

Fabrication and Microstructure of Gd₂O₂S:Tb Scintillation Ceramics from Water-bath Synthesized Nano-powders: Influence of H₂SO₄/Gd₂O₃ Molar Ratio

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Abstract: The Gd₂O₂S:Tb scintillation ceramics is extensively used for neutron radiography and industrial non-destructive testing due to its bright green emission, high intrinsic conversion efficiency and high thermal neutron capture cross-section. However, the existence of Gd₂O₃ secondary phase in Gd₂O₂S ceramics impedes the scintillation property. In this work, The Gd₂O₂S:Tb precursors were synthesized in water-bath with H₂SO₄ and Gd₂O₃ as starting materials. Molar ratio of H₂SO₄ to Gd₂O₃ defined as n was adjusted to synthesize the precursors., which influence on the properties of the precursors and powders was studied. Chemical composition of the precursors changes with the increase of n , from 2Gd₂O₃·Gd₂(SO₄)₃· x H₂O ($n < 2.00$) to Gd₂O₃·2Gd₂(SO₄)₃· x H₂O ($2.25 \leq n \leq 2.75$), and to Gd₂(SO₄)₃·8H₂O ($n = 3.00$). After being calcined and reduced, all the powders form pure Gd₂O₂S phase. Morphology of the Gd₂O₂S:Tb powders is closely related to the phase composition of the precursor. Increase of the XEL intensity shows two stages with n increase, corresponding to the phase transition of the precursor, respectively. The Gd₂O₂S:Tb scintillation ceramics were therefore fabricated by vacuum pre-sintering and HIP post-treatment. The ceramics were fabricated from the powders prepared with different n , achieving high relative density and XEL intensity, except the ceramics fabricated from the powders prepared with the $n = 2.00, 2.25, 2.50$. The increase of n is beneficial to the removal of the Gd₂O₃ secondary phase from the Gd₂O₂S:Tb ceramics. This work provides a way for eliminating the secondary phase in Gd₂O₂S:Tb scintillation ceramics.

Key words: water-bath method; molar ratio of H₂SO₄ to Gd₂O₃; Gd₂O₂S:Tb nanopowder; scintillation ceramics

Inorganic scintillation materials have been applied in many fields such as X-rays medical imaging, high energy physics and industrial manufacturing^[1-5]. Gadolinium oxysulfide (Gd₂O₂S) is an efficient and excellent matrix to produce phosphors and scintillation ceramics for luminescence and scintillation applications^[6-7], due to its wide bandgap (4.6–4.8 eV)^[8], high density (7.34 g/cm³)^[9], and high chemical stability^[10]. However, the Gd₂O₂S single crystal with high optical and scintillation quality,

meeting the requirements of practical application, has not been reported. While, the Gd₂O₂S-based phosphors have attracted considerable attention for decades^[11-14]. For instance, Terbium doped gadolinium oxysulfide (Gd₂O₂S:Tb) phosphor exhibits intensive green emission and high luminous efficiency^[15-16], which makes it widely used for display purposes in TV screens, cathode ray tubes, and X-ray intensifying screens^[17-21]. The Gd₂O₂S:Tb, applied for scintillation screens, mainly includes powder and

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ceramic scintillators^[22-24]. However, for the powder scintillation screen^[25], the poor thermal performance and radiation hardness limit its service lifespan. Due to the boundary scattering and the difference of refractive index among bubbles, powder particles and binders, the light output and optical uniformity are reduced. In contrast, ceramic scintillation screens can solve these problems well and effectively improve the light output. However, it is difficult to obtain high transparent ceramics for the birefringence caused by non-cubic structure^[26].

Gd₂O₂S belongs to hexagonal system (space group P3-m1 and lattice parameters $a=b=0.3851$ nm, $c=0.6664$ nm)^[27]. Each oxygen ion is surrounded by three gadolinium ions, while each sulfur ion is coordinated by six gadolinium ions to form a stable structure^[28-29]. However, the binding force of Gd toward S is much lower than that of O according to the hard and soft acid and base (HSAB) theory^[30]. As a result, the secondary phase of Gd₂O₃ is easily produced during the preparation of Gd₂O₂S ceramics. So, avoiding the existence of Gd₂O₃ is the main task of the Gd₂O₂S ceramics fabrication. At present, there are mainly two ways to synthesize Gd₂O₂S powders^[26]. One is to "supplement" the S element into the structure of Gd₂O₃. The other one is to synthesize the precursors which are calcined to provide Gd₂O₂SO₄, and then the Gd₂O₂SO₄ is reduced to Gd₂O₂S powders. In general, the sulfur supplementation method involves complicated procedures, high reaction temperatures and environmentally harmful sulfurization reagents such as S, CS₂, H₂S^[31-32]. The method produces micron-sized particles of irregular and uncontrolled morphologies^[33]. The reduction method usually involves mild reaction conditions, fewer by-products, and can obtain powders with smaller particles^[34-35]. The fine precursor powders can react more sufficiently in the reduction process, improving the uniformity of components^[36-37]. Meanwhile, the powders are conducive to the uniformity of ceramics sintering, and can reduce the formation of the secondary phase. The water-bath method is one of the reduction methods, which has the advantages of simple process and harmless by-products. Recently our group used the water-bath method to synthesize Gd₂O₂S powders^[34,36,38]. The morphology of the powders produced by the reduction method depends largely on the morphology of the precursors. The morphology, composition of the precursors can be affected by many factors, such as bathing temperature and time, volume of solution, solution pH and the molar ratio of H₂SO₄ to Gd₂O₃^[39-41]. The secondary phase of Gd₂O₃ in Gd₂O₂S ceramics is caused by the volatilization of sulfur. So, changing n is an effective strategy to make appropriate sulfur supplement in the process of synthesizing precursors.

Different n produce precursors with different chemical components, which change the morphology and property of the powders.

In this work, n was adjusted to synthesize the precursors in the water-bath method. Gd₂O₂S:Tb nanopowders were obtained *via* reducing in flowing mixture of argon and hydrogen (H₂-Ar). The chemical composition and phase evolution of the precursors were analyzed in detail. The influence of n on the morphology and X-ray excited luminescence (XEL) spectrum of the Gd₂O₂S:Tb powders were investigated. Gd₂O₂S:Tb scintillation ceramics were fabricated by the two-step sintering method comprised of vacuum pre-sintering and hot isostatic pressing (HIP) post-treatment. The influences of n on the chemical composition, morphology and microstructure of the Gd₂O₂S:Tb ceramics were investigated. The microstructure and chemical homogeneity of the obtained ceramics were analyzed by FESEM and EDS. The luminescence properties of the Gd₂O₂S:Tb ceramics were evaluated as well.

1 Experimental

The starting materials were commercial oxide powders: Gd₂O₃ (99.999%, Zhongkai New Materials Co., Ltd., Jining, China), Tb₄O₇ (99.995%, Zhongkai New Materials Co., Ltd., Jining, China) and concentrated H₂SO₄ (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Tb(NO₃)₃ solution was prepared by dissolving Tb₄O₇ in hot nitric acid. Gd₂O₃ was mixed with Tb(NO₃)₃ together in stoichiometric ratios of (Gd_{0.995}Tb_{0.005})₂O₂S. Then dilute H₂SO₄ solutions with different n were added to the suspension at 7 °C at a dripping speed of 8 mL/min. n was adjusted to 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, 2.75 and 3.00. After the reaction was conducted at 90 °C for 2 h in quartz beaker, the precursors were collected *via* centrifugation, and then dried in an oven at 70 °C for 48 h. The precursors were calcined in a tube furnace under flowing H₂-Ar. The Gd₂O₂S:0.5%Tb (in atomic) powders were uniaxially pressed into pellets of 18 mm in diameter at 30 MPa and then cold isostatically pressed under 250 MPa. For ceramics fabrication, the green pellets were pre-sintered at 1300 °C for 3 h in vacuum and subsequently HIP post-treated at 1450 °C for 3 h under 176 MPa in Ar atmosphere. At last, the samples were double-face polished to 1 mm thickness.

Phase identification was identified by the X-ray diffractometry (XRD, D/max2200 PC, Rigaku, Japan) using Cu K α radiation ($\lambda=0.15406$ nm) with a scanning speed of 5 (°)/min in the 2θ range of 10°–80°. The

morphologies of the reduced powders were observed by the field emission scanning electron microscope (FESEM, SU9000, Hitachi, Japan). The microstructures of the $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ ceramics were observed by a field emission scanning electron microscope (FESEM, SU8220, Hitachi, Japan). The chemical compositions of the ceramics were analyzed by the energy dispersive spectrum (EDS). X-ray excited luminescence (XEL) spectra were recorded by a homemade XEL spectrometer using a F30III-2 X-ray tube performed at 75 kV voltage and 1.5 mA current with a tungsten target and an Ocean Optics QE65000 collector.

2 Results and discussion

Fig. 1 shows the XRD patterns of the precursors after the reaction of H_2SO_4 and Gd_2O_3 with different n in hot water bath at 90 °C for 2 h. For the precursors with $n < 2.00$, all the precursors with similar diffraction patterns were obtained, indicating that the amount of sulfuric acid is not enough to make the occurrence of precursor phase transition. And the composition of the precursors can be formulated as $2\text{Gd}_2\text{O}_3 \cdot \text{Gd}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ^[42]. However, with the increase of n , some significant changes occurred in the diffraction peaks of the precursors, and the diffraction peaks of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ appear gradually. As reported in an American patent, the composition of the precursor is $\text{Gd}_2\text{O}_3 \cdot 2\text{Gd}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ with $n = 2.00\text{--}2.75$, but it was not described in detail^[43]. For the precursor with $n = 3.00$, all characteristic diffraction peaks of the precursor correspond well to the $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (PDF#31-0535). The precursor is consistent with the product of the complete reaction of H_2SO_4 and Gd_2O_3 with stoichiometric ratio of 3 : 1. According to the above results, with the increase of sulfuric acid usage, the proportion of SO_4^{2-} in the precursor increases. Considering the easy loss of S element in the preparation of $\text{Gd}_2\text{O}_2\text{S}$ powders, it is beneficial to replenish the sulfur in the powders.

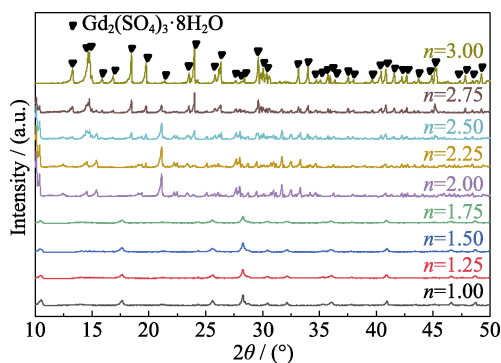
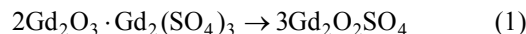


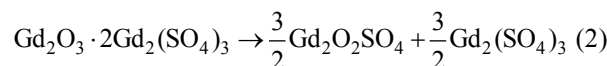
Fig. 1 XRD patterns of the products prepared with different n of H_2SO_4 and Gd_2O_3 in hot water bath at 90 °C for 2 h

Then the precursors were calcined in air at 600 °C for 3 h, and the phase composition of the calcined products were characterized, as shown in Fig. 2. It can be seen that the diffraction peaks of the products with $n < 2.00$ correspond well to the orthorhombic structured $\text{Gd}_2\text{O}_2\text{SO}_4$ (PDF#29-0613). For the products with $n = 2.00\text{--}2.75$, two phases of $\text{Gd}_2\text{O}_2\text{SO}_4$ and $\text{Gd}_2(\text{SO}_4)_3$ appeared after being calcined in air. And the increase of n leads to an increase in the XRD diffraction intensity of $\text{Gd}_2(\text{SO}_4)_3$, which is due to the appearance of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ phase in the precursor. It is noteworthy that the precursor with $n = 3.00$ is completely transformed into pure $\text{Gd}_2(\text{SO}_4)_3$, because diffraction peaks of the product correspond well to $\text{Gd}_2(\text{SO}_4)_3$ (PDF#39-0306). The reaction process of the precursors with different n calcined in air can be expressed as:

$n < 2.00$:



$2.00 \leq n \leq 2.5$:



$n > 2.50$:

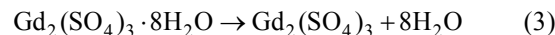


Fig. 3 shows the XRD patterns of the $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ powders with different n . After being calcined at 750 °C under hydrogen atmosphere, all diffraction peaks of the powders correspond well to the hexagonal crystal structure of $\text{Gd}_2\text{O}_2\text{S}$ (PDF#26-1422). Although the phase transitions of the precursors calcined in air are different to some extent, the phase compositions of the final powders are almost the same without any secondary phases observed. However, the XRD diffraction intensity of $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ powders changes with the composition of the precursors, which indicates that the crystallinity of the powders has changed. Theoretically, $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ powders with $n \geq 2.00$ have higher purity compared to others, because of the occurrence of following reactions:

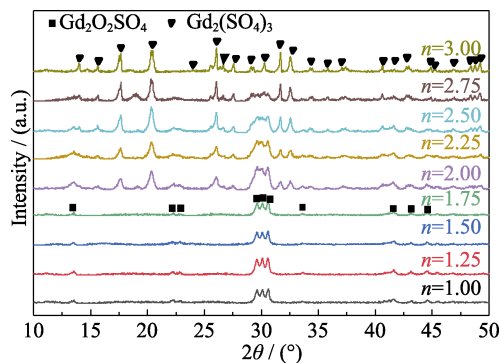
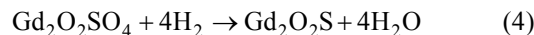
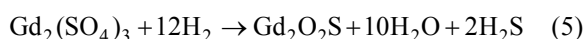


Fig. 2 XRD patterns of the products calcined in air at 600 °C for 3 h from the precursors prepared with different n



H₂S produced during reduction can not only inhibit the volatilization of S element, but also play a role in sulfidation, which is beneficial to the preparation of high purity Gd₂O₂S powder.

Fig. 4 shows the FESEM micrographs of Gd₂O₂S:Tb powders with different n . It can be seen that all Gd₂O₂S:Tb powders present layered or block structure with severe agglomeration. The fact that the reduced Gd₂O₂S:Tb powder retains the overall morphology of the composition, presenting overlapping and interlaced layered structures. With the component transformation of the precursor (*i.e.* the increase of SO₄²⁻ content in the precursor components), Gd₂O₂S:Tb powders gradually

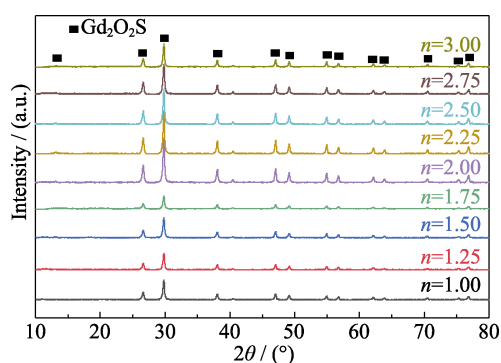


Fig. 3 XRD patterns of the products calcined in air and reduced in H₂ at 750 °C for 2 h from the precursors prepared with different n

precursor has been confirmed by our previous work. And it can be found from Fig. 1 and Fig. 4 that the morphology of the Gd₂O₂S:Tb powder is closely related to the phase composition of the precursor. Namely, the composition of the precursor determines the morphology of the reduced powder. For example, all Gd₂O₂S:Tb powders with $n < 2.00$ have the same chemical composition and show a superposed block structure, which is attributed to the bonding action of the SO₄²⁻ groups.

The XEL spectra of Gd₂O₂S:Tb powders with different n were measured and compared with the commercial micron Gd₂O₂S:Tb powders, as shown in Fig. 5. In Fig. 5(a), the characteristic emission peaks of Tb³⁺ can be observed from the Gd₂O₂S:Tb powders ranging from 350 to 700 nm under X-ray excitation, which are due to transitions from the ⁵D_{3,4} excited states to the ⁷F_{*J*} ($J=1-6$) ground multiples^[35-36,44]. The most prominent transition is in the spectral region of 545 nm (⁵D₄-⁷F₅ transition) giving rise to strong green emission. Fig. 5(b) shows the increase of luminous intensity in two stages, corresponding to the phase transition of the precursors respectively. The decrease of defect concentration of the Gd₂O₂S:Tb powders is one of the reasons for the increase of XEL intensity. The increasing proportion of S element in the precursors leads to the formation of more H₂S gas during the reduction, which effectively avoids Gd₂O₃ residue and inhibits the formation of S vacancies in the Gd₂O₂S:Tb powders. In addition, the improvement of

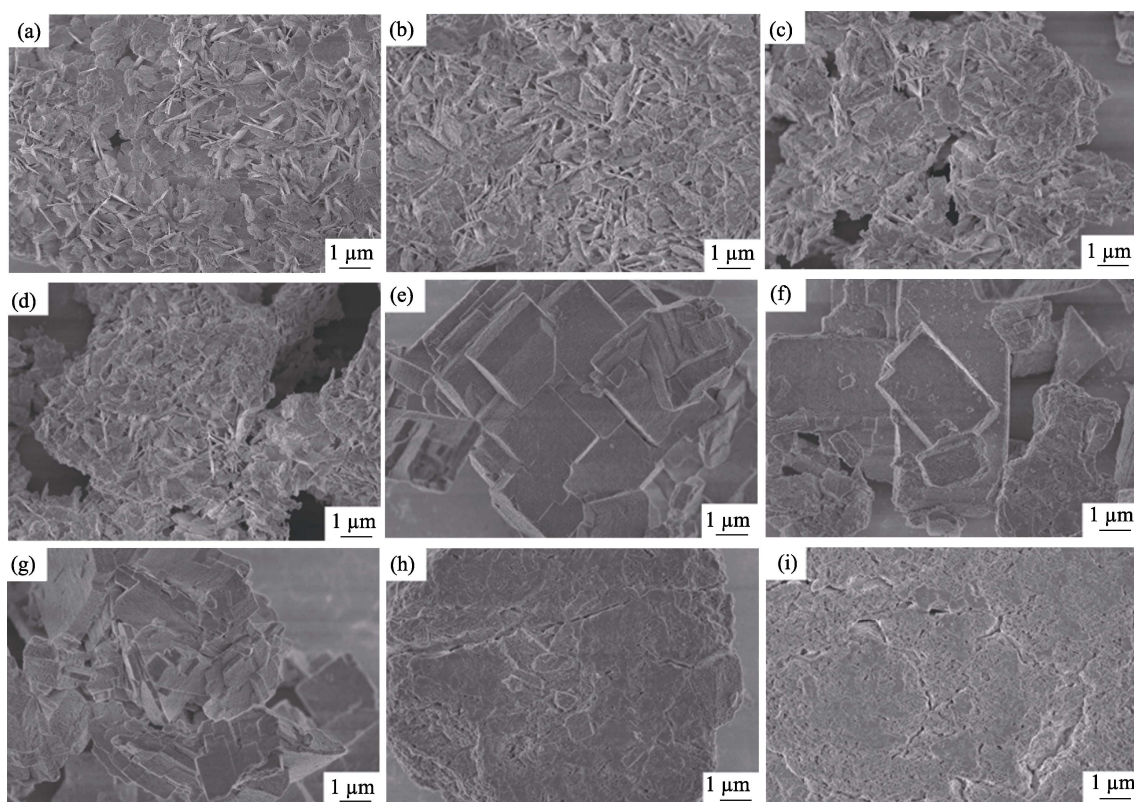


Fig. 4 FESEM morphologies of Gd₂O₂S:Tb powders with different n
(a) $n=1.00$; (b) $n=1.25$; (c) $n=1.50$; (d) $n=1.75$; (e) $n=2.00$; (f) $n=2.25$; (g) $n=2.50$; (h) $n=2.75$; (i) $n=3.00$

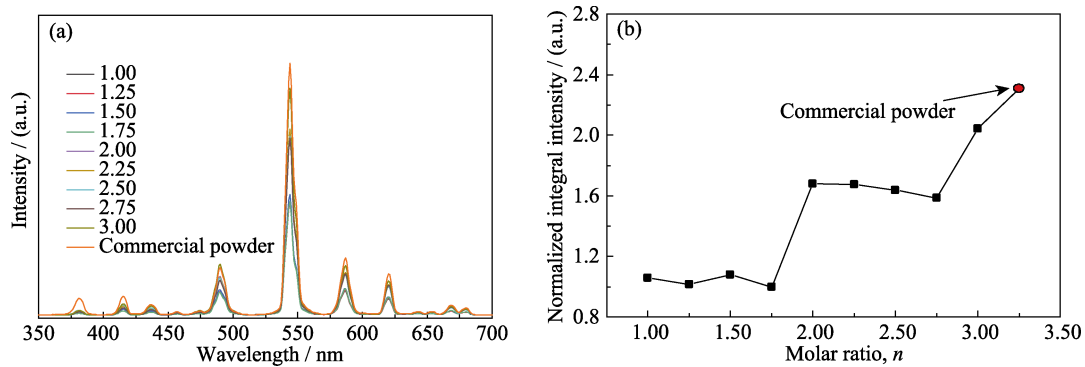


Fig. 5 XEL spectra and normalized integral intensity curves in the range of 350–700 nm of $\text{Gd}_2\text{O}_2\text{S:Tb}$ powders with different n
(a) XEL spectra; (b) Normalized integral intensity curves; Colorful figures are available on website

particle crystallization and the growth of particle size of the powders also affect its luminescent properties, as shown in Fig. 3 and Fig. 4. It also can be seen from Fig. 5(b) that the XEL integral intensity in the range of 350–700 nm of $\text{Gd}_2\text{O}_2\text{S:Tb}$ powders with $n=3.00$ is the closest to that of commercial micron powders, reaching 88% of XEL integral intensity of the commercial $\text{Gd}_2\text{O}_2\text{S:Tb}$ powder. And the luminescent properties of the synthesized powder can be further improved by increasing the calcination temperature of the precursor to promote the crystallinity and grain growth.

Fig. 6 shows the relative densities of the $\text{Gd}_2\text{O}_2\text{S:Tb}$ ceramics prepared with different n before and after HIP post-treatment. The relative densities of the pre-sintered ceramics decrease from 97.2% to 78.1% and then increase to 94.5% with n increasing from 1.00 to 3.00, corresponding to the morphology of the $\text{Gd}_2\text{O}_2\text{S:Tb}$ powders changes, respectively. The result shows that the sintering activity of the powders is significantly affected by their morphologies. Compared to the $\text{Gd}_2\text{O}_2\text{S:Tb}$ powder with block structure, the layered powders are easier to be broken in the molding process and the densification rate is faster. After the HIP post-treatment, the relative densities of all ceramics are increased. However, $\text{Gd}_2\text{O}_2\text{S:Tb}$ ceramics prepared with $n=2.00$, 2.25 and 2.50 were still not densified. Therefore, the subsequent work can be considered to introduce the ball milling process to break the agglomeration of the powders in order to obtain high-density ceramics.

The EDS analysis was performed on $\text{Gd}_2\text{O}_2\text{S:Tb}$ ceramics, as shown in Fig. 7. Two kinds of secondary phase can be found on the surface of the $\text{Gd}_2\text{O}_2\text{S:Tb}$ ceramics. From the EDS analysis results, it can be seen that the secondary phase in the white area is Gd_2O_3 . The secondary phase in the black area is aluminum-containing compound, which is introduced from the alumina crucible during the calcination and reduction of the powders. The black area on the ceramic surface

increases significantly when $n=3.00$, indicating that the precursor of this component is more likely to introduce Al element, so the alumina crucible should be avoided when calcination and reduction of the powders.

The FESEM micrographs of the $\text{Gd}_2\text{O}_2\text{S:Tb}$ ceramics vacuum pre-sintered at 1300 °C for 3 h and HIP post-treated at 1450 °C for 3 h are presented in Fig. 8. It can be seen that when $n=2.00$, 2.25 and 2.50, there are a lot of pores on the polished ceramics surface, indicating the ceramics are not completely compact. All ceramics have Gd_2O_3 secondary phase on the surface as mentioned above. When $n < 2.00$, the surface of ceramics has relatively more secondary phase, and the distribution of the secondary phase does not decrease with the increase of n . This is because the composition of the precursor is consistent when $n < 2.00$. The precursor is pure $\text{Gd}_2\text{O}_2\text{SO}_4$ after air calcination, and S element is not excessive during reduction. When $2.00 \leq n \leq 2.75$, the distribution content of the secondary phase decreases, which indicates the increase of S element proportion in the powders. The increase of n has a certain effect on the removal of the secondary phase in the ceramics, but the effect is not significant. When $n=3.00$, the Gd_2O_3 secondary phase on the ceramic surface decreases obviously.

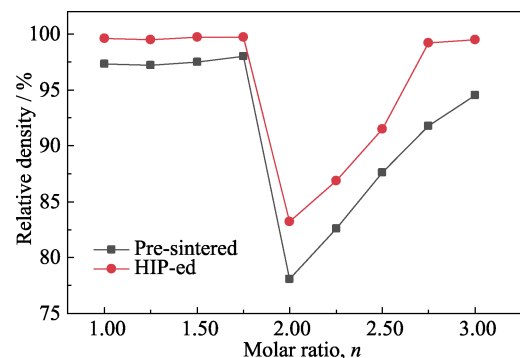


Fig. 6 Relative densities of $\text{Gd}_2\text{O}_2\text{S:Tb}$ ceramics vacuum pre-sintered at 1300 °C for 3 h and HIP post-treatment at 1450 °C for 3 h fabricated from the powders with different n

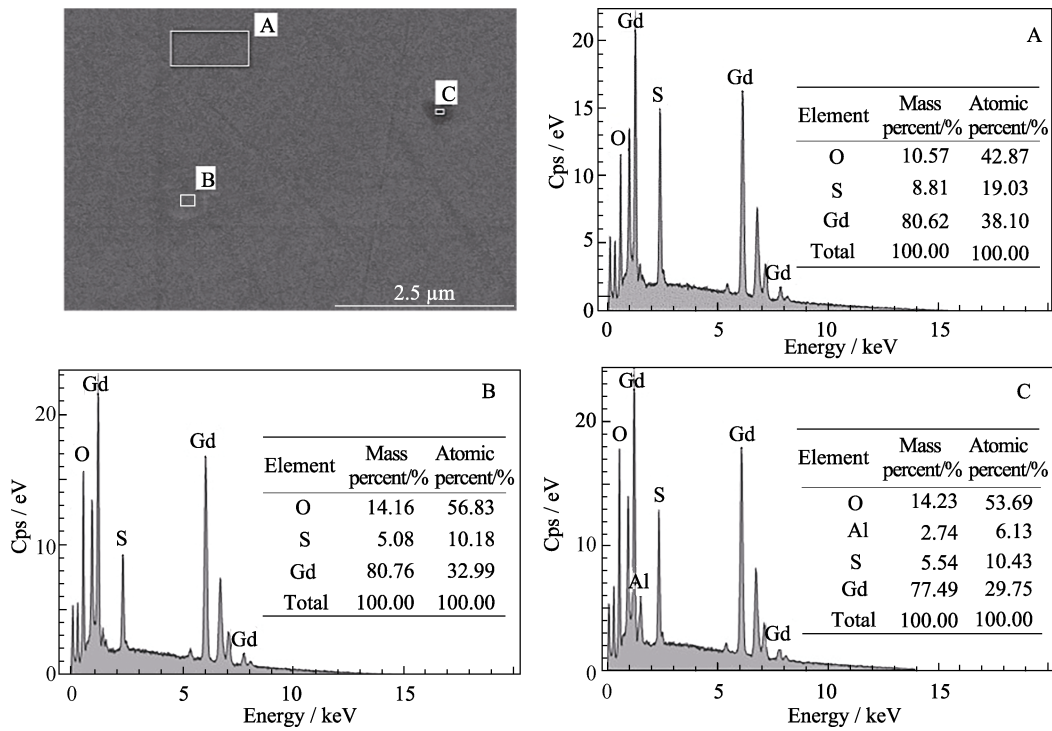


Fig. 7 FESEM micrograph and EDS patterns (white area) of the Gd₂O₂S:Tb ceramics vacuum pre-sintered at 1300 °C for 3 h and HIP post-treatment at 1450 °C for 3 h fabricated from the powders prepared with $n=1.00$

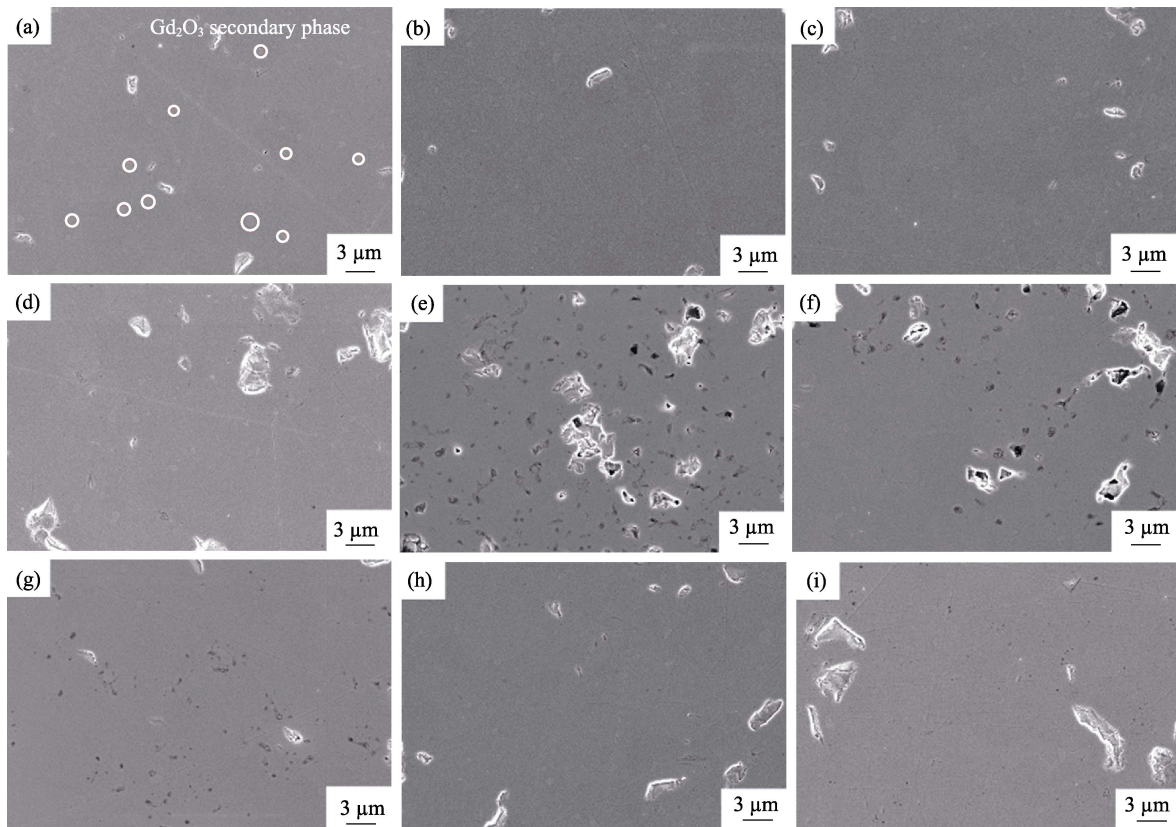


Fig. 8 FESEM morphologies of Gd₂O₂S:Tb ceramics fabricated from the powders prepared with different n (a) $n=1.00$; (b) $n=1.25$; (c) $n=1.50$; (d) $n=1.75$; (e) $n=2.00$; (f) $n=2.25$; (g) $n=2.50$; (h) $n=2.75$; (i) $n=3.00$

The XEL spectra of Gd₂O₂S:Tb ceramics fabricated from the powders prepared with different n are shown in Fig. 9(a). The emission bands of the Gd₂O₂S:Tb ceramics

in the range of 350–700 nm accords with the emission peaks of Tb³⁺. The strongest emission peak centered at 545 nm corresponds to the ⁵D₄-⁷F₅ transition^[35,44]. The

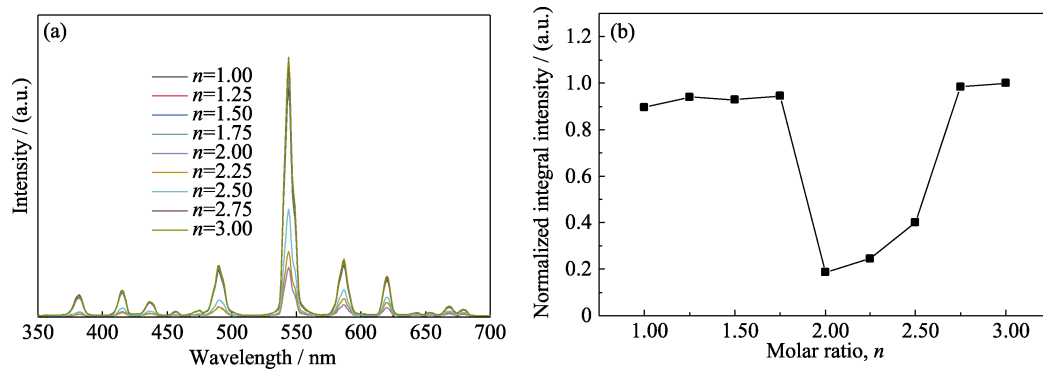


Fig. 9 XEL spectra and normalized integral intensity curves in the range of 350–700 nm of $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ ceramics fabricated from the powders with different n
(a) XEL spectra; (b) Normalized integral intensity curves; Colorful figures are available on website

normalized integral XEL intensity of $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ ceramics versus the powders n are shown in Fig. 9(b). For uncompact ceramics ($n=2.00, 2.25, 2.50$), the XEL intensity is relatively low, mainly due to the porosity. As the degree of densification of ceramics increases, the XEL intensity also gradually increases. For the compact ceramics ($n=1.00, 1.25, 1.5, 1.75, 2.75$ and 3.00), with the increase of n , the XEL intensity of the ceramic has a tendency to improve. But the secondary phase inside the ceramics will greatly reduce the scintillation performance of the ceramics. In addition, the ceramics has a higher XEL intensity when $n=3.00$, but there is no significant improvement compared with the ceramics fabricated from the powders prepared with other n . This is because more Al element may be introduced during the powders preparation, resulting in an increase in the content of aluminum-containing secondary phase in the ceramics.

3 Conclusions

The $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ precursors were synthesized with different molar ratios of H_2SO_4 to Gd_2O_3 in the hot water-bath. The $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ powders were obtained by reducing the precursors in H_2 -Ar at 750°C . The chemical composition of the precursors and the products calcined in air changes with the increase of n . The chemical composition of the precursors can be described as $2\text{Gd}_2\text{O}_3 \cdot \text{Gd}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ($n < 2.00$), $\text{Gd}_2\text{O}_3 \cdot 2\text{Gd}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ($2.25 \leq n \leq 2.75$), $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ($n=3$). After being calcined at 750°C under a hydrogen atmosphere, all powders form pure phase $\text{Gd}_2\text{O}_2\text{S}$ structure. The morphologies of the $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ powders are closely related to the phase composition of the precursor. With the increase of n , the XEL intensity of the $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ powders improves. The increase of the XEL intensity shows two stages, corresponding to the phase transition of the precursors respectively. $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ scintillation ceramics were fabricated by vacuum pre-sintering and HIP post-

treatment in an Ar atmosphere. The ceramics fabricated from the powders prepared with different n achieve high relative density except the ceramics fabricated from the powders with block structure ($n=2.00, 2.25, 2.50$). Only the dense ceramics achieve relatively high XEL intensity. Two kinds of secondary phase which is Gd_2O_3 and aluminum-containing compound can be found on the surface of the $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ ceramics. The secondary phase seriously reduces the optical quality and scintillation property of the ceramics. The increase of n has a certain effect on the removal of the Gd_2O_3 secondary phase from the FESEM morphologies of $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ ceramics. Therefore, our subsequent work mainly focuses on the elimination of the secondary phase in the ceramics.

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Photoluminescence and energy transfer in transparent glass-ceramics based on $GdF_3:RE^{3+}$ (RE = Tb, Eu) nanocrystals. *Journal of Rare Earths*, 2019, **37(11)**: 1137.

Gd₂O₂S:Tb 闪烁陶瓷的制备与结构: 水浴合成中 H₂SO₄/Gd₂O₃ 摩尔比的影响

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摘要: Gd₂O₂S:Tb 闪烁陶瓷以其明亮的绿色发光、高能量转换效率和高中子俘获截面而广泛应用于中子成像和工业无损检测等领域, 但 Gd₂O₂S:Tb 陶瓷中存在的 Gd₂O₃ 第二相影响其闪烁性能。本工作以 H₂SO₄ 和 Gd₂O₃ 为原料, 采用水浴法合成 Gd₂O₂S:Tb 前驱体, 研究了 H₂SO₄ 与 Gd₂O₃ 的摩尔比(n)对前驱体和 Gd₂O₂S:Tb 粉体性能的影响。前驱体的化学组成随 n 增大而变化: $2Gd_2O_3 \cdot Gd_2(SO_4)_3 \cdot xH_2O$ ($n < 2.00$)、 $Gd_2O_3 \cdot 2Gd_2(SO_4)_3 \cdot xH_2O$ ($2.25 \leq n \leq 2.75$) 和 $Gd_2(SO_4)_3 \cdot 8H_2O$ ($n = 3.00$), 经过空气煅烧和氢气还原后, 所有的粉体均形成 Gd₂O₂S 相。Gd₂O₂S:Tb 粉体的形貌与前驱体的相组成密切相关, 随着 n 增大, Gd₂O₂S:Tb 粉体的 XEL 强度增加呈现出两个阶段, 对应前驱体的相转变阶段。采用真空预烧结合热等静压烧结制备了 Gd₂O₂S:Tb 陶瓷, 相较于 n 为 2.00、2.25、2.50, 其他 n 制备的 Gd₂O₂S:Tb 陶瓷都达到了较高的相对密度和 XEL 强度, 不同 n 制备的陶瓷中都存在 Gd₂O₃ 第二相, n 增大有利于减少陶瓷内部的第二相, 为进一步消除 Gd₂O₂S:Tb 陶瓷中的第二相提供了思路。

关键词: 水浴法; H₂SO₄ 与 Gd₂O₃ 摩尔比; Gd₂O₂S:Tb 纳米粉体; 闪烁陶瓷

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