STUDY ON THERMOLUMINESCENCE PROPERTIES OF K$_2$GdF$_5$:Tb$^{3+}$

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ABSTRACT

In this article, K$_2$GdF$_5$ substance was doped by various Tb$^{3+}$ ion with concentrations 2, 5, 10, 15, 20 mol%, and the materials were synthesized by the solid state reaction method. The K$_2$GdF$_5$ material had orthorhombic structure of Pnam symmetry with the wrinkled surface structure shown on SEM images. The fluorescence spectrum indicated that the luminescence property of this material was due to the Tb$^{3+}$ ions. In the thermoluminescence (TL) investigation, the glow curves of K$_2$GdF$_5$:Tb$^{3+}$ owned three peaks at 196, 236 and 305 °C when measuring at 2 °C/s heating rate, the main peak (at 196 °C) could be used to determine the dose by the TL method. The sensitivity, linearity and responsivity to different radiation doses of materials were also examined. In addition, some of the thermoluminescence responses of materials with neutron doses were also investigated. The results showed this materials own thermoluminescence properties, which could be applied in measuring nuclear radiation including neutron doses.

Keywords: K$_2$GdF$_5$:Tb$^{3+}$, neutron dosimetry.

1. INTRODUCTION

Nowadays, the neutron sources have been widely used in many fields of material study, nuclear reaction, radiotherapy etc., thus it has required the development of neutron dosimetry methods, especially with accumulated neutron doses. However, until now, there are only a few studies about measuring the dose of the neutron by the thermoluminescence (TL) method, therefore, the investigation for creating neutron dosimeters is necessary. For application in dosimetry, the material has to be a uniform structure, stable during the measurement process, responsibility in a wide range of dose, linearity, and low thermal-fading effect.

With remarkable properties in the field of dosimetry, the K$_2$GdF$_5$ as well as the materials based on fluoride doped with rare – earth ions have been studied [1 – 4]. Recently, several studies have shown that the K$_2$GdF$_5$ crystals doped Tb$^{3+}$ ion with concentration 10 mol% has very high TL intensities [5]. This material can be used as a specialized dosimeter in measuring nuclear reaction doses, such as measuring the neutron doses. Because the neutron absorption cross section of gadolinium is high (4.9 × 10$^4$ barns), and the luminescent intensity of Tb$^{3+}$ in
visible range is very high also [6], thus K$_2$GdF$_5$:Tb$^{3+}$ is expected to be used in nuclear radiation dosimetry.

The main purpose is finding a material which having suitable TL properties for the measurement of nuclear radiation doses. The studies include the preparation of K$_2$GdF$_5$ doped with various Tb$^{3+}$ concentrations and investigation of the crystal structure and surface of the material. In addition, this study is expected the K$_2$GdF$_5$:Tb$^{3+}$ material is using as a dosimeter.

2. EXPERIMENTAL

K$_2$GdF$_5$ materials doped Tb$^{3+}$ ion with different concentrations 2, 5, 10, 15, 20 mol% were synthesized by solid state reaction method. The precursors were powders of KF, GdF$_3$, and TbF$_3$ in 99.99 % of purity (Aldrich). The mixture was ground to micro size in an agate mortar for 2 hours, then, the product was heated at 620 °C in a graphite tube under nitrogen gas flux for 5 days [7]. After the completion of the reaction, the product was crushed to micrometer size particles, then washed with distilled water and ethanol several times to ensure the excess KF was filtered out. The sample was dried at 120 °C for 30 minutes, then, annealed at 400 °C for 60 minutes.

The crystalline structure of samples was defined by X-ray powder diffraction (XRD) via X’Pert diffractometer from PANalytical. Fluorescence measurements were performed on Horiba spectroscopy, resolution of 0.5 nm with an excitation wavelength of 275 nm, and excitation spectra were measured with a monitor wavelength at 542 nm. SEM images were measured by MIRA-II Tescan instrument. For studying of TL response and their sensitivity, the samples were irradiated with various doses. The radiation sources were $^{60}$Co gamma, $^{90}$Sr/$^{90}$Y beta and $^{241}$Am/Be neutron, the neutron beam (10$^7$ n/s) with average energy $E_{\text{avg}} = 4.459$ MeV had doses of 0.9, 1.13, 1.42, 1.88, 2.58, 4.03, 5.77 mSv for investigation of the linear response with radiation dose. Then, the TL curves were measured and analyzed by the Harshaw TLD3500 reader with Winrem program, measurement parameters: 20 mg sample per each measurement, heat-treatment range from 50 to 400 °C and heating rate (β) with 2 and 10°C/s.

The TL curves of the K$_2$GdF$_5$:Tb$^{3+}$ materials were analyzed to determine values of the peaks and TL intensity. Then the properties of K$_2$GdF$_5$:Tb$^{3+}$ also were compared with CaSO$_4$:Dy common dosimeters for evaluating the TL sensitivities. The CaSO$_4$:Dy phosphors were used for this study were prepared by recrystallisation method, as shown in the paper of Lakshmanan et al [7].

From the measured data, the experimental TL curves were constructed, which were the peaks covered the individual peaks. Then the kinetic parameters of individual peaks were calculated by the curve fitting method between theory and experimental data. The deconvolution of glow curve was performed by changing the values of the trap depth E, the peaks intensity, and the order of kinetics to find the optimal values. The minimum value of FOM (formula 1) was a condition to determine the parameters of single peaks such as E and the order kinetics as well as the optimal values [8]:

$$FOM = \frac{\sum_p |y_{\text{exp}} - y_{\text{fit}}|}{\sum_p y_{\text{fit}}}$$

where theoretical values $y_{\text{fit}}$ were calculated by the corresponding equation for general-order kinetics of Randall and Wilkins [9], the processing program was designed on library of Matlab software.
3. RESULTS AND DISCUSSION

3.1. Material structure

The structure of the material was determined by the XRD measurement, and the pattern is shown in Fig. 1a. Almost all of the diffraction peaks match well with the orthorhombic structure of $\text{K}_2\text{GdF}_5$ and $\text{K}_2\text{TbF}_5$, so that the diffraction peaks in the pattern can be fitted to Miller index by JCPDS No. 77-1924, with the hkl indexes determined by the PCPDFWIN software version 2.4 (2003) of JCPDS-ICDD.

![X-ray diffraction pattern](image)

*Figure 1. X-ray diffraction pattern of sample, the coordination polyhedrons of Tb$^{3+}$ and F.*

The XRD results shown that the $\text{K}_2\text{GdF}_5$ material conforms to the synthesis method by solid-state reaction. The Gd$^{3+}$ ion was replaced by the Tb$^{3+}$ ion and material crystal structure is Pnma, space group 62 with cell parameters of: $a = 10.81$ Å, $b = 6.623$ Å, $c = 7.389$ Å; the coordination polyhedrons of Tb$^{3+}$ and F ions is modeled via Diamond program (Fig. 1b).

![SEM images](image)

*Figure 2. SEM images of sample with various Tb$^{3+}$ ion concentrations.*
In Figure 2, the SEM results show the surface structure and the morphological change with various Tb ion concentrations. At 10 mol% concentration of Tb, there are many small particles distributed in parallel on the surface of the host material, formed as a folding structure which has the large surface area. The surface structure affects the fluorescence intensity of the material, and the results of surface morphology analysis are in agreement with the thermoluminescence intensity investigation (in section 3.3) with various doping concentrations.

The surface structures can be due to the process of material synthesis by solid state reaction method, the K$_2$GdF$_5$:Tb$^{3+}$ material is formed by the diffusion of the KF and GdF$_3$ molecules components into each other.

### 3.2. Luminescence properties

In Figure 3a, the photoluminescence (PL) spectrum shows that all emission transitions are due to the transfer between $^5$D$_J$ ($J = 3, 4$) to $^7$F$_J$ ($J = 3, 4, 5, 6$) of Tb$^{3+}$ ion. The predominant green emission is due to $^5$D$_4$ $\rightarrow$ $^7$F$_5$ transition at 545 nm and this wavelength is well suitable to the sensitivity of photomultiplier tube in the TL reader.

![Photoluminescence (PL) spectrum](image)

Figure 3. The Photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy of K$_2$GdF$_5$:Tb$^{3+}$ material.

In Figure 3b, the photoluminescence excitation (PLE) spectrum shows that the appearance of the movement from the 8S$_{7/2}$ base level up to $^6$P$_J$ ($J = 3/2, 5/2, 7/2$) exciting levels of Gd$^{3+}$ ion at 312 nm. However, the emission transitions from $^6$P$_J$ ($J = 3/2, 5/2, 7/2$) to $^8$S$_{7/2}$ ($\sim 312$ nm) are not detected in the PL spectroscopy.

Thus, with the interaction of the Gd$^{3+}$- Tb$^{3+}$ pairs, the energy of exciting levels $^6$P$_J$ ($J = 3/2, 5/2, 7/2$) of Gd$^{3+}$ ions is efficiently transferred to Tb$^{3+}$ ions, this result is also consistent with recent studies of this ion pair [10, 11]. Therefore, the luminescence peaks of K$_2$GdF$_5$:Tb$^{3+}$ in the 300 - 700 nm range are due to Tb$^{3+}$ ions.

The issue of energy transfer from Gd$^{3+}$ to Tb$^{3+}$ ion is very important in the field of measuring neutron doses. When this material is irradiated by the neutron beam, the Gd$^{3+}$ ions will interact strongly with the neutron, Gd$^{3+}$ ions turn into excited state, and then transfer the energy to Tb$^{3+}$ ion when measuring TL.

### 3.3. Thermoluminescence properties
K$_2$GdF$_5$:Tb$^{3+}$ samples are investigated with various irradiation doses by different sources. Figure 4a shows the TL glow-curves of K$_2$GdF$_5$ doped Tb$^{3+}$ with 10 mol%, these samples have the same volume of 20 mg, irradiated by the $^{60}$Co gamma source and then measured TL glow curve with a heating rate of 2 °C/s. The glow - curves are simple shape with main peak at 196 °C and the second peak at 305 °C. The intensity of the main peak at 196 °C is higher than second peak and quite symmetric, corresponding to the second-order kinetic of TL theory [9]. The temperature of the main peak at 196 °C is in a suitable temperature range for dose measuring (150 - 300 °C). Because if the temperature of this peak is too high (> 300 °C) lead to infrared noise will overlap the TL signal, and if the temperature of the peak is too low (< 150 °C) lead to the quenching effect by thermal fading of time. In addition, Figure 4a shows that at various dose, the shapes of glow-curve are very uniform, and the TL intensities of samples are proportional to the doses.

![Gamma doses](image1)

![Beta doses](image2)

![Neutron Doses](image3)

![Am/Be neutron source](image4)

**Figure 4. Comparison of thermoluminescence glow curves**

Figure 4b shows the TL glow-curves of K$_2$GdF$_5$:Tb$^{3+}$ with 10 mol%, irradiated by $^{90}$Sr/$^{90}$Y beta source with various irradiation doses with a heating rate of 10 °C/s. The glow-curves have main peak at 223 °C. Similar to the case of the beta dose, the curves are uniform and the intensity is proportional to the dose.

When the K$_2$GdF$_5$: Tb$^{3+}$ with 10 mol% are irradiated with $^{241}$Am/Be neutron source, the shapes of glow-curves are heterogeneous, however, the linear rate of the TL intensity and the dose is still acceptable (Fig. 4c).
For comparative purposes, Figure 4d shows the TL curves of samples with various Tb\(^{3+}\) concentrations and CaSO\(_4\):Dy. These samples were irradiated with the \(^{241}\)Am/Be neutron source and the TL glow-curves are measured with a heating rate of 10 °C/s. The highest intensity was observed for Tb-doped with 10 mol% sample.

### 3.4. Dose response of material

To study the dose response of K\(_2\)GdF\(_5\) doped Tb\(^{3+}\) with 10 mol%, the relationship between the TL intensity of main peak and dose is drawn in Figure 5; with the gamma dose (Fig. 5a); beta dose (Fig. 5b) and neutron dose (Fig. 5c). The results show that the TL intensity of K\(_2\)GdF\(_5\):Tb\(^{3+}\) with 10 mol% is very responsive to the gamma, beta and neutron doses. The dose-responses of samples are very linear with deviations of the experimental and theoretical data are about 5 % - 7 %. These results indicate that the K\(_2\)GdF\(_5\):Tb\(^{3+}\) material is a candidate for application in nuclear radiation dosimetry field.

**Figure 5.** Linear response of luminescence intensity and irradiated dose on K\(_2\)GdF\(_5\):Tb\(^{3+}\) (10% Tb\(^{3+}\))

### 3.5. Study to separate TL glow curves into single peaks

Figure 6a presents the glow - curve of K\(_2\)GdF\(_5\):Tb\(^{3+}\) with 10 mol% irradiated by \(^{60}\)Co gamma at 20 Gy, measured with heating rate at 2 °C/s. The TL glow - curve was the overlap of many single peaks, a peak at 196 °C and another peak at 305 °C. In addition, on the down slope of the main peak may exist a low - intensity peak in the temperature range from 230 to 240 °C. To identify the peak that appeared on the down slope, the photo-transferred thermoluminescence (PTTL) method was used [9].

**Figure 6.** The single peak analysis of the TL glow curve
The sample was heated at 220 °C for 1 minute to remove the peak at 196 °C in TL glow-curve, and then irradiated ultraviolet light from the HBO lamp for 10 minutes, and then the sample was measured the TL curve. Fig. 6b shows the new peak appears at 236 °C and the second peak at 305 °C in the glow – curve. Thus, it can be concluded that the TL glow - curve of K$_2$GdF$_5$:Tb$^{3+}$ owns 3 individual peaks with the main peak at 196 °C and two low peaks at 236 °C and 305 °C. To determine the intensities of a individual peak in a curve, the fitting method of the experimental and theoretical data is used. The fitting result is shown in Fig. 6c, where the three theoretical curves are covered by the experimental curve.

4. CONCLUSION

The results of structural analysis of the material showed that K$_2$GdF$_5$:Tb$^{3+}$ material with the orthorhombic structure was successfully synthesized. The TL glow-curves of K$_2$GdF$_5$:Tb$^{3+}$ has the simple and suitable shape for the dosimetry applications. The TL sensitivity of K$_2$GdF$_5$:Tb$^{3+}$ is higher when compared with the CaSO$_4$:Dy common dosimeters. The K$_2$GdF$_5$:Tb$^{3+}$ satisfies the basic requirements for neutron dosimetry, it has the suitable thermoluminescence properties such as the linear of response dose and high sensitivity for the mix radiation.

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