

## Luminescence Properties Of Pure CaSO<sub>4</sub> Nanoparticles Produced By Co-Precipitation Method

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### Abstract

Thermoluminescence (TL) characteristics of pure CaSO<sub>4</sub> nanoparticles produced by co-precipitation method are presented. The formation of the nanoparticles was confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM). TL glow curve of this phosphor, exposed to gamma radiation exhibits five overlapping glow peaks in the complex glow curve at 463, 470, 483, 498 and 521(K) respectively, using a computerized glow curve deconvolution procedure. A photoluminescence (PL) emission band at 393 nm was observed for the synthesized nanoparticles. Different synthesis conditions were examined in order to achieve highest TL sensitivity. The produced nanoparticles exhibit superior thermoluminescent sensitivity compared to that of its bulk equivalent.

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## 1. Introduction

In recent decades, nanocrystals due to their outstanding properties have attracted much attention [1-5] and the optical behaviour of nanostructured semiconductors have found extensive industrial applications. Calcium sulphate is a well-tolerated, biodegradable, osteoconductive bone graft substitute

and a semiconductor with optically and electronically applications [6-7]. Together with the development of nanostructured materials, applications of calcium sulphate has been extended. CaSO<sub>4</sub> is one of the well known compound semiconductors suitable to be used as host matrix for large variety of dopants such as Dy, Mn, Eu, Ce and etc. [7-11].

Thermoluminescence and photoluminescence phenomena are generally used to study defects in semiconductor materials. Moreover, TL is successfully applied in radiation dosimetry. Many synthetic materials have been produced, developed and characterized to evaluate their feasibility as thermoluminescence dosimeters (TLD) in different dose levels [12, 13]. However, a particular material may or not be useful for radiation dosimetry depending on the kind of radiation field and the dose range to be measured. For low dose dosimetry, a high sensitive TL material should be used, while high dose dosimetry calls for a TL material having linear dose response up to high absorbed dose levels. In the present study, pure  $\text{CaSO}_4$  nanopowder was synthesized through a co-precipitation method. Novel optical properties of this pure nanocrystal are reported here for the first time. Investigations on the growth process explored in this paper accounts for new understandings of special properties such as TL and PL. Singly doped  $\text{CaSO}_4$  have been studied in detail in the past and two models have been presented for TL mechanism in  $\text{CaSO}_4$  based TL phosphor [14-18]. Recently, TL properties of  $\text{CaSO}_4$  nanostructure doped with Dy, Ce and Mn have been studied [19-21]. However TL of pure calcium sulphate has not been reported up till now. This study focuses on preparation and investigation of luminescence properties of pure  $\text{CaSO}_4$  nanocrystal using Co-precipitation method. The PL spectra, TL kinetic parameters and dosimetry features of this novel nanocrystalline are also presented and discussed.

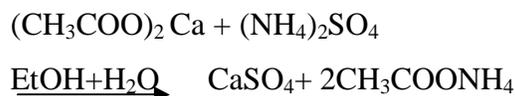
## 2. Experimental procedures

### 2.1 Materials and characterization

Nanoparticles were synthesized by a co-precipitation method. The following raw materials, used in the production stage, were obtained from the Merck chemicals: Calcium acetate ( $\text{C}_4\text{H}_4\text{CaO}_4\text{XH}_2\text{O}$ ), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), brij35 ( $(\text{C}_2\text{H}_4\text{O})_n\text{C}_{12}\text{H}_{26}\text{O}$ ), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and DI water. The structural characterization of nanoparticles was supported by X-ray diffraction (XRD) with Rigaku D-maxcIII diffractometer using  $\text{Cu } k_\alpha$  radiations. Shape of the nanoparticles was obtained using a scanning electron microscope (SEM) model Philips XL-30 ESEM, equipped with energy dispersive spectrometer (EDS). All irradiations were made with  $^{137}\text{Cs}$  source. The TL response was recorded by a Harshaw model 4500 computer based TL reader. A heating rate of  $1^\circ\text{C}/\text{sec}$  was used for recording the TL glow curves. Photoluminescence (PL) spectrum was obtained using a spectrometer model Perkin Elmer LS55 with photo multiplier tube and Xenon lamp at room temperature.

### 2.2. Synthesis of Pure $\text{CaSO}_4$ nanoparticles

Pure  $\text{CaSO}_4$  nanoparticles were synthesized by Co-precipitation method through the following chemical reaction:

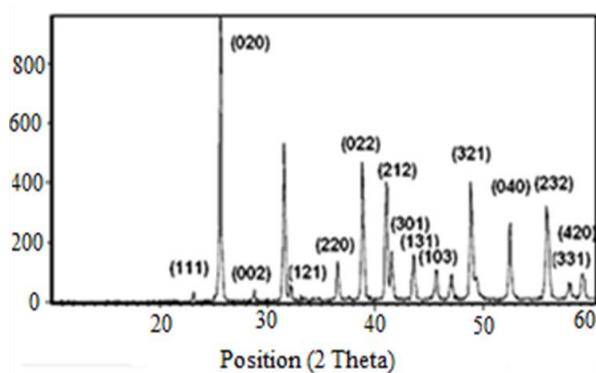


0.3954 g of calcium acetate was solved in 100 ml DI water on the stirrer for 5 min. Then 0.3035 g of ammonium sulfate was solved in the 100 ml mixture of ethanol and DI water on the stirrer for 10 min. 4.5

g of Brij35 was solved in 50 ml DI water on the stirrer for 5 min. The solution of brij35 and a few amount of sulfuric acid were then added slowly to calcium acetate solution to achieve pH=4. Then both solutions were mixed and stirred for 15 min. The solid part was collected by centrifuging the mixture and was thoroughly washed with ethanol for several times. The collected nanostructures were then dried in an oven for 2 h at 90 °C followed by annealing at 350 °C for 1 min under nitrogen atmosphere. The final product was pure CaSO<sub>4</sub> nanoparticles.

### 3. Results and discussion

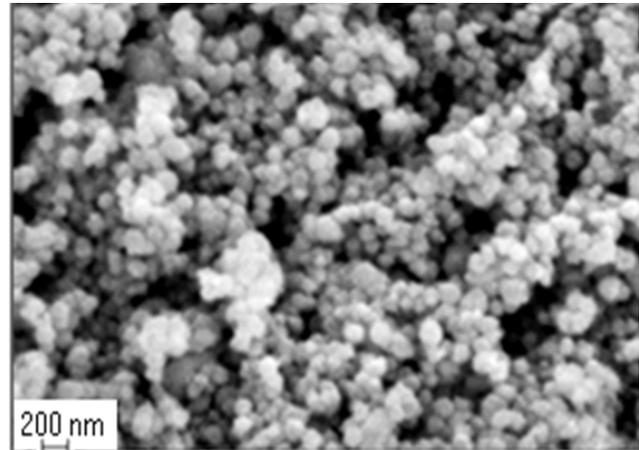
The crystalline structure of the produced CaSO<sub>4</sub> nanostructure was confirmed by XRD pattern shown in Fig. 1. The position of the diffraction peaks coincides very well with those of the standard bulk phase as shown in JCPDS card no.06-0226.



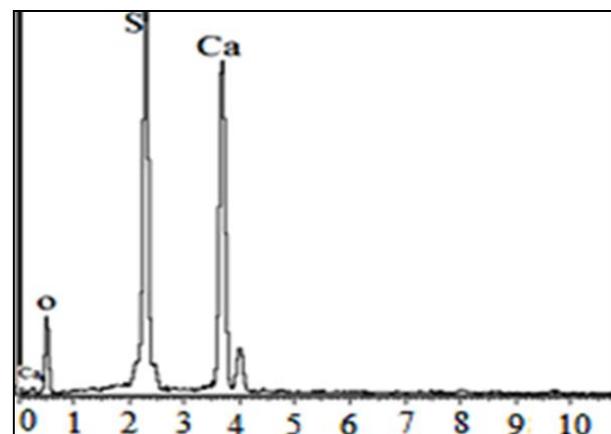
**Fig. 1.** XRD pattern of the pure CaSO<sub>4</sub> nanoparticles.

The particle size of the nanoparticles was calculated from FWHM by using Debye-Scherrer's equation [22]. An average particle size of about

50nm was obtained which is in good conformity with the SEM image. The SEM pattern of nanoparticles is shown in Fig. 2. As is evident, the products are uniform nanoparticles. The elemental concentrations obtained by EDX analysis is also observed in Fig. 3.



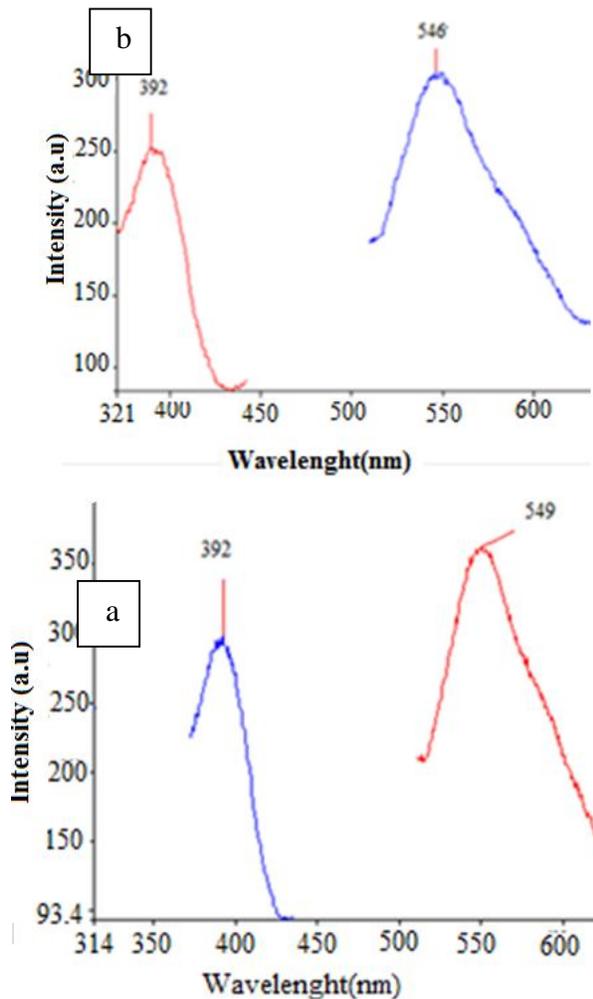
**Fig. 2.** SEM image of the produced CaSO<sub>4</sub> nanoparticles. The particles are uniform with the particles size is in conformity with that obtained from Scherrer's formula.



**Fig. 3.** EDS spectra of synthesized CaSO<sub>4</sub> nanoparticles

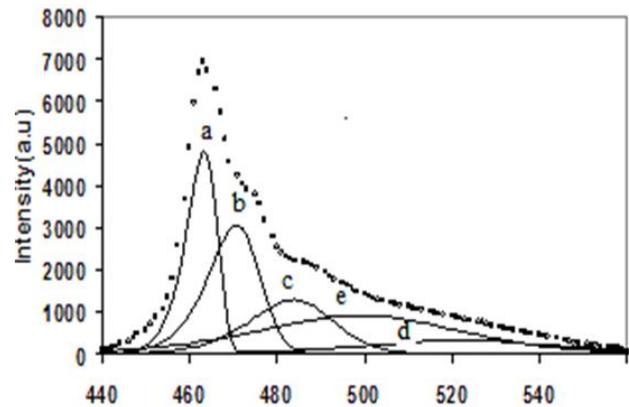
Figure 4 (a, b) shows photoluminescence spectra of the synthesized CaSO<sub>4</sub> nanoparticles and its bulk

counterpart. Photoluminescence pattern of bulk  $\text{CaSO}_4$  powders (Merck), shows a peak at 549 nm corresponding to the excitation at 392 nm, while the photoluminescence pattern of the synthesized  $\text{CaSO}_4$  nanoparticles exhibits a peak at 546 nm following excitation at 392 nm. The blue shifting is due to the size effect of materials. Decrease in particles size causes the band gap as well as the excited level spacing in the produced  $\text{CaSO}_4$  nanoparticles to be increased and the decrease in the emission wavelength of the nanostructures can be explained in this manner.



**Fig. 4.** Photoluminescence spectra of  $\text{CaSO}_4$  powders  
a) bulk powders (Merck) b) nanoparticles

Thermoluminescence properties of micro and nanocrystalline  $\text{CaSO}_4$  doped with different impurities has been studied, but the TL of pure  $\text{CaSO}_4$  nanocrystalline has not been reported yet. Fig. 5 shows TL glow curve of pure  $\text{CaSO}_4$  nanoparticles exposed to  $\gamma$ -rays from  $^{137}\text{Cs}$  source (open circles). The TL glow curve of pure  $\text{CaSO}_4$  nanoparticles exhibits five overlapping glow peaks at 463, 470, 483, 498 and 521 K respectively. Therefore, a computerized glow curve deconvolution technique was used to obtain the trapping parameters of the component glow peaks based on five overlapping peaks.



**Fig. 5.** TL glow curve of  $\text{CaSO}_4$  nanoparticles I (open circles) and component glow peaks (solid lines)

The computer program was produced in our laboratory using Levenberg-Marquart algorithm based on non-linear least square method. Thermoluminescence general order glow curve deconvolution function was employed in our program for curve fitting procedure. TL intensity in terms of  $I_m$  and  $T_m$  (the intensity and the temperature of peak maximum) is [23]:

$$I(T) = I_m b^{\frac{b}{b-1}} \exp\left(\frac{E}{kT} \cdot \frac{T - T_m}{T_m}\right) \times \left[ (b-1)(1-\Delta) \frac{T^2}{T_m^2} \cdot \exp\left(\frac{E}{kT} \cdot \frac{T - T_m}{T_m}\right) + Z_m \right]^{-\frac{b}{b-1}} \tag{1}$$

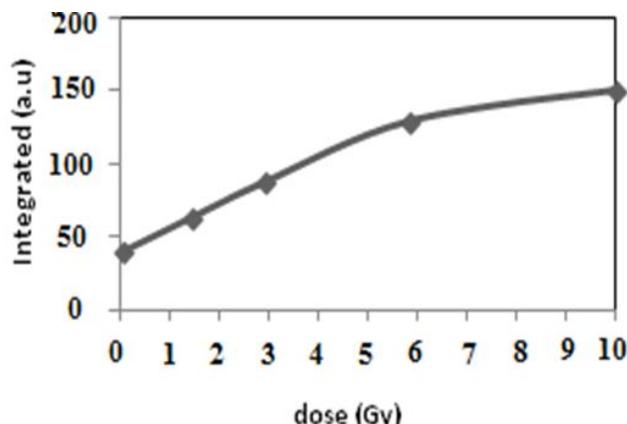
where *b* is the order of kinetics, *E* the activation energy, *k* the Boltzmann's constant, *T* the temperature,  $\Delta = \frac{2kT}{E}$ ,  $\Delta_m = \frac{2kT_m}{E}$  and  $Z_m = 1 + (b-1)\Delta_m$ . The parameters which are free to change by the program to achieve the best conformity between the glow curve obtained by experiment and that produced by Eq. 1 are *I<sub>m</sub>*, *T<sub>m</sub>*, *E* and *b*. The used glow curve deconvolution function( in terms of *I<sub>m</sub>*, *T<sub>m</sub>*, *E* and *b*) has advantage over the deconvolution function in terms of *n<sub>0</sub>*(initial concentration of electrons in trapping states),*s*( the pre exponential factor), *E* and *b* since *I<sub>m</sub>* and *T<sub>m</sub>* can easily be estimated from the experimental glow curve as the initial values for curve fitting process [24]. The Eq. 1 is more useful than the deconvolution functions for limiting cases of first and second- orders of kinetics as intermediate cases in which 1<*b*<2 can be taken into account and it smoothly goes to first and second orders when *b*→1 and *b*→2 respectively [25]. Results are shown in Table 1.

**Table 1.** Activation energy (*E*), peak maximum temperature(*T<sub>m</sub>*) and order of kinetics (*b*) of five

glow peaks contained in complex glow curve of pure CaSO<sub>4</sub> nanoparticles.

Peak	E	T <sub>m</sub>	I <sub>m</sub>	B
a	5.59	463	4856	1.1
b	3.73	470	3072	1.3
c	2.59	483	1292	1.5
d	1.15	498	920	1.6
e	1.34	521	318	1.9

Dose response curve of the synthesized nanoparticles irradiated to gamma radiation is depicted in Fig. 6.



**Fig. 6.** Dosimetric behaviour or TL response for pure CaSO<sub>4</sub>exposed by gamma-ray irradiation

As is evident, the TL dose response is linear for the absorbed doses up to about 5Gy and for the higher absorbed doses, due to the saturation of trapping states, sub-linear behavior is observed. There has been found a relationship between the TL sensitivity of a phosphor and its linear range of TL dose response [20], such that the higher the range of linear dose response, the lower the TL sensitivity. In contrast to the TL sensitivity of pure CaSO<sub>4</sub> nanoparticles which is 4 times

higher than that of commercial LiF:Mg,Ti (TLD-100), the region of its linear dose response is limited to doses up to 5 Gy.

As the capability of TL material for preserving the absorbed dose was in order, a number of samples irradiated to the same dose, was stored in dark environment followed by recording the TL signal at different storage times. TL fading studies showed that TL signal of the produced CaSO<sub>4</sub> nanoparticles remains almost unchanged by storing them in dark medium for one month (Fig. 7).

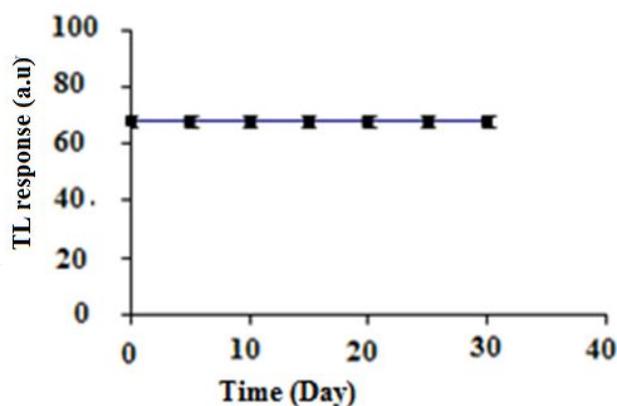


Fig. 7. TL fading of pure CaSO<sub>4</sub> nanocrystals exposed to 5Gy of  $\gamma$ -irradiation.

#### 4. Conclusion

1. XRD pattern shows that the synthesized nanocrystals are pure CaSO<sub>4</sub> nanoparticles.
2. TL glow curve of CaSO<sub>4</sub> nanophosphors following gamma-ray irradiation at room temperature revealed five overlapping peaks at 463, 470, 483, 498 and 521 (K). The particle size affects drastically the TL characteristics of nanoparticles. In case of nanocrystalline material the TL glow curve structure is very much different than that of the bulk materials.

3. Photoluminescence pattern of synthesized CaSO<sub>4</sub> nanoparticles shows a peak at 546 nm corresponding to the excitation peak at 392 nm.

4. The TL sensitivity of the synthesized nanocrystalline material was found to be more than that of bulk CaSO<sub>4</sub> at low exposures and is attributed to the particle size effect.

#### References

- [1] Y. Takeda, N. Umeda, V.T. Gritsyna, N. Kishimoto, Nucl.Instr. and Meth. B. 463 (2001), 175–177.
- [2] P. Zu, Z.K. Tang, G.K.L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Solid State Commun. 103 (1997) 459.
- [3] E.M. Wong, P.C. Searson, Appl. Phys. Lett. 74 (1999) 2939.
- [4] B.L. Zhu, C.S. Xie, D.W. Zeng, W.L. Song, A.H. Wang, Materials Chemistry and Physics, 89 (2005) 148–153.
- [5] Gong, X., Wu, P., Kin, Chan Wai, Chen, W., J. Phys. Chem. Solids, 61,(2000), 115–121.
- [6] S. Gitelis, P. Piasecki, T. Turner, W. Haggard, J. Charters, R. Urban, Orthopedics 24 (2001) 162
- [7] S. Lee, J. Kim, C.H. Lee, J. Membr. Sci. 163 (1999) 63
- [8] K.S.V. Nambi, V.N. Bapat, A.K. Ganguly, J. Phys. C 7(1974) 4403.
- [9] M. Maghrabi, T. Karali, P.D. Townsend, A.R. Lakshmanan, J. Phys. D 33 (2000) 470.
- [10] B.K.S. Nair, D. Sundar, A. Tomita, W. Hoffmann, A.R. Lakshmanan, J. Lumin. 86 (2000) 67.

- [11] R.L. Calvert, R.J. Danby, *Phys. Status Solidi* 83 (1984) 597.
- [12] McKeever, S.W.S., Cambridge University Press, Cambridge.(1985).
- [13]. Fox. P. J., Akber. R. A., Prescott. J. R.. J. *Phys. D: Appl. Phys.* 21,(1988)189-193.
- [14]. Bhatt B. C., Bhushan Dhabekar., Rajesh Kumar., Gundu Rao. T. K., Lakshmanan. A. R.. *Radiat. Prot. Dosim.* 119,(2006) 53–56.
- [15]. Ingle. N. B., Omanwar. S. K., Muthal. P. L., Dhopte .S .M. Kondawar. V. K.,Gunduraod .T. K., Moharil. S. V, *Radiat Meas.* 43,(2008) 1191-1197.
- [16]. Madhusoodanan. U., Jose. M. T., Tomita .A., Hoffmann .W., Lakshmanan. A. R. . *J.Lumin.* 82, (1999) 221-232.
- [17]. Menon. S. N., Sanaye. S. S., Dhabekar. B. S., Rajesh Kumar., Bhatt. B. C.*Radiat Meas.* 39, (2005).111 – 114
- [18]. Rivera. T., Roman. J., Azorin. J., Guzman.J. Serrano. A.k., Garcia.m. Alarcon. G.*Appl Radiat Isot.* 68,(2010), 623-625.
- [19].Salah. N., Sahare. P. D., Lochab. S. P., Kumar .P. *Radiat. Meas.* 41, (2006)40-47.
- [20]. M. Zahedifar, M. Mehrabi, S. Harooni, *Applied Radiation and Isotopes* 69 (2011) 1002–1006
- [21]. M. Zahedifar, M. Mehrabi, *Nuclear Instruments and Methods in Physics Research Section B*, 268, (2010) , 3517–3522
- [22] Cullity, B. D, 2nd edn (Addison–Wesley Publishing Company), (1956), 99.
- [23] G. Kitis, J. M. Gomez Ros, Tuyn. J .W. N, J. *Phys. D:Appl. Phys.* 31(1998) 2636-2641.
- [24] J.M. Gomez Ros and G.Kitis, *Radiat. Prot. Dosim.*101,1-4(2002) 47-52.
- [25] A.J.J. Bos, *Radiat. Meas.*,4, (2007) S45-S56.