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Contents

Thermoluminescence Studies in Europium Doped KSr_2Br_5 and $CsBa_2I_5$ Halide Phosphors

Chhagan D. Mungmode, Dhananjay H. Gahane, Chetan V. Chanmal, and Sanjiv V. Moharil

Abstract Divalent Europium (Eu^{2+}) doped alkali halides KSr_2Br_5 and $CsBa_2I_5$ phosphors are synthesized by wet chemical method. These phosphors are characterized for Thermoluminescence (TL) properties. Different γ-dose using Co^{60} source are used to irradiate the samples. For $CsBa_2I_5$:Eu^{2+}, thermoluminescence curve shows maxima at 207.5 °C and for KSr_2Br_5:Eu^{2+}, TL maxima peaks around 261.74 °C which are related to the defects at trap depths. Kinetic parameters of the peak are calculated. The activation energy value for $KSrBr_5$ and $CsBa_2I_5$ are 1.5 eV and 0.811 eV respectively, suggest a possible good stability of the trapped charges produced during irradiation. Hence, Eu (0.5%) doped KSr_2Br_5 and $CsBa_2I_5$ phosphors could be used for possible TL Dosimetry applications.

Keywords Thermoluminescence · Eu^{2+} · Kinetic order · Trap depth

1 Introduction

Thermoluminescence dosimetry has found numerous applications [1, 2] which includes areas of health science and other biological sciences, radiation protection and personnel monitoring. The phosphors show thermoluminescence phenomenon when it is illuminated by ionizing radiations; traps are created and electrons get trapped into it. These trapped electrons are released due to application of temperature and recombine with hole to emit radiation. Specifically tuned phosphor materials which

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are used in TLD badges has found wide applications in environmental and personnel radiation monitoring. New TLD phosphors have been established by researchers [3–7].

Thermoluminescence study can be efficiently used for the measurement of radiation dose and to study the electronic trap levels in crystals. Very large number of phosphor materials exhibits thermoluminescence but very few of them possesses all the perfect characteristics of an idle TLD [8]. Also, defects and impurities present in solids can be studied with the help of Thermoluminescence. In thermoluminescence study, ionizing radiations are used to irradiate a phosphor material for a particular time period. This phosphor is then annealed at a fixed rate and the emitted light output is measured as a function of temperature of the phosphor. The curve of emitted light intensity versus temperature is plotted.

The energy depth of the trapped electrons is given by the position of the peaks on the scale of temperature. How many numbers of electrons are transferred to these traps by the exciting radiations can be measured by area under the curve. The exciting radiations used for this purpose may be UV rays, Gamma rays, alpha particles, ion beams, electrons, neutrons, etc. TL studies give the distribution of traps in the band gap of solids.

Many Sulfides, Sulfates and fluorides of alkali and alkaline earth elements are extensively studied and widely used for Thermoluminescence Dosimetry (TLD). Phosphates and halo-phosphates of alkali and alkaline-earth metal elements were synthesized [9, 10] and also explored for their suitability as TLD materials (Welker 1991; Band et al. 1997; Kottaiswamy et al. 1997; Sanayee et al. 1997; Dhabekar et al. 2002). Schipper et al. (1993) studied X-ray storage phosphor $Ba_3(PO_4)_2$:Eu for trapping of electrons, Seshagiri et al. (1992) studied the thermally stimulated luminescence (TSL) and electron paramagnetic resonance (EPR) properties of calcium chlorophosphates doped with actinide [11].

Very few Eu^{2+} activated alkali halide materials are studied for thermoluminescence. In this work, synthesis and characterization of bromide and iodide-based phosphor is discussed. KSr_2Br_5:Eu^{2+} and $CsBa_2I_5$:Eu^{2+} are prepared using wet chemical synthesis method and their thermoluminescence study is discussed in this paper.

2 Experimental

All the reagents used in this work were of analytical purity manufactured by Merck and were used without further purification. $CsBa_2I_5$:Eu^{2+} sample was prepared using wet chemical method. Initially stoichiometric composition of metal carbonates and Eu_2O_3 were dissolved in HI. This solution was then heated on magnetic stirrer to boil off excess amount of acid and to get dry compound. This whole process was carried out in a glass distillation assembly which consists of a glass flask placed on hot plate with magnetic stirrer. One neck of the flask is connected to condenser unit, so that the evaporated acid can be cooled and collected in a receiving vessel at the lower end. The remaining compound was crushed to get fine powder and dried for 2 h in air.

After that the powder annealed for 1 h at 925 k in a reducing atmosphere provided by burning activated charcoal. Similarly, KSr_2Br_5:Eu^{2+} phosphor was also prepared. Thermally stimulated glow curves were recorded at room temperature. Phosphors under examination were irradiated with gamma dose of 23 kGy.

3 Result and Discussion

KSr_2Br_5 and $CsBa_2I_5$ has $TlPb_2Cl_5$ structure ($P2_1/c$, monoclinic) as shown in Fig. 1. In KSr_2Br_5, there are four formula units per unit cell. K^+ and half the Sr^{2+} cations are in a trigonal prismatic coordination of Br^- with three additional Br-ions capping the polyhedron. Such tricapped trigonal prisms are joined along [1 0 0] by common triangular faces, and they contain K^+ and Sr^{2+} alternatively. K^+ and half the Sr^{2+} ions are in a [6+2(+l)] coordination based on the geometry of a trigonal prism and the remaining half of the Sr^{2+} ions are in a [6 + 11] coordination of an extended octahedron [12].

Figure 2 shows TL glow curve observed in KSr_2Br_5:Eu^{2+} (0.5 mol%) phosphor and Fig. 3 shows TL glow curve observed in $CsBa_2I_5$:Eu^{2+} (0.5 mol%) phosphor irradiated with gamma dose of 23 KGy (75 min) recorded in the temperature range between room temperature to 400 °C. Heating rate was 0.11 °C/s. A dominant TL peak is observed at 261.74 and 213 °C.

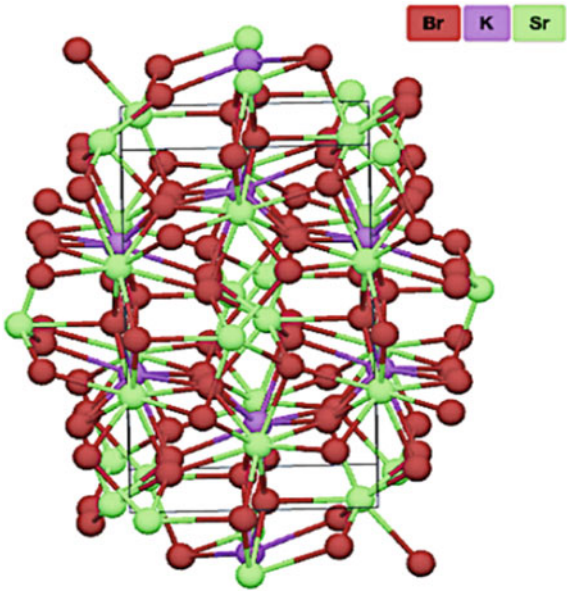

Fig. 1 Crystal structure of KSr_2Br_5

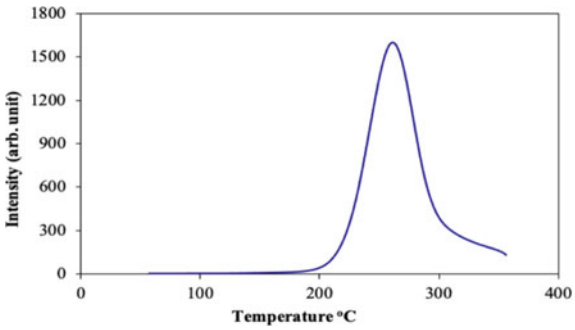

Fig. 2 Thermoluminescence glow curve of γ-irradiated $KSr_2Br_5:Eu^{2+}$ phosphor

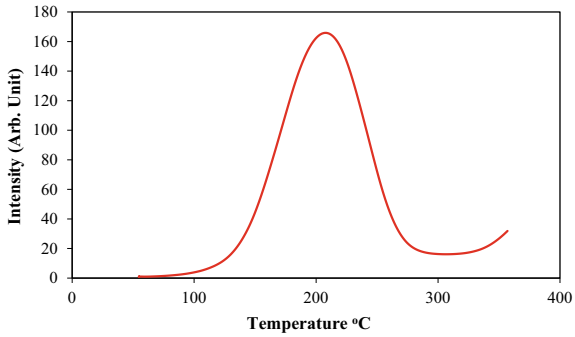

Fig. 3 Thermoluminescence glow curve of γ-irradiated $CsBa_2I_5:Eu^{2+}$ phosphor

The nature of the TL glow curve is decided by the order of kinetics. Half-width methods in which the temperatures T_m, T_1 and T_2 are the highest temperature, temperatures on the lower and upper sides related to half the highest intensity respectively and relied on the form of the glow curve, are utilized to make equations to relate E to all or any or a number of these temperatures.

The order of kinetics was calculated by Chen's Method [13] measuring the geometrical factor $\mu_g = \delta/\omega$, where δ is half width towards fall-off side of glow curve and ω is full width at half maximum of glow curve. These are calculated as $\delta = T_2 - T^m$, $\omega = T_2 - T_1$ and $\tau = T_m - T_1$, where Tm is peak temperature related to maximum intensity, T_1 and T_2 are temperature on either side of Tm corresponding to half of maximum intensity.

The calculated values of geometrical factor for $KSr_2Br_5:Eu^{2+}$ is $\mu_g = 0.48$ which corresponds to the kinetic order (l) 1.4 and that for $CsBa_2I_5:Eu^{2+}$ is $\mu_g = 0.4756$ which is less than 1 corresponds to the kinetic order (l) 1.38, shows that the kinetic order is first order estimated by the employment of Figs. 2 and 3 given by Chen [13].

The trap depth (E_τ) was calculated from the height parameters by the Chen's equation

$$E_\tau = C_\tau(kT_m^2/\tau) - b_\tau(2kT_m)$$

Table 1 Kinetic parameters of $KSr_2Br_5:Eu^{2+}$ and $CsBa_2I_5:Eu^{2+}$ phosphors calculated by the peak shape method

Material	Peak temp. *Tm* (K)	Geometric factor (μ_g)	Kinetic order (l)	Activation energy (E (eV))			Freq. factor ($s(s^{-1})$)
				$E\tau$	$E\delta$	$E\omega$	
$KSr_2Br_5:Eu^{2+}$	534.74	0.48	≈ 1.4	1.52	1.55	1.54	3.4×10^{12}
$CsBa_2I_5:Eu^{2+}$	480.57	0.4756	≈ 1.38	0.638	0.716	1.08	3.8×10^{12}

where,

$$C_\tau = [1.51 + 3(\mu_g - 0.42)] \text{ and } b_\tau = [1.58 + 4.2(\mu_g - 0.42)]$$
$$E_\delta = [0.976 + 7.3(\mu_g - 0.42)]kT_m^2/\delta$$
$$E_\omega = [2.52 + 10.2(\mu_g - 0.42)](kT_m^2/\omega) - 2kT_m$$

where, C_τ and b_τ are constants of Chen's equation, k is Boltzmann's constant and temperature is taken in kelvin. After determination of the trap depth and also the order of kinetics, the frequency factor s, in general, is estimated using the relation.

$$s = [(kT_m^2/\beta E)\, e^{(-E/kTm)}(1 + (l-1)2kT_m/E)]^{-1}$$

The calculated kinetic parameters for peak of $KSr_2Br_5:Eu^{2+}$ and $CsBa_2I_5:Eu^{2+}$ phosphors by the peak shape method are given in Table 1.

An important factor for a long-lasting phosphor is to supply an appropriate trap depth within the host. Due to too low trap depth, the electrons within the trap can return to the energy of the excited state easily, thus leading to a brief afterglow lifetime and if the trap depth is just too deep, the transition probability of electrons in the traps to the excited state is extremely low. In such a state, the after glowing is weakly intense. As per Sakai's report, a trap depth between 0.6 and 0.7 eV is suitable for an extended afterglow [14]. The frequency factor is also another important parameter that affects the lifetime of electrons in the traps. In this case, when the frequency factor is increased, the lifetime of the electrons in the traps is decreased.

4 Conclusion

We have synthesized the $KSr_2Br_5:Eu^{2+}$ and $CsBa_2I_5:Eu^{2+}$ phosphors using simple wet chemical method. TL of the $KSr_2Br_5:Eu^{2+}$ phosphor shows a maximum at 261.74 °C and for $CsBa_2I_5:Eu^{2+}$ phosphor TL maxima is around 207.57 °C. It shows linear response up to 23 kGy. Glow curve deconvolution and peak shape methods are used to find out the kinetic parameters. The activation energy value for $KSr_2Br_5:Eu^{2+}$ is 1.5 eV and for $CsBa_2I_5:Eu^{2+}$ is 0.811 eV, suggest a possible good stability of the

trapped charges produced during irradiation. $KSr_2Br_5:Eu^{2+}$ phosphor with a trap depth higher than 0.75 eV, a frequency factor of the order of 10^{12} s^{-1}.

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