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Controllable synthesis of Sm_2O_3 crystallites with the assistance of templates by a hydrothermal–calcination process

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ABSTRACT

Sm_2O_3 crystallites were controllably synthesized by the hydrothermal–calcination process with the assistance of different templates. The phase compositions, morphologies and optical properties of the as-prepared samples were characterized by X-ray diffraction, scanning electron microscope and ultraviolet–visible spectrophotometer. It is investigated that the influence of different templates on the structural and optical properties of Sm_2O_3 samples. Results showed that Sm_2O_3 crystallites with ribbon-like, granular and flake-like morphologies were obtained when $NaNO_3$, trisodium citrate and polyvinyl-pyrrolidone (PVP) were used as template agents. These templates effectively controlled the microstructure and optical properties of the as-prepared samples. The monoclinic phase Sm_2O_3 crystallites with ribbon-like morphology were prepared by using $NaNO_3$ as the template agent, which energy gap is only 4.827 eV.

1. Introduction

Lanthanides rare earth compounds were widely applied in various fields of modern science and technology due to their special optical [1–2], electrical [3], magnetic [4] and catalytic properties [5–6] arising from their unique 4*f* electrons. Sm_2O_3 is a kind of promising functional rare earth oxide materials because of their wide energy gap, high electrical resistivity, high dielectric constant and better chemical and thermal stability. It has been widely used in photoelectronic devices, nano sensors and micro-circuit batteries, which aroused considerable interest over the past several years [7–11].

According to current reports, pyrolytic process [12], sol–gel technique [13], microemulsion route [14] and solvothermal method [15] have been used to prepare Sm_2O_3 crystallites. Considered the difficulties of the morphology controlled, complicated operation and toxic solvent used of these methods, it is very necessary to design a facile and effective synthesis method of Sm_2O_3 nano/microcrystallites with controllable morphologies. Herein, the hydrothermal–calcination process was developed to prepare morphology controlled Sm_2O_3 crystallites with the assistance of different templates by using water as the reaction medium, which is a safe and environmentally friendly method [16–18].

In the present work, ribbon-like, granular and flake-like Sm_2O_3 crystallites with good ultraviolet light absorption property were successfully synthesized with the assistance of different templates by the hydrothermal–calcination process. The influence of different templates on the structural and optical properties of Sm_2O_3 crystallites was investigated.

2. Experimental

2.1. Synthesis of Sm_2O_3 crystallites

Firstly, 2.92 g $SmCl_3 \cdot 6H_2O$ (AR) was dissolved in 20 mL distilled water with magnetically stirring to prepare the solution with the concentration of 0.4 mol L^{-1}. Then 5 mol L^{-1} NaOH and 1 mol L^{-1} HCl solutions were used

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to adjust the pH value of the solution to 9.00 after 0.35 g $NaNO_3$ was added to get the precursor solution for the hydrothermal reaction. To investigate the influence of different templates on the Sm_2O_3 crystallites, 1.17 g of trisodium citrate ($C_6H_5Na_3O_7 \cdot 2\ H_2O$) and 1.39 g of polyvinylpyrrolidone (PVP) were used as template.

The above reactive precursor solution was transferred to the teflon-lined stainless steel autoclave with the packing ratio of 60% to heat at 200 °C for 48 h. And then, the mixture was cooled naturally down to room temperature. After the centrifugal separation, the obtained precursor was washed repeatedly several times with the distilled water and anhydrous ethanol. Afterwards, the precursor was dried in vacuum drying oven at 50 °C for 4 h. The as-prepared precursor was put into a muffle furnace and calcinated at 800 °C for 1 h. With the furnace cooled down to room temperature, Sm_2O_3 crystallites with different morphologies were finally obtained.

2.2. Characterization

The phase composition of the crystallites was characterized by X-ray diffraction (XRD, D/max2200PC, Rigaku, Japan) and the morphology of the crystallites was observed by a scanning electron microscope (SEM, JSM–6390A, JEOL, Japan). The UV–vis absorption spectra of the crystallites were determined by a UV–vis near-infrared spectroscopy (Lambda 950, Perkin Elmer Corporation, U.S.A.).

3. Results and discussion

3.1. XRD analysis of the precursor samples prepared by the hydrothermal process with the assistance of different templates

Fig. 1 shows the XRD patterns of the precursor samples prepared by the hydrothermal process with the assistance of different templates. It is found that different templates exhibited different effects on the phase compositions of the precursor samples. Sm_2O_3 as main crystalline phase with $Sm(OH)_2Cl$ phase were obtained without adding any template (Fig. 1a). In this case, Sm_2O_3 and $Sm(OH)_2Cl$ may be in the equilibrium state of the competitive growth in the reaction system. Pure $Sm(OH)_2Cl$ phase was achieved when $NaNO_3$ was added as the template (Fig. 1b). Na^+ and NO_3^- ions may restrain the further hydrolysis of the intermediate phase $Sm(OH)_2Cl$. Sm_4OCl_6 as main crystalline phase with $Sm(OH)_2Cl$ phase was obtained when trisodium citrate was used as the template (Fig. 1c). Trisodium citrate may restrain the hydrolysis of $SmCl_3$. Therefore, the incomplete hydrolyzed samples of Sm_4OCl_6 and $Sm(OH)_2Cl$ were obtained. In addition, the main crystalline phase of $Sm(OH)_3$ was achieved when PVP was used as the template (Fig. 1d). Therefore, it is indicated that PVP promoted the hydrolysis of $SmCl_3$ in the hydrothermal reaction so as to obtain the complete hydrolyzed $Sm(OH)_3$.

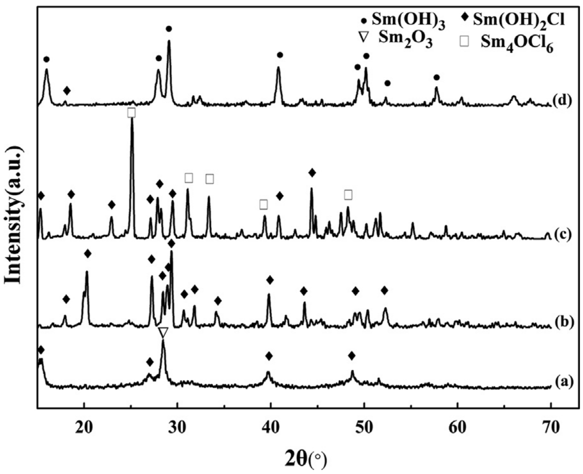

Fig. 1. XRD patterns of the precursor samples prepared by the hydrothermal method with the assistance of different templates: (a) no template; (b) $NaNO_3$; (c) trisodium citrate; (d) PVP.

3.2. SEM analysis of the precursor samples prepared by the hydrothermal process with the assistance of different templates

The SEM images of the precursor samples prepared by the hydrothermal process with the assistance of different templates are shown in Fig. 2. It can be obviously observed that the prepared precursor samples exhibited different morphologies. Without adding any template, the precursor sample exhibits dispersed nanorods morphology (Fig. 2a), which average length is about 2 μm and the diameter is less than 100 nm. The rod-like morphology precursor sample with uniform size was achieved when $NaNO_3$ was used as the template (Fig. 2b), which average length is about 6.5 μm and the diameter is about 300 nm. This means $NaNO_3$ may promote the crystallization process of $Sm(OH)_2Cl$ to form the rod-like structure with bigger size. When trisodium citrate was used as the template, the average size of the prepared precursor sample was 100 nm (Fig. 1c). The reason for this is that trisodium citrate can be used as ligand to form coordination compound with Sm^{3+} ion, which affected the nucleation way and restrained the crystal growth of the precursor sample [19]. In addition, the precursor sample prepared with PVP as the template was irregular particles agglomeration with nonuniform size (Fig. 2d). PVP may play an important role on the growth units of the precursor sample, which can promote the nucleation in the preliminary reaction and restrain the crystallization process of the particles. The irregular agglomeration morphology appeared due to the high surface energy of the particles.

3.3. XRD analysis of the samples prepared by the hydrothermal–calcination process with the assistance of different templates

Fig. 3 shows the XRD patterns of the samples prepared by the hydrothermal–calcination process with the assistance of different templates. It can be observed that Sm_2O_3 has been successfully prepared after the calcination process. The crystal structures of the samples were different in their orientation growth under the influence of different templates. Without adding any template, the peaks of the prepared sample were relatively weak and the main phase was indexed to the cubic phase Sm_2O_3 (JCPDS no. 74-1807), which is shown in Fig. 3a. When $NaNO_3$ was used as the template, the phase composition of the as-prepared sample