NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (3), P. 561–564

# Photoluminescence characteristics of nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$:EU by combustion method

P. Rubalajyothi, L. C. Nehru

Department of Medical Physics, School of Physics, Bharathidasan University, Tiruchirappalli–620024, Tamilnadu, India

lcnehru@yahoo.com

**PACS 61.43Gt, 88.20jj, 61.05cp, 61.50Lt** **DOI 10.17586/2220-8054-2016-7-3-561-564**

Nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$:Eu powder has been prepared by combustion method. XRD shows orthorhombic structure, the lattice parameter values are $a = 8.836$ Å, $b = 5.440$ Å, $c = 6.859$ Å. The nanocrystalline powder $Ba_{0.97}Ca_{0.03}SO_4$:Eu having a grain size of 47 nm, and also FTIR, PL, and three dimensional structure studies of the material and the results are presented in detail.

**Keywords:** $Ba_{0.97}Ca_{0.03}SO_4$:Eu, combustion method, XRD, computering software for structural bonding (JANA 2006, VESTA, PRIMA).

*Received: 5 February 2016*

*Revised: 10 May 2016*

## 1. Introduction

Thermoluminescene is the thermally stimulated emission of light from an insulator or semiconductor, following the previous absorption of energy from ionizing radiation such as gamma rays, X-rays, beta particles, alpha particles, neutrons and energetic ions. This phenomenon has been utilized for several applications. The main applications are in detection and measurement of absorbed radiation and dating of archaeological samples and detecting defects in solids. There are a number of commercially available TLDs for this purpose under different trade names the most popular are LiF:Mg,Cu,P, LiF:Mg,Ti, $Ba_{(1-x)}Ca_xSO_4$:Eu, $K_2Ca_2(SO_3)_4$, $CaSO_4$:Dy. Here, I have chosen the material $Ba_{(1-x)}Ca_xSO_4$:Eu, because this material is one that is having more prominence in the medical field. Here, calcium, sulfate and, barium materials were phosphorescent and these materials sensitivity and stability were high in the radiation dosimetry process. Sulfate is a common chemical in current everyday life and is used in a number of industrial processes. Sulfate is a major contributor to Climate change because when the light scattering it's efficiently increase the earth's albedo. $CaSO_4$ is another kind of chemical, mainly used in laboratory and industries. In precipitation processes, calcium sulfate is utilized to concentrate radioactive elements.

Photoluminescence (PL) is light emission from any form of matter after the absorption of photons. The observation of photoluminescence at a specific energy can be viewed as indication that the photon caused an excitation that populated an excited state associated with this transition energy. PL emission spectra of the nanomaterial without gamma irradiation, and the aim of this paper is to report on a preparations of $Ba_{0.97}Ca_{0.03}SO_4$:Eu to prepare the new method and I have include this structure and hkl calculations were included.

## 2. Methods and details

The thermoluminescene properties of nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$:Eu powder was successfully prepared by combustion method using a urea as fuel. Stoichiometric amounts of barium nitrate ($Ba(NO_3)_2$), calcium nitrate ($Ca(NO_3)_2{\cdot}4H_2O$), ammonium sulfate ($(NH_4)_2SO_4$) and doping material europium were dissolved in an aqueous solution of urea with constant stirring at room temperature. The solution was dried at 100 °C for 30 mins. After collect the powder to agate motor to grain and annealed at 500 °C for 1 h. The formation of the powder $Ba_{0.97}Ca_{0.03}SO_4$:Eu material is confirmed by XRD taken at room temperature using PANalytial X-ray diffractometer with Cu target (Cu-K$\alpha$), line $\lambda = 1.54060$ Åwith step size $\Delta 2\theta = 0.05$ °.

## 3. Result

### 3.1. X-ray diffraction

In X-ray diffraction experiment, hkl values were obtained for the $Ba_{0.97}Ca_{0.03}SO_4$:Eu powder sample. All the XRD peaks of the compounds have orthorhombic structure, as shown in Fig. 1. Hence, the lattice parameter is $a = 8.836$, $b = 5.440$, $c = 6.859$ values. The crystallite sizes were calculated using the Scherer formula. Based on this formula, the particle size was calculated to be 47 nm for the three dimensional structure for $Ba_{0.97}Ca_{0.03}SO_4$:Eu.

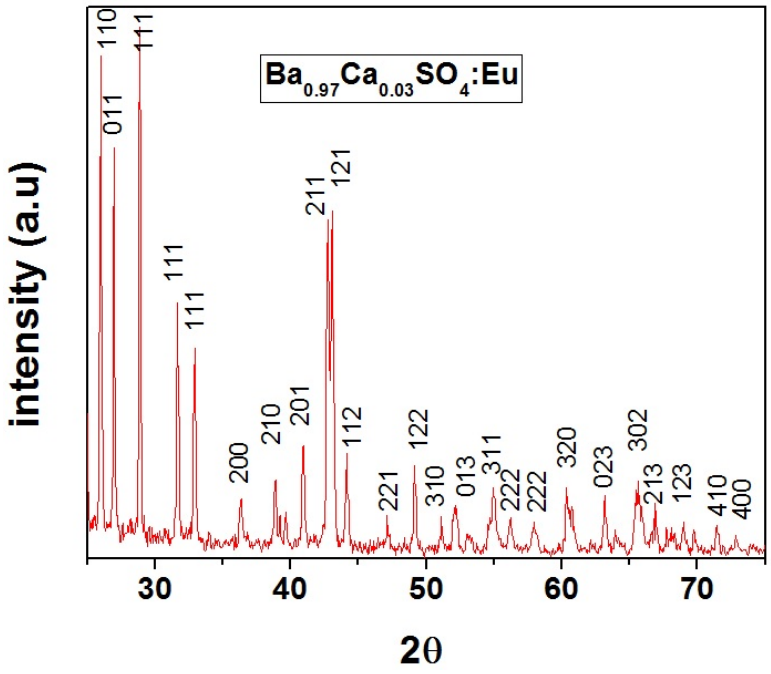


FIG. 1. X-ray Diffraction

TABLE 1. hkl calculation for $Ba_{0.97}Ca_{0.03}SO_4$:Eu

| **2$\theta$** | $\Theta$ | **sin$^2\theta$** | **sin$^2\theta$/k** | **h$^2$+k$^2$+l$^2$** | **hkl** |
|---|---|---|---|---|---|
| 19.9735 | 9.986 | 0.029 | 1.9 | 2 | 110 |
| 22.7881 | 11.394 | 0.038 | 2.59 | 3 | 111 |
| 26.8557 | 13.427 | 0.053 | 3.56 | 4 | 200 |
| 31.5432 | 15.77 | 0.073 | 4.89 | 5 | 210 |
| 36.1701 | 18.085 | 0.096 | 6.41 | 6 | 211 |

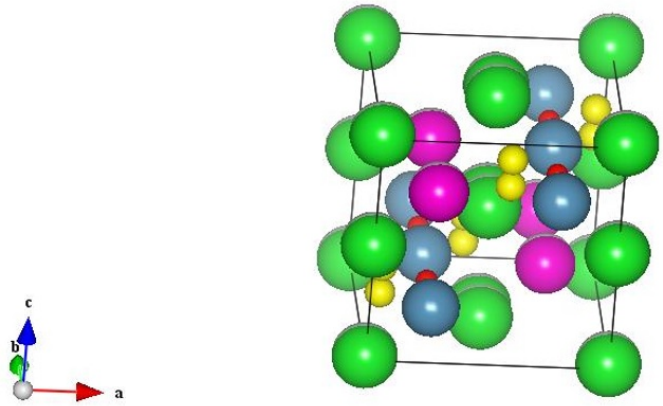


FIG. 2. By using the VESTA after the refinement method

The above diagram (Fig. 2) for $Ba_{0.97}Ca_{0.03}SO_4$:Eu shows the three dimensional structure obtained by using the VESTA software. The green color represents the barium and blue represents the calcium and red represents the oxygen and yellow represents sulfur and magenta color represents the europium.

By using the following formula to calculate the eletron density, we determined that the value is 0.08 e/Å3, meaning that this low electron mid bond density is ionic in nature:

$$\rho = 1/V f_0 \exp 2\pi i(hx + ky + lz),$$

where, $v$ is the volume of the material, $f_0$ is the structure factor value by refinement method, $hkl$ is the miller indices value, xyz is the carteisan co-ordinates.

### 3.2. Fourier transfer infrared spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy was also used to analyze the nanocrystalline $Ba_{0.97}$ $Ca_{0.03}SO_4$:Eu material. From this analysis, we confirmed the presence of many organic-based functional groups present in the $Ba_{0.97}Ca_{0.03}SO_4$:Eu sample. In the FTIR spectrum showed peaks at 3437.72 $cm^{-1}$, 2925.03 $cm^{-1}$, 2351.56 $cm^{-1}$, 2064.43 $cm^{-1}$, 1643.72 $cm^{-1}$, 977.47 $cm^{-1}$, 639.14 $cm^{-1}$, 608.75 $cm^{-1}$, which are indicative of alcohols, phenols, alkanes, alkynes, carbonyls, aliphatic amines, alkyl halides, as shown in Fig 3.

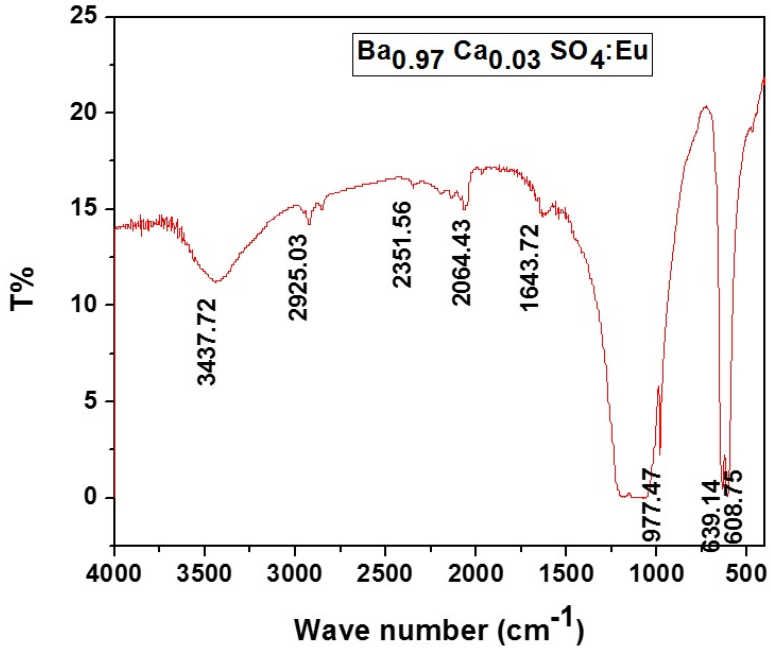


FIG. 3. Various functional group in FTIR

### 3.3. Photoluminescence

Figure 4 shows the PL emission spectra for un-irradiated nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$:Eu with an excitation wavelength of 325 nm. The un-irradiated phosphor has six peaks at 378, 412, 441, 494, 520 and 595 nm. The peaks at 412, 441 and 494 nm may be attributed to the same $Eu^{2+}$ emission arising due to the transition from $e$g to $t$2g levels of the 4f65dconfiguration to 8S7/2 levels of the 4f65d configuration but with $Eu^{2+}$ occupying different lattice sites [2,6]. The peak at 520 and 595 nm suggest that europium also enters the lattice in its trivalent state. This peak may be assigned to the $Eu^{3+}$ emission due to the transition 5D1 $\rightarrow$ 7F1 [4,7]. The disappearance of the 520 nm and 595 nm peak might be due to the conversion of $Eu^{3+}$ to $Eu^{2+}$ due to irradiation [1,3]. The disappearance of the 441 and 494 nm peak is quite surprising; however, it may be speculated that on irradiation, the 441 nm and 494 nm peak of $Eu^{2+}$ might be shifted to the lower wavelength side to show its emission at 378 nm along with the existing one at 378 nm [8].

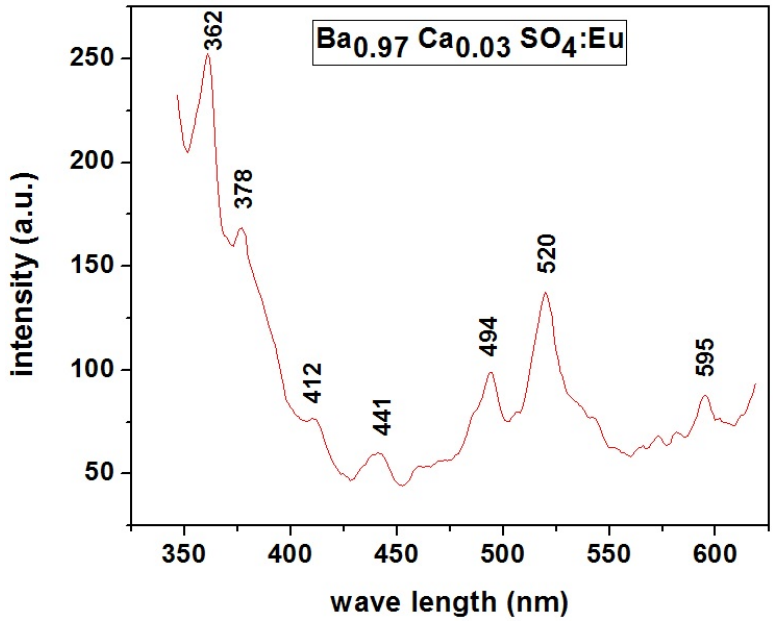


FIG. 4. Photoluminescence

## 4. Conclusion

Nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$:Eu powder has been prepared by the combustion method and subsequently confirmed by XRD. The $Ba_{0.97}Ca_{0.03}SO_4$ structure is orthorhombic in nature. The size of the Nanocrystalline is 47 nm. The size of the particle is calculated by using the Scherrer formula. Additionally, various organic-based functional groups are present in FTIR spectrum. The excitation wavelength is 325 nm for photoluminescence for the conversion of $Eu^{2+}$ to $Eu^{3+}$.

## References

[1] Merz J.L., Pershan P.S. Charge Conversion of Irradiated Rare-Earth Ions in $CaF_2$. II. Thermoluminescent Spectra. *Phys. Rev.*, 1967, **162**(2), P. 235.

[2] Blasse G. *Luminescence in Inorganic Solids*. Plenum, New York, 1978, P. 457–494.

[3] Bapat V.N. Thermoluminescence of $CaF_2$(Eu): influence of the presence of other lanthanide impurities. *J. Phys. C: Solid State Phys.*, 1977, **12**(19), P. 10L465–67.

[4] Pode R.B., Dhoble S. Radiation-induced defects in $Eu^{3+}$-activated yttrium vanadates. *J. Phys. D: Appl. Phys.* 1998, **31**(1), P. 146.

[5] Xiong G., Pengfei W., Wai K.C., Engju C. Effect of $\gamma$-irradiation on structures and luminescent properties of nanocrystalline $MSO_4:Eu_{x+3}$ (M = Ca, Ba, Sr, x = 0.001–0.005). *J. Phys. Chem. Solids*, 2000, **61**(1), P. 115–121.

[6] Pandey A., Sonkawade R.G., Sahare P.D. Thermoluminescence and photoluminescence characteristics of nanocrystalline $K_2Ca_2(SO_4)_3$ :Eu. *J. Phys. D:Appl. Phys.*, 2002, **35**(21), P. 2744–2747.

[7] Esparza-Garcia A.E., Garcia-Hipolito M., Aguilar-Frutis M. A, Falcony C., Cathodoluminescent and Photoluminescent Properties of $Al_2O_3$ Powders Doped with Eu. *Phys. Status Solidi A*, 2002, **193**(1), P. 117–124.

[8] Lochab S.P., Sahare P.D., Chauhan R.S., Numan S., Pandey A. Thermoluminescence and photoluminescence study of $Ba_{0.97}Ca_{0.03}SO_4$:Eu. *J. Phys. D: Appl. Phys.*, 2006, **39**(9), P. 1786–1792.

[9] Rangeela Y.D., Doredrajit S.S. Synthesis and TL glow curve analysis of BaSO4:Eu, Dy phosphor. *J. Luminescence*, 2012, **132**(6), P. 1575–1580.