

Absorption spectra of Calcium Barium tartrate crystals were recorded using a SHIMADZU UV-2450 UV-Vis spectrophotometer over the wavelength range 200 – 700 nm at Nano Research Laboratory, Department of Physics; Pratap College Amalner.Figure 2 shows UV absorption spectra of Calcium Barium tartrate crystals. From the spectrum, it has been inferred that Calcium Barium tartrate crystals have sufficient transmission in the entire visible and IR region. The absorption coefficient is high at lower wavelength and the wide transparency from 340 nm

suggesting their suitability for second and third harmonic generations of the 1064 nm radiation [26-27].

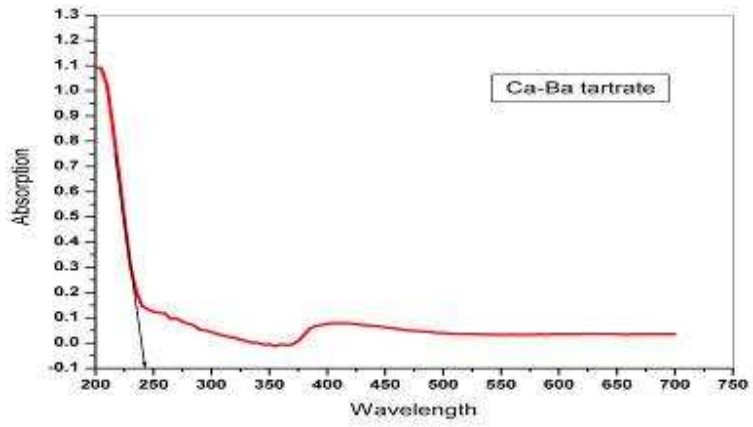


Figure 2: Optical absorption spectra of Calcium Barium tartrate

The band gap energy of the Calcium Barium tartrate crystals with the obtained wavelength are calculated using the following simple conversion equation;

Band gap energy (eV) = 1240/wavelength (nm).Band gap Energy is presented in the table 2.

Table 2: Band gap energy of Calcium Barium tartrate crystals

Crystal	λ (nm)	Band gap Energy (eV)
Calcium Barium tartrate	243	5.10

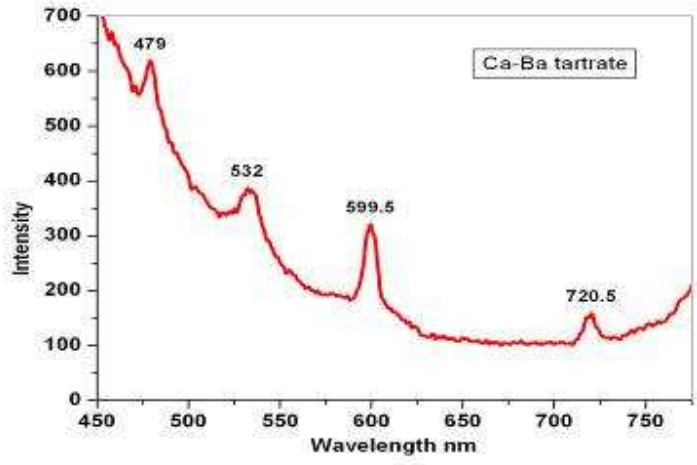
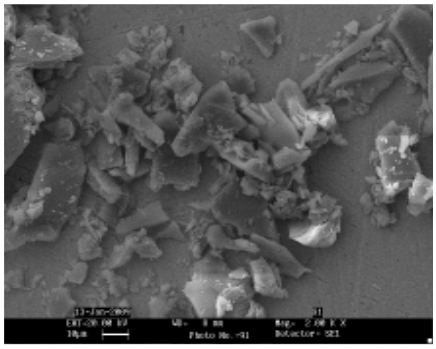


Figure3: Emission spectrum of Calcium Barium tartrate

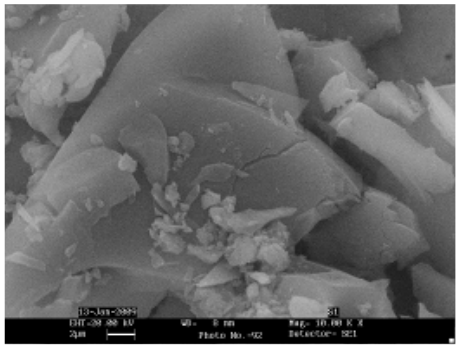
Photoluminescence (PL) characteristics:
A photo luminance spectrum was performed using Perkin Elmer LS55 florescent spectrophotometer at Nano Material Research Laboratory, Department of Physics Pratap College Amalner.

Figure 3 shows the emission spectrum of Calcium Barium tartrate crystal was recorded at room temperature. The emission spectrum shows the peaks mainly at 479nm, 532nm, 599 nm, and 720.5 nm when excited with 400 nm. Of these, the cyan emission at 479nm is the most intense of all emission, green emission at 535nm. The peak of orange emission at 599 nm is sharp and the peak of red emission at 720.5

4.3 SEM Analysis:
In the present work powdered sample of Calcium Barium tartrate crystals was examined by using SEM technique at the National Chemical Laboratory, Pune. The study of the surface of the crystal gives valuable information about its internal structure. Figure 4a illustrates SEM photographs of single crystals of Calcium Barium tartrate crystal. An enlarged SEM image is shown in Figure 4b. It shows plate like crystal morphology. These crystals are grown by layer deposition. Thick and thin layers are seen in figure. The individual plates of samples are flat and the plates with the sharp edges were observed. On some plates further plate like growth was observed.



4(a)



4(b)

Figure 4 (a): SEM image of Calcium Barium tartrate crystal. (b) Magnified SEM image.

CONCLUSION

Gel growth technique is suitable for growing crystals of Calcium Barium tartrate. Different habits of Calcium Barium tartrate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, concentration of reactants, etc. Calcium Barium tartrate crystals show the Cyan, green, orange and red emission when excited with 400 nm. SEM photographs shows plate like crystal morphology of the Calcium Barium tartrate.

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REFERENCES

[1] H. K. Henisch, J. Dennis and J. I. Hanoka, *J. Phys. Chem. Solids*, Volume 26, Page 493, **1965**.
[2] H. K. Henisch, *Crystal Growth in Gells*, Pennsylvania State University Press, University Park, Pennsylvania, **1970**.
[3] S. M. Dharma Prakash , P. Mohan Rao *Bull. Mater. Sci.* Volume 4 , Page 511-517 , **1986**.
[4] M. R. Shedam , Venkateswara Rao *Bull .. Mater. Sci*. Volume 16,Page 309- 315 , **1993**.
[5] S.L. Garud , K.B. Saraf *Bull. Mater. Sci* Volume 31 Page 639-643 2008.
[6] M.S. Joshi, P. Mohan Rao, A.V. Antony. *Bull. Mater. Sci.* Volume 2, Page 127 **1980**.
[7] S. M. Dharma Prakash , P. Mohan Rao *J.. Mater. Sci Lett.* Volume 5, Page 769, **1986**.
[8] M.H. Rahimkutty, Rajendra Babu ,K. Shreedharan *Bull. mater. Sci.,* Volume 24,Page 249-252, **2001**.
[9] H.K. Henisch., Crystal growth in gels, University park,PA ; The Pennsylvania university press **1973**.
[10] P.N. Kotru, N.K. Gupta, K. K. Raina,M.L. Koul, *Bull.Mater. Sci*. Volume 8 Page 547 **1986**.
[11] P.N. Kotru, N.K. Gupta, K. K. RainaL.B.Sarma, *Bull. Mater. Sci*. Volume 21,Page 83, **1986**
[12] M. M. Abdel-Kader, FI-Kabbany, S. Taha, M. Abosehly, K. K. Tahoon, and A. EI-Sharkay, *J. Phys. Chem. Sol*, Volume 52,Page 655, **1991**.
[13] H. B. Gon, *J. Cryst. Growth*, Volume 102,Page 501,**1990**
[14] C. C. Desai and A. H. Patel, *J. Mat. Sci. Lett*, Volume 6, Page 1066, **1987**.
[15] V. S. Yadava and V. M. Padmanabhan, *Acta. Cryst*, B Volume 29,Page 493, **1973**.
[16] L. V. Pipree and M. M. Kobklova, *Radio Eng. Electron Phys*, (USA),Volume 12,Page 33, **1984**.
[17] C. C. Desai , A. H. Patel and M. S. V. Ramana, *Ferroelectrics*, Volume 23,Page 102, **1990**.
[18] M. M. Abdel-Kader, FI-Kabbany and S. Taha, *J. Mater. Sci. Mater. Elect*, Volume 1, Page 201, **1991**.
[19] M. M. Abdel-Kader, FI-Kabbany, S. Taha, M. Abosehly, K. K. Tahoon and A. EI-Sharkay, *J. Phys. Chem. Sol*, Volume 52,Page 655, **1991**
[20] X. Sahaya Shajan and C. Mahadevan, *Bull. Mater. Sci.*,Volume 4, Page 327, **2004**.
[21] A. C. Yanes, T Topez, J. Stockel, J.F. Peraza and M. E. Torres, *J. Mater. Sci*, Volume 31,Page 2683,**1996**.
[22] T. Lopez, J. Stockel, J. F. Peraza and M. E. Torres, *Crys. Res. Technol*, Volume 30, 677,Page **1995**.
[23] S. K. Arora, V. Patel, R. G. Patel, B. Amin and Anjana Kothari, *J. Phys. Chem. Solids*, Volume 65,Page 965, **2004**.
[24] S. K. Arora, V. Patel, and Anjana Kothari, *Mater. Chem. Phys*, Volume 84, Page 323, **2004**.
[25] A. Jain, S. Bhat, S. Pandita, M. L. Kaul and P.N.Kotru, *Bull. Mater. Sci*, Volume 20,Page 1089, **1997**.
[26] P Nisha Santha kumaria ,S. Kalainathan,*Cryst.Res.Technol*.,Volume 4 page 317,**2008**.
[27] D.Kalaisevi, R Mohan Kumar, and R Jayavel, *Cryst. Res. Technol*.,Volume 8 page 851,**2008**.