STUDY ON THE THERMOLUMINESCENCE RESPONSE OF $K_2GdF_5$ CRISTALS DOPED WITH $Dy^{3+}$ TRIVALENT IONS TO X AND GAMMA RADIATION FIELDS

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ABSTRACT

Double Potassium Gadolinium Fluoride crystals [$K_2GdF_5$] doped with $Dy^{3+}$ optically active rare earth ions were investigated from the view point of its thermoluminescence (TL) response to X and gamma radiation fields. In this context, $K_2GdF_5$ crystals doped 0.2, 1.0, 5.0 and 10.0 at% $Dy^{3+}$ ions as well as undoped $K_2GdF_5$ crystals have been synthesized under hydrothermal conditions. The samples doped with 5.0 at% $Dy^{3+}$ and the undoped $K_2GdF_5$ have been found to have TL response, with good linearity. The samples show a single TL emission peak centered at 215 °C. After deconvolution this main peak is resolved into three common peaks for doped and undoped samples, respectively, and an additional peak at 234 °C for the sample doped with 5.0 at% $Dy^{3+}$. This peak is probably originated by the addition of $Dy^{3+}$ ions. The linear response was checked irradiating the samples with a Cs-137 gamma source with doses ranging from 0.1 mGy to 200 mGy. These results indicate that $K_2GdF_5$ undoped crystals an also those doped with 5.0 at% $Dy^{3+}$ have potential as promising materials for application in the fields of environmental, personal and clinical dosimetry.

1. INTRODUCTION

Since the suggestion of utilizing the thermoluminescence (TL) effect for the evaluation of ionizing radiation doses by Daniels et al. (1953) [1], a considerable number of various chemical compositions have been investigated in order to find the explanation of mechanisms for this effect and to discover promising TL phosphors for different dosimetric purposes. At present, TL dosimeters, in particular, those based on fluorides LiF and CaF$_2$ doped with trace quantities of transition metal or rare earth ions are actively used in environmental monitoring, personal and clinical dosimetry [2]. Recently, $K_2YF_5$ crystals singly doped with rare earth ions (RE), e.g. $Ce^{3+}$, $Tb^{3+}$, $Dy^{3+}$ or $Tm^{3+}$, have been shown to be attractive TL materials for detecting and discriminating different types of radiation [3]. The investigation of such
materials containing high concentrations of optically active RE ions is a promising direction for the developing of novel TL phosphors by taking into account that trivalent RE ions can efficiently capture electrons and/or holes and can be simultaneously recombination and luminescent centers [4]. In this context, recently, we have demonstrated that K$_2$YF$_5$ crystals doped with 10.0 at. % Tb$^{3+}$ and with 1.0 at. % Dy$^{3+}$ have high TL sensitivity to photon radiation fields [5-7].

Encouraged by these results and taking into account that others well known high sensitive thermoluminescent phosphors, e.g. CaSO$_4$ and CaF$_2$, have been successfully doped with Dy$^{3+}$ ions for use in radiation detection applications, we propose an investigation of the TL response of K$_2$GdF$_5$:Dy$^{3+}$ crystals to photon radiation fields.

2. EXPERIMENTAL

Within the present work, K$_2$GdF$_5$ crystals with concentrations with 0.0, 0.2, 1.0, 5.0 and 10.0 at.% of trivalent optically active Dy$^{3+}$ ions were synthesized with hydrothermal technique. Crystals of these fluoride compounds up to 1 cm$^3$ in size were grown by a direct temperature-gradient method as a result of the reaction of potassium fluoride aqueous solutions with appropriate mixtures of 99.99% pure rare earth oxides under hydrothermal conditions. Polished crystal platelets with thickness of about 1 mm and density around 4.2 g/cm$^3$ were utilized for the TL measurements. In addition, unmounted commercial LiF:Mg,Ti (TLD-100) chips manufactured by the Harshaw-Bicron Chemical Company were used in order to check the delivered doses used to obtain the relative TL sensitivities of synthesized K$_2$GdF$_5$ crystals.

The samples were exposed at room temperature (RT) to photon fields with gamma ray energy of 662 keV from $^{137}$Cs gamma sources, respectively, and with effective X-ray energies of 33.3, 41.1 and 52.5 keV, the last two ones of which were the W60 and W80 spectra as defined by ISO 4037-1 series. The measurements of TL glow curves were performed with a Harshaw-Bicron 3500 TLD reader operating with a linear temperature profile over the range from 50 up to 300º C in the resistive mode by using a heating rate of 10 $^0$C/s and reading cycles of 35s. Samples were annealed during secondary readings and the residual signal (reading 2 / reading 1) was 0.01 %. The samples were weighted and all data were normalized to the mass.

3. RESULTS AND DISCUSSION

In Table 1 we show the thermoluminescent output signal for different concentrations of Dy$^{3+}$ ions when irradiated with 10.0 mGy of gamma radiation dose. Computing the total integrated TL output between 50 and 300 $^0$C, we observe that the maximum sensitivity is obtained for crystals doped with 5.0 at.% of Dy$^{3+}$. However, in despite of the amount of emitted light, a glow curve analysis revealed that only this sample together with the undoped one shows a good TL peak shape.
Table 1. Integrated TL output signal from K$_2$GdF$_5$:Dy$^{3+}$ crystals after irradiation at 10.0 mGy of gamma doses

<table>
<thead>
<tr>
<th>% Dy</th>
<th>0.0</th>
<th>0.2</th>
<th>1.0</th>
<th>5.0</th>
<th>10.0</th>
</tr>
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<tbody>
<tr>
<td>TL (a. u.)</td>
<td>65.0</td>
<td>68.9</td>
<td>22.1</td>
<td>96.7</td>
<td>75.0</td>
</tr>
</tbody>
</table>

In this context, in Fig. 1 we present the glow curves for K$_2$GdF$_5$ crystals doped with 5.0 at% of Dy$^{3+}$ ions and for the undoped one. The glow curves were peak fitted using Gaussian lines. The glow curve for pure K$_2$GdF$_5$ was deconvoluted into three individuals peaks centered at 153.1, 185.3 and 216.1 °C, respectively. The glow curve for the doped sample can be deconvoluted into four peaks, three of them being at the same temperatures of the undoped crystal, and an additional peak at 234.2 °C. According to this approach, we think that the higher temperature peak (234.2 °C), which is present in the doped sample and absent in the undoped one, is probably originated by the addition of Dy$^{3+}$ ions.

![Graph showing glow curves for K$_2$GdF$_5$ and K$_2$GdF$_5$:Dy$^{3+}$ crystals](image)

Figure 1. TL output for undoped K$_2$GdF$_5$ and K$_2$GdF$_5$:Dy$^{3+}$ doped with 5.0 at% of Dy$^{3+}$, exposed to 300 mGy of a Cs-137 source. The peak fit show individual peaks at 153, 185, 216 and 234 °C.
Figure 2. Linear fitting for $K_2GdF_5$,$Dy^{3+}$ exposed to gamma doses ranging from 0.1 to 200 mGy.

In order to verify the linear behavior, the samples of $K_2GdF_5$,$Dy^{3+}$ doped with 5.0 at. % of $Dy^{3+}$ were irradiated with doses ranging from 0.1 to 200 mGy of gamma radiation. In Fig. 2, we plot the corresponding TL outputs. As one can see the linearity is observed over the full range of the utilized doses. The dose response function can be fitted as $I_{TL} = kD$, where $I_{TL}$ is the TL output intensity and $k$ is a linear constant. For this fitting $k = 3.035 \text{ nC/mGy}$. We have performed additional tests in order to estimate the lower limit of detection and the reproducibility and fading of the TL output signal. The lower limit of detection was found to be similar to that of LiF-100, i.e. between 0.01 and 0.1 mGy. The TL output has good reproducibility and for a 6-month storage period, fading was found to be less than 10%.

Another property that is very important to TL materials is their energy response behavior. The TL responses for lower radiation energies were measured for $K_2GdF_5$,$Dy^{3+}$ doped with 5.0 at. % of $Dy^{3+}$ at effective energies of 33.3, 41.1 and 52.5 keV. The TL outputs are summarized in Table 2 together with the data for irradiation with a Cs-137 source. We see that the maximum sensitivity is attained for X rays effective energy of 52.5 keV. In this energy, the relative response compared to Cs-137 is 15.1.

The high relative response to gamma energies is very appropriated to dosimetry in mixed X rays / gamma photon fields. The overall thermoluminescent properties of $K_2GdF_5$,$Dy^{3+}$ crystals suggest that they are good candidates for use at personal, environmental and clinical dosimetry, taking into account that some of the main TL properties can be largely enhanced with additional investigation, as for example, in the annealing and sensitization processes.

**Table 2. Relative TL intensity as a function of the effective photon energy of $K_2GdF_5$ doped with 5 at.% of $Dy^{3+}$.**

<table>
<thead>
<tr>
<th>Effective Energy (keV)</th>
<th>TL Output $K_2GdF_5$,$Dy^{3+}$ (nC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>662.0</td>
<td>7.57</td>
</tr>
<tr>
<td>52.5</td>
<td>114.3</td>
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<tr>
<td>41.1</td>
<td>67.8</td>
</tr>
<tr>
<td>33.3</td>
<td>48.6</td>
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</table>
4. CONCLUSIONS

An investigation has been performed to test the TL response of K$_2$GdF$_5$ crystals doped with various concentrations of Dy$^{3+}$ ions, which were grown under hydrothermal conditions. The crystals doped with 5.0 at.% of Dy$^{3+}$ ions, and also the undoped ones, have been discovered to be very sensitive to photon radiation fields, showing a TL glow curve that can be deconvoluted into four individual TL peaks centered at 153, 185, 216 and 234 °C. The peak at 234 °C, which is present in the doped sample and absent in the undoped one, is probably due to addition of Dy$^{3+}$. The lower limit of detection was found to be comparable to that of LiF-100, when exposed to gamma rays. For lower doses ranging from 0.1 to 200 mGy, the TL output has a linear behavior. Fading was found to be less than 10% in a 6-month period. The maximum TL output is attained for photons with 52.5 keV, with a relative response of 15.1 compared to Cs-137 source photons. Taking into account that the K$_2$GdF$_5$:Dy$^{3+}$ doped with 5.0 at.% TL properties can be highly improved with additional investigation at the annealing and sensitization processes, the results point out the K$_2$GdF$_5$:Dy$^{3+}$ as good candidates to be used as dosemeters in personal, environmental and clinical dosimetry.

ACKNOWLEDGMENTS

This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) and Comissão Nacional de Energia Nuclear (CNEN).

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