Effects of doping ions on the luminescence performance of terbium doped gadolinium polysulfide phosphor

Wenhua Zhang¹, ¹, a, Huamin Kou³, b, Lin Ge⁴, c, Ying Zhang⁵, d, Lin Lin⁵, e, Wei Li², *

¹University of Shanghai for Science and Technology, Shanghai 200093, China
²Shanghai University of Medicine & Health Sciences, Shanghai 201318, China
³Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
⁴The State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China
⁵National Engineering Research Center for Nanotechnology, Shanghai, 200241, China

*Corresponding author e-mail: 860130@gmail.com, awenhua950307@163.com,
huaminkou@mail.sic.ac.cn, gelin@sxicc.ac.cn, d17721013861@163.com,
linlin21023@163.com

Abstract. Gd₂O₂S: Tb (GOS) phosphor screen has been widely used in digital X-ray imaging, and so far, numerous studies have been focused on the doping ions to improve the luminescence performance of the GOS phosphors. GOS: Tb, Dy phosphors were synthesized by the solid-state reaction process, and their phase composition, particle size, morphology and luminescence properties were characterized. The results showed that co-doping Dy³⁺ can promote the luminescence and the optimal doping concentration of Dy³⁺ ions were about 0.2%, however concentration quenching will occur when the doping concentration exceeded 0.5%. Ta⁵⁺ ion was also studied in the GOS: Tb and GOS: Tb; Dy phosphors prepared by the same method. The results showed that when the Ta⁵⁺ co-doping concentration was 100ppm, the strongest emitted light intensity would be obtained for both phosphors. The photoluminescence spectra revealed a different influencing mechanism of Ta⁵⁺ ion comparing to Dy³⁺, which is by a strong energy transfer between Dy³⁺ and Tb³⁺.

1. Introduction

Terbium doped gadolinium oxysulfide (Gd₂O₂S:Tb³⁺) has a high density (7.34g/cm³) [1] and atomic number (Z=64), which gives rise to a high X-ray absorption efficiency. Meanwhile, a high conversion efficiency (~20%) and light yield, makes it an effective converter from X-ray to visible light [2]. A bright green light, emitted under the excitation of X-ray, matches good to the spectral of photodiode for photoelectric conversion. All these characteristics make it a widely used scintillator in industrial non-invasive detection, medical imaging equipment, mammography, dental X-ray and other X-ray detection fields.

A lot of studies have been focused on its synthesis process [3-7], characterization and luminescence mechanism. The characteristics of the GOS phosphors, such as phase composition, morphology,
particle size and specific surface area can influence their luminescence intensity and other properties. Furthermore, the doping ions in GOS is also one of the key factors on the luminescence properties of the phosphors and numerous studies have been focused on them to improve the luminescence performance of the GOS phosphors[8-10]. Different emission light wavelength (from red to blue) can be obtained by doping different ions, due to the rich 4f energy levels of trivalent rare earth ions. For example, GOS doped with Eu$^{3+}$ ions can emit red light with a main peak wavelength located at 623nm under the excitation of X-rays or ultraviolet light[11, 12], and is mainly used in some sensitive red detector and mammography detector. While, Pr$^{3+}$ ions doped GOS [13-15], which the main emission peak is around 512nm with a short life time of about 3μs, is an excellent fast decay scintillator material, and is widely used in CT detector.

Many reports have verified that Dy$^{3+}$, Tb$^{3+}$ co-doping GOS is an effective way to enhance the luminescence intensity of GOS: Tb phosphors [8, 16, 17]. Because there is a strong energy transfer between Dy$^{3+}$ and Tb$^{3+}$, which promotes the emission of Tb$^{3+}$ ions as the luminescence center. There are two main forms of this energy transfer: cross relaxation and non-radiative resonance. A noteworthy phenomenon is that when co-doped with Dy$^{3+}$, the concentration quenching range of Tb$^{3+}$ ions is greatly different and the quenching range of Dy concentration is slightly different among different GOS: Tb samples prepared by different synthetic methods. Other doping ions, such as Mg$^{2+}$ and Ti$^{4+}$ ions, have a great impact on the afterglow performance of GOS, leading to a long afterglow characteristics [18]. Ca$^{2+}$ and Ru$^{4+}$ ions even with a small doping amounts, will greatly affect the defect concentration in GOS, especially the defects caused by S vacancies [2].

In this paper, Dy$^{3+}$ co-doped GOS: Tb phosphors were synthesized by the solid state reaction process, and the concentration quenching properties of Dy$^{3+}$ ions were investigated. While, Ta$^{5+}$ co-doped GOS: Tb; Dy phosphors were also synthesized and the effects of co-doped Ta$^{5+}$ ions on the luminescence performance were firstly studied, and a possible influencing mechanism of Ta$^{5+}$ ion on the luminescence performance was proposed.

2.  Materials and Methods

2.1.  Preparation of the GOS: Tb; Dy phosphors

GOS: Tb; Dy phosphors were prepared using the solid state reaction process. Gadolinium (III) oxide (Gd$_2$O$_3$), Tetra terbium heptoxide (Tb$_2$O$_7$), Dysprosium (III) Oxide (Dy$_2$O$_3$) with high purity (99.99%) provided by Adamas were used as received. Sodium carbonate (99.99%) and potassium dihydrogen phosphate (99.99%), provided by Greagent, were used as molten salt, and sublimation sulfur (99.99%), provided by Alfa, played the role of sulfurizing agent of gadolinium oxysulfide phosphors.

All of the raw materials were weighed using a scale with a precision of 0.0001g according to the chemical formula (Gd$_{1-x-y}$Tb$_x$Dy$_y$)$_2$O$_2$S. We chose 0.3%, 0.5%, 0.8%, 1.2%, and 1.5% for the value x, and 0%, 0.1%, 0.2%, 0.5%, 0.8% and 1.2% were chosen for value y at each selected value x. After all the raw materials were weighed, they were mixed by ball milling at 120 rpm for 12 hours, and the mixture was dried and sieved (200 mesh). Then, the mixture was transferred into the alumina crucible with a lid and a larger crucible covering, aimed to prevent impurities pollution and hinder the invasion of O$_2$. The mixture was preheated at 330℃ for 2h and then calcined at 1200℃ for 2h in the atmosphere. The calcined product was dipped into nitric and stirred for 24 hours, and further washed by deionized water for three times, and ethyl alcohol for twice. Centrifugation of 3500rpm, 10min was used to remove the supernatant, and the precipitate was dried and sieved (200 mesh) to obtain the gadolinium oxysulfide phosphors.

2.2.  Preparation of the GOS: Tb; Ta and GOS: Tb; Dy; Ta phosphors

The Tantalum pentoxide (Ta$_2$O$_5$) with high purity (99.99%) was purchased from Adamas, and the same method was used to synthesis GOS: Tb; Ta and GOS: Tb; Dy; Ta phosphors. To verify the effect of Ta$^{5+}$ ions concentration on the luminescence properties of the GOS phosphors, here we prepared 4 different doping concentrations of Ta$^{5+}$:10ppm, 100ppm, 1000ppm and 5000ppm. For the GOS: Tb;
Ta phosphors, the concentration of Tb$^{3+}$ ions were set to 0.2%, 0.5% and 1.0%, and a small amount of Dy$^{3+}$(0.2%) was co-doped in the GOS: Tb; Dy; Ta phosphors.

2.3. Characterization

The characterization of morphology, particle size, and XRD of the GOS powders were as same as previous paper [19]. The morphology of the GOS powders was observed by a scanning electron microscope (SEM) of type JSM-6700F produced by JEOL Ltd. (Tokyo, Japan). The particle size distribution was measured by a particle size analyzer of type XDC produced by Brookhaven (Holtsville, USA). The phase composition of the GOS powders was analyzed by an X-Ray Diffraction (XRD) instrument of type D8 ADVANCE from Bruker (Karlsruhe, Germany). The photoluminescence spectrum measurements were carried out at room temperature using a fluorescence spectrometer (HORIBA QM-8075), with a 75W xenon lamp as the excitation source and a PMT F900 as the detection system.

3. Results and discussion

Figure 1a shows the XRD patterns of the GOS phosphor with Tb$^{3+}$ and Dy$^{3+}$ at the concentration of 0.5%. Comparing to the standard GOS phosphor pattern (PDF#26-1422, Figure 1b), there is no impurity phases appeared after doping Tb$^{3+}$ and Dy$^{3+}$ ions in the concentration range of this work. The morphology of the obtained GOS: Tb; Dy phosphors is granular shape with a particle size of several μm, as shown in Figure 2. The D50 of the powders is 5.88μm, consistent with the SEM results. Figure 3 shows the emission spectra of the GOS phosphors. It can be seen that the intensity of the emission peak corresponding to the $^5D_3—^7F_J (J = 3,4,5)$ energy levels decreases with the increase of Dy$^{3+}$ ion doping concentration, while that of the $^5D_4—^7F_J (J = 3,4,5,6)$ energy levels first increases and then decreases, and reaches the strongest at the Dy$^{3+}$ ion doping concentration of 0.2%. Therefore, the quenching concentration of co-doped Dy$^{3+}$ ion is 0.2% for the GOS phosphor with Tb$^{3+}$ ion concentration of 0.5%. Furthermore, GOS phosphors with different Tb$^{3+}$ ions concentration, which are 0.3%, 0.8%, 1.2% and 1.5% are prepared, and their PL spectra are measured at the same conditions. Figure 4 give the tendency of main emission peak ($^5D_4—^7F_5$ energy level) of those GOS: Tb; Dy with different concentration of Tb$^{3+}$. The results show the same trend after co-doping Dy$^{3+}$ ions with different concentrations of Tb$^{3+}$ ions, while the quenching concentration of GOS: Tb; Dy in different concentration group is slightly changed. From the results, the optimal doping concentration of Dy$^{3+}$ ion is about 0.2%, and it will be quenched after it exceeds 0.5%. However, the luminescence intensity increases all the while with the Tb$^{3+}$ ion concentration increases from 0.3% to 1.5%, indicating that1.5% does not reach the quenching concentration of Tb$^{3+}$ ion in GOS phosphors.
Figure 1. XRD of GOS with Tb$^{3+}$ and Dy$^{3+}$ at the concentration of 0.5%

Figure 2. SEM of samples of different co-doping concentration of Dy$^{3+}$: (a) 0%; (b) 0.1%; (c) 0.2%; (d) 0.5%; (e) 0.8%; (f) 1.2% with Tb$^{3+}$ concentration at 0.5%
Figure 3. PL spectra of GOS with 0.5% Tb$^{3+}$ and different concentration of Dy$^{3+}$

Figure 4. The luminescence intensity of the main emission peak (544nm) with increasing Dy ions concentration of different Tb$^{3+}$ concentration: (a)0.3%; (b)0.8%; (c)1.2%; (d)1.5%.
For GOS: Tb phosphors, it is obvious that co-doped Dy\(^{3+}\) ions increases the luminescence intensity, because there is a strong energy transfer between Dy\(^{3+}\) and Tb\(^{3+}\) ions [15-17]. As shown in Figure 5, on the one hand, when Dy\(^{3+}\) ion is activated as a sensitizer, the electron absorption energy transfers to a higher level in the 4f energy level, and then releases the energy to transfer back to a lower \( ^4F_{9/2} \) energy level. With the phonon emission, part of the energy in the \( ^4F_{9/2} \) energy level of the Dy\(^{3+}\) ion will be transferred to the \( ^4D_4 \) energy level of the Tb\(^{3+}\) ion through the dipole-dipole interaction, thereby enhancing the emission from the \( ^5D_4 \) energy level of Tb\(^{3+}\) ion. On the other hand, the energy gap between the \( ^4D_3 \) and \( ^4D_4 \) levels of Tb\(^{3+}\) ions is similar to that between the \( ^6H_{11/2} \) and \( ^6H_{15/2} \) levels of Dy\(^{3+}\) ions, which promotes the cross relaxation between Dy\(^{3+}\) and Tb\(^{3+}\), and to some extent, enhances the emission of the \( ^5D_4 \) level of Tb\(^{3+}\) ions.

![Diagram](image)

**Figure 5.** [20] Energy level diagram of Dy\(^{3+}\) and Tb\(^{3+}\)

XRD, SEM and PL spectra of GOS: Tb phosphors co-doped Ta\(^{5+}\)ions (10ppm, 100ppm, 1000ppm, 5000ppm) at a Tb\(^{3+}\) concentration of 0.5% are shown in Figures 6, 7 and 8 respectively. As we can see, there is no phase composition change shown in the XRD patterns and also no significant effect on the surface morphology shown by SEM when co-doping different concentration of Ta\(^{5+}\) ions. The PL spectra shows that the intensity of the main emission peak increases first and reaches the strongest at 100 ppm, after that decreases. Furthermore, the doping concentration of Tb\(^{3+}\) was changed to 0.2% and 1.0%, and the PL spectra of all samples were measured under the same conditions. The results show the same trend of increasing first and then decreasing, and the maximum of the emission peak also appears at the 100 ppm Ta\(^{5+}\) ion co-doping.
Figure 6. XRD of GOS: Tb with different concentration Ta$^{5+}$: (a) 10ppm; (b) 100ppm; (c) 1000ppm; (d) 5000ppm at a Tb$^{3+}$ concentration of 0.5%

Figure 7. SEM images of GOS with different concentrations of Ta$^{5+}$ ions at 0.5% Tb$^{3+}$: (a) 10ppm; (b) 100ppm; (c) 1000ppm; (d) 5000ppm.
We further studied the role of Ta$^{5+}$ ions in Tb$^{3+}$ and Dy$^{3+}$ co-doped GOS. Doping concentrations of Ta$^{5+}$ ions were still set to 10 ppm, 100 ppm, 1000 ppm, and 5000 ppm, while the doping concentration of Tb$^{3+}$ and Dy$^{3+}$ were fixed at 0.5% and 0.2%, respectively. The PL spectrum were measured under the same conditions and a similar result was obtained. After co-doping Ta$^{5+}$ ions, the luminescence intensity of Tb$^{3+}$ and Dy$^{3+}$ co-doped GOS can also be improved at the low doping concentration.
From the results of the PL spectra, the role of Ta$^{5+}$ ions in GOS: Tb is obviously different from Dy$^{3+}$ which can promote the energy transfer and enhance the emission of $^5D_4$ energy level of Tb$^{3+}$ ions. Regarding to the effect of Ta$^{5+}$ ion on the luminescence properties of GOS: Tb phosphors, the following possible explanations are proposed. Some studies have revealed that the main defect in GOS: Tb is caused by S vacancies [21]. It is the lower ionization potential of the sulphur ion relative to the oxygen, that the binding in the crystal lattice is weaker. Meanwhile, the S vacancy generally forms a relatively shallow cation trap. When Ta$^{5+}$ were doped in GOS: Tb, a fraction of Gd$^{3+}$ ions were replaced by Ta$^{5+}$ ions. Since there were two more positive charges, an anion trap was formed. Therefore, after co-doping with Ta$^{5+}$ ions, some cation traps caused by S vacancies will be eliminated, and the main emission peak of GOS: Tb will be enhanced. However, it will cause certain distortion of the crystal lattice after replacing and thus easily form new defects due to the difference in ion radius (the radius of Gd$^{3+}$ and Ta$^{5+}$ were 97pm and 64pm). And defects increase along with Ta$^{5+}$ and finally result in the decreases of the emission peak intensity. When co-doping Ta$^{5+}$ with Tb$^{3+}$ and Dy$^{3+}$, although the intensity of the main emission peak of GOS: Tb; Dy also showed a trend of increasing first and then decreasing as the Ta$^{5+}$ ions concentration increasing, it is worth noting that, after co-doping Dy$^{3+}$ in GOS: Tb, Ta, the luminous intensity were lower than those not doped ones at same concentration of Tb$^{3+}$ and Ta$^{5+}$. We speculate that this may be caused by the formation of new trap levels and hindering energy transfer between Dy$^{3+}$ and Tb$^{3+}$ ions after Ta$^{5+}$ doping. The mechanism needs to be further studied.

4. Conclusion

GOS: Tb; Dy phosphors were synthesized by the solid state reaction process. XRD showed that there was no impurity in GOS. The particle size distribution show that the D50 of the powders is 5.88μm.
and SEM show that the surface morphology of the powders was good and the PL spectrum of the powder was measured. The results give strong evidence to energy transfer between Dy³⁺ and Tb³⁺ and the optimum doping concentration of Dy³⁺ is about 0.2%, and the concentration quenching will occur when the concentration exceeds 0.5%. Ta⁵⁺ co-doped GOS: Tb; Ta and GOS: Tb; Dy; Ta were also synthesized by molten salt method. The concentrations of Ta⁵⁺ were 10ppm, 100ppm, 1000ppm and 5000ppm, respectively. The results show that the emission light intensity of GOS: Tb can be enhanced by doping 100ppm Ta⁵⁺, and it will weaken after doping higher concentration. The enhancement may be due to the elimination of some s vacancies, and the weakening may be due to the formation of new defect energy levels. Meanwhile, the luminescence of Dy³⁺ doped GOS: Tb; Ta also show same trend but the overall luminous intensity were lower than those undoped ones. This may be due to the formation of new defect levels and the blocking of energy transfer between Dy³⁺ and Tb³⁺ ions.

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