International Journal for Research in Engineering Application & Management (IJREAM)
ISSN : 2454-9150 Vol-04, Issue-05, Aug 2018

CaS : Bi nanocrystalline phosphors- T L Kinetic Analysis

Dr. Devendra Prasad

Assistant Professor, Department of Physics (Basic Science), U P Textile Technology Institute, 11/208, Souterganj Kanpur, (UP) INDIA. dev07.2007@rediffmail.com

Abstract - Phosphor materials are very useful for display devices as well as for dosimetric uses. Characterization of material is must for selection of suitable one. Thermoluminescence is one of the most efficient and convenient tool for characterization of material. In the present paper we reconsider the thermoluminescence studies of Bismuth doped Calcium Sulphidenanomaterial, already reported in literature, to evaluate order of kinetics involved. Here a new method of analysis is adopted to evaluate order of kinetics from the reportedthermoluminescence glow curves. Order of kinetics involved in process depends on extent of retrapping. It is found that order of kinetics increases with irradiation dose.

Keywords — Thermoluminescence, Orders of kinetics, Phosphors, Irradiation Dose, Retrapping.

I. INTRODUCTION

Alkaline earth sulphides are well known from their luminescent properties and their applications as phosphor materials in display screens, multicoloured fluorescent lamps, luminescent pigments, etc.These sulphides are traditionally known as Lenard phosphors, which in the past have not received due attention because of their poor reproducibility and chemical instability under normal conditions. After Lehmann and Ryan's findings [l-4] active research work is being carried out to develop efficient phosphor materials by using alkaline earth sulphides. Recent investigations on the screen materials developed by using the combination of the three phosphors, namely, CaS, SrS, and BaS, have yielded very promising results [5-6].These sulphides doped with certain rare earth (RE) impurities have exhibited emission bands from the ultraviolet (UV) to infrared (IR) region [7]. It is already well established that the luminescent properties of these materials which are related to the dopants are also controlled to a greater extent by native defects.Ionising radiations like UV, X-ray, gamma ray electrons, etc produce localized levels in the activated phosphors and the energy storage by such traps is studied by using the conventational Thermoluminescence (TL) glow curve method. The materials having dimensions in nanometer range are defined as nanomaterials. Within this dimension, the properties of matter are considerably different from the individual atoms, molecules and bulk materials. The physical, chemical, electricaland optical properties of these materials are size- and shape-dependent and they often exhibit important differences in the bulk properties.

During the last few years, very considerable progress has been made in the applications of the thermoluminescence (TL) technique for practical purposes. The most widely developed application, however, refers to its use in radiation dosimetry [8] which spans areas of health physics and other biological sciences, radiation protection and personnel monitoring. An equally impressive growth of the TL technique is reflected in its application to the study of various aspects of the role of defects and impurities in solids with suitable reliability. Among the different alkaline earth sulfide familyCalcium sulfide (CaS) is one of the members who dominates all sulfides in respect of their use in TL dosimetry. Marwaha et al [9] and Sweet and Rennie [10] give support to the significant potential of CaS phosphors as UV, γ-ray and x-ray dosimeter.

With the advent of nanotechnology, there is still a considerable amount of research involved in the search for new nanocrystalline phosphor materials with better TL and dosimetric properties. The potential of CaS:Binanocrystalline phosphor for UV dosimetry has recently been reported by Kumar et. al. [11]. It was found that due to nanocrystalline sizes the peak temperature shifts towards higher temperature due to the formation of deep traps. From dosemetric point of view, higher the temperature of the dosimetric peak the lesser the room temperature fading, is an important property. The importance of nanocrystalline materials has increased tremendously in the field of luminescence, especially as they exhibit enhanced optical, electronic and structural properties. They may be used as efficient phosphors in display applications such as flat panel displays with low-energy excitation sources because the lower the screen coating the larger its resolution. Thelarger surface to volume ratio of nanocrystalline materials also enhance the potential as because of which they are relatively stable with their phase to any external perturbation from heat, pressure, etc. Thus, in variable surrounding conditions they are an ideal material. Because of their stability deep traps are very useful. Therefore, for selecting a suitable material prior knowledge of traps and other kinetic parameters is desirable.

 DOI : 10.18231/2454-9150.2018.0583

ISSN : 2454-9150 Vol-04, Issue-05, Aug 2018

This paper reinvestigate the results of studies on the TL glow curves of CaS:Binanocrystalline phosphors exposed to γ-rays from a Cs^{137} source as reported by Kumar et. al.[12]. Here we calculate the order of kinetics parameter following a new method of analysis.

II. MATERIAL AND METHOD OF ANALYSIS

As reported by Kumar et. al.[12] for synthesis CaS:Binanocrystalline phosphors were prepared by the wet chemical co-precipitation method. Calcium chloride ($CaCl_2 \cdot 5H_2O$ (99.9%)), ethanol (99.9%), sodium sulfide ($Na_2S \cdot 9H_2O$), bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$ (99.5%)) and 1-thioglycerol (90%) are taken as starting material. The details of nanophosphors preparation have been reported Kumar et. al. [13].The TL response of CaS:Binanocrystalline phosphor with various $Bi3^+$ concentrations between 0.010 and 0.12mole% after a γ-ray dose of 40.48mGy as already reported in literature by Kumar et. al.[12] is shown in Fig.1.

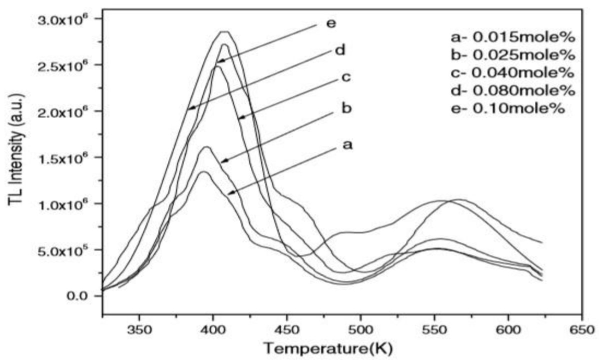

Fig.1 TL glow curve of CaS:Binanocrystalline phosphor irradiatited by γ-ray with 40h exposure at room temperature with different concentration of dopant Bi [12].

The trap parameters such as activation energy (E_A) and frequency factor(s) as calculated byKumar et. al.[12], for each deconvoluted peak of the CaS:Bi(0.08mole%) nanophosphors sample irradiated with a gamma dose of 40.48mGy(correspondsto40hexposure)atroomtemperature using Chen's [14] set of empirical formulae for the glow curveshapemethod. The Computer Glow Curve Deconvolution (CGCD) curve fitting for one sample under gamma ray irradiation is shown in Fig.2.

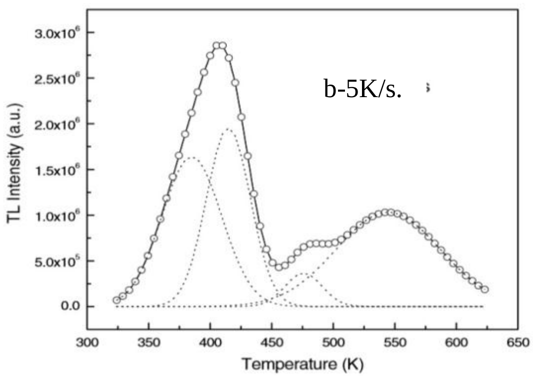

Fig.2 TL glow curve for CaS:Bi(0.08mole%) nanocrystalline phosphor after 40h γ-ray exposure. Dotted line represents the CGCD peaks [12].

III. RESULTS AND DISCUSSION

The trapping parameters, namely activation energy and frequency factor, as evaluated and reported in literature by Kumar et. al.[12] following Chen's method [14] are shown in Table.1. There are so many slightly different mechanisms responsible for appearance of TL glow reported in literature, but relation for peak temperature is same in all the mechanisms and is given by

$$T_m^2 = \frac{b\, E_a \tau_m}{k}$$

where T_m is peak temperature of curve, b is constant linear heating rate, E_a is trap depth or activation energy, k is Boltzmann's constant and τ_m is relaxation time at peak temperatue, which is given by Arrhenius relation as

$$\tau_m = \tau_0 \exp[\frac{E_a}{k\, T_m}]$$

Where τ_0 is inverse of frequency factor s. Considering the reported values of activation energy and frequency factor [12], LHS and RHS are calculated for each resolved peak and are shown in Table.1. The reported values of trapping parameters and peak temperature have to satisfy the equation of peak temperature. But the values shown in fifth and sixth columns of Table.1 are not same, means peak temperature relation is not satisfied. In order to remove this inadequacy here we apply a new method of analysis suggested by Prakash [15] and Prasad et al [16]. In his proposed mechanism, Prakash reconsider the process of

Table.1

Different reported [12] and evaluated parameters of various glow peaks of CaS:Bi(0.08mole%) nanocrystalline samples with 40.48mGy of γ-ray irradiation

b (K s^{-1})	T_m (K)	E_a (eV)	s (s^{-1})	T_m^2 (K^2)	$\frac{b\, E_a \tau_m}{k}$	ℓ
2	371	0.6	8.90E+04	137641	21996172.83	0.006257498
2	403	0.95	1.30E+09	162409	12764329.55	0.012723661
2	466	1.38	1.20E+14	217156	221956.7687	0.978370704
2	534	0.74	3.20E+07	285156	5145.246047	55.42125632
5	384	0.66	4.60E+07	147456	379916.2155	0.388127682
5	415	1.06	6.10E+11	172225	744976.9612	0.231181646
5	475	1.83	2.30E+19	225625	118737.4716	1.900200476
5	544	0.76	7.20E+07	295936	6693.175454	44.21458873
10	401	0.72	1.70E+	1608	5464559.	0.02942616

DOI : 10.18231/2454-9150.2018.0583

			07	01	358	
10	430	1.03	1.90E+12	184900	73598.4207	2.512282169
10	491	1.79	3.07E+18	241081	157632.3919	1.529387438
10	559	0.8	1.11E+08	312481	13570.35211	23.02674223

Recombination and retraping of excited electrons of conduction band and establish a new relation for TL intensity I at temperature T, and is given by

$$I = (1-x)\, n_0\, s\, exp[-\left(\frac{E_a}{k\,T}\right) - \frac{s\,(1-x)}{b}\int_{T_0}^{T} \exp(-\frac{E_a}{k\,T'})dT']$$

where x is extent of retrapping, n_0 is the initial concentration of trapped carriers per unit volume, T_o the temperature at which TL glow curve starts to appear, T′ any arbitrary temperature in the range $T_o$to T. Extent of retrapping is related with order of kinetics ℓ a

$$\ell = \frac{1}{1-x}$$

and accordingly peak temperature relation is modified as

$$T_m^2 = \frac{\ell\, b\, E_a\, \tau_m}{k}$$

As per the mechanism suggested by Prakash with changing b, the rate of recombinationchangesresultinginthechanged valueof T_m, which is again in agreement with reported [12] glow curve as shown in Fig.3.Changein initial concentration n_0, which is directly related with irradiation dose or exposure time, onlyinfluences the intensity of the TL glow curves which is again in agreement with the reported [12] TL glow curves of material under consideration as shown in Fig.4. As per the new method of analysis proposed by Prakash [15] and Prasad et al [16], order of kinetics is evaluated for all deconvoluted peak and and values are given in Table.1.

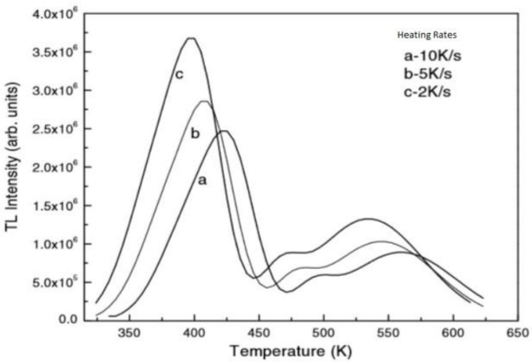

Fig.3 Influence of different heating rates on TL response of CaS:Bi(0.08mole%).

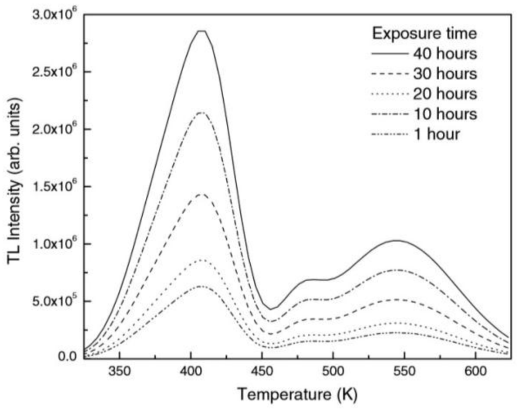

Fig.4 Influence of different irradiation exposure on TL glow curves of CaS:Bi(0.08mole%) at a heating rate of 5Ks^{-1}.

IV. Acknowledgment:

The author is thankful to the Director of his institute for providing the facilities and also thankful to Prof. Jai Prakash, Ex Pro Vice Chancellor, Pt. D D U Gorakhpur University, Gorakhpur for inculcating research temper.

V. Conclusion

Alkaline earth sulphides have been known for a long time as excellent and versatile phosphor materials. In the present investigation during reanalysis of already reported thermoluminescence glow curve, order of kinetics parameter is evaluated following a new proposed method. This parameter depends on extent of retrapping involved in thermoluminescence process. It has been found that reported influence of heating rate on glow curve is same as in new proposed mechanism, and the same result in the case of exposure time in terms of initial concentration. So, the discussed method of analysis may more helpful in characterization and accordingly selection of suitable luminescent phosphor material for different purposes like, in dosimeters or in display devices.

References:

[1]. W.Lehmann, "Alkaline Earth Sulfide Phosphors Activated by Copper, Silver, and Gold", J. Electrochem. Soc.,117, p1389-1393, 1970.

[2]. W. Lehmannand F. M. Ryan, "Cathodoluminescence of CaS : Ce3 + and CaS : Eu2 + Phosphors", J. Electrochem. Soc., 118, p477-482, 1971.

[3]. W. Lehmannand F. M. Ryan, "Fast Cathodoluminescent Calcium Sulfide Phosphors", J. Electrochem. Soc., 119, p275-277, 1972.

[4]. W. Lehmann, "Activators and co-activators in calcium sulfide phosphors", J. Luminescence, 5,p87-107, 1972.

[5]. Japanese Patent Jp 57,195,784, 'Alkaline earth metal sulfide phosphor', Hitachi Ltd, Kokai, TokkyoKoho, Dec. 82.

 DOI : 10.18231/2454-9150.2018.0583

[6]. Japanese Patent Jp 57,195,785, 'Phosphor', Toshiba Corporation, Kokai, TokkyoKoho, Dec. 82.

[7]. G. Blasse:'Handbook on the physics and chemistry of rare earths', (ed. K. A. Gschneider and L. R. Eyring), 237-274; 1979, Amsterdam, North-Holland Co.

[8]. G L Marwaha, N Singh , D R Vij and V K Mathur, "Spectral Variations and retrapping processes in CaS:Bi" 1980 Radiat. Eff. 53, p25, 1980.

[9]. G L Marwaha G L, N Singh N, D R Vij and V K Mathur, "CaS: Bi as U.V. dosimeter",Mater. Res. Bull. 14, p1489, 1979.

[10]. M A S Sweet and J Rennie , "Thermoluminescence studies of CaS : Bi nanocrystalline phosphors", Nucl. Instrum.Methods A 283, p330, 1989.

[11]. V Kumar ,R Kumar R, S P Lochab and N Singh, "Thermoluminescence studies of CaS : Bi nanocrystalline phosphors" ,Radiat. Eff. Defects Solids 161,p479, 2006.

[12]. V Kumar, R Kumar, S P Lochab and Nafa Singh., "Thermoluminescence studies of CaS : Bi nanocrystalline phosphors",J. Phys. D: Appl. Phys. 39, 5137, 2006.

[13]. V Kumar,N Singh,R Kumar and S P Lochab, " Synthesis and characterization of bismuth doped calcium sulfide nanocrystallites", J. Phys.: Condens Matter 18, p5029, 2006.

[14]. Chen R and Kirsh Y 1981 Analysis of Thermally Stimulated Processes (New York: Pergamon)

[15]. J Prakash, "Thermoluminescence glow curve involving any extent of retrapping or any order of kinetics",Pramana-j of Physics,2013, 81, 3, p521, 2013.

[16]. D Prasad, A N Thakur and J Prakash, "T L Glow Curve Analysis Technique for Evaluation of Decay Parameters and Order of Kinetics", Ultra Scientist, Vol.24(3)B,p489, 2012.

 DOI : 10.18231/2454-9150.2018.0583