Molten salt synthesis of SrFeO₃ nanocrystals

Jun YANG,^{*,†} Runsheng LI,^{*,**} Xiaoci LI,^{*} Yulin LONG,^{*} Junyi ZHOU^{*} and Yuanming ZHANG^{*}

^{*}Department of Chemistry, Jinan University, Guangzhou 510632, People's Republic of China

^{**}Guangzhou No.2 Middle School, Guangzhou 510530, People's Republic of China

Pure perovskite compound SrFeO₃ nanocrystals were successfully synthesized in molten NaNO₃–KNO₃ eutectic with Na₂O₂ from a mixture of strontium nitrate and ferric nitrate. The effect of metal precursors, salt medium, annealing temperature (mainly 400–800°C), and oxidizing properties of the melt on the phase composition, crystallite size and morphology of the resulting metal oxides were systematically studied by simultaneous TG/DSC, X-ray diffraction (XRD), scanning electron microscopy (SEM) methods. The results showed that the formation of the SrFeO₃ phase mainly depended on the nature of the metal precursor and salt medium. It was found that metal nitrates are the suitable precursors and NaNO₃–KNO₃ eutectic with Na₂O₂ is the suitable salt medium, which results in the formation of pure SrFeO₃ nanocrystals at a much lower temperature of 400°C.

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1. Introduction

Perovskite-type compound SrFeO₃ and related compounds have been one of the most attractive and interesting mixed oxides due to their innovative use in advanced technologies. These oxides have been used as functional material in many fields due to its special properties, including catalysts for direct methanol fuel cell,¹⁾ gas sensing devices,^{2)–6)} magnetic materials,^{7),8)} photocatalysts,⁹⁾ and redox materials for application in a membrane reactor.¹⁰⁾

The synthesis of SrFeO₃ and related compounds has been achieved by many methods including mechanochemical solid reaction,¹¹⁾ hydrothermal synthesis,¹²⁾ combustion synthesis,¹³⁾ co-precipitation method,¹⁴⁾ sol-gel method^{15),16)} and spray pyrolysis method.¹⁷⁾ Traditionally, strontium oxoferrates have been prepared by solid state reaction between SrCO₃ and Fe₂O₃ at a high calcination temperature (≈1300°C and above),¹⁸⁾ which is associated with drawbacks such as diffusional constrain and high temperatures resulting in uncontrolled particle size. Senzaki et al.¹⁷⁾ prepared strontium oxoferrate powders by spray pyrolysis of an aqueous solution of mixed metal nitrates and reported that phase-pure materials were typically obtained only at the highest temperatures investigated ($T > 1100^\circ\text{C}$). Furthermore, to obtain desired final powders with good crystalline structures, all the wet chemical methods need a very high calcination temperature, which waste time and energy.

Chemical methods of synthesis of materials play a crucial role in the design and discovery of new materials. It is well known that the molten salt synthesis method is one of the simplest, most versatile, and cost-effective approaches available for obtaining a pure perovskite phase at a relatively low temperature for a shorter soaking time. The intrinsic scalability, flexibility, and facility of this technique render it attractive for the fabrication of a range of ternary metal oxides. K_xNa_{1-x}NbO₃ with perovskite structure was produced in a molten salt with a Na₂CO₃/K₂CO₃ molar ratio of 1:1 at 650–900°C.¹⁹⁾ SrTiO₃ was produced in molten NaCl–KCl eutectic at 700°C, which was much lower than that (generally >1000°C) of the conventional solid state reactions.²⁰⁾ La-doped

NaTaO₃ was produced in molten Na₂SO₄–K₂SO₄ at 900°C for 0.5–1 h.²¹⁾ Single-crystalline perovskite BaZrO₃ particles were obtained using BaC₂O₄ and ZrO₂ as precursors, and NaOH/KOH as the molten reaction at 993 K.²²⁾ Rare earth orthoferrites of the general formula LnFeO₃ (Ln = La, Pr, Nd) phases were synthesized in molten NaOH flux at 673 K,²³⁾ and LaMO₃ (M = Mn, Fe, Co, Ni) were obtained in molten nitrates or nitrites.²⁵⁾ As far as we know, however, there is no report on the synthesis of SrFeO₃ perovskite using molten salt synthesis method.

In this communication, we systematically investigate the effect of metal precursor, salt medium, annealing temperatures (mainly 400–800°C) and annealing time (mainly 1–48 h) on product composition, morphology, size and shape in the synthesis of crystalline SrFeO₃ perovskite particles.

2. Experimental

2.1 Materials and synthesis

Principal raw materials: Fe(NO₃)₃·9H₂O (Shantou Guanghua Chemical Factory, 98.5%), Sr(NO₃)₂ (Tianjin Kernel Chemical Reagents Development Centre, 99.5%), KNO₃ (Guangzhou Chemical Reagent Factory, 99%), NaNO₃ (Tianjin Damao Chemical Reagent Factory, 99%), Na₂O₂ (Tianjin Dagu Chemical Co. Ltd., 92.5%).

The mixture of strontium and ferric precursors was obtained by mixing Sr(NO₃)₂ with Fe(NO₃)₃·9H₂O, SrCl₂·6H₂O with FeCl₃, and SrSO₄ with Fe₂(SO₄)₃, respectively, with a molar ratio of 1:1. Then salt medium, NaOH, KOH, NaNO₃–KNO₃ (molar ratio 1:1) eutectic, NaNO₃–KNO₃ eutectic with Na₂O₂ (molar ratio 2:2:1), NaCl–KCl–Na₂O₂ (molar ratio 2:2:1), or Na₂SO₄–K₂SO₄–Na₂O₂ (molar ratio 2:2:1), was mixed with the mixture of metal precursors in a molar ratio of Sr²⁺:Fe³⁺:NaOH = 1:1:20, Sr²⁺:Fe³⁺:KOH = 1:1:20, Sr²⁺:Fe³⁺:NaNO₃–KNO₃ = 1:1:20, Sr²⁺:Fe³⁺:NaNO₃–KNO₃ eutectic with Na₂O₂ = 1:1:25, Sr²⁺:Fe³⁺:NaCl–KCl–Na₂O₂ = 1:1:25 and Sr²⁺:Fe³⁺:Na₂SO₄–K₂SO₄–Na₂O₂ = 1:1:25, respectively. The mixture was placed into the ceramic crucible with a layer of corrosion resistant borosilicate ceramic glaze inside and kept at different temperatures for 1–48 h in a muffle furnace. After cooling down to room temperature naturally, the soluble compounds of the reaction

[†] Corresponding author: J. Yang; E-mail: tyangj@jnu.edu.cn

Table 1. Reaction conditions and results of the synthesis of SrFeO₃ powders in molten salts

No.	Reagent	Flux	Temperature (°C)	Time (h)	Products	Color	Crystallite size (nm)
01	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaNO ₃ -KNO ₃	400–800	24	SrFeO ₃ , SrO, Fe ₂ O ₃	Reddish-brown	—
02	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaOH	400–800	24	SrO, Fe ₂ O ₃	Reddish-brown	—
03	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	KOH	400–800	24	SrO, Fe ₂ O ₃	Reddish-brown	—
04	SrCl ₂ -FeCl ₃	NaCl-KCl-Na ₂ O ₂	500–800	24	SrFeO ₃ , SrO, Fe ₂ O ₃	Reddish-black	—
05	SrSO ₄ -Fe ₂ (SO ₄) ₃	Na ₂ SO ₄ -K ₂ SO ₄ -Na ₂ O ₂	500–800	24	SrFeO ₃ , SrSO ₄	Reddish-black	—
06	SrCl ₂ -FeCl ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	500–800	24	SrFeO ₃ , SrO, Fe ₂ O ₃	Reddish-black	—
07	SrSO ₄ -Fe ₂ (SO ₄) ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	500–800	24	SrFeO ₃ , SrO, Fe ₂ O ₃	Reddish-black	—
08	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	400	24	SrFeO ₃	Black	32
09	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	450	1–48	SrFeO ₃	Black	28–42
10	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	500	24	SrFeO ₃	Black	34
11	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	600	24	SrFeO ₃	Black	35
12	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	700	24	SrFeO ₃ , SrO, Fe ₂ O ₃	Reddish-black	—
13	Sr(NO ₃) ₂ -Fe(NO ₃) ₃	NaNO ₃ -KNO ₃ -Na ₂ O ₂	800	24	amorphous	Reddish-black	—
14	SrCO ₃ -Fe ₂ O ₃	—	850	12	SrFeO ₃ , Sr ₂ Fe ₂ O ₅	—	Ref. 18)

mixture dissolved in distilled water. The resulting solid product was filtered, washed with distilled water and dried at 80°C in a vacuum oven.

2.2 Characterization

The thermal behavior of the powder mixtures was determined by thermogravimetric analysis (TG/DSC) using a SDT Q600 V8.3 Build 101 instrument in an air stream from room temperature to 900°C with a heating rate of 10°C min⁻¹. Powder XRD patterns of the SrFeO₃ samples were recorded on a Siemens D-5000 diffractometer with monochromatized Cu Kα1 radiation ($\lambda = 0.15405$ nm) at 40 kV, 30 mA, at a scanning rate of 8°/min. SEM images were taken on a JEOL JSM-6330 F scanning electron microscopy. Sodium and potassium contents of the SrFeO₃ samples were determined using inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussions

3.1 Synthesis and characterization of SrFeO₃ nanocrystals

The molten salt synthesis method is one of the simplest, most versatile, and cost-effective approaches available for obtaining a pure perovskite phase at a relatively low temperature for a shorter soaking time. Physicochemical properties of the oxide powders synthesized by molten salt processes mainly depend on the nature of metal precursor and salt medium used. In order to identify the suitable metal precursor and salt medium for the synthesis of SrFeO₃, we tested various salt mediums such as NaOH, KOH, NaNO₃-KNO₃ (molar ratio 1:1) eutectic, NaCl-KCl-Na₂O₂ (molar ratio 2:2:1), Na₂SO₄-K₂SO₄-Na₂O₂ (molar ratio 2:2:1) and NaNO₃-KNO₃ eutectic with Na₂O₂ (molar ratio 2:2:1), and various metal precursors such as Sr(NO₃)₂-Fe(NO₃)₃·9H₂O, SrCl₂·6H₂O-FeCl₃ and SrSO₄-Fe₂(SO₄)₃. Among them, we found that Sr(NO₃)₂ and Fe(NO₃)₃·9H₂O are the best metal precursors and NaNO₃-KNO₃ eutectic with Na₂O₂ is the best salt medium, which resulted in the formation of pure and nano-size SrFeO₃ powders at a much lower temperature of 400°C. The results of the synthesis of SrFeO₃ in molten salts are summarized in Table 1.

In order to obtain strontium ferrum with Sr:Fe molar ratio 1:1, four systems were tested: Sr(NO₃)₂-Fe(NO₃)₃·9H₂O in NaNO₃-KNO₃ eutectic (A1); NaOH (A2); KOH (A3); and NaNO₃-KNO₃ eutectic with Na₂O₂ (A4).

In the case of system A1, A2 and A3, reddish-brown powders were obtained in the temperature range of 400–800°C. For

Fig. 1. XRD patterns of samples prepared from Sr(NO₃)₂-Fe(NO₃)₃·9H₂O in NaNO₃-KNO₃ eutectic with Na₂O₂ at different temperatures.

system A1, weak signals due to SrFeO₃ were observed in the powder diffraction patterns, whereas only SrO and Fe₂O₃ phases were obtained in system A2 and A3. In order to obtain pure SrFeO₃, Na₂O₂ was added to increase the oxidising nature of the system A1. Black SrFeO₃ nanocrystals were obtained in the temperature range of 400–600°C by adding Na₂O₂ to system A1. As shown in Fig. 1, the XRD patterns of samples could be assigned as cubic SrFeO₃ (JCPDS, 34-0641). No extra peaks were observed in the powder diffraction patterns, indicating that the obtained samples were single phase in nature. Sodium and potassium contents of the SrFeO₃ samples prepared in system A4 were determined using inductively coupled plasma mass spectrometry and these SrFeO₃ samples have sodium content of 0.08–0.12 wt % and potassium content of 0.03–0.06 wt %.

The TG and DSC curves of the mixture of Sr(NO₃)₂ and Fe(NO₃)₃·9H₂O in NaNO₃-KNO₃ eutectic with and without Na₂O₂ are shown in Figs. 2(a) and 2(b), respectively. Below 250°C, removal of the water of crystallization and decomposition of the nitrates cause the weight loss and the weight loss is about 16 and 17% in system A1 and A4, respectively. At 470°C, there is a very weak exothermal peak in DSC curves of system A1 [Fig. 2(a)], whereas a very strong exothermal peak was observed in DSC curves of system A4 [Fig. 2(b)]. At this temperature, the

Fig. 2. TG and DSC curves of $\text{Sr}(\text{NO}_3)_2\text{-Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ in (a) $\text{NaNO}_3\text{-KNO}_3$ eutectic; (b) $\text{NaNO}_3\text{-KNO}_3$ eutectic with Na_2O_2 .

reaction between SrO and Fe_2O_3 occurred, which is accompanied by the release of heat²⁴⁾ and XRD signals due to SrFeO_3 were recognized in the XRD patterns of the samples. In the temperature range of 410–490, the weight loss is about 4% in system A4. The weight loss at 470°C in the A4 system as shown in Fig. 2(b) is attributed to decomposition of Na_2O_2 , and the oxygen released from Na_2O_2 facilitated the reaction between SrO and Fe_2O_3 . However, in the case of system A1, the reaction between SrO and Fe_2O_3 was not thorough and the resulting product was a mixture of SrFeO_3 , SrO , and Fe_2O_3 phases, while a pure cubic SrFeO_3 phase was obtained in system A4. This strongly suggests that the effect of Na_2O_2 could facilitate the reaction between SrO and Fe_2O_3 and the phase $\text{Sr}_3\text{Fe}_2\text{O}_{7-8}$ transform to SrFeO_3 phase, so it could improve the purity of SrFeO_3 . By raising the temperature to 700°C, a very strong endothermic peak was observed in DSC curves (Fig. 2) and the weight loss may be regarded as the decomposition temperature of molten salts.²⁵⁾ As the certification of XRD patterns in Fig. 1, at 700°C, SrFeO_3 began to decompose and very weak signals due to SrFeO_3 and Fe_2O_3 appeared. Above 800°C, amorphous powders were obtained.

In order to investigate how the different temperatures affect the microstructure of SrFeO_3 , SEM analyses of samples synthesized at 400–600°C in $\text{NaNO}_3\text{-KNO}_3$ eutectic with Na_2O_2 (system A4) are presented in Fig. 3. It can be clearly seen that SrFeO_3 prepared at different temperatures exhibited varied microstruc-

Fig. 3. SEM photographs of SrFeO_3 prepared at (a) 400°C; (b) 450°C; (c) 500°C; (d) 600°C in $\text{NaNO}_3\text{-KNO}_3$ eutectic with Na_2O_2 .

Fig. 4. XRD patterns of samples prepared from $\text{Sr}(\text{NO}_3)_2\text{-Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ in $\text{NaNO}_3\text{-KNO}_3$ eutectic with Na_2O_2 at 450°C for different times.

tures in particle size and morphology. The SrFeO_3 powders obtained at 400°C are of agglomerates with fine particles, while those obtained at 450°C are of fine cubic particles, exhibiting a more uniform morphology. Further increasing the annealing temperature, the particle size increased sharply from about 1 μm at 450°C to 4 μm at 500–600°C.

3.2 Effect of annealing time on the crystallinity of SrFeO_3

Figure 4 shows the XRD patterns of the samples prepared in molten $\text{NaNO}_3\text{-KNO}_3$ eutectic with Na_2O_2 at 450°C at different annealing time. Black SrFeO_3 powders were obtained at 450°C for 1–48 h. The diffraction peak intensity of SrFeO_3 powders obtained after an annealing time shorter than 4 h was weak and the crystallite size was about 27 nm. With the increase of annealing time, the intensity of SrFeO_3 peaks increased and the crystallite size increased from 27 nm to about 40 nm (annealing time 12 h). However, further increasing the annealing time to 48 h, there was a trivial change in diffraction peak density of the as-synthesized SrFeO_3 , indicating the effect of annealing time on crystallinity of SrFeO_3 became insignificant.

Fig. 5. SEM photographs of SrFeO_3 prepared at 450°C for (a) 2 h; (b) 6 h; (c) 24 h; (d) 48 h in $\text{NaNO}_3\text{--KNO}_3$ eutectic with Na_2O_2 .

SEM micrographs of SrFeO_3 synthesized at 450°C at different annealing time are presented in Fig. 5 and a time-dependent morphology evolution process from agglomerates to uniform cubic shapes can be observed. Large-scale SrFeO_3 contained agglomerates of primary fine particles were obtained after 2 h [Fig. 5(a)]. Prolonging the annealing time to 6–24 h, SrFeO_3 with cubic shapes became more and more, but in contrast, the agglomerates gradually diminished (images b and c in Fig. 5). SrFeO_3 powders obtained after 24 h are of fine cubic particles, exhibiting a more uniform morphology. With the increase of annealing time, the particle size decreased from about 3–4 μm to 1 μm .

4. Conclusions

Flux synthetic conditions, using a molten $\text{NaNO}_3\text{--KNO}_3$ eutectic with Na_2O_2 at $400\text{--}600^\circ\text{C}$, can be used to prepare SrFeO_3 nanocrystals in high purity and homogeneity at much lower temperature and shortened reaction time compared to conventional solid-state techniques. SrFeO_3 nanocrystals can be synthesized in molten $\text{NaNO}_3\text{--KNO}_3$ eutectic with Na_2O_2 rather than molten NaOH , KOH , and $\text{NaNO}_3\text{--KNO}_3$ eutectic. The addition of Na_2O_2 facilitated the reaction between SrO and Fe_2O_3 , leading to the formation of SrFeO_3 at a much lower temperature of 400°C , which was much lower than that ($\approx 1300^\circ\text{C}$ and above) of the conventional solid state reactions.

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