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Preparation of Tb^{3+}-doped K_2GdF_5 Used to Neutron Dosimetry

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Abstract: The neutron absorption section of gadolinium atom is very high, so that the K_2GdF_5 crystals doped with Tb^{3+} ions have been studied for neutron dosimetry by the thermoluminescence (TL) method. The K_2GdF_5 crystals doped 2%, 3% and 5% concentrations of Tb^{3+} ions were synthesized by solid state reaction method. The TL properties were studied after the exposure of the samples to neutron source. The experimental results showed that the TL glow-curves of K_2GdF_5:Tb^{3+} has the simple, suitable shape for the dosimetry applications. The TL sensitivity of this material is higher than that of commercial TLD-100 and TLD-900 dosimeters. The thermal fading effect of Tb^{3+}-doped K_2GdF_5 is very low. The glow curve consists of the main peak at temperature of 202°C. The glow curve deconvolution into individual the peaks showed that the curve had a main peak at 202°C, and kinetic order b = 2. The study results indicated that the K_2GdF_5 doped with Tb^{3+} is very remarkable material can be applied in neutron dosimetry field.

Keywords: *K_2GdF_5, Tb^{3+}, thermoluminescence , neutron dosimeter.*

I. INTRODUCTION

Nowadays, the neutron sources have been widely used in many fields as the material research, the nuclear reaction, the radiotherapy … so it is required the development of neutron dosimetry methods, especially with accumulated neutron doses for a long time.

Many papers have been reported on the neutron dosimeter field [1,2]. Since the neutron absorption cross section of gadolinium is very high, about 4.9 x 10^4 bars, and the double fluoride compounds doped rare earth ions have strongly TL characteristics [3]. But the expensive, complex techniques were required for those dosimeters. Therefore, the simple methods for preparing neutron dosimeters are necessary. But until now, almost researches were focused on gamma, beta dosimeters [4-6]. The commercial dosimeters such as TLD-100 and TLD-900 have been studied so detail, but they are less sensitive to neutron irradiation. So, if measuring dose of mixed radiation including neutron beam, TLD100 and TLD900 dosimeters will not give accurate results.

K_2GdF_5 materials doped with Tb ion were expected to be able to used in neutron dosimetry [7]. Recently several studies have showed that the K_2GdF_5 crystals doped Tb with 10% concentration have very high TL intensity [8]. Therefore, the study of new materials which can be measured neutron dose with high sensitivity, linearity and low fading effect is an essential problem in actuality.

Several TL properties have to be examined for the choice of a material used to the dosimetry application. The main peak of glow curve should have a peak temperature at the maximum in the range 170°C - 250°C.

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Because at higher temperatures the infrared emission from both TLD sample and TLD holder may interfere giving up to a source of errors in the reading data. On other hand, if peak temperature is too low, the fading effect will increase in during the period storage time from irradiating to dose reading.

The materials need to response with low neutron dose. The linearity, low thermal fading effect of dosimeter are important factors for the application. In addition, the materials need to have uniform shape and stability with environment.

In this study, the thermoluminescence properties of K_2GdF_5 crystals doped Tb^{3+} ions for the purpose of neutron dosimetry were studied.

II. EXPERIMENTAL

The initial compounds such as KF, GdF_3, TbF_3 are purchased from Sigma-Aldrich company with a purity of 99.99%. The K_2GdF_5 crystals doped Tb^{3+} ions were synthesized by solid state reaction method, with stroichimetric of $2KF + GdF_3 + Tb^{3+} \rightarrow Tb^{3+}$-doped K_2GdF_5 [8].

In the typical, the mixture of KF, GdF_3 and TbF_3 with molar ratio of 2: 1: 0.02, respectively, were ground in an agate mortar for 2 hours to ensure the mixture has small particle size and homogeneous. After grinding, the mixture was heated in a graphite boat in nitrogen gas flux at a temperature of 620°C for 6 days. After heating, the samples were obtained of white hard pellets, they were crushed to a particle size of about 50 – 100 µm, then washed with distilled water and ethanol several times. The samples were dried at the temperature 120 °C for 30 minutes. After then, they were annealed at a temperature of 400°C for 60 minutes. Finally, the powder samples were put in and sealed in the plastic tubes to be used as dosimeters, the weight of each dosimeter was 20 mg.

The crystallographic structure of samples was confirmed by X-ray diffraction (XRD) using D5000-SIEMENS at Institute of Materials Science. The samples were irradiated by neutron source and then measured their TL glow-curves. The irradiation was performed on the neutron Am – Be source at Nuclear Research Institute. This neutron source was shielded by the lead plates to reduce gamma radiation. Although the materials had a purity of 99.99%, we can not yet determined gamma dose by the neutron activate reactions. However, to estimate gamma dose, the K_2GdF_5:Tb samples were irradiated together with the TLD100 and TLD900, these commercial dosimeters were very sensitive to gamma dose. The study results on the TLD100 and TLD900 dosimeters showed that the gamma dose was very low.

The neutron beam had dose rate is 0.132 mGy/h. The samples were irradiated by the absorbed doses 3.14 mGy, 6.32 mGy, 9.06 mGy, 17.03 mGy, 21.90 mGy, 25.06 mGy to investigate the linear response of the dosimeter.

The TL glow curves were measured on a thermoluminescence reader (Harshaw LTD 3500 with Winrem software). The measured parameters were setup with the range of temperature from 50°C to 350°C and heating rate of 2°C/s. The TL intensities were calculated by nA unit corresponding to the current of photomultiplier tube following the Winrem program. The TL glow curves were analyzed to calculating values of the peak temperature and TL intensity. The thermal fading effect was obtained from the change of period storage time after irradiation. Addition, the TL intensity results were compared between Tb^{3+}-doped K_2GdF_5 and commercial dosimeters TLD-100 and TLD-900.

After measured the TL glow-curve, the data were extracted by export program and were recorded on files. The experimental TL glow-curves were analyzed to individual peaks, then the kinetic parameters of peaks were calculated by the curve fitting method between theory and experimental data [9, 10]. The deconvolution of glow curve was performed as follows, changing the values of the trap depth, the peak intensities, and the order of kinetics to find the optimal values. The minimum value of FOM is a condition to determine the optimal values, with

$$FOM = \frac{\sum_p \left| y_{experimental} - y_{fit} \right|}{\sum_p y_{fit}}$$

where $Y_{experimental}$ is experimental values of TL intensity derived from measurement program, and Y_{fit} is theory values calculated by the corresponding equation for general-order kinetics of Randall and Wilkins [9, 10]:

$$I(T) = I_m b^{\frac{b}{b-1}} \exp\left(\frac{E}{kT} \frac{T - T_m}{T_m} \right)$$

$$\times \left(\begin{array}{l} 1 + (b-1) \dfrac{2kT_m}{E} \\ +(b-1)\left(1 - \dfrac{2kT}{E}\right)\left(\dfrac{T^2}{T_m^2} \exp\left(\dfrac{E}{kT} \dfrac{T - T_m}{T_m}\right)\right) \end{array} \right)^{\frac{-b}{b-1}} \quad (1)$$

where I(T) is the TL intensity of a single peak, T_m is the temperature corresponding to the maximum TL intensity I_m, E is the trap depth, b is the order of kinetic.

The trap depth parameters and the order kinetics were determined by FOM minimum condition.

III. RESULTS AND DISCUSSION

A. The study the structure of materials.

Fig. 1 shows XRD pattern of synthesized K_2GdF_5 sample. All of the diffraction peaks match well with the orthorhombic structure (JCPDS No. 77-1924).

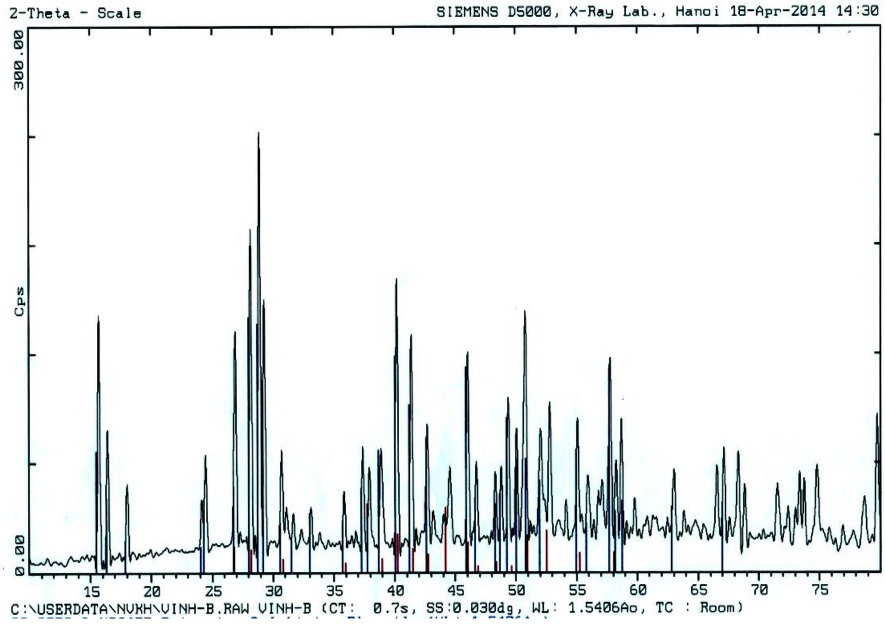

Fig. 1. X-ray diffraction pattern of K_2GdF_5 materials

The results demonstrated that the synthesis process by the solid state reaction method, at high temperature and in inert gas, had the desired results.

B. The study on TL intensity of K_2GdF_5:Tb.

The Tb^{3+}-doped K_2GdF_5 with 2%, 3% and 5% mol of Tb^{3+} were irradiated with neutron dose of 25.06 mGy and then measured thermoluminescence intensity with heating rate $\beta = 2°C/s$. The TL glow curves were showed in Fig 2. The main peak of glow curves located at temperature 202°C, this range of temperature is suitable for using of TL dosimeter. With the same conditions, the TL peak intensities of Tb^{3+}-doped K_2GdF_5 materials are much higher than of TLD-900. In other hand, the glow-curve shape of Tb^{3+}-doped K_2GdF_5 has only a single peak, which is quite symmetric, that is corresponding to the second-order kinetic of TL theory [9].

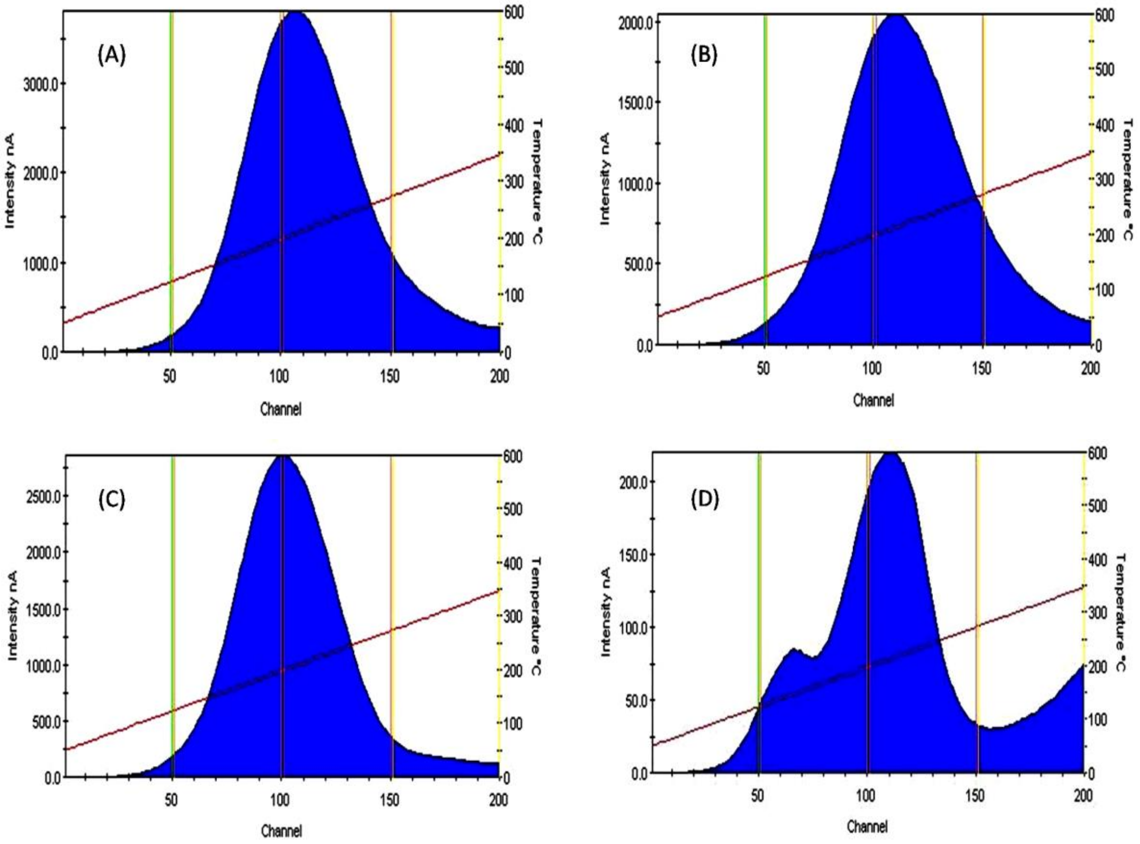

Fig. 2. The TL glow-curves of K_2GdF_5 doped Tb^{3+} with 5% (a), 3% (b), 2% (c) mol concentrations and TLD-900 (d).

Tab.1 presents the dependence of thermoluminescence intensity of main peak on neutron doses of Tb^{3+}-doped K_2GdF_5 and TLD-900. The results show that the TL intensity increases with increasing of Tb^{3+} ion concentration. The TL intensity of Tb^{3+}-doped K_2GdF_5 is about 10 times higher than that of TLD-900 dosimeters. That indicated, in case of the neutron irradiation, Tb^{3+}-doped K_2GdF_5 have TL sensitivity higher than $CaSO_4$:Dy (TLD-900). In addition, the measurement results on TLD-100 dosimeter, irradiated with the same neutron dose, shown that the TL intensities of TLD-100 are very low.

Table I. The dependence of TL intensities of main peak to different neutron doses.

Absorbed Dose	The intensity of main peak (nA)			
(mGy)	K_2GdF_5:Tb 5%	K_2GdF_5:Tb 3%	K_2GdF_5:Tb 2%	TLD-900
3.14	845	268	265	28
6.32	1410	605	649	68
9.06	2023	914	784	79
17.03	3091	1800	1746	182
21.90	3473	2518	2521	220
25.06	3803	2928	2864	258

C. TL response of the Tb^{3+}-doped K_2GdF_5 material to neutron irradiation.

Fig. 3 shows the response of TL intensity of different materials on the neutron doses. The neutron dose response of samples is very linear; the deviation of the experimental and theory data is about 5% - 7%. These values indicate that the Tb^{3+}-doped K_2GdF_5 materials are candidate for apply in neutron dosimeter field.

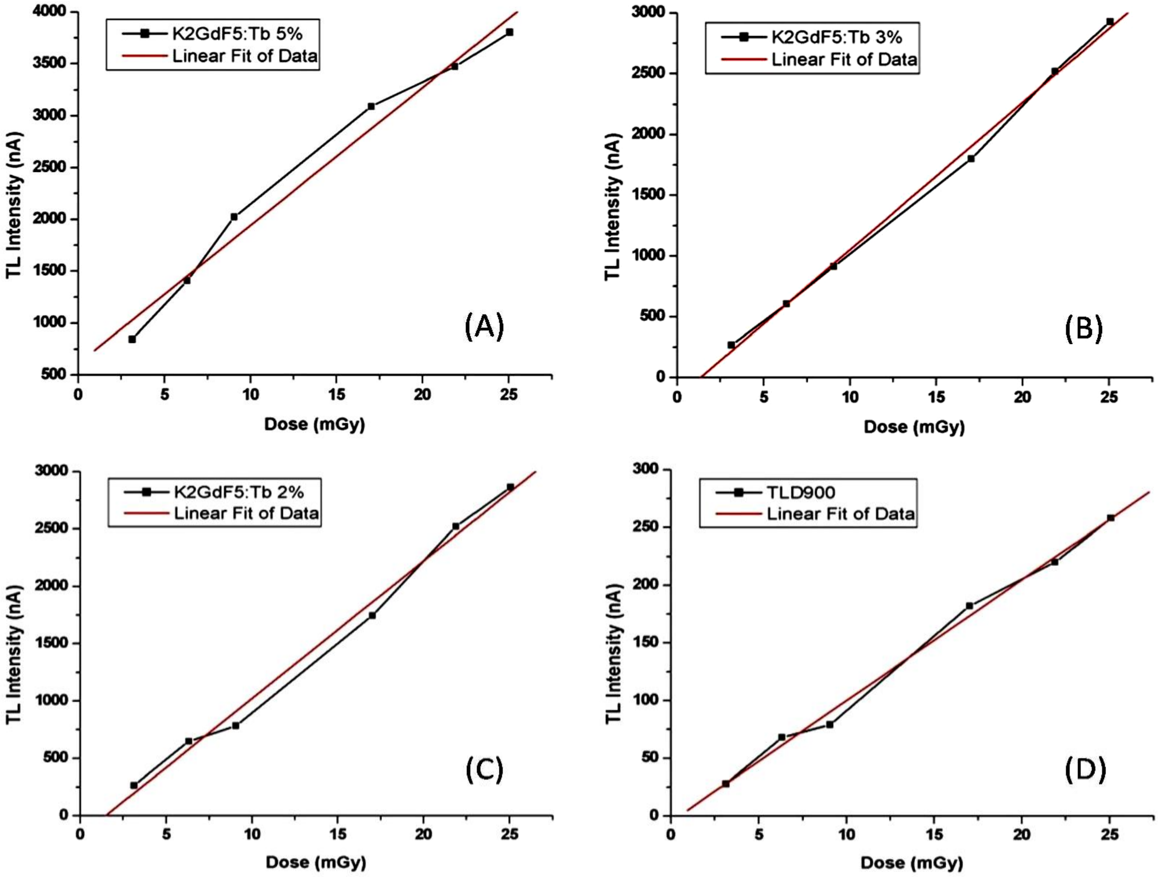

Fig. 3. The neutron dose response of peak intensity of K_2GdF_5 doped with 5% (a), 3% (b), 2% (c) mol of Tb^{3+}, TLD-900 (d).

D. The thermal fading effect

In order to estimate the thermal fading effect, the TL intensities of samples were measured for given periods of time after irradiating. In this experiment, the samples were irradiated with absorbed doses of 2 mGy and 16 mGy, the periods of time from irradiating to TL measuring are 2, 27, 50 days. The results show that the decline of TL intensity was rather low, as shows in Tab. 2. The average fading values are 5% and 15% after 27 and 50 days of storage, respectively. This decline is independent on the irradiated doses.

Table II. The thermal fading of Tb^{3+}-doped K_2GdF_5 with neutron irradiation.

Absorbed Dose	Storage period (day)	Imax (nA)	fading (%)
2 mGy	2	385.55	0
	27	366.20	5
	50	319.46	17
16 mGy	2	3257.85	0
	27	3055.93	6
	50	2788.97	14

E. The calculation of the kinetic parameters

The shape of glow curves of Tb^{3+}-doped K_2GdF_5 are almost symmetrical. This characteristic proves TL glow peaks corresponding to second-order kinetic of thermoluminescence theory [9, 10]. However, for calculating the kinetic parameters E and b of the peaks, we analyzed the glow-curve into the individual peaks by curve fitting method between experimental and theory data. The theory data were obeyed the general-order kinetic equation (eq. 1) [9, 10]. The fitting condition of curve is minimum of FOM value. Results of fitting process allowed obtaining the values of kinetic parameters E trap depth and b order of kinetic of main peak. The E values were varied from 0 to 3 eV with step 0.05 eV; b values were varied from 1 to 2 with step 0.05. Some of results collecting from program are illustrated in Fig. 4a, b, c, corresponding to b of 1, 1.5 and 2, where values of fitting FOM decrease from FOM = 0.268 to 0.065 (in table 3).

The results of TL curve fitting with only a main peak determined value of order kinetic b equals 2. In addition, when fitting with only a main peak at temperature 202°C (Fig. 4c), the values of experimental TL intensity at about temperatures 300°C were higher than the theory values, it confirmed that the curve had a peak at this temperature range. So the FOM value of fitting curve was lowest when the fitting was performed with two peaks: 1st peak at temperature 202°C and 2nd peak at 302°C. The received fit curve is showed in Fig 4d with FOM = 0.042. In this case, the trap depth values were 0.8 eV, 1.0 eV for peak at 202°C and 302°C, respectively.

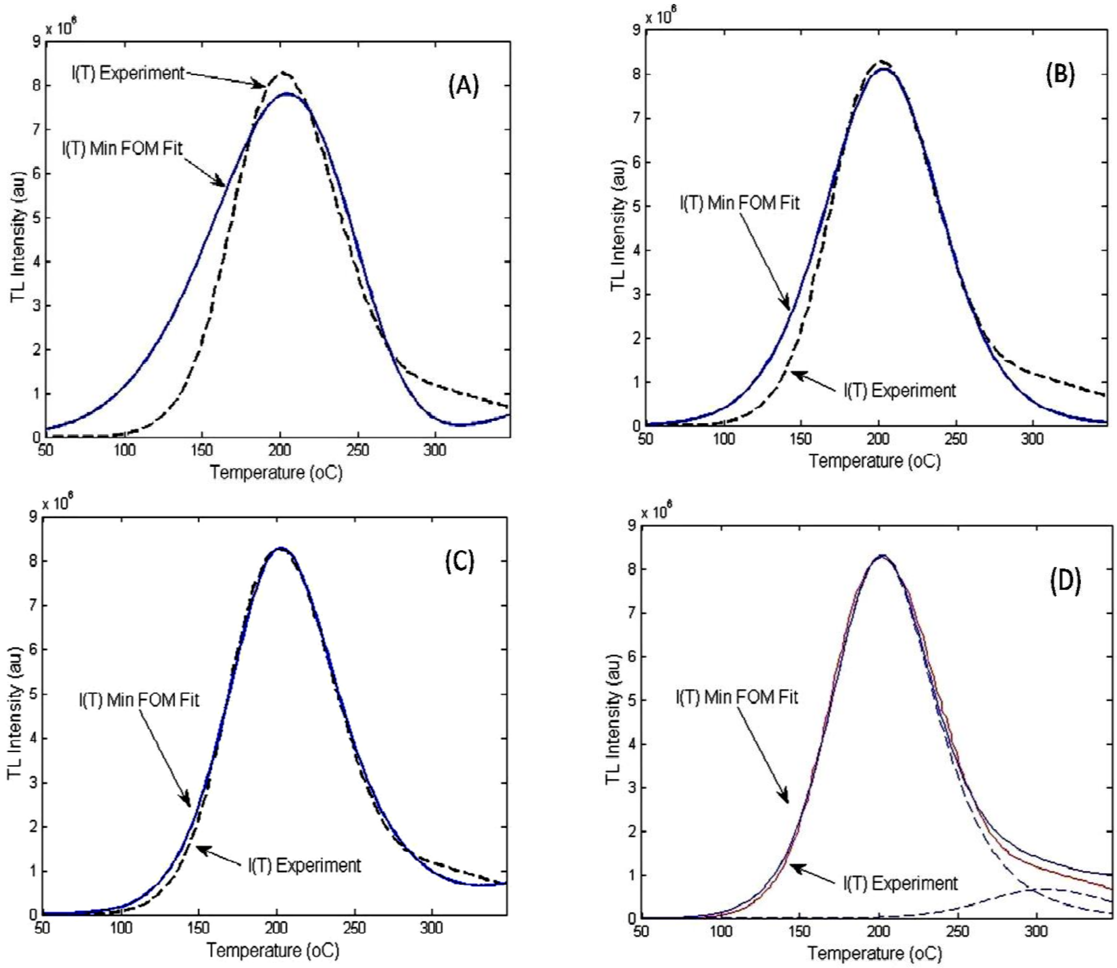

Fig. 4. The shapes of glow curve fit with different order kinetic: (a) 1st order of kinetic with b = 1, fitting 1 peak; (b) General-order of kinetic, with b = 1,5, fitting 1 peak; (c) 2nd order of kinetic, with b = 2, fitting 1 peak and (d) 2nd order of kinetic, with b = 2, fitting 2 peaks

Table III. The kinetic parameters of dosimetry peak of Tb^{3+}-doped K_2GdF_5

Number of peaks to fit	Trap depth E (eV)	Order of kinetic b	Fit FOM
1	E1 = 0.40	1.0	0.268
1	E1 = 0.50	1.25	0.196
1	E1 = 0.60	1.5	0.136
1	E1 = 0.65	1.75	0.105
1	E1 = 0.75	2.0	0.065
2	E1 = 0.8 E2 = 1.0	2.0	0.042

The result shows that the E trap depth of the main peak accords with the TL theory. The thermoluminescence kinetics with b = 2 corresponds to the electrons re-trap at trap centers are larger than recombine with holes for luminescence in the recombination center. This characteristic increased electron density in trap centers during irradiated, and the TL sensitivity of the material also was enhanced.

IV. CONCLUSION

Tb^{3+} doped K_2GdF_5 material was successful synthesized. This material has the orthorhombic structure. The TL sensitivity of this new material is about 10 times higher than that of TLD-100 and TLD-900. The Tb^{3+}-doped K_2GdF_5 is satisfied the basic requirements for the neutron dosimetry material, such as simple glow curve, high TL sensitivity, linearity and low fading effect. The glow curve of corresponds to second-order kinetics with dosimetric peak at 202°C, and this peak correspond to the trap depth is 0.8 eV. The Tb^{3+}-doped K_2GdF_5 is material having remarkable TL characteristics, so this material may be suitable for neutron dosimetry and the other rays in the mix radiation.

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