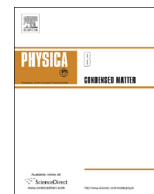




ELSEVIER

Contents lists available at ScienceDirect

Physica B

journal homepage: [www.elsevier.com/locate/physb](http://www.elsevier.com/locate/physb)

# Reaction kinetics of the double perovskite $\text{Sr}_2\text{FeMoO}_6$ by gas–solid reactions

J.L. Valenzuela<sup>a,b</sup>, T.E. Soto<sup>b,c</sup>, J. Lemus<sup>a</sup>, O. Navarro<sup>b</sup>, R. Morales<sup>a,\*</sup>

<sup>a</sup> Instituto de Investigaciones Metalúrgicas, Universidad Michoacana de San Nicolás de Hidalgo, Ciudad Universitaria, Francisco J. Mújica S/N, Colonia Felicitas del Ro, C.P. 58030 Morelia, Mexico

<sup>b</sup> Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, 04510 Mexico D.F., Mexico

<sup>c</sup> Facultad de Ciencias Físico-Matemáticas, Universidad Michoacana de San Nicolás de Hidalgo, Ciudad Universitaria, Francisco J. Mújica S/N, Colonia Felicitas del Río, C.P. 58030 Morelia, Mexico

## ARTICLE INFO

### Article history:

Received 26 December 2013

Accepted 18 July 2014

Available online 30 July 2014

### Keywords:

Double perovskite  
Thermogravimetric  
Strontium ferrate  
Thermal decomposition

## ABSTRACT

Double perovskite  $\text{Sr}_2\text{FeMoO}_6$  is characterized by its colossal magnetoresistance, however, its production route is not well established. Therefore, the objective of this work is to study the reaction kinetics involved in the formation of  $\text{Sr}_2\text{FeMoO}_6$ . Firstly, precursor phases  $\text{Sr}_2\text{Fe}_2\text{O}_5$  and  $\text{SrMoO}_4$  were synthesized by gas–solid reactions from starting reagents such as  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$  y  $\text{MoO}_3$ . The thermogravimetric technique was employed to analyze the kinetics of formation of the double perovskite from the precursor phases given the optimized process variables. Microstructural characterization of the products obtained was performed by X-ray diffraction and Rietveld analysis. Results showed that the instability of  $\text{SrFeO}_{2.5}$  during the reduction stage led to a formation of a disordered double perovskite  $\text{Sr}_2\text{Fe}_{0.71}\text{Mo}_{1.29}\text{O}_6$ .

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

The double perovskite  $\text{Sr}_2\text{FeMoO}_6$  (SFMO) has magnetotransport properties that have drawn attention in view of their application in magnetic recording devices [1]. This compound is half-metallic ferromagnetic oxide with colossal magnetoresistance (CMR) and Curie temperature of  $\sim 400$  K [2,3]. The ordered lattice structure of SFMO consists of body centered cubic lattice with alternating  $\text{FeO}_6$  and  $\text{MoO}_6$  octahedra at the corners, strontium atom in its center [4]. In this configuration, the Fe has a +3 valence (spin quantum  $S=5/2$ ) and Mo has +5 valence ( $S=5/2$ ) with antiferromagnetic superexchange interaction between  $S=5/2$  spins and  $S=1/2$  spins which might produce the large ferromagnetic magnetization below  $T_C$  [2,5].

The most common method for the synthesis of SFMO is by solid state reaction, that is, calcination and reduction of initial reactants in controlled atmosphere [6–9]; TGA studies on the formation of SMFO are very limited; Jacobo et al. [10] performed a TGA experiment on precursor samples, prepared by wet chemical method towards the formation of SMFO, to only determine the water content in the sample. On the other hand, Hu et al. [11] showed that the ordering of the Fe and Mo cations in SFMO

structure improves with increasing sintering time. Kircheisen et al. [12] reported that the SFMO is stable between  $10.2 \leq \log(p\text{O}_2) \leq -13.7$  at  $1200^\circ\text{C}$  below this range the SFMO is reduced into a lower oxide, and above that range, it decomposes into  $\text{SrMoO}_4$  and  $\text{SrFeO}_{3-x}$ . This work studies the kinetics of the reactions for the formation of SFMO by thermogravimetric analysis (TGA) under well controlled experimental conditions.

## 2. Material and methods

Reagent powders of  $\text{Fe}_2\text{O}_3$  (Alfa Aesar, 99.5%),  $\text{SrCO}_3$  (Aldrich, 99.9%) and  $\text{MoO}_3$  (Merck, 99.5%) were used to prepare separately the precursor phases  $\text{SrFeO}_{2.5}$  ( $\text{Sr}_2\text{Fe}_2\text{O}_5$ ) and  $\text{SrMoO}_4$  (SMO). Reagent powders were first dried at  $100^\circ\text{C}$  for 10 h in a muffle furnace. Both the precursor powders were synthesized by weighing stoichiometric ratios of  $\text{SrCO}_3/\text{Fe}_2\text{O}_3$  and  $\text{SrCO}_3/\text{MoO}_3$ . The powders were thoroughly mixed in an agate mortar for 30 min. Then, the powder mixtures were calcined in helium and then heated in a reducing atmosphere to form the double perovskite  $\text{Sr}_2\text{FeMoO}_6$ , the experimental details are explained below.

### 2.1. Thermogravimetry

To follow the gas solid reactions involved in the formation of  $\text{Sr}_2\text{FeMoO}_6$ , thermogravimetric analyses (TGA) were performed

\* Corresponding author. Tel.: +52 443 3223554.

E-mail address: [rmorales@umich.mx](mailto:rmorales@umich.mx) (R. Morales).

isothermally and nonisothermally using a Setaram, Setsys Evolution 16/18, which has an accuracy of 0.03  $\mu\text{g}$  and is fully controlled through a personal computer. The calcination process was performed nonisothermally under a stream of helium gas (99.999%) with an oxygen concentration of  $< 3 \times 10^{-6}$  atm. The reduction experiments were carried out in a mixture of 5% $\text{H}_2$ /He and 1.25%  $\text{H}_2$ /He for nonisothermal and isothermal experiments, respectively. The purity of  $\text{H}_2$  was 99.999%. 40 mg of powder sample was held into an alumina crucible (10 mm ID  $\times$  1 mm H) which was hung from one end of the beam balance, using a 0.4 mm diameter Pt wire, and placed in the hot zone of the vertical furnace. The mass change during TGA experiments was recorded at 2 s intervals. The reactor furnace was made of dense alumina with an 18 mm inner diameter. The temperature of the furnace was controlled by a Pt–Pt/13% Rh (S-type) thermocouple placed just below the crucible. To perform nonisothermal experiments the analysis chamber was evacuated to less than 10 Pa, then the chamber was back filled with the desired working gas (He or  $\text{H}_2$ /He). Once the atmospheric pressure was achieved, the reaction chamber was heated at a rate of 5  $^\circ\text{C}/\text{min}$  under a constant flow of the working gas of 100 ml/min. When the maximum temperature was reached, the furnace chamber was cooled down to room temperature at a maximum rate of 50  $^\circ\text{C}/\text{min}$  without changing the parameters of the working gas. For the isothermal reduction experiment, after the evacuation stage, the reaction chamber was heated at a rate of 40  $^\circ\text{C}/\text{min}$ , under 40 ml/min of He gas, up to 1150  $^\circ\text{C}$ . After the temperature in the chamber was stabilized,  $\text{H}_2$  gas was led into the system for the reduction reaction to start. When no more significant weight loss was observed, the experiment was terminated manually allowing the furnace to reach room temperature in about 30 min. The reducing atmosphere was kept during the cooling stage to avoid oxidation of the sample.

## 2.2. X-ray diffraction and Rietveld refinement

Calcined and reduced samples were structurally studied by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer at 30 mA, 50 kV and 0.2 $^\circ$ /12 s step size with  $\text{Cu K}\alpha$  radiation. Rietveld method was employed for the determination of the crystalline structure using a computer software GSAS (Toby, 2001). The structures used for refinement were  $\text{Sr}_2\text{Fe}_{0.8}\text{Mo}_{1.2}\text{O}_6$  and  $\text{SrFeO}_{2.7341}$  that correspond to the Powder Diffraction Files (PDF) 98-006-9936 and 98-010-5739, respectively.

## 3. Results

The weight loss obtained from the calcination experiments of mixtures of  $\text{SrCO}_3/\text{MoO}_3$  and  $\text{SrCO}_3/\text{Fe}_2\text{O}_3$  powders indicated the complete formation of SMO and  $\text{SrFeO}_{2.5}$  precursor phases, respectively. These findings were confirmed by XRD analyses as seen in Fig. 1.

The obtained Bragg peaks revealed that the precursor phases were highly crystalline and matched the reference patterns of  $\text{SrFeO}_{2.5}$  ( $\text{Sr}_2\text{Fe}_2\text{O}_5$ ) (PDF: 98-000-3411) and  $\text{SrMoO}_4$  (PDF: 98-000-7961); no other phases were detected in each precursor phase.

The nonisothermal reduction of the mixed precursors is shown in Fig. 2, the total weight loss from room temperature up to 1250  $^\circ\text{C}$  was 7.5%. To understand the process of weight loss in the reduction of the double perovskite, each precursor was reduced separately as shown in Fig. 3. As it can be seen the weight loss for SMO suggests that the reduction reaction starts at about 850  $^\circ\text{C}$  and ends about 1150  $^\circ\text{C}$ , in contrast, the weight loss of  $\text{SrFeO}_{2.5}$  starts from room temperature and keeps losing weight at the end of the heating cycle.

Fig. 4 shows the percentage weight loss curves of the  $\text{SrFeO}_{2.5}$  for different atmospheres, it can be seen that the oxide phase loses weight from very low temperatures independent of the atmosphere.

Based on the above preliminary experiments, the optimum process parameters were chosen to perform an isothermal reduction experiment as shown in Fig. 5. It is clearly seen that after 120 min, the reduction reaction seemed to keep losing weight at a very low rate.

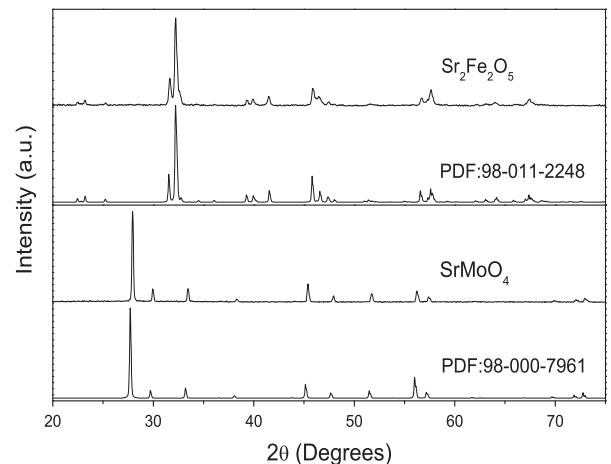


Fig. 1. XRD results of the precursor powders  $\text{SrFeO}_{2.5}$  and  $\text{SrMoO}_4$  obtained by calcination of the reagents  $\text{SrCO}_3/\text{Fe}_2\text{O}_3$  and  $\text{SrCO}_3/\text{MoO}_3$ , respectively. Also shown are the corresponding reference standards.

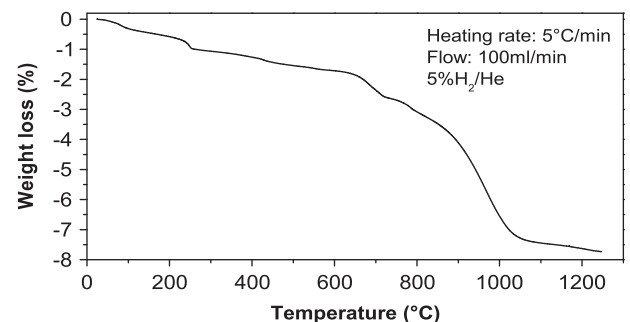


Fig. 2. Nonisothermal reduction curve of mixed precursors, SMO and  $\text{SrFeO}_{2.5}$ , by TGA.

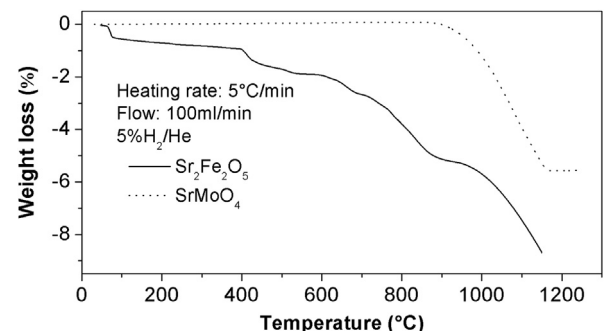


Fig. 3. Kinetic behavior of precursor phases,  $\text{SrMoO}_4$  and  $\text{Sr}_2\text{Fe}_2\text{O}_5$ , under non-isothermal reducing conditions.

Download English Version:

<https://daneshyari.com/en/article/1809341>

Download Persian Version:

<https://daneshyari.com/article/1809341>

[Daneshyari.com](https://daneshyari.com)