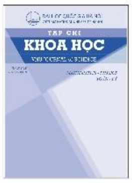
VNU Journal of Science: Mathematics – Physics, Vol. 36, No. 4 (2020) 29-34

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP



Original Article

Investigation on the Thermoluminescence Properties of $KGdF_4:Sm^{3+}$ Polycrystalline

Phan Van Do*

Thuy Loi University, 175 Tay Son, Dong Da, Hanoi, Vietnam

Received 09 March 2020
Revised 17 April 2020; Accepted 18 August 2020

Abstract: $KGdF_4$ polycrystalline doped with the different concentration of Sm^{3+} ions were synthesized by hydrothermal technique. Thermoluminescence (TL) glow curves of samples were measured in the range from 50 °C to 400 °C after irradiating beta, neutron and X-ray radiations. The response of TL intensity to impurity concentration and neutron dose were studied in detail. The TL kinetic parameters such as activation energy (E) and frequency factor (s) were estimated by using the method of heating rate variation.

Keywords: $KGdF_4$ polycrystalline, Thermoluminescence.

1. Introduction

In recent decades, the search of the new dosimeter materials is always an interesting research field for scientists. So far, thermoluminscence (TL) materials based on LiF, CaF_2, Al_2O_3 and $CaSO_4$ have been being used widely for the commercial dosimeter. However, there is always a strong demand in TL phosphors for the measurements of neutron dose in environment and the distinction of radiation field [1, 2]. In particular, the traditional TL materials have not responded well to these requirements yet [1-4]. Recently, $KLnF_4$ and K_2LnF_5 (Ln = Gd or Y) crystals doped with trivalent rare earths (e.g. Ce^{3+}, Tb^{3+}, Tm^{3+} and Dy^{3+} ions) have been shown to be promising materials for detecting and discriminating different types of radiation fields [1,2, 5-9]. It is known that the thermal neutron absorption cross-sections of ^{155}Gd and ^{157}Gd isotopes are 255,000 b and 61,000 b, respectively [2]. These values are much higher than that of other lanthanides. Thus, the TL materials containing gadolinium can yield a high sensitivity with environment neutron [2, 10].

---

*Corresponding author.
Email address: phanvando@tlu.edu.vn

https//doi.org/ 10.25073/2588-1124/vnumap.4485

In this work, the dependence of TL glow curves of $KGdF_4:Sm^{3+}$ polycrystalline on types of radiation (e.g. beta, neutron and X-ray) have been presented. The TL kinetic parameters and the dose response to thermal neutron of $KGdF_4:Sm^{3+}$ have been discussed in detail. To the best of my knowledge, this is the first study about the TL properties of $KGdF_4$ material.

2. Experiment

$KGd_{1-x}F_4:xSm^{3+}$ (x = 0.25, 0.5, 1.0, 1.5 and 2.0 at.%) polycrystalline were fabricated by the hydrothermal method [6]. The initial chemicals were solutions of KF, $Gd(NO_3)_3$ and $RE(NO_3)_3$ and catalyst PEG. The mixture was poured into a 60 ml Teflon bottle held in a stainless steel autoclave and sealed. Temperature of mixture was raised to 450 K and kept stable for 72 hours, then cooled down to room temperature. The product was rinsed with ethanol and distilled water, finally dried in air at 350 K for 24 hours. The phase structure and morphology of the products have been reported in our previous studies [6], in which $KGdF_4:Sm^{3+}$ polycrystalline crystallizes in hexagonal phase with the average particle size of about 30 nm.

All samples were irradiated β, n and X-ray radiations at room temperature from the ^{90}Sr sources, Cyclone 30 System and Faxitron X-ray System, respectively. After being irradiated the ionizing radiations, the samples were stored in the sealed metal box for 1.5 hours. Then, the TL glow curve measurements of all samples in the range from 50 to 400 °C were carried out with the Harshaw-Bicron 3500 TLD reader.

3. Results and Discussion

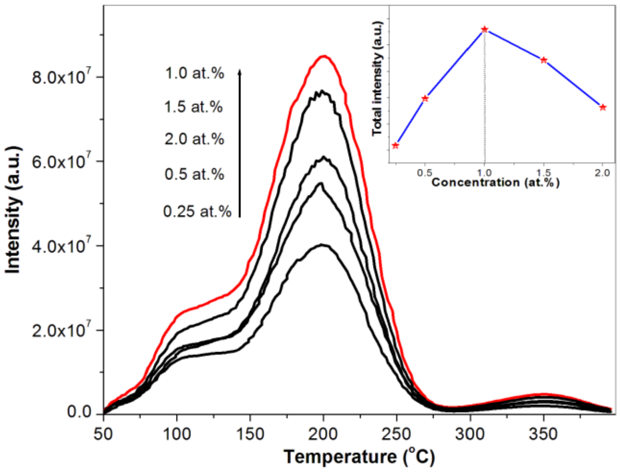


Figure 1. TL glow curves of $KGd_{1-x}F_4:xSm^{3+}$ (x = 0.25, 0.5, 1.0, 1.5 and 2.0 at %) polycrystalline after irradiating 25 mSv of β radiation.

The TL glow curves of $KGd_{1-x}F_4:xSm^{3+}$ polycrystalline after irradiating 25 mSv of β radiation are presented in Figure 1. These measurements were carried out with a heating rate of 2.0 °C/s. The dependence of integrated TL intensity on the Sm^{3+} concentration is indicated in inset of Figure 1. It can be seen that at the beginning the total TL intensity increases with the increase of Sm^{3+} concentration and reaches the maximum value at 1.0 at%, then decreases. For the X-ray and neutron radiation, the obtained results are the same as that of β radiation. For this reason, the $KGdF_4$ sample doped with 1.0 at.% of Sm^{3+} ion (denoted by KGF1) would be used for the next investigations

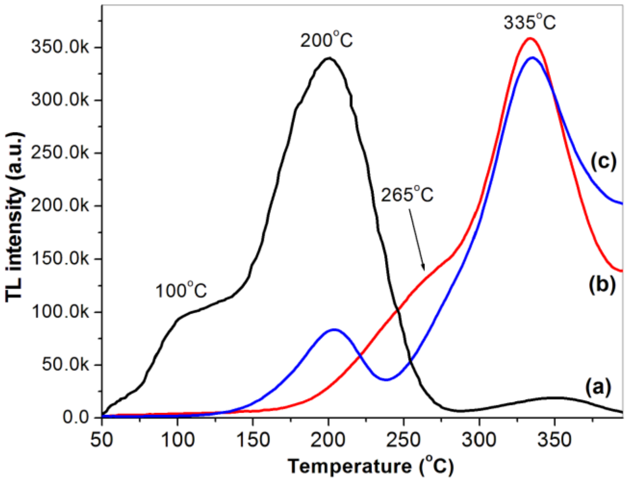


Figure 2. TL glow curves of $KGd_{0.99}F_4$:$0.01Sm^{3+}$ sample following 5 mSv radiation dose of (a) beta, (b) neutron and (c) X-ray.

Figure 2 shows the TL glow curves with a heating rate of 2.0 °C/s for the $KGd_{0.99}F_4$:$0.01Sm^{3+}$ sample following different radiations. For the β irradiated sample, the TL glow curve consists of three peaks at temperature around 100, 200 and 335 °C. Among of them, the peak at 200 °C has the strongest intensity. For the neutron radiation, the TL glow curve expresses a main peak at ~ 335 °C and a shoulder around 265 °C. In the TL glow curve measured after irradiating X-ray there is a strong peak at ~ 335 °C, a weaker peak at ~200 °C and a shoulder at temperature around 265 °C.

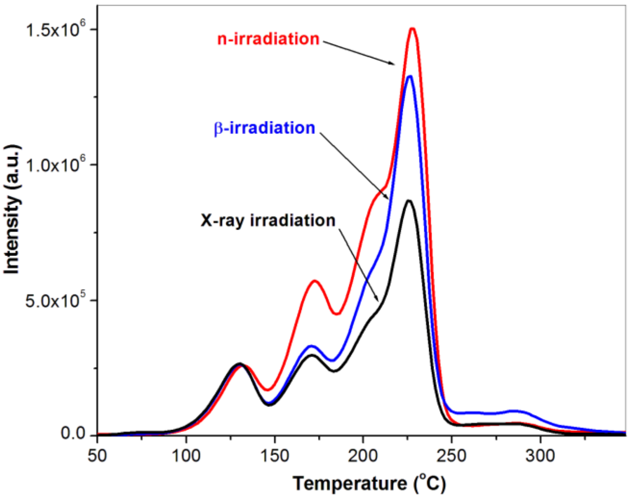


Figure 3. TL glow curves of TLD100 dosimeter following different radiations.

As shown in Figure 2, the shape of TL glow curves depends strongly on the type of the radiation that was irradiated for the sample. This characteristic of $KGdF_4$:Sm^{3+} polycrystalline is different from that of the TLD100 commercial dosimeter. For TLD100 dosimeter, the TL glow curves are the same for all types of radiation that have been absorbed by the material (see Figure 3). From the obtained results, it can be found that $KGdF_4:Sm^{3+}$ polycrystalline has a high potential for development TL phosphors in order to identify radiation fields [1, 2].

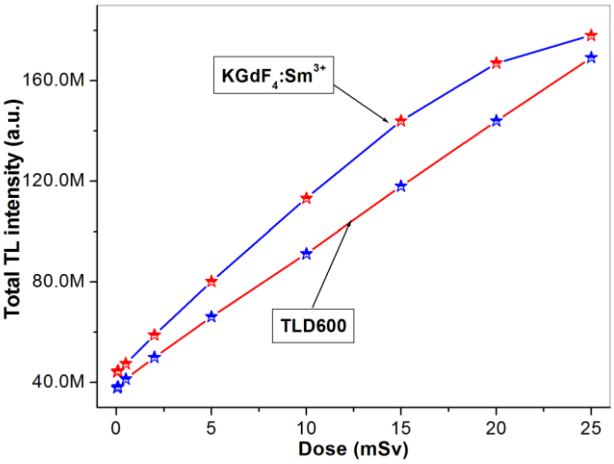


Figure 4. The dependence of integrated TL intensity on neutron dose in the range from 0.05 to 25 mSv

To estimate the application ability of the $KGdF_4:Sm^{3+}$ material for measuring neutron doses in environment, the TL glow curve of KGdF1 sample was measured after it was irradiated neutron radiation with different doses. The results were compared with that of the neutron dosimeter TLD600. It is noted that a material can be used for dosimeter when its dose response is linear [1, 11, 12]. Figure 4 exhibits the relationship between integrated TL signals and neutron dose for the KGdF1 sample and TLD600 dosimeter. Taking into account the correction for mass, it can be seen that the dose response in the range from 0.05 to 15 mSv of KGdF1 sample is linear and higher than that of TLD600. However, the relative sensitivity of $KGdF_4:Sm^{3+}$ seems to be lower than that of TLD600 for doses that are higher than 25 mSv. Beside the high sensitivity with the thermal neutron, the TL glow curve of $KGdF_4:Sm^{3+}$ also gives a simple structure (see Figure 2). For these reasons, $KGdF_4:Sm^{3+}$ polycrystalline can be a promising material for making environment neutron dosimeters.

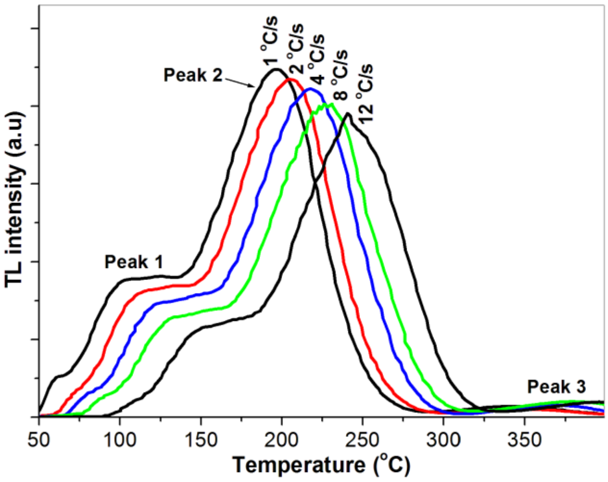


Figure 5. The TL glow curves of KGdF1 sample after irradiating β 250 mSv with different heating rate.

In order to have better knowledge of TL features of the $KGdF_4:Sm^{3+}$ polycrystalline, it is necessary to determine the kinetic parameters characterizing the trapping centers, namely the activation energy (E) and the frequency factor (s). These parameters for $KGdF_4:Sm^{3+}$ would be evaluated by using the method of various heating rates. To estimate the kinetic parameters for $KGdF_4:Sm^{3+}$, the TL glow curves are simulated by using the first order kinetic, then the relationship between the temperature at peak of TL glow curve (T_m) and the heating rate (β) is given by following formula [2, 12]:

$$\ln\frac{T_m^2}{\beta} = \frac{E}{k} \times \frac{1}{T_m} + \ln\frac{E}{ks} \qquad (1)$$

where k is the Boltzmann constant. The kinetic parameters can be found by analyzing the graphical of plots $\ln(T_m^2/\beta)$ vs. $1/T_m$.

Figure 5 presents a series of TL glow curves measured at heating rate of 1.0 °C, 2.0 °C, 4.0 °C, 8.0 °C and 12.0 °C. It can be seen the TL peaks are shifted towards high temperatures with the increase of the heating rate. This result is the same as that of other studies [2, 9, 12].

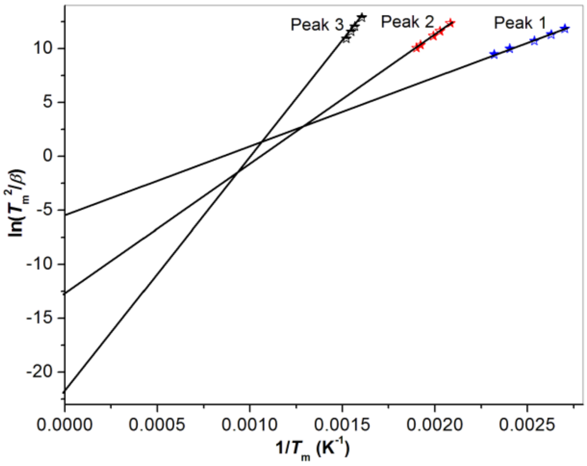


Figure 5. The dependence of $\ln(T_m^2/\beta)$ on $1/T_m$ for KGdF1 sample.

Table 1.The temperature at peaks (T_m), activation energies (E) and frequency factor (s) for TL glow curve of $KGd_{0.99}F_4:0.01Sm^{3+}$ polycrystalline following β radiation.

Peaks	T_m°C at β = 2 °C/s	E, eV	s, s^{-1}
1	100	0.54	1.2×10^{7}
2	200	1.04	3.2×10^{9}
3	335	2.04	3.9×10^{12}

Figure 6 shows the dependence of $\ln(T_m^2/\beta)$ on $1/T_m$ for three peaks of TL glow curve after irradiating β radiation. It can be seen that the plots for all peaks are the straight lines. The slope of lines gives the value of E/k, and the y-intercept of the lines at $1/T_m$ provides value of $\ln(E/sk)$. From these values, the activation energy (E) and frequency factor (s) have been evaluated and displayed in Table. 1. Usually, the value of activation energies can be obtained by the method of heating rate variation having a high reliability whereas the accuracy of frequency factor is rather low. In addition, the TL peaks do not obey exactly to the first order kinetic. This also leads to error in the analysis of kinetic parameters. Therefore, one can only consider the orders of *s* parameters that are given in Table 1.

4. Conclusion

For $KGdF_4:Sm^{3+}$ polycrystalline, the TL intensity is strongest at dopant concentration of 1.0 at.% Sm^{3+} ion for all ionizing radiations. The shape of TL glow curves depends strongly on kind of ionizing radiation on samples. The neutron dose response of TL intensity in the range from 0.5 to 15 mSV of $KGdF_4:Sm^{3+}$ is linear and better than TLD600. Thus, the $KGdF_4:Sm^{3+}$ material has a promising for discriminating the radiation fields and developing the thermal neutron dosimeter. Using the method of heating rate variation, the activation energies are found to be 0.54 eV, 1.04 eV and 2.04 eV; the frequency factor are 1.2×10^{7} s^{-1}, 3.2×10^{9} s^{-1} and 3.9×10^{12} s^{-1} for peaks 100 ^{o}C, 200 ^{o}C and 335 ^{o}C, respectively.

References

[1] H.W. Kui, D. Lo, Y.C. Tsang, N.M. Khaidukov, V.N. Makhov, Thermoluminescence properties of double potassium yttrium fluorides singly doped with Ce^{3+}, Tb^{3+}, Dy^{3+} and Tm^{3+} in response to α and β irradiation, J. Lumin. 117 (2006) 29-38. https://doi.org/10.1016/j.jlumin.2005.03.012.

[2] H.K. Hanh, N.M. Khaidukov, V.N. Makhov, V.X. Quang, N.T. Thanh, V.P. Tuyen, Thermoluminescence properties of isostructural K_2YF_5 and K_2GdF_5 crystals doped with Tb^{3+} in response to α, β and X-ray irradiation, Nucl. Instrum. Methods Phys. Res. B 268 (2010) 3344-3350. https://doi.org/10.1016/j.nimb.2010.06.041.

[3] P. Dewangan, D.D. Bisen, N. Brahme, R.K. Tamaraka, K. Upadhyay, S. Sharma, I.P. Sahu, Studies on thermoluminescence properties of alkaline earth silicate phosphors, J. Alloys Compd. 735 (2018)1383-1388. https://doi.org/10.1016/j.jallcom.2017.11.293.

[4] Y. Wang, Y. Zhao, D. White, A.A. Finch, P.D. Townsend, Factors controlling the thermoluminescence spectra of rare earth doped calcium fluoride, J. Lumin. 184 (2017) 55-63. https://doi.org/10.1016/j.jlumin.2016.12.011.

[5] P.V. Do, V.X. Quang, V.P. Tuyen, L.D. Thanh, N.M. Khaidukov, V.N. Makhov, N.T. Thanh, Sensitization of luminescence from Sm^{3+} ions in fluoride hosts K_2YF_5 and K_2GdF_5 by doping with Tb^{3+} ions, J. Lumin. 209 (2019) 340-345. https://doi.org/10.1016/j.jlumin.2018.12.057.

[6] P.V. Do, V.X. Quang, L.D. Thanh, V.P. Tuyen, N.X. Ca, V.X. Hoa, H.V. Tuyen, Energy transfer and white light emission of $KGdF_4$ polycrystalline co-doped with Tb^{3+}/Sm^{3+} ions, Opt. Mater 92 (2019) 174-180. https://doi.org/10.1016/j.optmat.2019.04.013.

[7] J. Azorin, A. Gallegos, T. Rivera, J.C. Azorin, N.M. Khaidukov, Determination of kinetic parameters of K_2YF_5:Tb from isothermal decay of thermoluminescence, Nucl. Instrum. Methods Phys. Res.A 580 (2007) 177-179. https://doi.org/10.1016/j.nima.2007.05.077.

[8] J.A. Nieto, N.M. Khaidukov, A.S. Rodriguez, J.C. Vega, Thermoluminescence of terbium-dopeddouble fluorides, Nucl. Instrum. Methods Phys. Res.B 263 (2007) 36-40. https://doi.org/10.1016/j.nimb.2007.04.082.

[9] E.C. Silva, N.M. Khaidukov, M.S. Nogueira, L.O. Faria, Investigation TL response of $K_2YF_5:Dy^{3+}$ crystals to X and gamma radiation fields, Radiation Measurement 42 (2007) 311-315. https://doi.org/10.1016/j.radmeas.2007.02.056.

[10] A. Kadari, N.M. Khaidukov, R. Mostefa, E.C. Silva, L.O. Faria, Trapping parameters determination and modeling of the thermoluminescence process in $K_2GdF_5:Dy^{3+}$, Optik 127 (2016) 3959-3963. https://doi.org/10.1016/j.ijleo.2016.01.097.

[11] S. Hashim, Y. Alajerami, A.T. Ramli, M.H. Mhareb, Thermoluminescence Dosimetry Properties and Kinetic Parameters of Lithium Potassium Borate Glass Co-doped With Titanium and Magnesium Oxides, Appl. Radiat. Isot 91 (2014) 126–130. https://doi.org/10.1016/j.apradiso.2014.05.023.

[12] A. Kadari, S. Delice, N.M. Gasanly, Dose dependence effect of thermoluminescence process in $TlInS_2$:Nd single crystals, Optik138 (2017) 372-376. https://doi.org/10.1016/j.ijleo.2017.03.062.