Gd$_2$O$_2$S: Pr Scintillation Ceramics from Powder Synthesized by a Novel Carbothermal Reduction Method

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Gd$_2$O$_2$S: Pr ceramics were fabricated by spark plasma sintering using the powders synthesized by carbothermal reduction method. The calcination temperature, carbon content, and other preparation conditions of the powders are optimized. The results indicate that the carbon content in the raw mixture has a great influence on the final phases of the phosphor powders. A possible reaction process and mechanism are also proposed. The spectroscopic properties of Gd$_2$O$_2$S: Pr phosphors and ceramics are studied by photoluminescence (PL) and X-ray excitation luminescence (XEL) spectra, in which show a green emission at 513 nm was detected as the main emission under the UV and X-ray excitation.

I. Introduction

The rare-earth oxysulfide phosphors generally show excellent luminescent performance, good chemical stability, and innocuity, thus these phosphors have been widely used in safety indicators, color television picture tube, and urgent illumination system. Among them, the Gd$_2$O$_2$: Pr has been considered as the most appropriate phosphors for the fabrication of scintillation ceramics because of its high density (7.34 g/cm$^3$) and high X-ray stopping power. Furthermore, the Gd$_2$O$_2$: S doped with Pr$^{3+}$ and Ce$^{3+}$ exhibits extremely high light yield (35 000 photons/MeV), short decay time, and relatively low afterglow, which are important properties as scintillation material used in X-ray computed tomography (X-CT).

At present, many methods have been developed for the synthesis of Gd$_2$O$_2$: S phosphors, such as the rare-earth oxide reaction with S gas method, solid-state reaction method, hydrogen reducing doped gadolinium sulfite method, combustion method, solvothermal method, and vacuum firing method. However, it is still difficult to synthesize Gd$_2$O$_2$: X (X = Pr, Tb, Eu) phosphors with high purity, low cost, and excellent luminescence. For example, the solid-state reaction (SSR) method has the advantage of considerable productivity, but the size and particle morphology of powders are unable to control due to the high reaction temperature. In addition, the high-purity fluxes (S, Na$_2$CO$_3$) lead to increasing the preparation cost. The combustion method uses some organic solvents as fuels causing environment pollution. Vacuum firing and hydrogen reducing doped gadolinium sulfite are the complicated and high cost synthesis process. Thus, some new preparation methods are starred of developing to solve the problem mentioned above.

Carbothermal reduction method, with many advantages, including high yield, low cost, easily controllable reaction process, and no toxic gas during synthesis process, has been successfully used in a number of areas, such as preparation of transparent ceramic materials (AION), nanostructure materials (SiC), and electroactive materials. However, there has not been any published paper about Gd$_2$O$_2$: Pr phosphors synthesized by the carbothermal reduction method to the best of our knowledge. The transition phase of Gd$_2$O$_2$SO$_4$ needs to be firstly synthesized using the commercially available Gd$_2$O$_3$ and H$_2$SO$_4$. A number of methods have been used for preparation of Gd$_2$O$_2$: S$^4$ powders, such as electrospinning reaction with S gas method, solid-state reaction method, and homogeneous precipitation. Up to now, the solid-state reaction is one of the most widely used fabrication routes due to its high efficiency and simple process, and this method was used to synthesize the Gd$_2$O$_2$: S$^4$ powders.

Spark plasma sintering (SPS) is a relatively new and distinctive technique, which fabricates the materials with small grain sizes due to the fast heating, short holding time, and much lower sintering temperature. The A$_2$O$_3$ and Sr$_3$(PO$_4$)$_2$:F$^{2-}$ ceramics with a birefringence effect caused by the noncubic structure were reported transparent or translucent by SPS. The translucent Gd$_2$O$_2$: Pr ceramics were fabricated by SPS using the powders synthesized by carbothermal reduction method. The single-phase Gd$_2$O$_2$: Pr phosphors were easily obtained by this method. The optimal ratio and reaction temperature will be discussed in details.

II. Experimental Procedure

(1) Sample Preparation

Gd$_2$O$_3$ powders (99.999%, Alfa Aesar, Tianjin, China), Pr$_2$(SO$_4$)$_3$ powders (99.99%, Alfa Aesar), Carbon powders (99.999%, Alfa Aesar), H$_2$SO$_4$ (GR; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as raw materials to synthesize Gd$_2$O$_2$: Pr phosphors. Pr$_2$(SO$_4$)$_3$ and Gd$_2$O$_3$ powders were gradually added into the dilute H$_2$SO$_4$ solution and maintained powders in suspension by mild stirring. Thereafter, the mixture was put into a temperature-holder box which can regulate the temperature from 20°C to 100°C and kept at 96°C for 2 h. The precursor was filtered three times using water and alcohol, respectively. The precursor was subsequently calcined to obtain Gd$_2$O$_2$: SO$_4$ phase in a muffle furnace. Finally, the carbon and Gd$_2$O$_2$: SO$_4$ were mixed together with the variation of molar ratios between 1:0.1 and 1:0.58, and the reference ratio was based on carbon reaction with Gd$_2$O$_2$: SO$_4$ forming CO$_2$, in which the reaction...
ratio was 1:0.5 between carbon and Gd$_2$O$_2$SO$_4$. The powder mixtures were calcined at different temperatures for 3 h to obtain the single-phase Gd$_2$O$_2$S. Gd$_2$O$_2$S: Pr ceramic was sintered in a 2040 SPS apparatus (Sumitomo Coal Mining Co., Tokyo, Japan). The powders were weighed and then put into an inner diameter of 15 mm graphite mold, separated by graphite paper from the mold. After that, the powder was prepressed at 5 MPa for 1 min to create a green body. The green pellet was sintered under uniaxial pressure at 50 MPa under vacuum, with a heating rate of 80°C/min from room temperature to 1300°C. The sample was held for 5 min at 1300°C, and it was cooled gradually to the room temperature. The sintering temperature was monitored using a thermocouple wire. The sample was polished on both surfaces with thickness of 0.5 mm.

(2) Characterizations

The grain morphology of the Gd$_2$O$_2$S: Pr powders were observed by a field-emission scanning electron microscopy (Model S-4800, Hitachi, Tokyo, Japan). The phase of the synthesized powder was identified by X-ray diffraction (XRD, Bruker AXS GmBH, Model Bruker D8 DISCOVER, Karlsruhe, Germany). The photoluminescence (PL) spectrum was collected with a fluorescence spectrophotometer (Model Fluoromax-4 fluorescence spectrophotometer, HORIBAJOBYN, Paris, France) using xenon arc lamp as the excitation source. The XEL (X-ray excited luminescence) spectra were recorded on X-ray excited spectrometer (self-assembly Shanghai). Thermal analysis of the precursor was performed by a TG-DTA instrument (Model STA449C; Netzsch Co., Bavaria, Germany). The sample was heated from 30°C to 1000°C in flowing air with a heating rate of 10°C/min. Fourier-transform infrared spectra (FTIR) of the synthesized precursor and the powders calcined at 650°C for 2 h were measured using a Fourier-transform infrared spectrometer (Model 7000-C, Nicolet, Madison, WI) over the 400–4000 cm$^{-1}$ wave number range with a resolution of 4 cm$^{-1}$ with powders dispersed in KBr. The residual carbon content in final product was carried out with an ELTRA CS-2000 apparatus (Eltra GmbH, Neuss, Germany).

III. Results and Discussion

(1) Preparation Mechanism of the (Gd$_{1-x}$Pr$_x$)$_2$O$_2$SO$_4$ Powders

During the Gd$_2$O$_3$ and Pr$_2$(SO$_4$)$_3$ added into the dilute H$_2$SO$_4$ solution, the following reaction occurs:

\[
(3-x)\text{Gd}_2\text{O}_3 + x\text{Pr}_2(\text{SO}_4)_3 + 3(1-x)\text{H}_2\text{SO}_4 + (m-3-3x)\text{H}_2\text{O} = 2\text{Gd}_2\text{O}_3 \cdot (\text{Gd}_{1-x}\text{Pr}_x)_2(\text{SO}_4)_3 \cdot m\text{H}_2\text{O}
\]

(1)

Figure 1 shows the morphologies of the starting powder and the precursor. The initial Gd$_2$O$_3$ powder was of bulk agglomeration shape. The particle of precursor was spherical with slight agglomeration and the size distribution was between 100 and 500 nm.

DTA-TG curves for the precursor obtained in flowing air are shown in Fig. 2. On the TG curve for the precursor, two main steps of weight loss are observed in TG curve and the overall weight loss is about 16.41%. The first weight loss between 200°C and 300°C is caused by the elimination of crystal water in the precursor. The second sharp weight loss from 360°C to 400°C is attributed to the dehydroxylation of the hydroxyl water in the precursor. The corresponding DTA curve is also shown in Fig. 2. It can be seen that there are two broad endothermic peaks at 270.3°C and 390.0°C, indicating the removal of crystal water and hydroxyl water. From 500°C to 750°C, the weight loss is measured to be 1%. When the temperature is higher than 750°C, the weight changes little according to the TG curve, thus this temperature is used as the reasonable calcination temperature.

Figure 3 gives the FTIR spectra of the precursor and the powder calcined at 650°C 2 h, respectively. FTIR analysis of the synthesized samples is important both for understanding the composition of the products and decomposition mechanism. The absorption bands located at 3200 and 3612 cm$^{-1}$ can be assigned to the OH band stretch in the precursor,
indicating the existence of crystal water and hydroxyl water in the precursor. The absorption peaks centered at 1645 and 3478 cm\(^{-1}\) are attributed to O–H stretching and bending vibrations of the absorbed water in the precursor, respectively. The bands centered at about 585 and 1131 cm\(^{-1}\) can be attributed to the variation of SO\(_4^{2-}\) group. According to FTIR spectra and references,\(^5,19,23\) the precursor is mainly composed of gadolinium, sulfate groups, and crystal water, and it may be formulated as Gd\(_2\)O\(_2\)SO\(_4\)·\(\text{Gd}_{1-x}\Pr_x\text{SO}_4\)·\(m\)H\(_2\)O. After the precursor was calcined at 650°C, the absorption band at about 3200 and 3612 cm\(^{-1}\) almost disappeared, suggesting the removal of hydroxyl and crystal water.

To study the phase transformation of the precursor after calcination at different temperatures, the XRD analysis was performed directly on the precursor. The XRD patterns of the precursor and its calcination products in air are shown in Fig. 4. It shows the precursor has the very strong diffraction peaks, which prove the structure of precursor is not amorphous, as shown in Fig. 4(a). All diffraction peaks of the calcination products [Figs. 4(b)–(d)] can be well indexed to the standard JCPDS cards nos. 41-0683 and 29-0613. It indicates that the precursor changes to Gd\(_2\)O\(_2\)SO\(_4\) during the calcination in the muffle furnace.

(2) Preparation Mechanism of the Single-Phase Gd\(_2\)O\(_2\)S Powders

To investigate the effect of calcination temperature on the carbothermal reduction synthesis of Gd\(_2\)O\(_2\)S powders, samples synthesized with different carbon contents were calcined in the temperature range 850°C–1150°C for 3 h. The calcination temperature is critical for improving the properties of (Gd\(_{1-x}\Pr_x\))\(_2\)O\(_2\)S phosphors, including optical spectrum, structure, granularity, and appearance aggregation degree. Figure 5 shows the XRD patterns of reaction products obtained at different temperatures for 3 h. The mixtures with ratios of 1:0.46 and 1:0.41 calcined at 850°C and 950°C fail to convert completely into the Gd\(_2\)O\(_2\)S phase, as can be observed from Fig. 5. It is concluded that the reaction temperature should be above 1000°C for obtaining pure phase Gd\(_2\)O\(_2\)S at relatively low temperature may decrease powder agglomeration.

A mixture of carbon and Gd\(_2\)O\(_2\)SO\(_4\) will react with each other based on the followed reaction equations:

\[
\begin{align*}
2C + \text{Gd}_2\text{O}_2\text{SO}_4 & = \text{Gd}_2\text{O}_2\text{S} + 2\text{CO}_2 \uparrow & (2) \\
4C + \text{Gd}_2\text{O}_2\text{SO}_4 & = \text{Gd}_2\text{O}_2\text{S} + 4\text{CO} \uparrow & (3) \\
4\text{CO} + \text{Gd}_2\text{O}_2\text{SO}_4 & = \text{Gd}_2\text{O}_2\text{S} + 4\text{CO}_2 \uparrow & (4)
\end{align*}
\]

It is a complicated reaction process according to formulas listed above, and all the reaction processes have the chance of happening. Thus, the theoretical reaction molar ratio is hardly calculated from the formula. Therefore, the different molar ratios, which changed from 1:0.10 to 1:0.58 between
carbon and Gd$_2$O$_2$SO$_4$ were designed to obtain the optimal condition. The XRD patterns of the reaction products obtained from different ratios are shown in Fig. 6. When the ratios change from 1:0.10 to 1:0.46, all the diffraction peaks can be well indexed as the hexagonal structure and they are perfectly congruent with standard Gd$_2$O$_2$S ([P3$_1$/m; 164] JCPDS # 26-142) and 65-3449; lattice constants: $a = b = 3.851$ Å, $c = 6.667$ Å) data. When excessive carbon was added, it would be exist as impurities in the final products, causing the negative influence of luminescence properties with high cost. For the sake of obtaining high-quality phosphors, the carbon concentration of the initial mixtures should have a minimum value. However, if the content of carbon is insufficient in the initial mixtures, no sufficient reducing agent reacts with oxidant, the final product will contain other phase. The other diffraction peaks can be seen in the Fig. 6 with a ratio of 1:0.58. In conclusion, the optimal ratio was 1:0.46 in this experiment. The SEM micrograph of Gd$_2$O$_2$S powders synthesized at 1000°C for 3 h with a ratio of 1:0.46 between carbon and Gd$_2$O$_2$SO$_4$ is shown in Fig. 7. The morphology of Gd$_2$O$_2$S particles is a hexagonal plate shape with a thickness of 200 nm.

(3) PL and XEL Spectra of the (Gd$_{0.9987}$Pr$_{0.0013}$)$_2$O$_2$S Phosphors and Ceramics

Figure 8 shows the residual carbon weight ratio in final product. With increase in carbon content in the mixture, the residual carbon content increases accordingly. The PL excitation and emission spectra of the (Gd$_{0.9987}$Pr$_{0.0013}$)$_2$O$_2$S phosphors synthesized by different ratios between carbon and (Gd$_{0.9987}$Pr$_{0.0013}$)$_2$O$_2$SO$_4$ are shown in Fig. 9. The excitation spectra were monitored by 513 nm. The $^6$S$_{5/2}$→$^4$P$_J$ transitions of the Gd$^{3+}$ ions are responsible for the peaks (at 313 and 311 nm) of excitation band. These peaks indicate a highly efficient energy transfer from the Gd$^{3+}$ ions to the Pr$^{3+}$. The broad absorption band centered at 270 nm is observed from the excitation spectra, which is the matrix absorption band. The band broadened at 300 nm is generated by $4f$→$5d$ transition of Pr$^{3+}$ ions. Although the emission location of (Gd$_{0.9987}$Pr$_{0.0013}$)$_2$O$_2$S phosphors synthesized by the different concentrations of carbon is similar, the relative intensity of the emission bands is different from each other, the high concentration of carbon shows negative property due to the pollution of carbon. The emission spectra of the (Gd$_{0.9987}$Pr$_{0.0013}$)$_2$O$_2$S phosphors were excited by 300 nm monochromatic light from a xenon (Xe) lamp. The strongest line corresponding to the $^3$P$_0$→$^1$H$_4$ transition of Pr$^{3+}$ ions is shown in Fig. 9(b), which shows green emission at 513 nm. The sharp emission peak at 500 nm belongs to the $^3$P$_1$→$^1$H$_4$ transition of Pr$^{3+}$ ions, which is next to the most prominent peak. The weak peaks located at 545 and 665 nm correspond to the $^3$P$_1$→$^1$H$_3$ and $^3$P$_0$→$^1$F$_2$ transitions of Pr$^{3+}$ ions, respectively. The emission intensity of different samples has the same tendency with the excitation spectra. In addition, all the data are perfect agreement with the references.

The photoluminescence spectra of Gd$_2$O$_2$S: Pr ceramics at room temperature are given in Fig. 10. The photoluminescence spectra of ceramics and phosphors are similar. Figure 11 shows the XEL spectrum of Gd$_2$O$_2$S: Pr ceramic fabricated by SPS at 1300°C for 5 min. The inset (a) of Fig. 11 shows the XEL spectrum of (Gd$_{0.9987}$Pr$_{0.0013}$)$_2$O$_2$S phosphors. The measurement was operated at 65 kV, 2.3 mA. The XEL spectrum of Gd$_2$O$_2$S: Pr ceramic is similar to that of (Gd$_{0.9987}$Pr$_{0.0013}$)$_2$O$_2$S phosphors. It can be seen that these emission peaks show the characteristic emission of Gd$_2$O$_2$S: Pr ceramics.
Pr\(^{3+}\). The most intense peak still exhibits green emission at 513 nm, which is attributed to the \(^3P_0\rightarrow^3H_4\) transition of Pr\(^{3+}\) ions. However, in contrast to the PL spectra, there is a slight difference in emission intensities and emission peak locations, especially for emission bands at 665 nm corresponding to \(^3P_0\rightarrow^3F_2\) transition of Pr\(^{3+}\) ions. The possible origin for the differences is that the excited mechanism is different between ultraviolet and X-ray excitation. The ultraviolet excitation is a simple process, in which the ultraviolet energy reacts directly with the activator Pr\(^{3+}\) ions. On the contrary, the X-ray excitation is a more complicated process including three continuous steps. The interaction of a high-energy photon with Gd\(_2\)O\(_2\)S host lattice generates a quantity of electrons in conduction band and many holes in valence band. The electron–hole pairs transport through the material, and the luminescence centers Pr\(^{4+}\) capture the electrons as radiative combination and emit light.\(^{28}\) Meanwhile, the defects in Gd\(_2\)O\(_2\)S host lattice can also capture the electron–hole pairs as nonradiative combination.

**IV. Conclusions**

The pure phase Gd\(_2\)O\(_2\)S: Pr phosphors were synthesized by a low cost and high productive carbothermal reduction method. The precursor can be transformed into Gd\(_2\)O\(_2\)SO\(_4\) during the calcination in air at 750°C. The reaction temperature between carbon and Gd\(_2\)O\(_2\)SO\(_4\) should be above 1000°C, and the optimal molar ratio is 1:0.46. Gd\(_2\)O\(_2\)S: Pr scintillation ceramics were fabricated by SPS at 1300°C for 5 min. The results show the powders synthesized by carbothermal reduction are promising for the industrial production and sintering Gd\(_2\)O\(_2\)S: Pr ceramics.  

![Fig. 9. PL excitation spectra (a) and emission spectra (b) of (Gd\(_{0.998}\)Pr\(_{0.0013}\))\(_2\)O\(_2\)S phosphors produced by different ratios between carbon and (Gd\(_{0.998}\)Pr\(_{0.0013}\))\(_2\)O\(_2\)SO\(_4\).](image)

![Fig. 10. PL excitation spectrum (a) and emission spectrum (b) of Gd\(_2\)O\(_2\)S: Pr ceramic fabricated by spark plasma sintering.](image)

![Fig. 11. The XEL spectra of Gd\(_2\)O\(_2\)S: Pr ceramic fabricated by spark plasma sintering. The inset (a) is the XEL spectra of (Gd\(_{0.998}\)Pr\(_{0.0013}\))\(_2\)O\(_2\)S phosphors.](image)
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