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Preparation, kinetic analysis and thermoluminescent dosimetry features of highly sensitive SrF_2:Dy phosphor

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ABSTRACT

Dy doped SrF_2 microcrystalline was prepared by co-precipitation technique. Thermoluminescence (TL) glow curve of γ irradiated SrF_2:Dy phosphor consists of a main glow peak at 485 K with small shoulders at around 384 K and 590 K. The effects of different dopant concentrations and annealing regimes on TL sensitivity were investigated and the optimum conditions were achieved at 1 mol% of Dy dopant and annealing at 700 °C for 30 min. Initial rise, variable heating rate, isothermal decay and computerized glow curve deconvolution (CGCD) methods were applied to obtain kinetic parameters of the prepared material. TL sensitivity of this phosphor is about 10 times more than that of LiF;Mg;Ti (TLD-100). Based on the obtained results, the synthesized phosphor is appropriate for dosimetry applications.

1. Introduction

TL from rare earth doped materials has widely been studied for several years because of their special characteristics due to atomic structures (the incomplete 4f shell) (Sharma et al., 2011; Anishia et al., 2011; Zahedifar et al., 2016). Certain rare earth doped fluorides such as CaF_2 and LiF with different dopants are amongst the well-known commercial TL dosimeters. Lithium fluoride is used in personal monitoring because of its chemical stability and near tissue equivalence ($Z_{eff}=8.14$). Other phosphors recognized as good materials for TL dosimetry are CaF_2 and BaF_2. In recent works, CaF_2 with different dopants like Dy,Ce, Cu, Tm and Mn have been studied (Salah et al., 2009; Zahedifar et al., 2013; Wang et al., 1986; Zahedifar and Sadeghi, 2012). Calcium fluoride doped with different impurities such as Dy, Tm and Mn are commercially available thermoluminescent dosimeters (TLDs). These TLDs are commonly used in various branches such as personal, environmental, UV and mixed field dosimetry (McKeever et al., 1995; Wulf and Gniadecka, 1996).

There are limited researches on TL dosimetry features of other rare earth doped fluorides such as strontium fluoride.

Chen et al. have investigated the TL properties of Nd^{+3},Pr^{+3},Tb^{+3} and Tm^{+3} doped SrF_2 crystals exposed to β and UV (Kristianpoller et al., 2004). In another research on TL properties of SrF_2:Pr^{+3}, its dose response at the administrated dose of 90 Gy was determined to be higher than that of TLD-100 by a factor of ~3. Two glow peaks were identified in TL glow curve of SrF_2:Pr^{+3} (Kristianpoller et al., 2010)

In a recent work, TL dosimetry features SrF_2 nanoparticles with different dopants of Dy and Cu was studied. 7 glow peaks were observed in TL glow curve of SrF_2:Dy nanoparticles at 384, 406,421, 449, 469, 495 and 508 K. Since the TL dose response of SrF_2:Dy nanoparticles is linear in absorbed dose ranging from 1 Gy to 1KGy, it has been recommended for high dose dosimetry. Also, the amount of dysprosium as dopant was optimized at 0.5 mol% (Zahedifar et al., 2015).

It has been found that TL sensitivity of crystals are strongly modified by changing the type and amount of dopant and the preparation method (Kim et al., 2004). Dysprosium is reported to be one of the most effective dopants in increasing the TL response. In this study SrF_2:Dy is introduced as a new highly sensitive TL phosphor, and its dosimetry properties is compared with those of TLD-100. Kinetic parameters of TL glow peaks contained in its complex glow curve are also presented and discussed. Because of proper TL sensitivity, low fading (especially for glow peak 4) and good reusability, the prepared phosphor is quite hopeful for environmental dosimetry. High effective atomic number of about 33.4 causes over response of SrF_2:Dy phosphor when it is irradiated with low energy photons. This energy dependence of TL response limits the application of SrF_2:Dy phosphor in personal dosimetry.

2. Sample preparation

Microcrystalline SrF_2:Dy phosphor was prepared by the co-

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precipitation method. The preparation procedure was similar to that of SrF_2:Dy nanoparticles except for using surfactant. In production process of SrF_2:Dy nanoparticles, bridge surfactant was used to prevent enlargement of particle size and to keep it in nanometer scale, while in fabricating microcrystalline SrF_2:Dy, surfactant was not used in order to allow the particle size to increase.

Strontium nitrate, ($Sr(NO_3)_2$, 99.99% purity), ammonium fluoride (NH_4F, 99.99% purity), dysprosium nitrate ($Dy(NO_3)_3$, 99.99% purity), distilled deionized water and acetone from Merck Chemicals were used. To prepare the microcrystalline SrF_2:Dy powder, firstly 1.00 g strontium nitrate was dissolved in a mixture of acetone and deionized water. Equal volumes of

10 cc aceton and 10 cc deionized water were used in the above solutions. After that, different amounts of dysprosium nitrate (0.1, 0.3, 0.5, 0.7, 1, 1.4 and 2 mol%) was added to the strontium nitrate solution while it was placed on a stirrer and then stoichiometric amount of NH_4F in a mixture of acetone/water was added drop wise to the final product. A white precipitate was produced immediately which was separated in a centrifuge, washed several times with mixture of acetone/water, and dried in an oven at 90 °C for 2 h. Finally, a white powder was obtained.

The sample formation and crystalline phases were identified using an X-ray diffractometer (Bruker D8 Advance) with Cu K_α radiation ($\lambda = 1.54$ Å) at a step size of $2\theta = 0.02^\circ$. A scanning electron microscope model Philips XL-30 ESEM equipped with energy dispersive spectrometer (EDS) was used for taking SEM images and elemental analysis. All the irradiations were made using a ^{60}Co gamma source with dose rate of 74.25 mGy/min at room temperature. TL glow curves were recorded using a commercial TLD reader, Harshaw model 4500 computer based TL reader using a heater strip as contact heating and indicator of temperature with accuracy of 1 °C/s. Since TL response depends directly on mass of the sample, the mass of samples for different tests were fixed at 0.007 by using a SHIMADZU Ax120 (max = 120 g, d = 0.01 mg).

3. Results and discussion

3.1. XRD, SEM and EDS pattern

The X-ray diffractogram of the synthesized SrF_2:Dy sample is shown in Fig. 1. The recorded XRD pattern exhibits the cubic structure of strontium fluoride and corresponds to data in the literature as JCDPS Card No: 86–2418. From XRD results, the average crystalline size of approximately 1.89 μm was calculated by Scherrer's formula using the dominant (111) peak. The SEM image of the prepared SrF_2:Dy phosphor is observed in Fig. 2. EDS spectrum is used for qualitative elemental

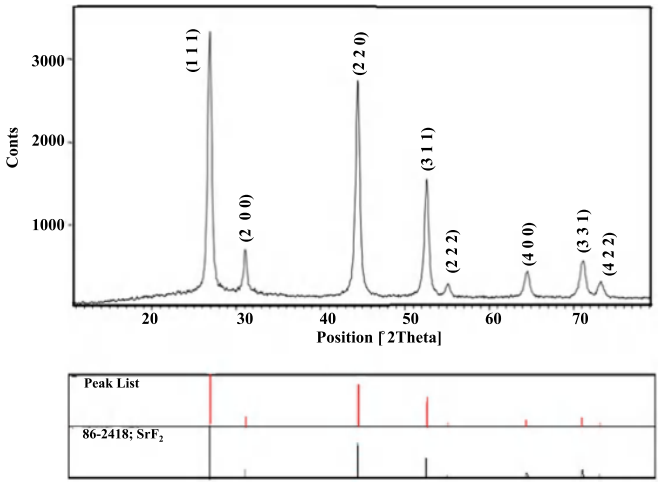

Fig. 1. XRD pattern of SrF_2 phosphor.

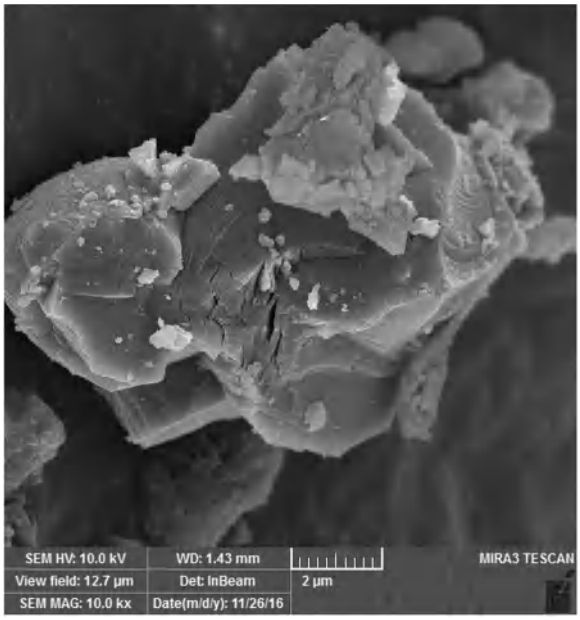

Fig. 2. SEM images of the produced SrF_2:Dy phosphor.

analysis, which identifies the elements and their relative abundance in the sample. This analysis confirmed the presence of Sr, F and Dy as dopant in expected ratios.

3.2. TL characteristics

TL sensitivity is highly dependent on the kind and amount of impurity ions. TL response of SrF_2:Dy phosphor with various Dy^{+3} concentrations ranging from 0.1 to 2 mol% after irradiating the samples to 5 Gy dose from ^{60}Co gamma source are shown in Fig. 3(a). As is shown, the TL intensity is maximum for 1 mol% concentration of Dy impurity. The corresponding TL glow curves for different amounts of dysprosium are observed in Fig. 3(b). The variation in TL sensitivity may be assigned to the change in trap distribution due to lattice perturbation caused by the incorporation of activator ions (Dy^{+3}) in the host lattice SrF_2.

To study the TL characteristics of a certain material, it is necessary to determine a suitable annealing program. Effect of annealing regime on TL sensitivity in the temperature region ranging from 400 to 800 °C and for different annealing times was studied. For annealing temperatures between 600 and 800 °C, the TL glow curves showed similar structure except for the main dosimetry peak which shifted towards higher temperatures with increased intensity. On decreasing the annealing temperature to 400 and 500 °C, glow curve structure changed and the main dosimetry peak shifted towards lower temperatures with decreased intensity. Considering the results obtained, heating the sample at 700 °C for 30 min was identified as the optimum annealing regime.

The TL dose response as a function of gamma-ray dose for SrF_2:Dy phosphor is shown in Fig. 4. The integrated area underneath the glow curve was used as indicator of TL response. The TL dose response curve is observed to be linear in the absorbed dose range from 20 mGy to 10 Gy and beyond 10 Gy the trapping states become saturated.

The stability of TL signal by storing the TL material at room temperature is an important point which should be considered in selecting a TLD. Here, samples were exposed to gamma dose of 10 Gy and stored in a dark place at room temperature. Then the samples were readout at different time intervals within the period of 1 month. The results demonstrated that the low temperature peak disappears after 10 days storage and the reduction in area of glow curve without peak 1,2 and without peaks 1,2,3 are 28% and 5% correspondingly after 1 months

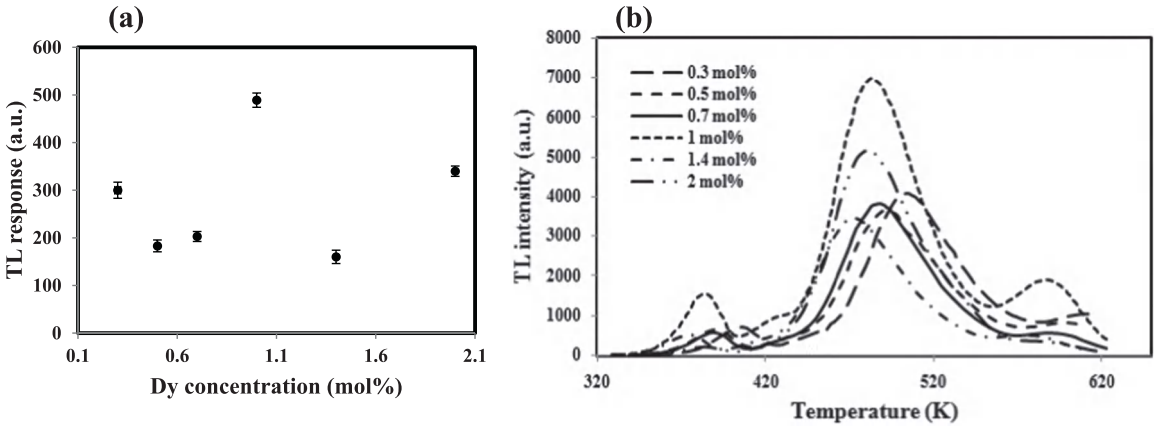

Fig. 3. TL responses for different dysprosium concentrations in SrF_2:Dy phosphor (a) and the corresponding TL glow curves (b) after 5 Gy gamma irradiation.

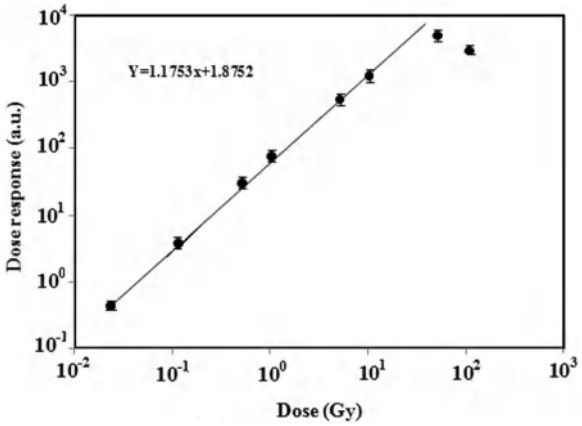

Fig. 4. Dose response of SrF_2Dy sample.

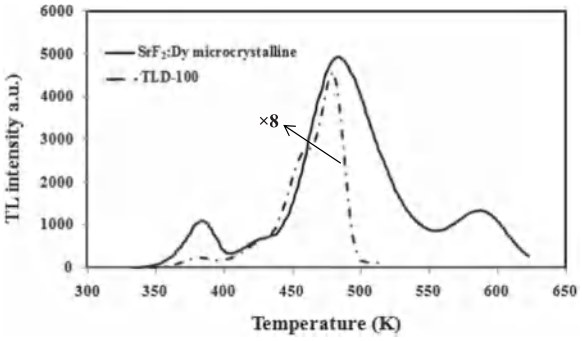

Fig. 5. Comparison of TL sensitivities of SrF_2Dy powder and LiF:Mg,Ti (TLD-100) after 1 Gy gamma irradiation. TL glow curve of TLD-100 was enlarged by a factor of 8 for better presentation.

storage. In Fig. 5 the TL glow curve of SrF_2:Dy is compared with that of TLD-100 after 1 Gy gamma ray irradiation which reveals that the TL sensitivity of SrF_2:Dy phosphor is 10 times more than LiF:Mg,Ti(TLD-100).

To confirm the reusability of the prepared phosphor, six cycles of annealing, irradiation and readouts were performed for the same material. For this test, freshly prepared powder was irradiated to 1 Gy dose from ^{60}Co, followed by read-out the samples and annealed at 700 °C for 30 min before subsequent irradiation.

3.3. Glow curve analysis

For kinetic analysis of SrF_2:Dy phosphor, T_m-T_{stop} and computerized glow curve deconvolution (CGCD) methods were used. The computer program was produced in our laboratory. The T_m –T_{stop}, is a technique for estimating the number of glow peaks included in TL glow curves of the phosphor. Using this method, the irradiated sample was first heated in TLD reader with a constant heating rate of 5 °C/s to the temperature T_{stop}, then were cooled quickly down to room temperature without emerging the sample from the reader. After that, the glow curve with heating rate of 2 °C/s was recorded to obtain the peak temperature T_m. By repeating this procedure for higher T_{stop} values between 90 and 330 °C with the step size of 10 °C and recording the corresponding T_m, the T_m-T_{stop} plot was obtained. The plot of T_{stop} against T_m is presented in Fig. 6 for SrF_2:Dy phosphor. The region in which T_m remains approximately unchanged can be attributed to a single glow peak. The plateaus with lower slopes (flat regions) indicate that the corresponding glow peak obeys near first-order kinetics and higher kinetic orders correspond to higher slopes (McKeever, 1985). In Fig. 6, four smooth regions and three sudden jumps are observed. Therefore, the minimum number of four component glow peaks were estimated for the complex glow curve of SrF_2:Dy phosphor.

To obtain the shape of TL glow peaks, the glow curve of SrF_2:Dy phosphor was de-convoluted using the computerized de-convolution program based on Levenberg-Marquart algorithm. Curve fitting procedure was done based on the solution of the general order kinetics equation and is given by (McKeever, 1985; Bos, 2007).

$$I(T) = I_m b^{\frac{b}{b-1}} \exp\left(\frac{E(T-T_m)}{kTT_m}\right)\times \left\{\frac{T^2}{T_m{}^2}(b-1)\left(1-\frac{2kT}{E}\right)\exp\left(\frac{E(T-T_m)}{kTT_m}\right) + 1 + (b-1)\frac{2kT_m}{E}\right\}^{\frac{-b}{b-1}} \quad (1)$$

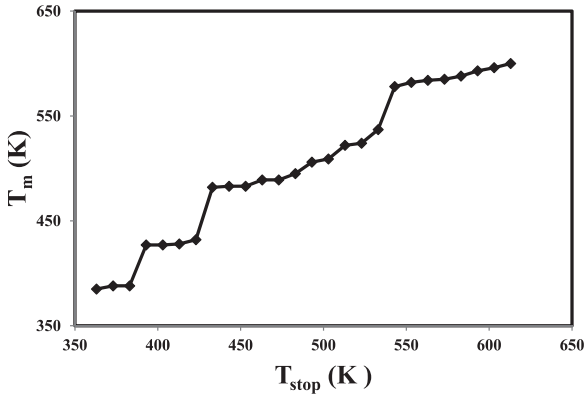

Fig. 6. Variation of peak maximum (T_m) versus T_{stop} for the produced SrF_2:Dy phosphor.

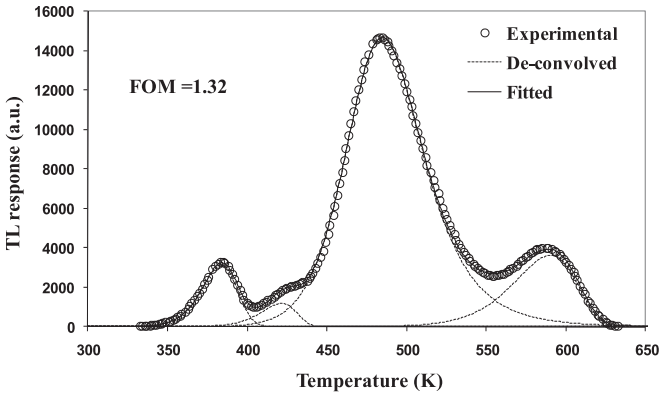

Fig. 7. Experimental TL glow curve (hollow circles), fitted glow curve (solid curve) along with component glow peaks (dashed curves) for the SrF_2:Dy for absorbed dose of 5 Gy.

$$S = \frac{\beta E}{KT_m^2}\frac{1}{(1+(b-1)\Delta m}exp\left(\frac{E}{KT_m}\right) \quad \Delta m = \frac{2KT_m}{E} \tag{2}$$

Where, I_m is the TL intensity, T_m the maximum temperature, T the absolute temperature, E the activation energy, k the boltzmann's constant, b the kinetic order, β the heating rate and s the frequency factor. Goodness of fit was tested using the figure of merit (FOM), given by (Balian and Eddy, 1977)

$$FOM = \sum_{j_f}^{j_l} \frac{100[Y_i - Y(X_i)]}{A} \tag{3}$$

For curve fitting procedure, the temperature interval in which the glow curve appears is divided into definite intervals (channels). j_f and j_l are the numbers that correspond to the first and the last temperature interval ΔT. y_i and $y(x_i)$ are TL intensities obtained from experiment and generated from Eq. (1) respectively and A is the area of the fitted glow curve. A good fit to the experimental glow curve is achieved when the amount of FOM is lower than 2.5.

Fig. 7 shows a typical glow curve for Dy-doped SrF_2 phosphor and its deconvoluted glow peaks obtained after 5 Gy gamma irradiation which reveals that glow peaks 1, 2, 3 and 4 are located respectively at 384 and 421, 485 and 590 K.

The low FOM value of 1.32% shows that the experimental glow curve is fairly fitted to that generated by the program. In addition, the activation energy, kinetic order and peak temperatures of the constructing glow peaks of SrF:Dy are presented in Table 1.

3.4. Determination of kinetic parameters

Isothermal decay method was used to obtain the order of kinetics, b. Employing this method, TL intensity is recorded as a function of time while the sample is held at a constant temperature. A plot of log (dI/dt) versus log (I) using isothermal decay curve leads to straight line with slope of 2–1/b from which the values of 1.43 and 1.89 were obtained for kinetic orders of TL glow peaks 1 and 3 respectively. The attained results are inserted in Table 2. As can be seen, these data are in accordance with those obtained by CGCD.

The validity of the acquired values for activation energies were checked by measuring them by using variable heating rate and initial rise methods. The effect of different heating rates between 1 ks^{-1} to 5 ks^{-1} on the TL response was investigated in SrF_2:Dy phosphor. It is known that the peak temperature T_m shifts towards higher temperature as the heating rate increases. For glow peaks obeying general order of kinetics, ln $[I_m^{b-1}(\frac{T_m^2}{\beta})^b]$ is plotted versus $\frac{1}{T_m}$ for different heating rates according to the equation: $I_m{}^{b-1}(\frac{T_m}{\beta})^{b} = (sn_0)^{-1}(\frac{n_0E}{bk})^{b} \exp(\frac{E}{KT_m})$ (Chen and Winer, 1970). For obtaining variable heating rate plots, the samples were heated in temperature range of 50–350 °C by 5 different heating rates. In Fig. 8 the straight lines resulting from plotting ln $[I_m^{b-1}(\frac{T_m^2}{\beta})^b]$ against $\frac{1}{T_m}$ are shown for different separated glow peaks of SrF_2:Dy phosphor, each with the slop of $\frac{E}{K}$. The results are introduced in Table 2, which are in accordance with those obtained from CGCD method.

The initial rise method was also used to determine the activation energies. It is well established that in rising part of the glow peak, the TL intensity is proportional to exp($\frac{-E}{KT}$). So, plotting lnI against $\frac{1}{T}$ gives a straight line with slope of $\frac{-E}{K}$, from which the activation energy can be obtained (Singh et al., 1988). The comparative results of three different methods are shown in Table 2. Having the activation energy, kinetic order and the peak maximum temperature of a TL glow peak, the frequency factor, s was calculated from Eq. (2).

As is observed in Table 2, there is not exact convergence between the results obtained for the kinetic parameters by different methods. A short discussion on the scatter in the results is given here. CGCD while is an efficient method for estimation of trapping parameters of the TL glow curve, the figure of merit is a criterion to compare the deviations of experimental from the expected values obtained from the model. Therefore, by increasing the FOM value from zero, the uncertainty in the kinetic parameters extracted from the CGCD method increases. The variable heating rate method uses the fact that the maximum temperature of TL glow peaks shift to higher temperature by increasing the heating rate. But this methods fails to precise determination of activation energy when applies to overlapping glow peaks, since the maximum peak temperature cannot be assessed exactly in this case which results in uncertainty in estimation of activation energy.

Table 1
Kinetics parameters of SrF_2:Dy phosphor extracted from CGCD method.

peak	b	E (eV)	T_m (K)	I_m (a.u)
1	1.21	1.26	384	3147
2	1.00	1.35	421	1183
3	2.00	1.22	485	14670
4	1.00	1.43	590	3618

Table 2
The obtained activation energies of SrF_2:Dy phosphor from CGCD, variable heating rate and initial rise methods.

Peak	b (Isothermal decay)	E_{CGCD} (eV)	E_{VH} (eV) (Various heating rate)	E_{IR} (eV) (Initial rise)	s (s^{-1})
1	1.43	1.26	1.41	1.19	4.58×10^{12}
2		1.35	–	1.16	1.79×10^{14}
3	1.89	1.22	1.22	1.36	10.53×10^{13}
4		1.43	1.40	1.43	7.83×10^{10}

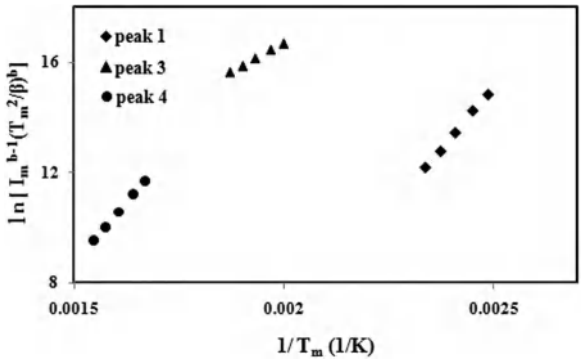

Fig. 8. ln $[I_m^{b-1}(\frac{T_m^2}{\beta})^b]$ against $\frac{1}{T_m}$ for different glow peaks of SrF_2:Dy phosphor. The slope of each line is equal to $\frac{E}{K}$.

The initial rise method uses the initial rise part of the glow peak to evaluate the activation energy; hence in the case of overlapping glow peaks it is necessary to eliminate the preceding glow peaks by thermal bleaching technique. The initial rise method is sensitive both to previous annealing condition for removal of low temperature glow peaks and also on the temperature region in the raising part of the glow peak used for the analysis which are the sources for imprecise determination of the activation energy by this method.

4. Conclusion

The synthesis process, important TL dosimetry features and kinetic analysis of the high sensitive SrF_2:Dy phosphor were presented in this work. Optimum concentration for Dy impurity was found at 1 mol%. The remarkable TL property of this phosphor is that while its TL sensitivity is significantly high, its linear dose response extends to dose levels higher than 10 Gy. TL kinetic parameters of the synthesized phosphor were obtained using different methods of isothermal decay, variable heating rate, initial rise and CGCD. Even though the results are closed to each other, it is not expected to obtain the same results from different methods, since it is difficult to precisely evaluate the experimental peak parameters needed for kinetic analysis by different methods. The relatively simple glow curve structure with separated glow peaks makes it easy to remove the unstable low temperature components by pre-heating the sample and use the stable main glow peak for dosimetry purposes. Considering the results obtained in this work, SrF_2:Dy is suggested for TL dosimetry applications.

Acknowledgements

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References

Anishia, S.R., Jose, M.T., Annalakshmi, O., Ramasamy, V., 2011. Thermoluminescence properties of rare earth doped lithium magnesium borate phosphors. J. Lumin. 131, 2492–2498.

Balian, H.G., Eddy, N.W., 1977. Figure of merit (FOM), an improved criterion over the normalized chi squared test for assessing goodness-of-fit of gamma-ray spectra peaks. Nucl. Instrum. Methods 145, 389–393.

Bos, A.J.J., 2007. Theory of thermoluminescence. Radiat. Meas. 41, 45–56.

Chen, R., Winer, S.A.A., 1970. Effects of various heating rates on glow curves. J. Appl. Phys. 41, 5227–5232.

Kim, J.L., Lee, J.I., Chang, S.Y., Chung, K.S., Choe, H.S., 2004. The glow curve structure for the LiF:Mg,Cu,Na,Si TL detector with dopants concentrations and sintering temperatures. Radiat. Meas. 38, 435–438.

Kristianpoller, N., Chen, W., Khaidukov, N., Chen, R., 2010. Optical properties of some fluoride compounds and their application to dosimetry. Radiat. Meas. 45, 566–568.

Kristianpoller, N., Weiss, D., Chen, R., 2004. Optical and dosimetric properties of variously doped SrF_2 crystals. Radiat. Meas. 38, 719–722.

McKeever, S.W.S., 1985. Thermoluminescence of Solids. Camb. University Press, Cambridge.

McKeever, S.W.S., Moscovitch, M., Townsend, P.D., 1995. TL Dosimetry Materials: Properties and Uses. Nuclear Technology Publishing, Ashford.

Salah, N., Khan, Z.H., Habib, S.S., 2009. Copper activated LiF nanorods as TLD material for high exposures of gamma-rays. Nucl. Instrum. Methods Phys. Res. B 267, 3562–3565.

Singh, T.S.C., Mazumdar, P.S., Gartia, R.K., 1988. On the determination of activation energy in thermoluminescence by the initial rise method. J. Phys. D: Appl. Phys. 21, 1312–1314.

Sharma, G., Lochab, S.P., Singh, N., 2011. Thermoluminescence characteristics of CaS doped with rare earth ions Ce and Sm. Curr. Appl. Phys. 11, 921–925.

Wang, T.K., Hsu, P.C., Weng, P.S., 1986. Application of TLD-200 dosimeters to the discrimination of α, β and γ radiation. Radiat. Prot. Dosim. 16, 225–230.

Wulf, H.C., Gniadecka, M., 1996. CaF_2:Dy and CaF_2 crystal-based UV dosimeters. Skin. Res. Technol. 2, 108–113.

Zahedifar, M., Almasifard, F., Sadeghi, E., Kashefi biroon, M., Ramazani moghaddam-Arani, A., 2016. Thermoluminescence kinetic analysis and dosimetry features of $MgSO_4$:Dy and $MgSO_4$:Cu nano-rods. Radiat. Phys. Chem. 125, 127–133.

Zahedifar, M., Sadeghi, E., 2012. Synthesis and dosimetric properties of the novel thermoluminescent CaF_2:Tm nanoparticles. Radiat. Phys. Chem. 81 (1856-186).

Zahedifar, M., Sadeghi, E., Mozdianfard, M.R., Habibi, E., 2013. Synthesis, characteristics and thermoluminescent dosimetry features of γ-irradiated Ce doped CaF_2 nanophosphor. Appl. Radiat. Isot. 78, 125–131.

Zahedifar, M., Sadeghi, E., Kashefi biroon, M., Harooni, S., Almasifard, F., 2015. Thermoluminescence dosimetry features of DY and Cu doped SrF_2 nanoparticles under gamma irradiation. Appl. Radiat. Isot. 105, 176–181.