Luminescence and scintillation properties of Gd$_2$O$_2$S:Tb,Ce ceramics

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Abstract—Optical quality Gd$_2$O$_2$S:Tb,Ce ceramics have been sintered by the uniaxial hot pressing method. The heat-treated ceramics offer high transparency in a wide spectral range from 400 to 1000 nm and good scintillation characteristics: high intensity of X-ray stimulated luminescence in the green spectral region and a low level of afterglow.

Index Terms—ceramic scintillators, energy efficiency, hot pressing method

I. INTRODUCTION

Terbium-doped gadolinium oxysulfide is known as a superior X-ray powder phosphor with an energy efficiency of emission in the visible spectral region up to 0.2 [1,2]. Besides Gd$_2$O$_2$S:Tb has a high density, 7.34 g/cm$^3$, and shows a not too long decay time, $\sim$ 600 µs [1]. These properties make forming ceramic scintillators from this powder phosphor attractive. Ceramic scintillators are profitably employed in X-ray tomography [3,4]. As early studies show, the ceramic quality depends heavily on the sintering conditions: temperature, pressure, type of activator and co-activator, flux, and heat-treatment [5,6]. The goal of the present work is to continue and extend the earlier studies of the optical and luminescent properties of Gd$_2$O$_2$S:Tb in order to obtain a better understanding of the physical processes in the ceramics and to find a way of improving their scintillation characteristics.

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II. EXPERIMENTAL

Optical Gd$_2$O$_2$S:Tb ceramics were sintered by uniaxial hot pressing of powders in vacuum, with the composition differing in the concentration of Tb. The method of densification and sintering of powders into ceramics has been developed in the St. Petersburg State Optical Institute [5]. The equipment provides to carry out the sintering at temperatures $\leq$ 1300 °C and pressures $\leq$ 300 MPa. Hot pressing of the powder phosphors was done in the presence of low-melting-point fluorine-containing impurities. Several samples with a Tb content of 0.08 and 0.4 wt.% were prepared for the investigation. We studied also samples co-activated with Ce (0.002 wt.%), which was introduced to reduce afterglow.

The grain size of the original Gd$_2$O$_2$S powder varies in the range from 3 to 5 µm. Ceramic samples of $\sim$ 10 mm diameter and 1.6 mm thickness were used in the experiments. The measurements have been performed on both as sintered samples and samples with additional heat treatment. All samples were checked by X-ray diffraction. The microstructure of the powder and ceramic samples was studied using an optical microscope.

The emission spectra were recorded under excitation by means of a steady-state X-ray source (40 kV, 10 mA) or a Xe lamp. The experimental set-up for measurement of luminescent and optical characteristics was described in paper [7]. The same set-up was used for measurement of the excitation spectra in the range from 200 to 600 nm, and thermostimulated luminescence (TSL) in the range from 80 to 800 K. The scintillation efficiencies of the ceramics were measured in transmission: the photomultiplier tube was placed behind the sample in line with the X-ray beam.

III. RESULTS AND DISCUSSION

Ceramics obtained from undoped Gd$_2$O$_2$S powder were opaque. Introduction of fluorine ions makes it possible to obtain ceramics transparent over a wide spectral range (fig. 1). An optimal content of fluorine ions was found to be 0.06 wt.%. Gd$_2$O$_2$S(F) ceramic shows a relatively high transparency from 0.4 to 0.5 (curve 1, fig. 1). Gd$_2$O$_2$S:Tb(0.08 wt. %),Ce(0.002 wt. %)(F) shows an even higher transparency of $\sim$ 0.53 in the region of the main emission maximum at 545 nm of Tb $^{3+}$ (curve 2, fig.1). This corresponds to an absorption coefficient $k$ = 4.0 cm$^{-1}$ and this is a good result for ceramic sintering of a
compound with a hexagonal crystal structure (Gd₂O₂S). The minimum of the transparency near 460 nm is related to efficient 4f-5d absorption of Ce³⁺ ions [8]. The drastic decrease of transparency in the short wavelength region can be assigned to 4f-5d absorption of Gd³⁺ ions. The effect of heat treatment on the transparency of the ceramics is a reduction of absorption in the short wavelength region.

The samples with 0.08 wt.% of Tb show larger scintillation efficiency than those with 0.4 wt.% of Tb. Introduction of Ce slightly decreases the efficiency, but it reduces the afterglow level significantly. Heat treatment enhances the efficiency of all samples. Heat treated Gd₂O₂S:Tb(F) ceramic shows an energy efficiency for X-ray excitation of about 0.15. All our experiments were focused on the Gd₂O₂S:Tb(0.08 wt.%) (F) as well as Gd₂O₂S:Tb(0.08 wt.%),Ce(0.002 wt.%) (F) samples. Hereafter we shall not denote the percentage of the impurities any longer.

Fig. 1. Optical transmission spectra: 1 - Gd₂O₂S(F) and 2 - Gd₂O₂S:Tb, Ce(F) ceramics. Sample thickness 1.6 mm.

Fig. 2. Microstructure of Gd₂O₂S:Tb, Ce(F) ceramic.

Investigation of the microstructure of the Tb-activated Gd₂O₂S ceramics shows that they contain grains of at least an order of magnitude larger than the particles of the original powder, e.g., see fig. 2. The ceramics do not contain pores and their density is more than 99.9 % of that of a single crystal.

Fig. 3. Excitation spectra of the main emission line at 545 nm in Gd₂O₂S:Tb(F) ceramic: 1- before and 2 - after heat treatment.

Fig. 4. X-ray stimulated emission spectrum of Gd₂O₂S:Ce(F) ceramic: 1 - before and 2 - after heat treatment.

The excitation spectra of the main emission line at 545 nm of the Gd₂O₂S:Tb(F) ceramic sample demonstrate the effect of the heat treatment (fig. 3). The as-sintered ceramic shows a structure (307 and 313 nm lines) superposed on a wide band related to Tb⁵⁺ interconfiguration transitions (long wavelength part). The band of the heat-treated sample is more intense. The short wavelength part of the excitation spectra is appropriate to fundamental absorption of the matrix because the energy gap of Gd₂O₂S is 4.39 eV [9] (it corresponds to 282 nm). One can see that the shape of the short wavelength band (~ 270 nm) is the same for the as-sintered and heat-treated Gd₂O₂S:Tb(F) ceramics. The 307 and 313 nm peaks on the long wavelength side of the wide band (curve 1, fig.3) are typical for ⁸S₇/₂ → ⁴P₉/₂ transitions of Gd³⁺ ions. Existence of these peaks confirms the known energy transfer process from Gd³⁺ to Tb³⁺. Very weak excitation peaks in the long wavelength region (magnified curve) are related to the f-f transitions of Tb³⁺ ions: ⁷F₆ → ⁵D₃ (380 nm) and ⁷F₆ → ⁵D₄ (490 nm).

The X-ray stimulated emission spectrum of the Gd₂O₂S:Ce(F) ceramic shows a wide band peaking at 520 nm (curve 1, fig. 4) The intensity of this intrinsic luminescence, which arises supposedly from donor-acceptor recombination [1], increases in going from powder to the ceramic state. It points to an increase of the number of structure defects in ceramics. Moreover, it has been found that the lattice constant a grows from 3.846 [Å] in powder to 3.855 [Å] in the Gd₂O₂S:Tb(F) ceramic. The emission spectrum of the Gd₂O₂S:Tb, Ce(F) ceramic (curve 2, fig. 4) is quite similar to
that of the corresponding powder. The spectrum shows a number of lines related to f-f transitions of the Tb$^{3+}$ ion. The radiative transitions occur from the excited $^5D_3$ and $^5D_4$ states to the different levels of the $^7F_3$ term. Heat treatment of the Tb-doped ceramics results in an increase of the intensity of each emission line.

Fig. 4. X-ray stimulated emission spectra: 1 - Gd$_2$O$_2$S(F) and 2 - Gd$_2$O$_2$S:Tb,Ce(F) ceramics

The TSL measurements have revealed complicated glow curves for the non-heat-treated ceramics. The curves contain a number of TSL peaks in the range from 150 to 500 K, suggesting that a number of shallow as well as deep traps exist in the ceramics. The heat-treated samples show only low-temperature peaks (fig. 5). The “pure” Gd$_2$O$_2$S(F) ceramic (curve 1) exhibits two TSL peaks at 130 and 240 K. Introduction of Tb suppressed these peaks (curve 2). The Gd$_2$O$_2$S:Tb,Ce(F) ceramic shows one intensive peak at 140 K, but in this case the TSL signal is very low at $T \geq 300$K (curve 3). Cerium is known as a co-dopant creating a level in the forbidden band, which can capture efficiently a hole from the valence band as well as an electron from the conduction band [8]. This improves radiation hardness and decreases the afterglow of the Ce-doped crystals. The Gd$_2$O$_2$S:Tb,Ce(F) ceramic shows a very low afterglow indeed. The emission intensity is less than 4.10$^{-5}$ of the maximum intensity at 500 ms after stopping irradiation.

The temperature dependence of intensities of the main two emission lines (416 and 545 nm) has been measured. In as-sintered Gd$_2$O$_2$S:Tb(F) ceramic both lines show a maximum intensity at 170 K and a drastic thermal quenching at room temperature. The heat-treated ceramic shows a similar dependence for the 416-nm line, while the intensity of the 545-nm line increases significantly with temperature (inset of fig. 5). In the Ce-doped ceramic the growth of the 545-nm line intensity continues up to 400 K.

![TSL glow curves](image)

**Fig. 5.** TSL glow curves of 1 - Gd$_2$O$_2$S(F), 2 - Gd$_2$O$_2$S:Tb(F), 3- Gd$_2$O$_2$S:Tb,Ce(F) ceramics irradiated by X-rays at 80 K during 2 min. Inset: Temperature dependence of emission line intensities: 1 - 416 nm ($^5D_4 \rightarrow ^7F_3$) and 2 - 545 nm ($^5D_1 \rightarrow ^7F_4$). Intensities are normalized.

**TABLE 1. MAIN CHARACTERISTICS OF CERAMIC SCINTILLATORS:** $\rho$ is density, $Z_{eff}$ is effective atomic number, $\eta$ is energy efficiency under 40-80 keV X-ray excitation, $\lambda_{em}$ is emission wavelength maximum, $\tau$ is decay time constant, and Aft. is afterglow measured 100 ms after stopping irradiation.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Gd$_2$O$_2$S:Tb,Ce</th>
<th>Gd$_2$O$_2$S:Pr,Ce</th>
<th>Lu$_2$O$_3$:Eu,Tb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$, g/cm$^3$</td>
<td>7.34</td>
<td>7.34</td>
<td>9.4</td>
</tr>
<tr>
<td>$\rho Z_{eff}^2$ ($10^6$)</td>
<td>103</td>
<td>103</td>
<td>211</td>
</tr>
<tr>
<td>$\eta$, %</td>
<td>15</td>
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<td>$\lambda_{em}$, nm</td>
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<td>510</td>
<td>611</td>
</tr>
<tr>
<td>$\tau$, ms</td>
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<td>0.003</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td>Aft., %</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.3</td>
</tr>
</tbody>
</table>

It is unlikely that the thermal quenching of Tb$^{3+}$ emission at $T > 170$ K (curve 1 in inset of fig. 5) is associated with multiphonon relaxation. In powder this process is assigned to thermal ionization of the Tb$^{3+}$ excited states [5]. We have to take into account also that the high scintillation yield of Gd-based compounds is due to the transfer of energy to an activator center via Gd$^{3+}$ excited states [5,8]. This mechanism should work in the Gd$_2$O$_2$S:Tb owing to overlapping of the Gd$^{3+}$ emission and Tb$^{3+}$ (4f-5d) excitation spectra (fig. 2). The energy transfer process can be controlled by different defects, which change the capture ability with temperature. At present we have not got enough experimental data to understand the origin of the different temperature dependencies of the two main emission lines of the Gd$_2$O$_2$S:Tb,Ce ceramic (inset of fig. 5). It can only be
said with confidence that the green emission predominates in the heat-treated ceramics. The main characteristics of Gd$_2$O$_2$S:Tb,Ce ceramic and two other well known ceramic scintillators are tabulated in table 1. The data for Gd$_2$O$_2$S:Pr,Ce and Lu$_2$O$_3$:Eu,Tb ceramics are taken from papers [3,4]. One can see that the Gd$_2$O$_2$S:Tb,Ce exhibits good properties, its main advantage being a high energy efficiency.

IV. CONCLUSION

Variation of the parameters of the sintering process allows us to make optical ceramics with predetermined characteristics. The studied heat-treated Gd$_2$O$_2$S:Tb,Ce ceramics offer rather good characteristics:
- high optical transparency in the visible region;
- high intensity of the X-ray stimulated luminescence, which is comparable with that for powder samples;
- low level of afterglow;
- predominant green emission.

The elaborated hot pressing method can be used for forming other ceramic scintillators from powder compounds, from which it is not possible to grow as large single crystals.

V. REFERENCES