



A hydrothermal assisted method to prepare Samarium Tungstate sheets at lowered reaction temperature

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ABSTRACT

In the present work, a hydrothermal-assisted synthesis of sheet-like Samarium Tungstate powders is developed. The structures and morphology of these powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Results show that a new phase of $\text{SmWO}_4(\text{OH})$ was obtained during the hydrothermal reaction. This phase was further used as precursor to obtain Sm_2WO_6 crystallites with much lowered heating temperature during the calcination. Furthermore, both of the $\text{SmWO}_4(\text{OH})$ and Sm_2WO_6 products were found to exhibit sheet-like microstructures without obvious morphological differences, suggesting that controlling the precursor microstructure is an effective approach to maintain the calcined Sm_2WO_6 morphology. Finally, the schematic comparison between hydrothermal assisted method and conventional solid state reaction method was presented.

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1. Introduction

As a kind of typical rare earth tungstate, Samarium Tungstate (Sm_2WO_6 , $\text{Sm}_2\text{W}_2\text{O}_9$ and $\text{Sm}_2\text{W}_3\text{O}_{12}$) were found to present excellent performance in luminescence [1], paramagnetic behavior [2] and conductors in solid oxide fuel cell as anodes materials [3], and photocatalytic water splitting process [4]. At present, solid state reaction (SSR) has been the most frequently applied method for preparing rare earth tungstate powders [5], providing a conventional method for inorganic materials preparation with simplicity, low cost and high yield in the product preparation. However, studies [6,7] have pointed out that lack of homogeneity, large particle sizes with a drastic decrease in the surface area were found during the long time process. This is considered to be the major shortcomings of the SSR method, which is not favorable for various applications of rare earth tungstate powders. On the other hand, wet chemical approaches, especially hydrothermal method, were successfully employed to synthesize rare earth metal tungstates, obtaining products with controllable particles sizes and morphologies [8–10]. Furthermore, hydrothermal method provides not only an effective method to control the product morphology in solution system, but also a homogeneous crystallization environment that allows the synthesis of metastable phases with special properties [11]. Therefore, it is expected that employing wet chemical methods

to prepare Samarium Tungstate materials may lead to enhanced morphology-related properties.

Herein, we report the synthesis of pure Sm_2WO_6 by a topotactical hydrothermal-calcination method. This method were found to form a new phase of $\text{SmWO}_4(\text{OH})$ structure during the hydrothermal process, which is crucial to obtain the Sm_2WO_6 product at lowered temperature. Moreover, a schematic comparison between hydrothermal assisted method and conventional SSR method was presented.

2. Experimental

Generally, analytical grade $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water separately and then mixed together to form a suspension, of which the pH value is then adjusted to 8 before transferring to an autoclave. Then the autoclave is heated at 180 °C for 24 h. After cooled down to room temperature, the products were washed and dried to obtain white powder. Afterwards the powder was calcined to obtain pure Sm_2WO_6 . Detailed experimental procedure is in the Supplementary material.

To compare our approach with reported conventional solid state method [2,12], analytical grade Sm_2O_3 and WO_3 (molar ratio 1:1) were ball-milling mixed and heated at different temperatures (650 °C and 900 °C) for 12 h.

The phase composition of the as-prepared powders were characterized by X-ray diffraction (XRD, D/MAX-2200PC) with Cu

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$K\alpha$ radiation ($\lambda=0.15406$ nm, scanning rate: 8° min^{-1} , 2θ range: 10° – 60°). Surface morphologies of the samples were observed by using scanning electron microscopy (SEM, S4800). Transmission electron microscopy (TEM) images were taken on a JEM-3010 high-resolution transmission electron microscope operated at 300 kV.

3. Results and discussions

Fig. 1 shows the XRD patterns of samples prepared via different methods. It can be seen that various products were obtained through different processes. Fig. 1a (i) presents a pattern that is unable to be indexed in the JCPDS cards with both Sm and W in the crystal structure, but it is highly similar to monoclinic $\text{NdWO}_4(\text{OH})$ phase with JCPDS card No. 74-1798, except for two peaks at around 20° which can be indexed as Sm_2WO_6 (see Supplementary material). Since Sm and Nd are both lanthanides with similar atomic structure, we consider the hydrothermal product may possess a structure which is similar to $\text{NdWO}_4(\text{OH})$. This is further confirmed by EDS result (see Supplementary material), which shows that the molar ratio of Sm:W is 1:1, being exactly the molar ratio of Nd:W in the known $\text{NdWO}_4(\text{OH})$ phase. This indicates that the hydrothermal product may possess similar chemical composition and can be written as $\text{SmWO}_4(\text{OH})$. Similar research on niobates has been reported [13]. For the product calcined at 650°C for 2 h, Fig. 1a (ii) presents an XRD pattern of pure monoclinic Sm_2WO_6 structure, suggesting the $\text{SmWO}_4(\text{OH})$ phase in the hydrothermal product was completely decomposed during the calcination process.

For comparison, conventional solid state reaction (SSR) method of using Sm_2O_3 and WO_3 (molar ratio Sm/W=2) as raw materials to prepare Sm_2WO_6 [2,3] was carried out. From Fig. 1a (iii), it can be found that the SSR product obtained at 650°C shows mixed phases of Sm_2O_3 (major phase), WO_3 and $\text{Sm}_2\text{W}_3\text{O}_{12}$ (minor phases), indicating the SSR method may not be able to obtain Sm_2WO_6 when using Sm_2O_3 and WO_3 as raw materials at 650°C . When the reaction temperature is increased to 900°C , a mixture of Sm_2WO_6 , $\text{Sm}_2\text{W}_2\text{O}_9$ and Sm_2O_3 is found in Fig. 1a (iv). This suggests most of the Sm_2O_3 and WO_3 finally reacted at much higher temperature to produce Sm_2WO_6 and $\text{Sm}_2\text{W}_2\text{O}_9$ while some of the raw material (Sm_2O_3) still remains to become impurities after a long time calcination process.

Combining the above XRD results reveals that the formation of Sm_2WO_6 in our experiment may greatly reduce the calcination temperature with the hydrothermal product ($\text{SmWO}_4(\text{OH})$) as calcination precursor when compared with the SSR method, suggesting a much lower activation energy of phase transition from $\text{SmWO}_4(\text{OH})$ to Sm_2WO_6 structure. This is due to the different mechanisms processes of these two methods. During SSR process, an obvious lattice rearrangement of both Sm_2O_3 and WO_3 structures are needed to form Sm_2WO_6 structure in the product, requiring high energy during the reaction. For the hydrothermal product $\text{SmWO}_4(\text{OH})$, it is considered to be analogous to Sm_2WO_6 structure since they both possess monoclinic structures. This may greatly reduce the energy for the transition between these two phases.

For further comparison of the hydrothermal-assisted and conventional SSR methods, the morphologies of as-prepared samples were observed by SEM images. As can be seen in Fig. 1b and c, the hydrothermal product obtained before and after calcination both exhibit irregular sheet-like microstructures without obvious morphological differences, although their XRD patterns were found to greatly vary from each other in Fig. 1a. When employing the SSR method at 650°C , a mixed microstructure of flake-like and rod-like particles is observed (see Supplementary material), suggesting different crystal structures of the product. This corresponds well with the different phases shown in XRD results. Further increasing the calcination temperature to 900°C leads to an obvious change in morphology (see Supplementary material), presenting two different shapes of the SSR product. By combining these shapes with the XRD patterns, it is believed that at least two different phases were prepared. Concluding from the above discussion, we believe using the hydrothermal product for calcination may effectively control the final product morphology, which is similar to the reported topotactically synthesis approach [14]. However, the SSR method product exhibits different morphologies in the SEM images, resulting in more difficulties of product morphology control.

Typical TEM observations of the $\text{SmWO}_4(\text{OH})$ and Sm_2WO_6 products are shown in Fig. 2. Fig. 2a and b present a single-crystal structure of the as-prepared $\text{SmWO}_4(\text{OH})$ sheet structure. Further measuring the clear lattice spacing (Fig. 2b) finds the (1 0 0) face of the $\text{SmWO}_4(\text{OH})$ structure, indicating the crystal structure of these sheets corresponds well with the XRD results shown in Fig. 1a. No lattice spacing of Sm_2WO_6 can be found. The TEM image of the

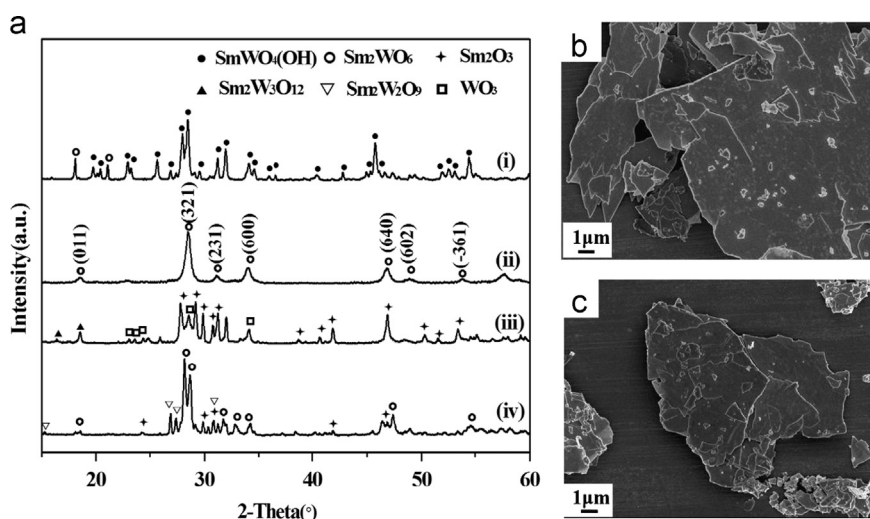


Fig. 1. XRD patterns (a) of samples prepared by different methods: (i) hydrothermal (180°C , 24 h); (ii) calcined (650°C , 2 h) after hydrothermal reaction; (iii) solid state reaction (650°C , 12 h); (iv) solid state reaction (900°C , 12 h), and SEM images of hydrothermal product (b) and calcined hydrothermal product (c).

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