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Thermoluminescence Properties of β-Ray Irradiated $CaZnF_4$:Dy Phosphor

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ABSTRACT

In this paper, thermoluminescence studies of $CaZnF_4$: Dy phosphor, irradiated with beta-rays, has been reported. A series of $CaZnF_4$: Dy phosphors were prepared by the wet chemical method and characterized for photoluminescence (PL) and Thermoluminescence (TL) properties. Under the photoluminescence study, the characteristic emission spectrum of Dy^{3+} corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (483 nm) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (576 nm) transitions were observed. The Thermoluminescence (TL) glow curves of the prepared sample showed two well-defined glow peaks at 103 °C and 162 °C, respectively, indicating that two sets of traps is being activated within the particular temperature range. The trapping parameters associated with the prominent glow peak of $CaZnF_4$: Dy was calculated by using Chen's method.

Keywords: Photoluminescence (PL); thermoluminescence (TL); beta-rays; wet chemical synthesis; fluoride.

I. INTRODUCTION

Rare-earth activated fluoride phosphors have gained huge attention for their interesting optical properties [1–3]. Fluoride phosphors produce a very high quantum yield compared to oxide phosphors due to lower probability of non-radiative decay of rare-earth ions in fluoride phosphors. This is an outcome of low phonon energies in fluoride-based phosphors. The bond formation between rare-earth ions and fluoride ions is often highly ionic nature and this results in the lower value of phonon energy and a wider band gap [4,5].

Fluoride materials have shown interesting luminescence properties, both in terms of thermoluminescence dosimetry (TLD) and lamp phosphors [6–8]. The synthesis of these phosphors by solid state diffusion method is often accompanied with incorporation of several unwanted impurities which can quench the luminescent centres [9]. Halide phosphors are very susceptible to hydrolysis and there is practically a lot of difficulty in preparing complex halide phosphors through solid state diffusion method [5,10,11]. The varying melting points of the precursor materials in the solid state diffusion hamper the stoichiometry and the formation of the final product will not assure the nonexistence of the unreacted constituent materials. To avoid this dilemma, wet-chemical methods are more preferable for the synthesis of halide phosphors.

A convenient one-step synthesis i.e. wet chemical synthesis of $CaZnF_4$: Dy phosphor and investigations on its photoluminescence and thermoluminescent properties have been reported in this paper. This paper also includes the trapping parameters of β -rays irradiated $CaZnF_4$ phosphor which was calculated by Chen's half width method.

II. EXPERIMENTAL

A series of $CaZnF_4$:Dy^{3+} (Dy = 0.1 mol%, 0.2 mol%, 0.5 mol% and 1 mol%) phosphor were synthesized by a facile wet chemical method. The AR grade precursors, namely, $CaCl_2$, $ZnCl_2$, NH_3F and Dy_2O_3 were taken in stoichiometric proportion. Since Dy_2O_3 is insoluble in water, it was converted into nitrate form by preparing a

stock solution of Dy_2O_3 dissolved in Nitric Acid (HNO_3). This stock solution was heated in an oven at 60 ^oC for 5 minutes to confirm complete conversion of oxide to nitrate form of Dy. All the precursors were separately dissolved in deionized distilled water stirred well until complete solution resulted. These solutions were added one by one and mixed well using a magnetic stirrer, and heated at 60 ^oC until complete evaporation of water took place. The prepared samples were allowed to cool down slowly at room temperature. The resultant polycrystalline mass was crushed to fine powder in a porcelain mortar with pestle.

The prepared phosphors were characterized for their photoluminescence and thermoluminescence properties. The photoluminescence (PL) excitation and emission spectra were recorded on the Shimadzu RF-5301PC spectrofluorophotometer. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. For the thermoluminescence (TL) measurements, samples were exposed to β- rays from a ^{90}Sr source at room temperature at the rate of 0.58 $kGyh^{-1}$. After desired exposure, TL glow curves were recorded for 5 mg of sample each time at a heating rate of 5 ^oC/sec. The TL glow curves were recorded using thermoluminescence reader (Integral PC Based) NUCLEONIX - (TL-1009 I), with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, photomultiplier tube, dc amplifier and millivolt recorder. For comparison, glow curves were also recorded under identical conditions for commercially available dosimetry grade TLD-$CaSO_4$: Dy.

III. RESULTS AND DISCUSSION

3.1 PL characteristics of Dy^{3+} activated $CaZnF_4$ Phosphor

It is essential to have the understanding of the transition probabilities of intra-configurational 4f transitions of rare-earth ions to recognize the luminescence properties of materials. Luminescent materials doped with Dy^{3+} ions show the blue emission at 470–500 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and the yellow emission at 570–600 nm corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ hypersensitive transition. These transitions are observed when the crystal field environment is favourable for Dy^{3+} doping in the host.

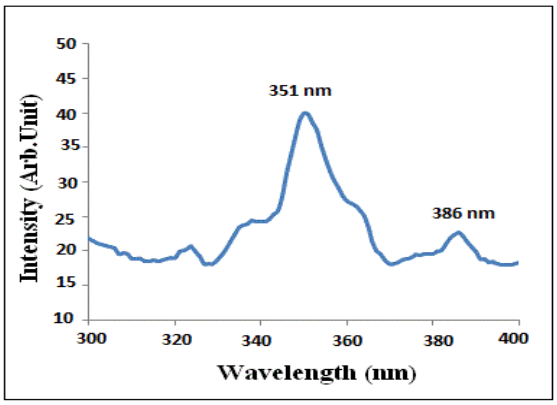

Figure 1. Excitation spectrum of $CaZnF_4:Dy^{3+}$ phosphor monitored at 576 nm.

In case of $CaZnF_4:Dy^{3+}$ phosphor, two characteristic emission peaks were observed at 483 nm and 576 nm for 351 nm excitation. The excitation spectrum of $CaZnF_4:Dy^{3+}$ phosphor, monitored at 576 nm, is shown in Fig. 1. The spectrum shows a sharp and most intense peak at 351 nm corresponding to the $^6H_{15/2}$ to $^6P_{7/2}$ transition of Dy^{3+}. Another peak at 389 nm corresponding to $^6H_{15/2}$ to $^4F_{7/2}$ transition is also observed. However, these peaks are blunt and are not intense. The emission spectra, as shown in Fig. 2, also have a similar blunt nature. This is due to the fact that $CaZnF_4$ does not offer a favourable crystal field environment for the doped Dy^{3+} ions. The peaks centred at 483 nm (blue) and 576 nm (yellow) correspond to the transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$, respectively [12,13]. The variation of Dy^{3+} ions shows slight variation in the intensity of the PL emission. The PL intensity has shown an increase with the dopant concentration and no concentration quenching was observed up to 1 mol% Dy^{3+} doping.

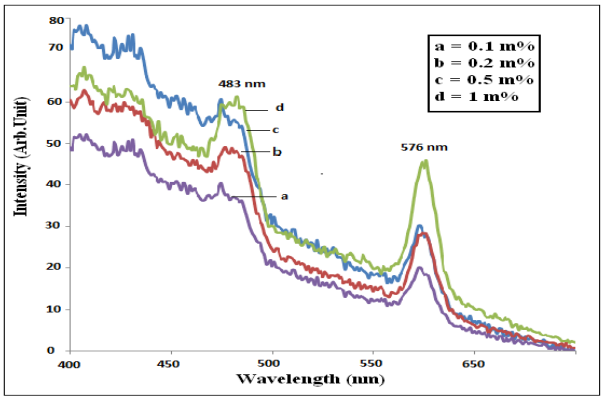

Figure 2. Emission spectrum of $CaZnF_4:Dy^{3+}$ phosphor when excited at 351 nm.

3.2 TL characteristics of Dy^{3+} activated $CaZnF_4$ Phosphor

Figure 3 shows TL glow curves of $CaZnF_4:Dy^{3+}$ (0.1 mol%) phosphor irradiated by different doses β-rays using ^{90}Sr source. The TL glow curves were recorded at a linear heating rate of 5 ^oC/sec in the temperature range between 50 to 300 ^oC. 5 mg sample of $CaZnF_4:Dy^{3+}$ was used to record the glow curves. The TL peak intensity of β-irradiated $CaZnF_4:Dy^{3+}$ (0.1 mol%) phosphor increased up to 30 Gy dose. The TL glow curve has a broad nature arising from 60 ^oC to 280 ^oC which also depicts the presence of two different peaks inside the glow curve. The glow curves of the irradiated sample presented two well separated peaks for all the doses of β-rays. This means that there is a shallow trapping level leading to a peak at 103 ^oC and a deeper trapping level leading to a peak at 162 ^oC. Another observation is that the intensity of the higher temperature peak (162 ^oC) is slightly greater than the lower temperature peak (103 ^oC). This means that the trapping of charge carriers is more towards the deeper trap levels than the shallower ones. The deconvoluted TL glow curves can be seen in Fig. 4. No TL glow curve was recorded for unirradiated samples of $CaZnF_4:Dy^{3+}$ (0.1 mol%) phosphor.

To discover its application as a thermoluminescence dosimeter (TLD), a material should show a linear response with the absorbed dose of radiation. Many TL materials show a nonlinear response with the absorbed dose over certain amount of dose range. The relationship between the TL intensity and absorbed doses of β-rays for $CaZnF_4:Dy^{3+}$ (0.1 mol%) phosphor has been shown in Fig. 5. The TL response is found to be linear in the dose range 1.5 to 29 Gy. Fig. 6 shows the comparison of TL glow curve of $CaZnF_4$: Dy with the standard $CaSO_4$: Dy TLD phosphor irradiated by β –rays. The TL intensity of the $CaZnF_4$: Dy phosphor is six times smaller than that observed in case of commercial $CaSO_4$: Dy TLD phosphor.

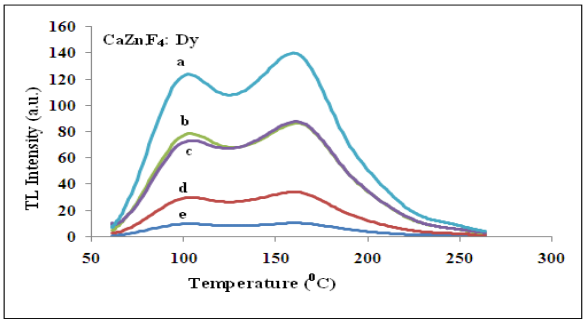

Figure 3. TL glow curve of $CaZnF_4$: Dy phosphor with different exposure of Dy ions at β –rays exposure (0.58 $kGyh^{-1}$). (i) a=29 Gy (ii) b=19 Gy (iii) c=10 Gy (iv) d=5 Gy (v) e=1.5 Gy.

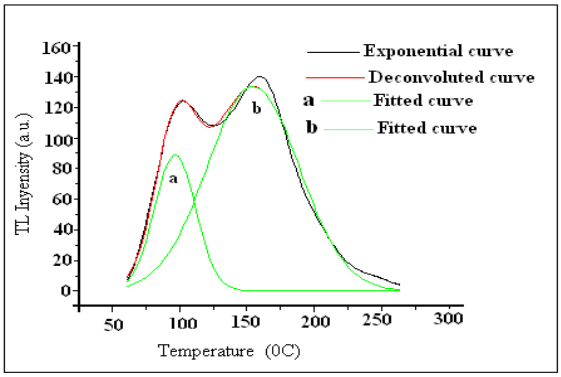

Figure 4. An analyzed TL glow curve of $CaZnF_4$: Dy phosphor irradiated with a 29 Gy dose of β –rays at room temperature.

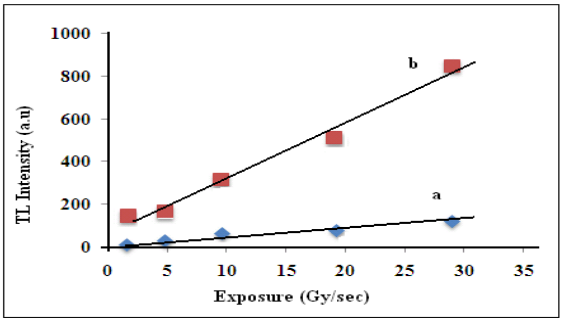

Figure 5. Dose response curve of (a) $CaZnF_4$: Dy and (b) $CaSO_4$: Dy phosphor.

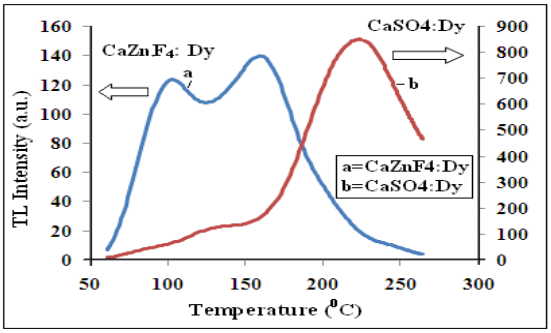

Figure 6. TL glow curve of $CaZnF_4$: Dy compared with standard $CaSO_4$: Dy TLD phosphor for β -ray exposure.

3.3 TL kinetic and trap depth analysis

Trapping parameters such as order of kinetics (b), activation energy (E), and frequency factors (s) were calculated for the glow peak of $CaZnF_4$:Dy phosphor for 29 Gy dose by using Chen's method [14]. According to Chen's method order of kinetics (b) is determined by geometrical shape or symmetry factor (μ_g), as given in Eq. (1).

$$\mu_g = (T_2-T_m)/ (T_2-T_1) \text{ -------- } (1)$$

where T_m is the peak temperature, and T_1 and T_2 are temperatures on either side of T_m. Here, $T_m-T_1 = \tau$, the half width towards the rising side of the glow peak; $T_2-T_m = \delta$, the half-width towards the fall-off side of the glow peak; and $T_2-T_1 = \omega$ is the total half-width.

Chen's method was employed to determine the energy depth of local trapping levels. For kinetic and trap depth analysis, TL glow curve were recorded at a heating rate of 5 ^oC /sec. Inserting the values of T_1, T_m and T_2 in Eq. (1), geometrical factor μ_g turns out to be about 0.49 for peak-1 and 0.33 for peak-2 respectively, indicating that they obey general order kinetics. Therefore, the activation energy (E) and the frequency factor (s) can be estimated with following equations,

$$E = c_\alpha \left(\frac{kT_m^2}{\alpha}\right) - b_\alpha (2kT_m)$$

and

$$s = \frac{\beta E}{T_m^2 k}\left[\frac{1}{1+(b-1)\left(\frac{2kT_m}{E}\right)}\right]\exp\left(\frac{E}{kT_m}\right)$$

Here α stand for τ, δ or ω respectively. The Peak shape parameters and the kinetic parameters are given in Table 1 and 2, respectively.

Table 1. Peak shape parameters of $CaZnF_4$: Dy (0.1 m %) Phosphor

Peaks	T_1 (°C)	T_m (°C)	T_2 (°C)	τ (°C)	δ (°C)	ω (°C)	μ_g
Peak-1	80	103	125	23	22	45	0.49
Peak-2	115	162	185	47	23	70	0.33

Table 2. Kinetic parameters of $CaZnF_4$: Dy (0.1 m %) Phosphor

Peaks	E_τ	E_δ	E_ω	E (eV)	s_τ	s_δ	s_ω	s (sec^{-1})
Peak-1	0.788	0.891	0.808	0.805	1.10×10^{10}	2.95×10^{10}	2.05×10^{10}	2.03×10^{10}
Peak-2	0.339	0.219	0.295	0.284	7.22×10^{2}	0.171×10^{2}	1.88×10^{2}	3.09×10^{2}

IV. CONCLUSION

A series of $CaZnF_4$:Dy phosphor was prepared by the wet chemical synthesis method. The PL emission spectra shows two peaks centered at 483 and 576 nm originating from the $^4F_{9/2}$-$^6H_{15/2}$ and $^4F_{9/2}$-$^6H_{13/2}$ transitions of Dy^{3+}, respectively. The strongest PL emission intensity was observed for 1 mol% doping of Dy^{3+} ions. No concentration quenching was observed up to this range of doping. The TL response curve of the prepared phosphor, irradiated with high dose β – rays, is linear and the TL peak intensity is six times less as compared to that obtained for $CaSO_4$:Dy commercial TLD phosphor. The trapping parameters of $CaZnF_4$:Dy phosphor were calculated by Chen's method. The mean value of trap depth for peak-1 was found to be 0.805 eV, whereas for peak-2 the value was 0.284 eV. The present TL characteristics indicate that this phosphor may be applicable for radiation dosimetric purpose.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

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