Journal of Alloys and Compounds 501 (2010) 190–192

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Thermoluminescence characteristics of gamma irradiated CaS:Ce nanophosphors

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ARTICLE INFO

Article history:
Received 11 November 2009
Received in revised form 8 April 2010
Accepted 15 April 2010
Available online 20 May 2010

Keywords:
Nanophosphors
Thermoluminescence
Luminescence

ABSTRACT

Thermoluminescence behavior of gamma irradiated CaS:Ce nanophosphors have been presented. CaS:Ce (0.2 mol%) shows two peaks one around 400 K and a high temperature peak around 560 K at a heating rate of 5 K/s. TL intensity increases up to 5.76 kGy of gamma exposure and afterwards it decreases. The linearity of CaS:Ce nanophosphors over a wide range of dose is explained on the basis of track interaction model (TIM) and large surface to volume ratio of nanoparticles. Effect of different heating rates on the TL glow curve has also been investigated. The trapping parameters: activation energy (E) and order of kinetics (b) for CaS:Ce (0.2 mol%) have been calculated.

1. Introduction

Sulphide phosphors are long investigated for their multi-field applications such as television screens, fluorescence lamps, thermoluminescence dosimetery and high pressure mercury lamps [1–6]. CaS, a Lenard phosphor, exhibits long afterglow [7] owing to its defect structure since it possess S and Ca vacancies [8–10] giving rise to unique thermoluminescence characteristics. Being a wide bandgap (4.43 eV) [7] semiconductor, it is investigated with wide range of dopants such as Sm^{3+}, Ce^{3+}, Eu^{2+}, Bi^{3+}, etc. [11–14]. These days nanotechnology has stimulated interest in the properties of nano form of the matter. Kumar et al. has studied the thermoluminescence characteristics of CaS:Bi nanophosphors with different irradiation sources [12,15]. Vij et al. has studied the thermoluminescence properties of SrS:Ce nanophosphors both with gamma and UV irradiations [16,17]. In this paper we have reported the thermoluminescence behavior of CaS:Ce nanophosphors with gamma irradiation. To the best of our knowledge there are no reports on the thermoluminescence characteristics of CaS:Ce nanophosphors for gamma irradiation.

2. Experimental

The nanoparticles for the study were prepared by solid state diffusion method [13]. Calcium sulphate, cerium nitrate, sodium thoisulphate, carbon powder and ethanol were the starting materials. Carbon reduces sulphate to sulphide at high temperature and cerium acts as an activator. Sodium thoisulphate (15%) acts as a flux for the reaction. The calculated quantity of calcium sulphate, carbon powder, cerium nitrate (0.2 mol%) and the flux were taken and mixed thoroughly with the help of an agate pestle and mortar. The charge was placed in clean graphite crucible (which was already baked at the firing temperature) and a thin layer of carbon powder was spread over it. This crucible was covered with another similar crucible. The thin layer of the carbon over the charge created a reducing environment over the charge at high temperature. This whole arrangement was placed in a muffle furnace and charge was fired at 950 °C for 2 h. The firing at high temperature causes the incorporation of cerium in the host lattice. After 2 h the charge was taken out and rapidly crushed while red hot with the help of pestle and mortar. The details of the nanoparticle preparation are reported elsewhere [18].

For recording TL, nanoparticles were irradiated with different doses of ^{60}Co γ-rays at room temperature. Prior to gamma exposure, the samples were annealed at 300 °C for 10 min and then quenched on a metallic plate at room temperature to erase any residual information. TL glow curves were recorded on a Harshaw TLD reader (Model 3500) fitted with 931B photomultiplier tube (PMT) by taking 5 mg of sample each time.

3. Results and discussion

CaS:Ce (0.2 mol%) nanoparticles so formed have cubic crystalline phase with an average grain size of 53–60 nm and posses irregular shape. The structural properties and luminescence characteristics of these nanoparticles are reported elsewhere [18].

4. Thermoluminescence characteristics

The dependence of TL intensity on the cerium concentration is shown in Fig. 1. Intensity was recorded for different concentrations of cerium after an exposure of 144 Gy. It increases with the increasing cerium concentration and becomes maximum for a particular concentration of cerium (0.2 mol%), and with further increase in the activator, the intensity decreases. This is in good agreement with the phenomenon of concentration quenching. Hence 0.2 mol% of cerium is found to be the optimum concentration for the TL intensity.

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doi:10.1016/j.jallcom.2010.04.138

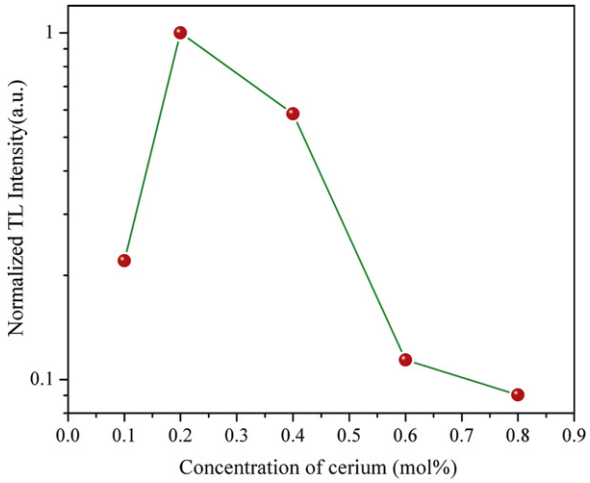

Fig. 1. TL intensity as a function of cerium concentration in CaS after a gamma exposure of 144 Gy.

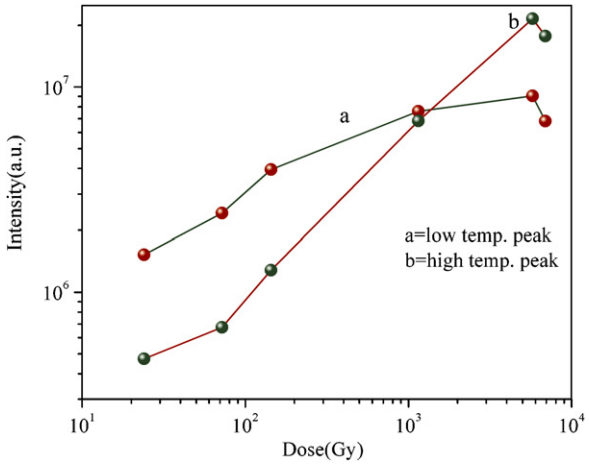

Fig. 3. Variation in TL intensity with the exposure of gamma rays for CaS:Ce (0.2 mol%).

Effect of different doses of gamma rays on the TL glow curve of CaS:Ce (0.2 mol%) at heating rate of 5 K/s is shown in Fig. 2. Glow curve shows two peaks one around 400 K and a high temperature peak around 560 K. With increasing dose there is slight variation in the peak position and the intensities of both low and high temperature peaks have been observed to increase but there is rapid rise in the intensity of high temperature peak indicating deep traps are formed at high doses. Some authors have also reported such shifts in the TL peak position with ion beam bombardment and attributed this effect to disorganization of the initial energy bands [19,20]. TL intensity is found to be maximum for 5.76 kGy of Gamma rays. It increases almost linearly up to exposure of 5.67 kGy of gamma rays and afterwards a fall is recorded.

Variation in TL intensity with the exposure of gamma rays for both low and high temperature peak is shown in Fig. 3. The linear behavior over a wide range of dose can be explained on the basis of track interaction model (TIM) [21,22]. According to this model, the number of traps generated by the high energy radiation in a track depends upon the cross section and the length of the track inside the matrix. In case of nanomaterials the length of the track generated by high energy radiation is of the order of few tenths of nanomaterials. At low doses there exist few trap centers (TC)/luminescent centers (LC). As the dose increases, the TL intensity increases as still some particles exist that would have missed while targeting by the high energy radiation, owing to the small size of the particles. This gives good linearity over a wide range of dose. After a gamma exposure of 5.76 kGy, a decrease in TL intensity has been noticed with further increase in dose. The fall in the TL intensity at higher doses has been reported earlier by several authors [23,24] and usually a consequence of competition between radiative and non-radiative center or between different kinds trapping centers [25].

4.1. Effect of heating rate

The influence of different heating rates on TL glow curve of CaS:Ce (0.2 mol%) (exposed to 1.152 kGy of gamma rays) is shown in Fig. 4. Fig. 4 shows the TL glow curves at heating rates 2 K/s, 5 K/s and 10 K/s. With increase in the heating rate the peak temperature of the high temperature peak shifts to higher side while the peak intensity decreases which may be due to thermal quenching of TL due to increase in the heating rate [26–29]. While the low temperature peak shows a shift in the peak temperature to higher side but the peak intensity increases with increasing heating rate which indicates some complex distribution of traps in the lattice.

4.2. Calculation of trapping parameters

For analysis of glow curve it was firstly deconvoluted using glow fit deconvolution software which is based on the first order kinetic

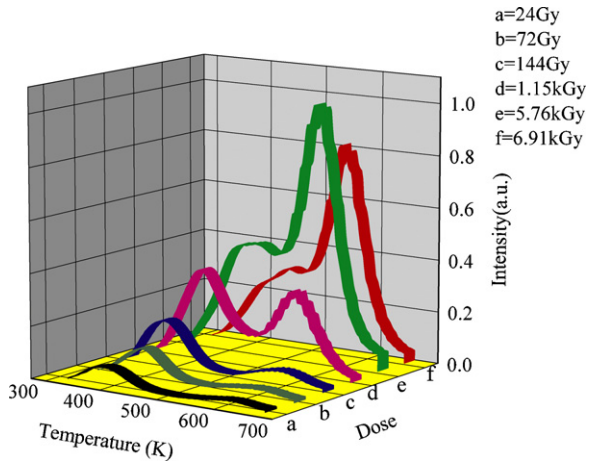

Fig. 2. Effect of different doses of gamma rays on the TL glow curve of CaS:Ce (0.2 mol%).

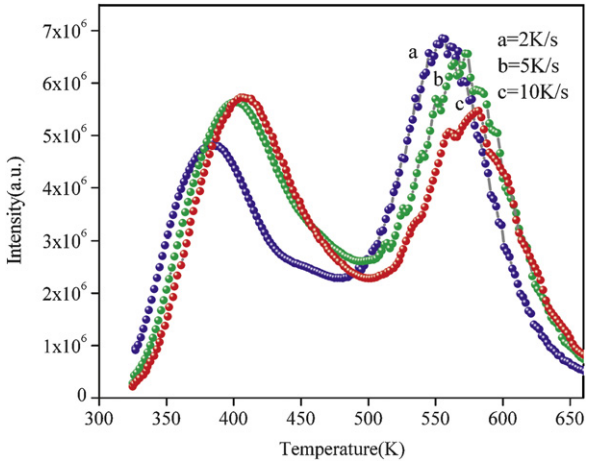

Fig. 4. Influence of different heating rates on TL glow curve of CaS:Ce (0.2 mol%) (exposed to 1.152 kGy of gamma rays).

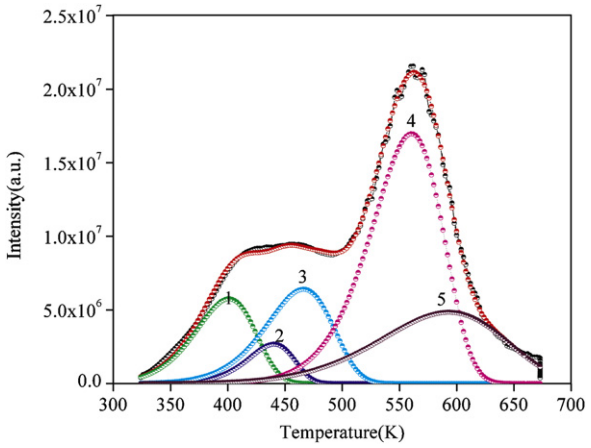

Fig. 5. Deconvolution of experimental TL glow curve of CaS:Ce (0.2 mol%) for 5.76 kGy of gamma exposure at a linear heating rate of 5 K/s.

Table 1
Trapping parameters of various glow peaks of CaS:Ce (0.2 mol%) nanocrystalline sample for 5.76 kGy of gamma exposure at a linear heating rate of 5 K/s.

Peak	T_m (K)	Order of kinetics	E (eV)
1	401	1.06	0.501
2	441	1.13	0.794
3	466	1.06	0.609
4	561	1.02	0.824
5	593	1.04	0.509

model [30] and the glow curve fitting is done using an iterative Levenberg Marquardt algorithm [31]. And the activation energy (E) needed to free the trapped electrons was obtained. To determine the order of kinetics (b) the form factor μ_g [$\mu_g = (T_2 - T_m)/(T_2 - T_1)$], which involves T_1 and T_2 (temperature corresponding to the half of the intensities on either side of the maximum) was calculated. Theoretically the form factor which ranges from 0.37 and 0.56 is close to 0.42 for first order kinetics and 0.52 for second order kinetics [32]. The form factor is independent of the activation energy, E and strongly depends upon the order of kinetics. To determine the general order of kinetics (other than first or second order), the correlation between order of kinetics (b) and the form factor (μ_g) given by Chen was used [32]. A theoretical peak was generated using these parameters. The thermal activation energy (E) was again calculated using Chen set of empirical formulae [33]. The procedure was repeated for all the TL peaks till a theoretical glow curve was obtained by their convolution to overlap the experimental one.

Fig. 5 shows the experimental glow curve for CaS:Ce (0.2 mol%) nanoparticles at a heating rate of 5 K/s deconvoluted into five peaks (using Glow curve deconvolution software) which were also confirmed by thermal cleaning method [34]. The trapping parameters obtained from the deconvoluted glow peaks are shown in Table 1. The goodness of fit is obtained by figure of merit (FOM) which is 0.019 indicating a good fit between experimental and theoretical fitted peak.

5. Conclusions

A thermoluminescence study of gamma irradiated Ce doped CaS nanoparticles has been presented. TL intensity shows an increase for a wide range of gamma exposure (5.76 kGy). This has been explained on the basis of track interaction model (TIM) and increased surface to volume ratio in case of nanocrystalline Ce doped CaS phosphor. Glow curve shows two peaks one around 400 K and a high temperature peak around 560 K. The kinetic parameters have also been evaluated.

Acknowledgement

One of the authors GS is thankful to I.U.A.C., New Delhi for financial help in the form of a fellowship under the project UFUP-44305.

References

[1] H.-J. Sung, Y.-S. Cho, Y.-D. Huh, Y.R. Do, Bull. Korean Chem. Soc. 28 (2007) 1280.
[2] H.S. Bhatti, R. Sharma, N.K. Verma, J. Mod. Opt. 53 (2006) 2021.
[3] H.S. Bhatti, R. Sharma, N.K. Verma, Radiat. Eff. Defects Solids 161 (2006) 113.
[4] A.G.J. Green, B. Ray, I.V.F. Viney, J.W. Brightwell, Phys. Status Solidi (a) 110 (2006) 269.
[5] G.L. Marwaha, N. Singh, D.R. Vij, V.K. Mathur, Mater. Res. Bull. 14 (1979) 1489.
[6] M.A.S. Sweet, J. Rennie, Nucl. Instrum. Methods A 283 (1989) 330.
[7] D. Jia, R.S. Meltzer, W.M. Yen, J. Lumin. 99 (2002) 1.
[8] N. Singh, G.L. Marwaha, V.K. Mathur, Phys. Status Solidi (a) 66 (1981) 761.
[9] Y. Kojima, K. Aoyagi, T. Yasue, J. Lumin. 126 (2007) 319.
[10] C. Guo, D. Huang, Q. Su, Mater. Sci. Eng. B 130 (2006) 189.
[11] B.Q. Sun, G.S. Yi, D.P. Chen, Y. Zhou, J. Cheng, J. Mater. Chem. 12 (2002) 1194.
[12] V. Kumar, R. Kumar, S.P. Lochab, N. Singh, J. Phys. D: Appl. Phys. 24 (2006) 5137.
[13] V. Singh, T.K.G. Rao, J.J. Zhu, M. Tiwari, Mater. Sci. Eng. B 131 (2006) 195.
[14] X. Gong, W.J. Chen, P.F. Wu, W.K. Chen, Appl. Phys. Lett. 73 (1998) 2875.
[15] V. Kumar, H.C. Swart, O.M. Ntwaeaborwa, R. Kumar, S.P. Lochab, V. Mishra, N. Singh, Opt. Mater. 32 (2009) 164.
[16] A. Vij, S.P. Lochab, S. Singh, R. Kumar, N. Singh, J. Alloys Compd. 486 (2009) 554.
[17] A. Vij, S.P. Lochab, R. Kumar, N. Singh, J. Alloys Compd. 490 (2009) L33.
[18] G Sharma, P. Chawla, S.P. Lochab, N. Singh, Radiat. Eff. Defects Solids 164 (2009) 763.
[19] J. Gaikwad, S. Thomas, S. Kamble, P.B. Vidyasagar, A. Sarma, Nucl. Instrum. Methods B 156 (1999) 231.
[20] N. Salah, P.D. Sahare, J. Phys. D: Appl. Phys. 39 (2006) 2684.
[21] S. Mahajna, Y.S. Horowtz, J. Phys. D: Appl. Phys. 30 (1997) 2603.
[22] Y.S. Horowitz, O. Avila, M. Rodrigues-Villafuerte, Nucl. Instrum. Methods Phys. Res. B 184 (2001) 85.
[23] V. Pagonis, R. Chen, J.L. Lawless, Radiat. Meas. 42 (2007) 198.
[24] J.R. Cameron, N. Suntharalingam, G.N. Kenney, Thermoluminescent Dosimetry, The University of Wisconsin Press, Madison, 1968.
[25] J.L. Lawless, R. Chen, D. Lo, V. Pagonis, J. Phys.: Condens. Matter 17 (2005) 737.
[26] S.P. Kathuria, C.M. Sunta, J. Phys. D: Appl. Phys. 15 (1982) 497.
[27] S.P. Kathuria, S.V. Moharil, J. Phys. D: Appl. Phys. 16 (1983) 1331.
[28] N. Vana, G. Ritzinger, Radiat. Prot. Dosim. 6 (1984) 29.
[29] R.K. Gartia, S.J. Singh, P.S. Mazumdar, Phys. Status Solidi (a) 106 (1988) 291.
[30] A.J.J. Bos, Radiat. Meas. 41 (2007) S45.
[31] M. Puchalska, P. Bilski, Radiat. Meas. 41 (2006) 659.
[32] R. Chen, J. Electrochem. Soc. 116 (1969) 1254.
[33] R. Chen, Y. Kirsh, Analysis of Thermally Stimulated Processes, Pergamon Press, New York, USA, 1981, p. 162.
[34] P.D. Sahare, N. Salah, S.P. Lochab, T. Mohanty, D. Kanjilal, J. Phys. D: Appl. Phys. 38 (2005) 3995.