Powder Technology 305 (2017) 382–388

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Ultrafine Gd_2O_2S:Pr powders prepared *via* urea precipitation method using SO_2/SO_4^{2-} as sulfuration agent—A comparative study

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ARTICLE INFO

Article history:
Received 25 July 2016
Received in revised form 30 September 2016
Accepted 5 October 2016
Available online 11 October 2016

Keywords:
Scintillator
Urea precipitation
Luminescent phosphor
Oxysulphide

ABSTRACT

Nano-rods and tremelliform Gd_2O_2S:Pr powders were prepared *via* a urea precipitation method using SO_2 and SO_4^{2-} as sulfuration agent, respectively. Gd_2O_2S:Pr nano-rods with diameter of about 200 nm were obtained while the scale of tremelliform Gd_2O_2S:Pr reaches tens of microns. Gd_2O_2S:Pr nano-rods exhibits better crystallinity and stronger luminescence intensity compared to that of tremelliform Gd_2O_2S:Pr. Intensive study on their formation process and mechanism is presented in this work. It is proposed that Gd_2O_2S:Pr nano-rods were obtained from $Gd_2(SO_3)_3 \cdot 3H_2O$ nano-rods synthesized *via* a dissolution-deposition process while tremelliform Gd_2O_2S:Pr is prepared *via* an oriented growth process using SO_4^{2-} as sulfuration and regulation agent. As prepared Gd_2O_2S:Pr powders show strong green emission light at 512 nm under excitation of 318 nm ultraviolet light. Optimal concentration of Pr^{3+} is around 1 mol% since it exhibits the highest luminescence intensity at that concentration. This study is extremely prospective for the preparation and morphology control of sulphide luminescent materials.

1. Introduction

Luminescent material is of an energy conversion medium that can emit photons under high energy excitation [1–3]. Among which, inorganic luminescent material plays important role in the mediation of scintillation applications, synthetic spectrum, display and LED lighting, *etc.* [4–7]. Sulphide phosphor is of an important luminescent material with many prospective applications [8–10]. Among which, Gd_2O_2S is of a typical material that obtains advantage properties such as excellent chemical durability, high thermal stability, high melting point and density which makes it appropriate matrix material for activator atoms [11]. Especially, its successful application as detector material in CT equipment manufactured by Siemens, Philips, *etc.* is worthy to be mentioned [12].

Morphology and microstructure control of luminescent material has attracted much attention since extremely high luminescent efficiency and novel designation of luminescent material can be achieved accordingly [13,14]. Particularly, low-dimensional structures are the fundamental units for anisotropic shape control, presenting general shape and assembly control strategies for more complex structures. For example, nanorods and nanowires with restricted dimension have also been extensively explored and investigated about the influence of shape and dimensionality on the physical properties [15]. Material microstructure designation and control have profound impact on the luminescence of phosphor [16,17]. Urea precipitation method has been developed as an important approach for the preparation of ultrafine inorganic particles [18–20]. Stable pH obtained during the thermal decomposition of urea in aqueous solution makes it quite promising for precise composition control of nanopowders. Clear decomposition mechanism of urea provides researchers possibility to analyze the evolution process of ultrafine particles from its initial forming period. That is quite important for morphology control of particles prepared *via* this approach. Especially this method can accomplish both homogenous and anisotropic growth of precursor particles according to experimental parameter regulation [21]. In 2013, Qin [22] reported the process and mechanism of anisotropic absorption of SO_4^{2-} on different facets of the Y_2O_3 precursor nucleus using $(NH_4)_2SO_4$ as regulation agent. That also provides new approach to introduce S element into precipitant. After that, Lian reported in 2015 the preparation of Gd_2O_2S using urea precipitation method [23]. Previously, many researchers have also reported synthesis of Gd_2O_2S in solid state method (SSR) [24–26] and emulsion liquid membrane (ELM) [27,28]. Among the synthesis methods above, SSR method has an advantage of considerable productivity based on its high reliability. Nevertheless, such a method is based on the high temperature reaction of mixed powders, which is difficult to obtain ultrafine powders with high purity and defined morphology. ELM precipitation method

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http://dx.doi.org/10.1016/j.powtec.2016.10.014

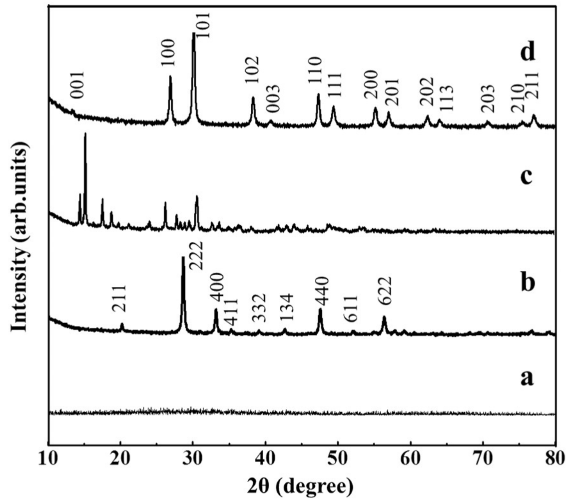

Fig. 1. X-ray diffraction pattern of powders at different stages of Pso_2 (a) precursor, (b) powders calcined at 800 °C in air, (c) sulfonated powders using SO_2 at 450 mL/min for 15 min, (d) reduced powders calcined at 800 °C in 20% N_2 and 80% H_2 hybrid atmosphere.

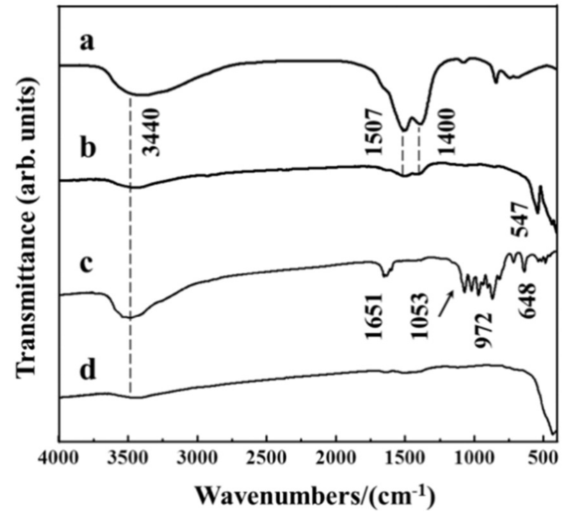

Fig. 3. FTIR spectra of powders at different stages of Pso_2: (a) precursor, (b) powders calcined at 800 °C in air, (c) sulfonated powders using SO_2 at 450 mL/min for 15 min, (d) reduced powders calcined at 800 °C in 20% N_2 and 80% H_2 hybrid atmosphere.

has been proved a possible synthesis technique for preparing various morphological Gd_2O_2S phosphors. Formation of precipitation is by a means of which the metal ions can be extracted from external water phase into organic membrane and then stripped into internal water phase. However, such method is quite complicated and time consuming, which leads to its low yield. Hence it is difficult to achieve sulphide phosphors such as Gd_2O_2S with defined morphology effectively. Back in the 1990s, SO_2 sulfuration method was also recorded in some patents [29,30] for the preparation of sulphide phosphors, which is believed to be an effective way to get particles sulfonated. However, no reports have been covered in research papers.

In present work, urea precipitation method was performed to prepare Gd_2O_2S precursor powders with defined morphology. A comparative study on two sulfuration approaches was then introduced. In the first case, SO_2 was applied as the sulfuration agent of the calcined oxide prepared *via* urea precipitation method. While in the second case, SO_4^{2-} was introduced into the urea precipitation system as the sulfuration agent. Nano-rods and tremelliform Gd_2O_2S were prepared by using SO_2 and SO_4^{2-} as sulfuration agent, respectively. Gd_2O_2S nano-rods with diameter of about 200 nm were obtained while the scale of tremelliform Gd_2O_2S reaches tens of microns. Intensive study on their formation process and mechanism are presented in this work. It is proposed that Gd_2O_2S nano-rods were obtained from $Gd_2(SO_3)_3 \cdot 3H_2O$ nano-rods synthesized *via* a dissolution-deposition process while tremelliform Gd_2O_2S was prepared *via* an oriented growth process using SO_4^{2-} as sulfuration agent and regulation agent. Praseodymium (Pr) ion is the most widely used active ion in Gd_2O_2S medium for its appropriate energy level system and high efficiency for scintillation application [12]. In present work, Pr^{3+} was added in Gd_2O_2S matrix as active ion. It is found that Gd_2O_2S:Pr nano-rods exhibited better crystallinity and stronger luminescence intensity compared to that of tremelliform Gd_2O_2S:Pr. As prepared Gd_2O_2S:Pr powders showed strong green emission light at 512 nm under excitation of 318 nm ultraviolet light. Optimal concentration of Pr^{3+} is around 1 mol% since it exhibits the highest luminescence intensity at that concentration range. Work accomplished in this paper is prospective for the efficiency improvement and feasibility in the preparation of sulphide phosphors.

2. Experimental

Commercially available Gd_2O_3 powders (GanZhou QianDong Rare Earths Group Co. Ltd. China, 99.99%), Pr_6O_{11} powders (Alfa Aesar, 99.99%), HNO_3 (Sinopharm chemical reagent), urea (Aladdin, 99.99%), $Na_2(SO_3)_3$ (Sinopharm chemical reagent, 99%) and $(NH_4)_2SO_4$ (Aladdin, 99.99%) were used as starting materials.

In a typical synthetic procedure for Gd_2O_2S:Pr powders using SO_2 as sulfuration agent (the procedure is denoted as Pso_2), Gd_2O_3 and Pr_6O_{11} mixture powders were dissolved in diluted HNO_3 to get transparent solution. 25 mL as prepared solution and urea were dissolved in 975 mL distilled water. In all cases, concentration of Gd^{3+} was kept at 0.015 M while urea was kept at 0.5 M. Pr^{3+} was added according to ratio Pr/

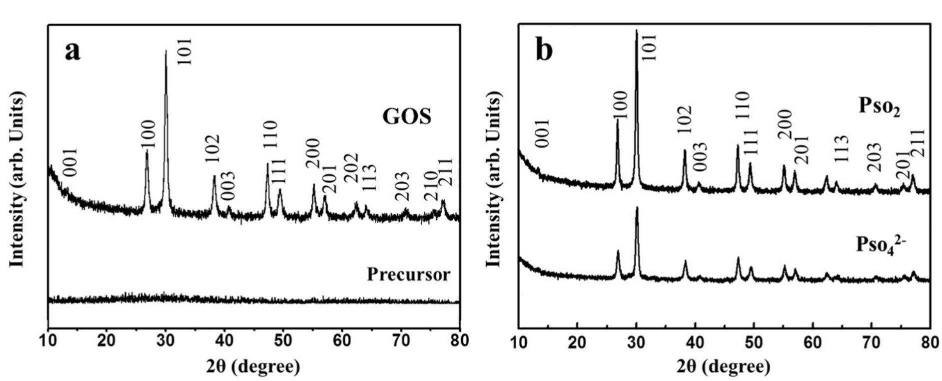

Fig. 2. (a) X-ray diffraction pattern of precursor and reduced powder calcined at 800 °C in 20% N_2 and 80% H_2 hybrid atmosphere prepared in Pso_4^{2-} (b) X-ray diffraction intensity comparison of the final products prepared in Pso_2 and Pso_4^{2-}.