Optical and scintillation properties of Gd$_2$O$_2$S: Pr, Ce, F ceramics fabricated by spark plasma sintering

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Abstract

Gd$_2$O$_2$S: Pr, Ce, F scintillation ceramics were fabricated by the spark plasma sintering (SPS) method. Optical absorption, phase evolution, luminescence spectra, and microstructures are investigated. Temperature dependent radio-luminescence under X-ray excitation has been performed in the 77–500 K range on Gd$_2$O$_2$S: Pr, Ce, F ceramics. The intensity of the X-ray emission peaks decreases with increase of the temperature from 250 K to 450 K. The effect of the sintering temperature on the light yield of Gd$_2$O$_2$S: Pr, Ce, F ceramics is also discussed, and the highest light yield reaches to 84% of that of the commercial sample. Some traps are proposed to be the main reason for degradation of the scintillation properties.

Keywords: Scintillation ceramics; Gd$_2$O$_2$S: Pr, Ce, F; Spark plasma sintering

1. Introduction

As is well known, the scintillation materials are widely used in the modern medical imaging, high energy physics (HEP), environmental applications and homeland security [1–3]. Take X-ray computed tomography (X-ray CT) as an example, (Y,Gd)$_2$O$_3$: Eu, Gd$_2$O$_2$S: Pr, Ce, F and Gd$_3$Ga$_5$O$_{12}$: Cr, Ce ceramics have been commonly applied [4]. Among these, Gd$_2$O$_2$S: Pr, Ce, F is one of the most widely used scintillation materials due to its high effective atomic number, high density, low afterglow, and high light yield [5]. A number of sintering methods have been developed for preparing Gd$_2$O$_2$S: X (X = Pr, Tb, Ce) ceramics, including hot pressing (HP) under vacuum [6–8], hot isostatic pressing (HIP) with argon atmosphere [9], pressure-less reaction sintering under flowing hydrogen atmosphere [10] etc. However, HP and HIP need to keep a high pressure at the final temperature, resulting in high cost [9]. The pressure-less reaction sintering [10] requires the high densification temperature and long holding time. On the contrary, spark plasma sintering (SPS), known as a fast and efficient sintering method, has been developed for many years [11]. A pulse electric current is applied directly to the graphite die during the sintering process. Thus, the graphite die acts as heating elements which is different from the HP sintering process. SPS can provide dense and fine-grained ceramics at low temperature and short time due to high heating rates and high density and good scintillation properties of Gd$_2$O$_2$S: Pr, Ce, F ceramics can be prepared by SPS within a few minutes.

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In our present work, Gd$_2$O$_2$S: Pr, Ce, F ceramics were fabricated by SPS using commercially available LiF or Li$_2$GeF$_6$ as sintering aids. The effects of the sintering temperature on the optical and scintillation properties were studied.

2. Experimental

2.1. Preparation of the Gd$_2$O$_2$S: Pr, Ce, F ceramics

The original powders used in this paper were purchased from the LWB Company with average grain size of 5 μm. The high-purity powders of Li$_2$GeF$_6$ or LiF (≥ 99.99%, Alfa Aesar Company, USA) were used as sintering aids. The doping concentration of sintering aids can be found in some other papers [16,17]. The mixture of powders was pressed into 20 mm diameter disks by dry pressing at 10 MPa. The green body was further cold-isostatically pressed at 300 MPa for 1 min. Finally, the green body was put into the graphite die with an inner diameter of 20 mm and then sintered by SPS. During the sintering process, the green body was heated at a linear heating rate, and a pressure of 50 MPa was slowly applied to the sample. The translucent Gd$_2$O$_2$S: Pr, Ce, F ceramics were annealed in air at 1050 °C for 3 h. A schematic of the model 2040 SPS apparatus is shown in Fig. 1.

2.2. Characterization

Absorption spectra of various samples were obtained by a Cary5000UV–vis–NIR spectrophotometer. The fracture surfaces of the Gd$_2$O$_2$S: Pr, Ce, F ceramics were observed by scanning electron microscopy (SEM, JSM-6700F). Phase analysis of the prepared Gd$_2$O$_2$S: Pr, Ce, F sample was identified by X-ray diffraction (XRD, Model D/MAX-2550 V, Rigaku Co., Japan). Fluorescence spectrum was collected with a fluorescence spectrophotometer (Model Fluoromax-4 fluorescence spectrophotometer; HORIBA JOBIN YVON, Paris, France). The X-ray excited luminescence (XEL) spectra at various temperatures were measured with test equipment assembled in Shanghai. It consisted of four parts; an X-ray source to irradiate the sample, an Oxford Instrument cryostat (Optistat DN2-V) to stabilize the sample, an Ocean Optics QE65000 Spectrometer to collect luminescence, a mechanical pump to obtain vacuum atmosphere. The X-ray tube was operated at 60 kV, 2.2 mA. These spectra were measured within 77–500 K under vacuum. Thermoluminescence (TL) was measured by the same equipment. The ceramic was firstly excited by X-ray tube (60 kV, 2.2 mA) at 77 K for 10 min, and then the sample was heated at 0.2 K/s from 77 K to 500 K by a temperature programmer. TL emission spectrum was continuously measured in the range 200–950 nm by QE65000 Spectrometer. The pulse height spectrum under gamma-ray excitation ($^{137}$Cs source, 662 keV) was detected by a photomultiplier (R878, Hamamatsu, Japan) with working voltage at 1200 V. The shaping time was 2 μs.

3. Results and discussion

The absorption spectra of Gd$_2$O$_2$S: Pr, Ce, F ceramics sintered at different temperatures are presented in Fig. 2. The comparison of their amplitude reveals that the absorbance of the higher sintering temperature is weaker in the whole region. With increasing sintering temperature, optical quality becomes better at the same pressure. The result also agrees with Fig. 3. The short-wavelength limit for Gd$_2$O$_2$S: Pr, Ce, F ceramics lies in the 330–350 nm region [17]. The optical absorption bands in the 450–500 nm and 600–630 nm regions are assigned to the transitions $^{3}H_{j} ightarrow ^{3}P_{j}$, $^{1}J_{o}$, and $^{3}H_{j} ightarrow ^{4}D_{2}$ of the Pr$^{3+}$. The broad absorption band in the 460 nm region can be seen from the inset, caused by the 5d–4f transition of Ce$^{3+}$ [7].

Fig. 3(a) shows the mirror-polished surface after etching by Ar ions, and the sample was sintered at the 1280 °C. Many pores can be clearly observed in the Fig. 3(a). The fracture surface images of the Gd$_2$O$_2$S: Pr, Ce, F ceramics sintered at different temperatures are also shown in Fig. 3. The quantity of residual pores decreases with the increase of sintering temperature.
temperature from 1280 °C to 1320 °C. Unfortunately, many pores still exist in the Gd$_2$O$_2$S: Pr, Ce, F ceramic sintered at 1320 °C for 5 min. Samples tend to break when the sintering temperature is higher than 1320 °C, and more carbon atom contamination generated by graphite die will penetrate into the sample due to the higher sintering temperature. Thus, the optimized SPS sintering temperature is 1320 °C in our case. It was reported in Ref [9] that, pores also remain in the sample prepared by the HIP.

Heat treatment is a necessary process, which can significantly improve the optical and scintillation properties [18]. If the Gd$_2$O$_2$S powders are heated up to 470 °C in air, it will react with oxygen as follows [18,19]:

\[
\text{Gd}_2\text{O}_2\text{S} + 2\text{O}_2 = \text{Gd}_2\text{O}_3 + \text{SO}_3 \uparrow \quad (470–815 \degree C)
\] (1)

\[
\text{Gd}_2\text{O}_3\text{SO}_4 = \text{Gd}_2\text{O}_3 + \text{SO}_3 \uparrow \quad (1100–1260 \degree C)
\] (2)

However, when the O$_2$ partial pressure and heat treatment temperature are limited at a low value, the Gd$_2$O$_2$S powders are able to keep the original phase. There is a great difference in oxidative behavior between ceramic and powder. The ceramic has a much higher density, so the speed of oxidation of ceramic is slower during heat treatment in air. In addition, the outer layer will form a thin oxidation layer decreasing oxidation speed, so the inner layer of the ceramic can keep the original phase. The samples were polished on both surfaces to eliminate the thin oxidation layer after heat treatment at 1050 °C for 3 h. Fig. 4b shows the XRD pattern of the Gd$_2$O$_2$S ceramic after polishing, no Gd$_2$O$_3$SO$_4$ and Gd$_2$O$_3$ phases can be detected, all peaks observed can be well indexed as the pure hexagonal phase and they are perfect consistent with standard Gd$_2$O$_2$S data (JCPDS card no.26-1422; lattice constant: \(a=b=3.851 \text{ Å}; c=6.667 \text{ Å}\)). The XRD pattern of raw powders is also presented in Fig. 4.

Fig. 5 shows the excitation and emission spectra of the Gd$_2$O$_2$S: Pr, Ce, F ceramics sintered at 1320 °C for 5 min. The broad band centered at 313 nm is associated with the 4f–5d transition of Pr$^{3+}$ ions [10], as can be observed in the excitation spectrum. From the emission spectra of the Gd$_2$O$_2$S: Pr, Ce, F ceramics under 313 nm UV excitation, the main fluorescent wavelength locates at 513 nm and shows the green emission.
band, which is characteristic of Pr$^{3+}$ in the Gd$_2$O$_2$S matrix. The green emission band corresponding to the $^3P_0 \rightarrow ^3H_4$ transition dominates for almost any excitation [17]. In addition, the sharp peak around 500 nm is caused by the $^3P_1 \rightarrow ^3H_4$ transition of Pr$^{3+}$ ions, which location is next to the most prominent peak. The $^3P_1 \rightarrow ^3H_5$ and $^3P_0 \rightarrow ^3F_2$ transitions of Pr$^{3+}$ ions are responsible for the weak peaks around 550 nm and 665 nm, as also shown in Fig. 5.

Fig. 6 shows XEX spectra of the Gd$_2$O$_2$S: Pr, Ce, F powders and ceramics under the same excitation conditions. The ceramics and powders have the same emission location. The dominant emission peak is the green emission band at 513 nm due to the $^3P_0 \rightarrow ^3H_4$ transition, which is one of the basic characteristic peaks of Pr$^{3+}$ in the gadolinium oxysulfate crystal lattice under X-ray excitation. The emission bands at 547 nm, 639 nm, and 767 nm are shown in Fig. 6, which are caused by transitions from $^3P_1 \rightarrow ^3H_6$, $^3P_1 \rightarrow ^3H_6$, $^3P_0 \rightarrow ^3F_3$, respectively. The heat-treated sample has stronger luminescence intensity, which is because that the ceramics were sintered in graphite die under high sintering temperature, and graphite would penetrate into the Gd$_2$O$_2$S: Pr, Ce, F ceramic lattice causing contamination. Meanwhile, the graphite die generated a strong reducing atmosphere around the sample during sintering. Thus, oxygen defects, which are harmful to the scintillation properties, are generated. Heat treatment in air results in reducing the quantity of the oxygen defects, and this process improves the optical quality and scintillation efficiency.

The temperature dependence of X-ray excitation luminescence spectrum was measured, as shown in Fig. 7. The measurement was carried out on the Gd$_2$O$_2$S: Pr, Ce, F ceramic sintered at 1320 °C from 77 K to 500 K. The peak location of green emission bands has no changing from 77 K to 500 K, and no new peaks appear in the region of 400–850 nm. At 77 K, the green emission band with maximum wavelength located at 513 nm corresponds to the $^3P_0 \rightarrow ^3H_4$ transition of Pr$^{3+}$ ions, which is in agreement with the room temperature spectrum. With increasing the temperature, the emission lines become broader due to interaction with phonons [20], which can be seen in the inset (a) of Fig. 7. The luminescence intensity of $^3P_0 \rightarrow ^3H_4$ is significantly decreased from 250 K to 450 K, can be clearly seen in the inset (b) of Fig. 7. Temperature quenching of Gd$_2$O$_2$S: Pr, Ce, F ceramic luminescence was also reported in other papers [20,21]. The mechanism of high temperature quenching is complicated, and involved some trivial effects [21].
increasing the temperature, the 4f–5d excitation and the host lattice excitation will cross more and more. The chance of the excitation energy lost as non-radiative combination increases, and this process causes the decreasing luminescence intensity of $^3\text{Pr}^\text{f} \rightarrow 4\text{H}_4$ [20]. However, considering that the traps can also capture the electrons leading to non-radiative combination. Hence the high temperature quenching may have strong relationship with traps [21]. The samples contain a large number of electronic traps can be revealed by thermoluminescence (TL). The TL is described later in detail.

The gamma-ray-excited pulse height spectra of these Gd$_2$O$_2$S: Pr, Ce, F ceramics are shown in Fig. 8. The highest channel number is 743, and the light yield is 84% of that of the commercial ceramic. When the measurements were carried out at a shaping time of 2 μs, as for the nonheat-treated samples, no clear response can be detected under gamma-ray excitation due to the same reason as the X-ray excitation luminescence. Among the many known sintering aids, the most effective reagent is Li$_2$GeF$_6$, and the optimal concentration is 0.15% [9]. The Li$_2$GeF$_6$ as sintering aids is not only promoting densification but also improving the luminescent properties at the optimal concentration [9]. SPS is very similar to traditional HP in that a uniaxial pressure is applied across the graphite piston during sintering. Hence we change nothing about sintering aids during sintering. Without the sintering aids, the light yield of samples is comparatively low even the sintering temperature up to 1300 °C, and no peak can be recorded under $^{137}\text{Cs}$ 662 keV gamma-ray excitation. It is difficult to obtain high density samples without any sintering aids because the average size of raw powders is about 5 μm. The scattering phenomenon appears when the photons pass through ceramic, it has negative influence on the detection efficiency of photomultiplier and the light yield is low. Gorokhova et al. [17] showed that the relative density of the Gd$_2$O$_2$S ceramics prepared without sintering aids is no higher than 0.93% of the theoretical values. When the low-melting additive is added into the samples, the liquid phase appears at lower temperature during the sintering and can significantly accelerate the shrinkage of the samples. The light yield also becomes higher with increasing the sintering temperature from 1280 °C to 1320 °C, but it cannot change too much. Compared with the relatively low sintering temperature, the samples sintered at 1340 °C and 1360 °C contain more carbon penetrated by graphite die, which causes the extremely low light yield.

In Fig. 9 we report the TL glow curves of Gd$_2$O$_2$S: Pr, Ce, F ceramic sintered at 1320 °C and commercial sample measured after X-ray irradiation at 77 K in the same conditions, obtained by integration of the whole emission range. The TL peaks of commercial sample were multiplied by a factor of 10. As can be seen, the TL glow curve of the sample sintered at 1320 °C is composed of a prominent peak observed at temperatures from 116 K to 122 K and some other peaks with extremely low intensity. The TL intensity of the commercial sample is much weaker than that of the sample fabricated by our laboratory. The high TL intensity is evidence of a high concentration of electron traps in the sample. The sample was fabricated by SPS under vacuum, which is very defective in oxygen and sulfur leading to a large number of electronic traps in Gd$_2$O$_2$S crystal lattice. Furthermore, the sample was annealed in air, which meant that the oxygen defects were significantly reduced after heat treatment. Sulfur vacancies were still generated during heat treatment. Hence the main electronic traps in gadolinium oxysulfate crystal lattice are ascribed to sulfur vacancies [20]. These traps decrease the light yield as non-radiative combination centers. The insets (a)–(d) of Fig. 9 show TL emission spectra of Gd$_2$O$_2$S: Pr, Ce, F ceramic at selected temperatures. TL emission spectra at 120 K and XEL spectra at room temperature are similar, which proves Pr$^{3+}$ ions still act as the luminescence centers.

Fig. 10 shows the room temperature afterglow profiles of Gd$_2$O$_2$S: Pr, Ce, F ceramic sintered at 1320 °C and commercial sample after exposure to X-ray pulse excitation. It is well known that the afterglow is caused by the deep traps [18]. The afterglow of Gd$_2$O$_2$S: Pr, Ce, F ceramic is mainly attributed to some electronic traps, [20] such as sulfur vacancies. The sample sintered by SPS has a quantity of electronic traps, as can be proved in Fig. 9. The electrons are captured by electronic traps during X-ray excitation, thereafter, it will be released to the conduct band again.

![Fig. 8](image1.png)  
**Fig. 8.** The pulse height spectra of Gd$_2$O$_2$S ceramics (heat treatment at 1050 °C for 3 h) under gamma-ray excitation ($^{137}\text{Cs}$).

![Fig. 9](image2.png)  
**Fig. 9.** Thermoluminescence glow curves of Gd$_2$O$_2$S: Pr, Ce, F ceramic sintered at 1320 °C for 5 min and commercial sample.
4. Conclusions

The Gd$_2$O$_2$S: Pr, Ce, F ceramics with good scintillation characteristics were fabricated by SPS. The heat treatment is very important for improving the property of Gd$_2$O$_2$S: Pr, Ce, F ceramics. Luminescence spectra of Gd$_2$O$_2$S: Pr, Ce, F ceramics under UV excitation show a green emission at 513 nm as the most prominent peak. Microstructure analysis indicates diminishing concentration of residue pores with increasing the sintering temperature from 1280°C to 1320°C. The light yield also improves slightly with higher sintering temperature. The channel number of the sample sintered at 1320°C is 743, and the light yield is 84% of that of the commercial ceramic. The TL and afterglow studies reveal that a high concentration of traps exists in the sample to reduce the light yield and increase afterglow.

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