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Short communication

Low-temperature synthesis of $SrWO_4$ nano-particles by a molten salt method

Xiaohui Jiang [a,b,*], Junfeng Ma [b], Yan Yao [b], Yong Sun [b], Zhensen Liu [b], Yang Ren [b], Jun Liu [b], Botao Lin [b]

[a] Department of Physics, Jining University, Qufu 273155, PR China
[b] State Key Laboratory of Green Building Materials, China Building Materials Academy, Beijing 100024, PR China

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Abstract

$SrWO_4$ nano-particles with a scheelite structure were successfully prepared by a molten salt method at 270 °C. The structure, morphology and luminescent property of the resultant powders were characterized by X-ray diffraction (XRD), transmission electron microcopy (TEM), and photoluminescence (PL), respectively. The resultant samples are a pure phase; the size, morphology and properties of $SrWO_4$ nano-particles were affected by the calcining time and weight ratio of the salt to the $SrWO_4$ precursor has little influence on it. PL spectra results also show that the optical properties of the $SrWO_4$ nano-particles strongly relied on their crystallinity.

Keywords: A. Calcination; B. Nano-composites; C. Optical properties

1. Introduction

Tungstate materials have attracted special interest because of their unique structure, luminescent behavior, and potential applications [1–8]. Among those materials, $SrWO_4$ and $CaWO_4$ have found practical importance as laser host materials [9,10] in quantum electronics and scintillators in medical applications. Both of them belong to a body-centered tetragonal system with scheelite crystal structure where WO_4^{2-} molecular ions are loosely bound to Sr^{2+} or Ca^{2+} cations, and their space groups are denoted by C_{4h}^6 [11]. Luminescence of $CaWO_4$ with the scheelite structure is explained as originated from transition from $^3T1 \rightarrow {}^1A1$ in the WO_4^{2-} group [12], and in this article, we assume that the PL property of $SrWO_4$ nano-particles is strongly dependent on their morphology and crystallization besides the transition.

The synthesis of $SrWO_4$ has been offered by several different routes such as solid-state reaction, hydrothermal, sputtering, and Czochralski method [13–16]. However, there are still some limitations, e.g. the as-prepared samples are either irregular in morphology and large in particle size or inhomogeneous in composition. So it is very significant whether in fundamental or applied field to explore new routes to $SrWO_4$, especially for $SrWO_4$ crystallites with nanometer size, which would have unique properties compared to traditional products [17–21].

Molten salt method has attracted considerable attention because of its simple instrumentation and easy manipulation, being environmental friendly and available to a large-scale production. Here, we report on the synthesis of $SrWO_4$ nano-particles by a molten salt method at as low temperature as 270 °C for the first time.

2. Experiment

Sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) and strontium chlorate ($SrCl_2{\cdot}6H_2O$) were used as starting materials, and both of them were of analytical grade without any further purification. Appropriate amounts of $Na_2WO_4{\cdot}2H_2O$ and $SrCl_2{\cdot}6H_2O$ were dissolved in distilled water to form an aqueous solution with 1 M concentration, respectively. The two solutions were mixed together with strongly magnetic stirring at room temperature, and a white precipitate was formed. The precipitate was washed and filtered with distilled water for several times, and dried in

* Corresponding author at: Department of Physics, Jining University, Qufu 273155, PR China. Tel.: +86 537 5226238; fax: +86 537 5226238.
E-mail address: xiaohuijiang721@Gmail.com (X. Jiang).

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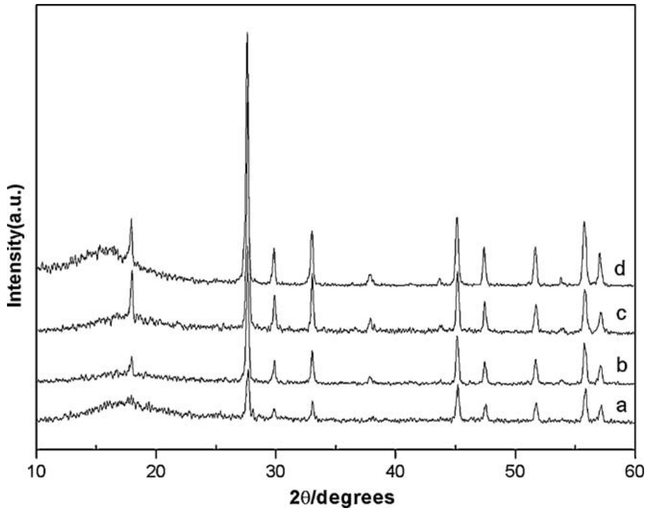

Fig. 1. XRD patterns of the samples synthesized at 270 °C for (a) 8 h, (b) 10 h, (c) 12 h and (d) 24 h, respectively, with 6:1 weight ratio of the salt to the $SrWO_4$ precursor.

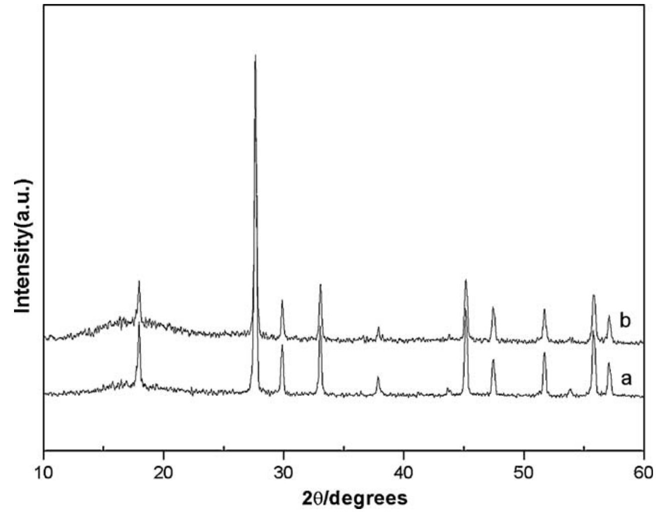

Fig. 2. XRD patterns of the samples synthesized at 270 °C for 8 h, with different weight ratios of the salt to $SrWO_4$ precursor: (a) 1:1 and (b) 10:1.

an oven at 60 °C for 5 h to obtain $SrWO_4$ precursors. By ball milling in absolute ethanol for 1 h, the as-prepared $SrWO_4$ precursors was mixed with $LiNO_3$ salt, where the weight ratio of the salt to the $SrWO_4$ precursor was selected as 1:1, 6:1 and 10:1, respectively. Then, the mixture was put into an alumina crucible, and calcined at 270 °C with the holding time ranging from 8 h to 24 h. Finally, the resultant products were thoroughly washed and filtered with distilled water and absolute ethanol, and dried at 60 °C in an oven for 5 h. XRD analysis was carried out using an X-ray powder diffractometer (XRD, D8 ADVANCE, Germany) with Cu Kα radiation. The morphology and particle size of the as-prepared powders were observed by using a transmission electron microscope (TEM, H-8100, Japan) and scanning electron microscope (SEM, XL30 S-FEG, Holland). The room temperature luminescent spectra were recorded on a spectrofluorometer (PL, Fluorolog-3, Jobin Yvon Inc, USA).

3. Results and discussion

Fig. 1 shows XRD patterns of the samples synthesized by the molten salt method at 270 °C for the holding time of 8 h, 10 h,

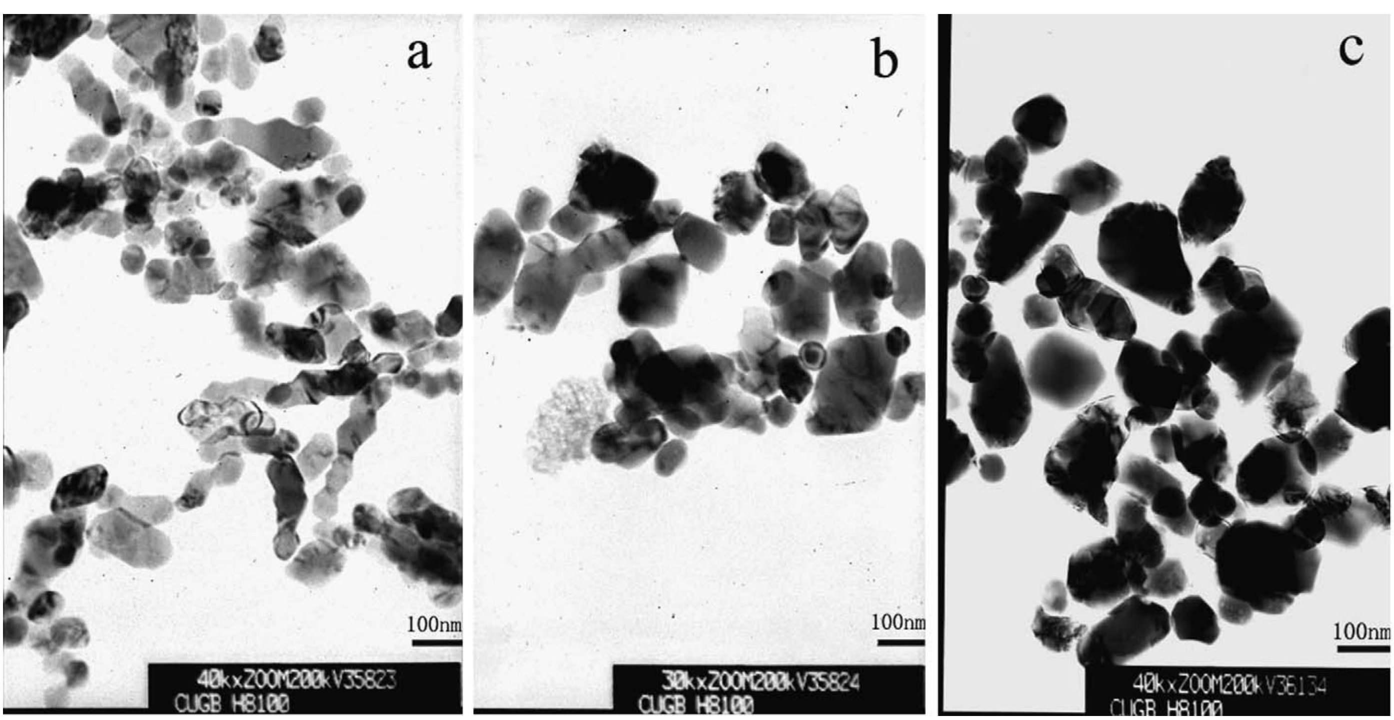

Fig. 3. TEM images of $SrWO_4$ crystallites obtained at 270 °C for different holding times: (a) 8 h, (b) 12 h, and (c) 24 h, respectively, with 6:1 weight ratio of the salt to $SrWO_4$ precursor.

12 h and 24 h, respectively; where 6:1 weight ratio of the salt to the $SrWO_4$ precursor was used. All of them can be indexed to a pure tetragonal phase of $SrWO_4$ with a scheelite-type structure, and well consistent with the reported data (JCPDS: 85-0587), no other impurities can be found. Moreover, the intensity of the diffraction peaks progressing increases as the calcining time is prolonged.

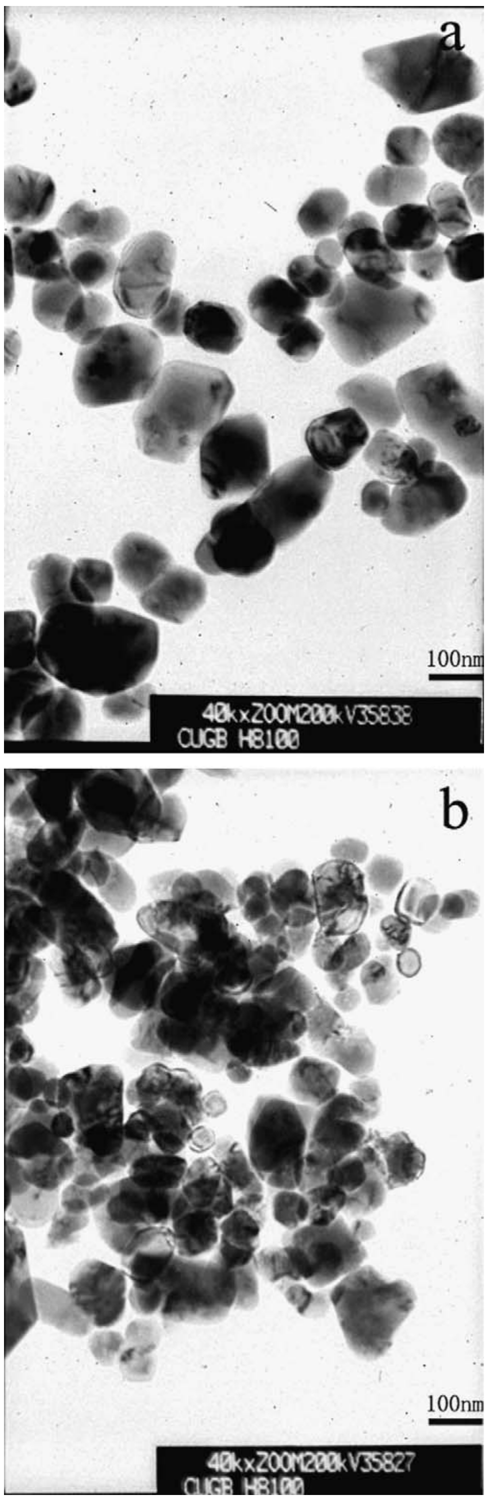

Fig. 4. TEM images of the $SrWO_4$ crystallites obtained at 270 °C for 8 h with the weight ratio of the salt to the $SrWO_4$ precursor: (a) 1:1 and (b) 10:1, respectively.

Fig. 2 shows XRD patterns of the samples synthesized by the molten salt method at 270 °C for 8 h, varying the weight ratio of the salt to the $SrWO_4$ precursor 1:1 and 10:1, respectively. It is obvious that the two XRD patterns are similar, and all the patterns can be indexed to a pure tetragonal phase of $SrWO_4$. As shown in Fig. 2, further increasing the ratios of the salt to the precursor does not have obvious changes in the diffraction peaks intensity.

Fig. 3 shows TEM images of $SrWO_4$ crystallites obtained at 270 °C for the holding time 8 h, 12 h and 24 h, respectively, with 6:1 weight ratio of the salt to $SrWO_4$ precursor. It can be found that the particle size of the $SrWO_4$ crystallites grows bigger as the holding time increases, which also confirm the above XRD results. On the other hand, as the holding time increases, the morphology of the $SrWO_4$ crystallites become more homogeneous and also have better crystallinity.

Fig. 4 shows the effect of the weight ratio of the salt to the precursor on $SrWO_4$ crystallizing morphology, where $SrWO_4$ crystallites were obtained by the molten salt method at 270 °C for 8 h, with the weight ratio of the salt to $SrWO_4$ precursor 1:1 and 10:1, respectively. One can find that the morphologies of the $SrWO_4$ crystallites become inhomogeneous with the increasing weight ratio of the salt, which further suggests that the weight ratio of the salt has little influence on the morphologies.

Fig. 5 shows the representative PL spectra of the $SrWO_4$ crystallites synthesized by the molten salt method at 270 °C for the holding time 8 h, 10 h, 12 h and 24 h, respectively, with the weight ratio of the salt to the $SrWO_4$ precursor 6:1. Both samples exhibit a same emission peak position around 430 nm using a 350 nm excitation line. It indicates that PL spectra of nano-sized $SrWO_4$ crystallites are strongly relied on their particle size and crystallinity. The better crystallinity, the higher PL emission peak is.

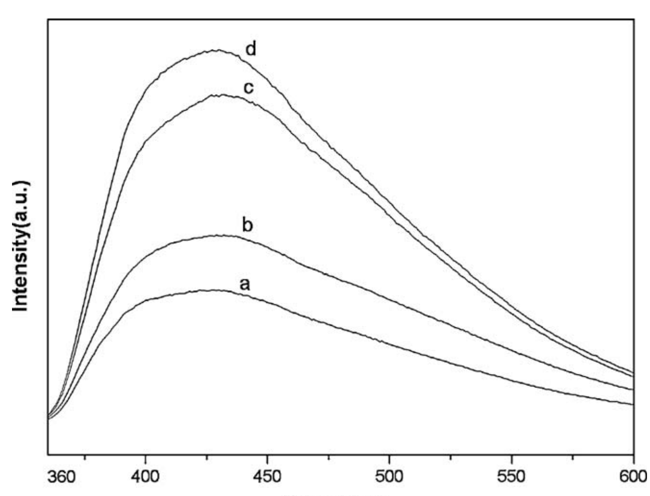

Fig. 5. PL spectra of $SrWO_4$ crystallites obtained at 270 °C for different holding times: (a) 8 h, (b) 10 h, (c) 12 h, and (d) 24 h, respectively; with 6:1 weight ratio of the salt to $SrWO_4$ precursor.

4. Conclusion

$SrWO_4$ nano-particles can be successfully synthesized at 270 °C by a molten salt method. The particle size, morphology, and crystallinity of $SrWO_4$ crystallites are strongly relied on the holding time, and weight ratio of $LiNO_3$ salt to $SrWO_4$ precursor has little influence on it. The improved PL properties of $SrWO_4$ crystallites are strongly relied on their particle size and crystallinity. The better crystallinity, the higher PL emission peak is.

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