Thermoluminescence Glow Curve Analysis of Dy^{3+} Activated $Ca_2Na_3(SO_4)_3Cl$ Phosphor

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Abstract:

This paper presents the Thermoluminescence study of $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ phosphor synthesized by wet chemical method. The TL glow curve and trapping parameters of $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ phosphor are reported. The samples were irradiated by ^{60}Co gamma-ray source at a dose rate of 0.3712kGy/hr and heating rate of 5°C/s. The samples were characterized by XRD, SEM, PL and TL techniques. Single glow peak is observed for all concentrations of Dy^{3+} activated $Ca_2Na_3(SO_4)_3Cl$ phosphor. The trapping parameters are calculated by Chen's peak shape method. TL glow curves obey the second order kinetics with a single glow peak.

Keywords: XRD, TL, SEM, Wet chemical method

Introduction:

According to McKeever et.al.**[1]**thermoluminescence is one of the processes in Thermally Stimulated Phenomenon. Over last two decades, inorganic phosphors have been widely used in luminescent devices. TL is normally utilized for dosimetry. The other important applications include dating of ancient archeological pottery samples, geological samples, TLD badge for whole body monitoring, etc. TL dosimetry is a low cost, easy technique for measuring the radiation doses using TLD material. Much attention has been paid in developing new TLD phosphors which includes various host materials as sulphates, phosphates, vanadates, borates, chlorides, fluorides, oxides, tungstates. **[2]** Different preparation methods and properties of several thermoluminescent materials have been investigated so far and it is found that sulphates constitute good performer TLDs reports B. Koreet. al. **[3].**Mixed sulphates like $K_2Ca_2(SO_4)_3$:Eu **[3]**, Na_3SO_4C l**[4]**, and other **[5-9]**halosulphate phosphors have been studied and found to be good TL phosphors.

In the present paper we report synthesis and TL properties of dysprosium activated $Ca_2Na_3(SO_4)_3Cl$ phosphors prepared by the wet chemical method. This phosphor also shows excellent photoluminescence property. The structure and morphological properties were studied by XRD and SEM.

Experimental

The phosphor $Ca_2Na_3(SO_4)_3Cl: Dy^{3+}$ was prepared by wet chemical method. For the preparation of $Ca_2Na_3(SO_4)_3Cl: Dy^{3+}$, high purity Na_2SO_4, $CaCl_2$, $Ca(NO3)_2$, $(NH_4)_2SO_4$ and Dy_2O_3 (all AR grade of 99.99% purity) were used as initial raw material. Each initial raw material was weighed using the high precision (0.00001 gm) electronic monopan balance. The concentrations 'x' of Dy in the form of nitrate,

(obtained by mixing with nitric acid) were mixed with host, (where x= 0.05, 0.1, 0.2, 0.5, and 1 mole %). By taking the raw materials in stoichiometric ratio, they were dissolved separately in distilled water and then mixed together to give desired compound.

The compound $Ca_2Na_3(SO_4)_3Cl$: Dy^{3+} is prepared by heating in oven at 80° C for 10-12 hrs. The dried samples were then slowly cooled at room temperature. The resultant polycrystalline mass was flattened to fine particle in crucible. The powder was used for further study.

The photoluminescence (PL) emission spectra of the sample were recorded using fluorescence spectrometer (RF -5301). Equal amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. TL glow curves were recorded with the normal setup consisting of a small metal plate heated directly using a temperature programmer, photomultiplier tube (931B), dc amplifier and millivolt recorder. Five milligram of phosphor was heated every time at the rate of $5°Cs^{-1}$. Samples were exposed to γ - rays using a ^{60}Co source at room temperature at the rate of 0.3712 kGy h^{-1} for different doses in the range 3-87Gy. The glow curves were recorded with a TL glow curve reader (TL10091).

Results and Discussion:

X-ray diffraction

Figure.1, shows the XRD pattern of $Ca_2Na_3(SO_4)_3Cl$ phosphor. It depicts good crystalline nature of the sample. In the XRD pattern starting compound or intermediate compounds lines are not observed, therefore, we consider that the compound is prepared successfully.

Scanning Electron Microscopy

In order to study the morphological structure of phosphor prepared by wet chemical method, scanning electron microscopy has been performed. **Figure.2** shows the SEM images of $Ca_2Na_3(SO_4)_3Cl$ phosphor with different magnifications. The images show that the phosphor consists of clustered structure of micro crystals. The particle size ranges from 3µm to 10 µm.

Thermoluminescence study

TL glow curves of $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ phosphor

Figure. 3 shows the TL glow curves of $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ phosphor prepared by wet chemical method exposed to ^{60}Co γ- radiation source for 30sec at the rate of 0.3712kGy/hr. It is seen that only one glow peak is obtained and the shape of glow curve is same for all the concentrations of the activator Dy^{3+}.

All the curves have single peak at ~ 156°C, which indicates that only one set of trapping parameters have been activated at a particular temperature. This also indicates that the electron traps involved are deep and high energy is required to release the trapped electrons. It is also observed that the intensity of TL increases with increase in Dy^{3+} concentration. Maximum intensity is obtained for 1mol%

concentration of Dy^{3+} ions in $Ca_2Na_3(SO_4)_3Cl$ phosphor. The change in relative intensity may be due to change in population of trapping centers. The electronic and optical properties of luminescent materials depend upon defects in the crystal, the chemical composition and doping of impurities.

Effect of radiation dose on TL intensity

Figure.4 illustrates the TL response of $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (1mol%) irradiated with different doses of γ-radiations. Here also we find that the TL intensity increases with the increase of exposure time and the peak position shifts to higher temperature side. Maximum TL intensity corresponds to the 156°C,176°C, 178°C, 184°C, 189°C, 195°C for the dose value of 3 - 86 Gy resp. Enhancement in TL intensity with increase in doses may be due to the increase in the number of traps with the increase in the dose.

When these traps release the charge carriers after thermal stimulation, they combine with their counterparts to increase the TL intensity. This increase in TL intensity is depicted in **Figure.5**. It is seen that the TL dose response of the $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (1mol%) phosphor is almost linear with slight irregularity. The desirable characteristic of a TLD detector is linear relationship between TL intensity and absorbed dose. Saturation is not found up to 86Gy dose.

Trapping parameters

There are numerous methods for calculating trapping parameters like initial rise method, Ilich method, Lushchik's method, Halperine and Braner method and Chen's peak shape method. Here we have calculated the trapping parameters by Chen's peak shape method.

Using the Chen's peak shape method, the kinetic order can be related to the geometrical factor (μ_g) by the relation $\mu_g = \frac{T_2 - T_m}{T_2 - T_1} = \frac{\delta}{\tau}$, where T_1, T_m and T_2 represent the temperatures of half intensity at low temperature side peak temperature and high temperature side of TL peak. And $\delta = T_2 - T_m$, $\tau = T_2 - T_1$

Therefore E_δ, E_τ, and E_ω are the corresponding activation energy.

For first order kinetics μ_g = 0.42 and for second order kinetics μ_g = 0.52. And another symmetry factor to identify the order of kinetics proposed by Balarin (ρ) can be given as,

$$(= (T_12 - T_1M)/(T_1M - T_11)$$

For the first order kinetics ρ ranges from 0.7 to 0.8 and for second order kinetics ρ ranges from 1.05 to 1.20. From calculated values of μ_g and ρ it is seen that the single peak corresponding to $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (1mol%) is of second order kinetics. The activation energy (E) can be calculated from Chen's [**10**] method and formula for activation energy can be given as,

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

Where α stands for ω,τ and δ respectively. c_α and b_α can be given as,

$c_\tau = 1.51 + 3.0(\mu_g - 0.42)$ and

$b_\tau = 1.58 + 4.2(\mu_g - 0.42)$

$c_\delta = 0.976 + 7.3(\mu_g - 0.42)$ and $b_\delta = 0$

$c_\omega = 2.52 + 10.2(\mu_g - 0.42)$ and $b_\omega = 1$

And the frequency factor 's' can be calculated by the formula

$$s = \frac{\beta E}{kT_m^2}\left(1 + \frac{(b-1)\delta}{c}\right)\exp\left(\frac{E}{kT_m}\right)$$

Where b is the order of kinetics and β is the heating rate.

The trapping parameters calculated are listed in Table 1. The peaks obey second order kinetics. The values of activation energy lie between 0.58 to 0.73 eV. The values of frequency factor lie between 0.28×10^6 to 1.23×10^8 .

Table. 1- Shape factors (μ), Balarin's parameter (ρ), Activation energy (E) and order of kinetics (b) and frequency factor(s) for gamma irradiated $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (1mol%) doped phosphor

γ-dose	T_1 (°C)	T_m (°C)	T_2 (°C)	τ	δ	ω	μ=δ/ω	ρ	b	Activation energy(eV)	Frequency factor
3Gy	122	156	213	34	57	91	0.62	1.67	2	0.73	1.23×10^8
12.37Gy	137	176	228	39	52	91	0.57	1.33	2	0.69	1.3×10^7
24.7Gy	139	178	231	39	53	92	0.57	1.36	2	0.70	1.4×10^7
37Gy	145	184	237	39	53	92	0.57	1.35	2	0.72	1.9×10^7
61.8Gy	147	189	243	42	54	96	0.56	1.28	2	0.69	0.4×10^7
86.6Gy	148	195	242	47	47	94	0.5	1.0	2	0.58	0.28×10^6

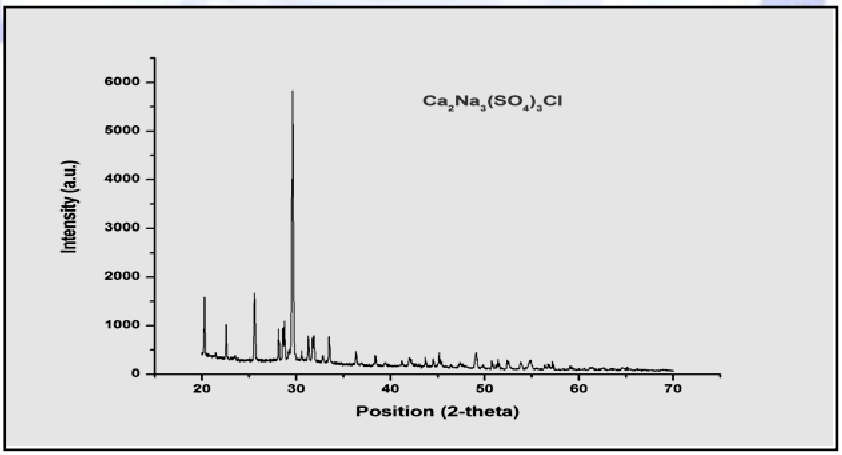

Figure.1-XRD pattern of $Ca_2Na_3(SO_4)_3Cl$

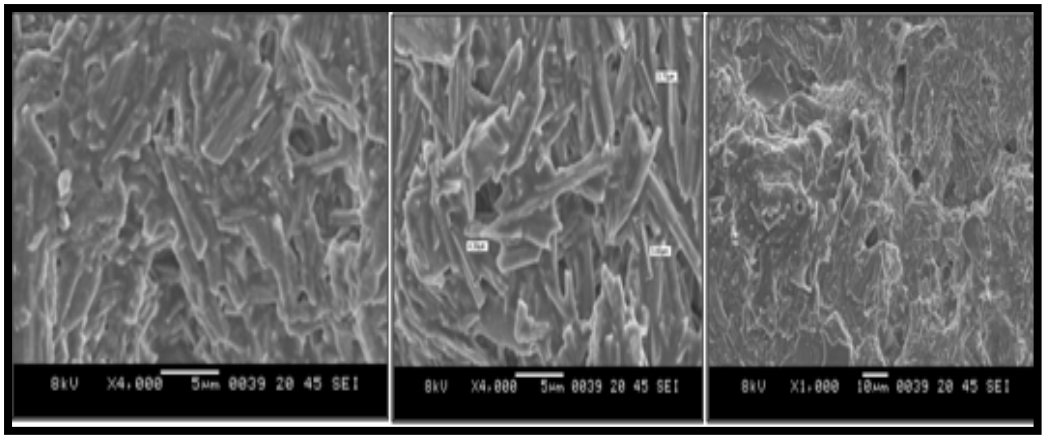

Figure.2-SEM images showing surface morphology of $Ca_2Na_3(SO_4)_3Cl$

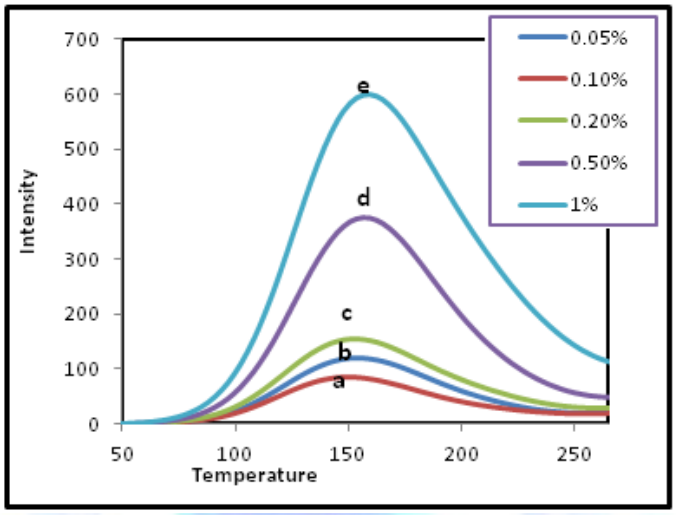

Figure. 3- TL glow curves $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (a) 0.05 mol%, (b) 0.1 mol%, (c) 0.2 mol%, (d) 0.5 mol% (e) 1mol% phosphors exposed to γ-rays.

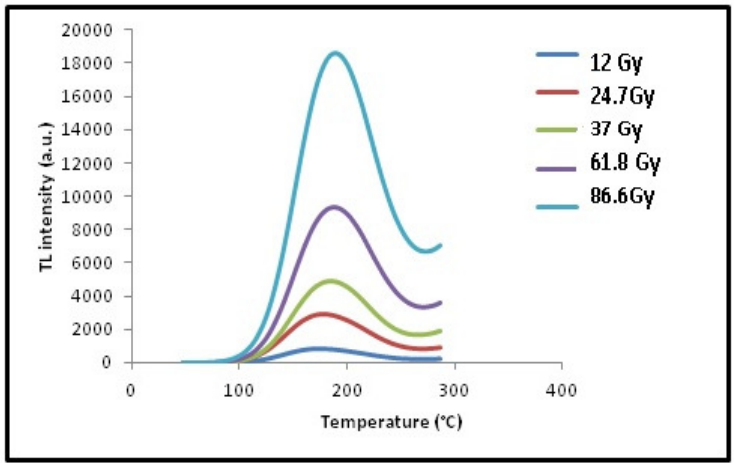

Figure. 4-Variation of TL intensity with exposure time for$Ca_2Na_3(SO_4)_3Cl:1\%Dy^{3+}$

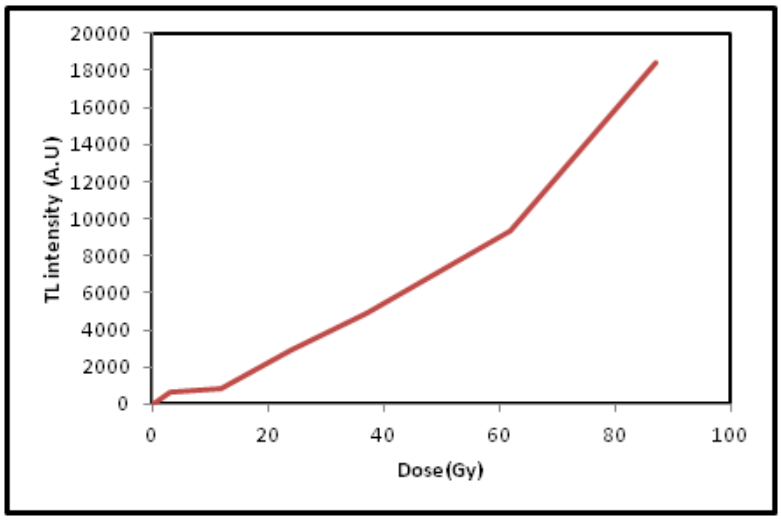

Figure. 5-Dose response curve of $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (1mol%)

Conclusion:

The phosphor $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ was synthesized successfully by wet chemical method. Synthesis is confirmed by SEM and XRD, showing crystalline nature with sizes ranging between 3 to 10µm range. The TL analysis showed a single glow peak obeying second order kinetics, which indicates that only one set of trapping parameters is activated. The TL intensity increases with the increase in the dopant Dy^{3+} concentration and maximum intensity is obtained for $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (1mol%) . Also the TL intensity increases with the increase in the γ-ray dose. The phosphor was found to be almost linear in the dose range from 3 to 86 Gy dose. The kinetic parameters of the phosphor $Ca_2Na_3(SO_4)_3Cl:Dy^{3+}$ (1 mol%) are evaluated as 0.73, 0.69, 0.7, 0.72, 0.69 and 0.58eV for glow peaks centered at 156°C, 176°C, 178°C, 184°C, 189°C, 195°C respectively, and the corresponding estimated frequency factors are 1.23×10^8, 1.3×10^7, 1.4×10^7, 1.9×10^7, 0.4×10^7, 0.28×10^6 s^{-1}. Thus the prepared phosphor may be useful in high dose TL dosimetry.

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