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Formation kinetics of Sr_2FeMoO_6 double perovskite

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The formation kinetics of Sr_2FeMoO_6 (SFMO) was diagnosed during the solid-state reaction of $SrFeO_{3-x}$ and $SrMoO_4$ at different temperatures and heating rates. The reaction kinetics was analyzed by X-ray diffractometer, and the extent of the reaction was quantified by the internal standard method. The non-isothermal kinetic empirical model was proposed to evaluate the activation energy and rate constant of SFMO and further justified to be valid to picture the reaction kinetics of SFMO.

1. Introduction

Recently, the magnetotransport properties of the ordered double-perovskite Sr_2FeMoO_6 (SFMO) have been exhaustively re-examined in view of their potential applications in magnetic recording devices for which large magnetoresistance at low field is desirable. The ideal structure of this $A_2BB'O_6$ double perovskite consists of an ordered array of Fe and Mo atoms alternating on the B and B′ site. A large antiferromagnetic superexchange interaction between the $s = 5/2$ spins of Fe^{3+} and $s = 1/2$ spins of Mo^{5+} induces a ferrimagnetic half metallic state with a saturation moment of 4 μ_B [1]. However, most of the experiments showed a reduced saturation moment [1–3]. This fact has been claimed to be related to antisite defect, where some of the Fe and Mo ions interchange their crystallographic positions [4, 5], which was further considered as a possible reason for the low field magnetoresistance (LFMR) [6]. Moreover, other effects such as grain size [7] and degraded surface [8] were also invoked to explain LFMR.

It is apparent that the origin of the enhancement of the LFMR for SFMO double perovskite is still not completely known. Moreover, the fact that control of stoichiometry and valence state of the distinct species is very subtle and required critical reducing conditions for the synthesis has posed serious difficulties to progress. Therefore, the understanding of the formation mechanism and kinetics of SFMO double perovskite during processing would lend support not only to produce high-quality samples but also to provide deep insight for realizing the origin of LFMR of this oxide. The formation mechanism of SFMO double perovskite had recently been detailed [9, 10], in which formation of SFMO could be considered as the reaction between $SrFeO_{3-x}$ and $SrMoO_4$. In this investigation, we will further explore the formation kinetics of this oxide.

2. Experimental procedure

High-purity powders of $SrCO_3$, Fe_2O_3, and MoO_3 were used to prepare the precursor powders. The precursor powder of $SrFeO_{3-x}$ (SFO) was prepared by calcining the mixed powders of $SrCO_3$ and Fe_2O_3 at 1000°C for 4 h in 5% H_2-95%N_2. The precursor powder $SrMoO_4$ (SMO) was synthesized by milling the mixed powders of $SrCO_3$ and MoO_3. SFMO was prepared by mixing SFO and SMO with a ratio of 1:1 for 12 h. The mixture was rapidly dried by using microwaves to reduce the segregation of SFO and SMO and then ground lightly with a mortar and pestle. The reaction pellets were prepared by pressing in a die (with a diameter of 12 mm) at a pressure of 100 Mpa. The reaction rate of the powder compacts was measured at different heating rates (2, 5, and 10°C/min) from room temperature to the desired temperature.

XRD (Model D/MAX III.V XRD, Rigaku, Tokyo, Japan) analysis was performed on samples that had been heated at various temperatures and different heating rates. The samples were ground for analysis, and MgO was used as an internal standard to determine the amount of SMO. It should be noted that the strongest peak of SFMO overlaps with that of SFO, so the extent of reaction was determined by SMO. The scanning rate was set to 1° (2θ) per min over a range of 25–45° (2θ), which contained the strongest diffraction-line intensities of SMO and MgO. These peaks were selected to measure the extent of SMO, and the counts that were collected for the peaks were fitted and integrated to extract the peak area.

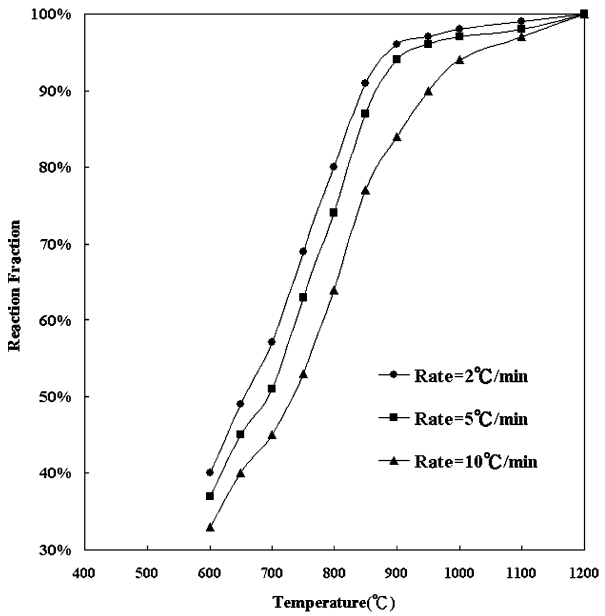

Figure 1 Formation of SFMO versus temperature at different heating rates.

3. Results and discussion

3.1. Formation of Sr_2 $FeMoO_6$ at different temperatures

Quantitative XRD was used to determine the extent of reaction as a function of temperature. The extent of reaction was evaluated by the ratio of the area (integrated intensities) of the major peak of MgO to that of the major peak of the product of SMO, using an X-ray-calibration curve fitting. The formation of SFMO as a function of temperature, at a heating rate of 2, 5, and 10°C/min, is shown in Fig. 1. These curves show a sigmoid shape; however, the higher the heating rate, the higher the temperature that is required to attain the same reacted fraction.

3.2. Nonisothermal kinetic analysis of the formation of SFMO

There are several models [11–15] concerning the solid-state reaction. The major difference between these models is based on the rate-limiting process that is involved in the reaction. In solid-state reactions, the reactants are not mixed on an atomic level and, therefore, must diffuse or penetrate into each other if the reaction is to start and propagate within the solid phase. Thus, space coordinates would play a significant role during the reaction. There are two fundamental processes that are involved in the solid-state reaction: (I) the chemical reaction itself and (II) the transport of matter to the reaction zone. Usually, there is specific activation energy for each process, so each reaction assumes a specific rate constant. The procedure [16] for the analysis of the nonisothermal reaction kinetics was modified to evaluate the activation energy of the SFMO. The time rate conversion, $d\alpha/dt$, is given as

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

where k is a rate constant and $f(\alpha)$ may be dependent on the particle size. The specific rate constant can be expressed as an Arrhenius equation, i.e. $k = A\exp(-\frac{Q}{RT})$, where A is a frequency factor, Q the activation energy for the reaction, R the gas constant, and T the absolute temperature. For a constant heating rate, $\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT}$ where β is the heating rate. Therefore, the kinetic Equation 1 can be further expressed as

$$\ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = \ln[\mathrm{Af}(\alpha)] + \left(-\frac{\mathrm{Q}}{\mathrm{RT}}\right). \qquad (2)$$

In this investigation, the $f(\alpha)$ values were assumed to be constant at a fixed α value, and the activation energy can be evaluated by plotting $\ln[\beta(d\alpha/dT)]$ vs. $1/T$ at different heating rates for a constant α value. If only one mechanism dominates during the reaction, the lines would be parallel. If more mechanisms occur during the reaction, they would show unparallel lines. Fig. 2 shows a plot of $\ln[(\beta d\alpha/dT)]$ vs. $1/T$ for SFMO at different heating rates and for a constant α value, in which the values of $d\alpha/dT$ had been evaluated from the slopes of the lines in Fig. 1. As observed, these lines are linear and parallel, which implies that this empirical model is valid to describe the nonisothermal reaction kinetics and that only one mechanism dominates. It is noted that when $\alpha > 0.9$, the reaction fraction would become too small, leading to the slow kinetics observed in Fig. 1 and invalidity of the model. The activation energy obtained from slopes of the line in Fig. 2 has an average value of 185 kJ/mol, which is very low compared with strontium barium niobate of 650–1300 kJ/mol depending on the composition [17]. In previous work [17], the activation energy was suggested to be related to the interdiffusion of ions and affected by the structure distortion in ceramics. Because the formation of SFMO was via the reaction between SFO and

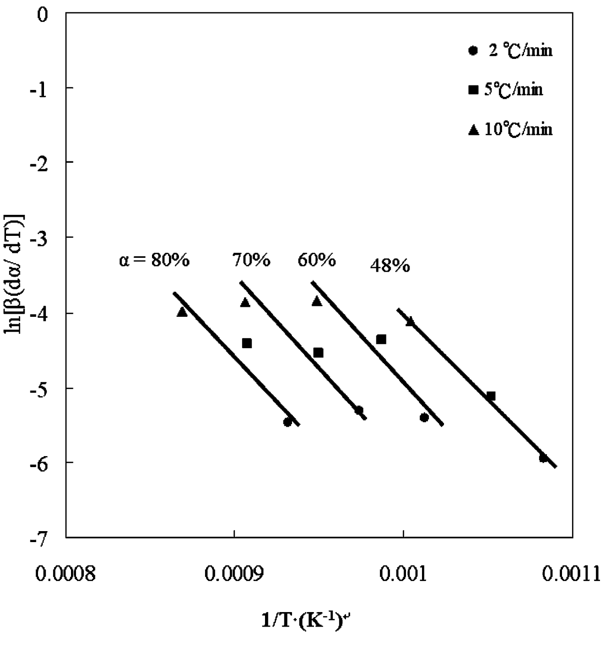

Figure 2 Plot of $\ln[\beta(d\alpha/dT)]$ versus $(1/T)$ for the SFMO at different heating rates with a constant α value.

SMO and essentially, the structure was developed based on the skeleton of SFO [9, 10] the structure distortion would be minimized. The low value of the activation energy obtained for SFMO would lend support to this suggestion.

If $f(\alpha)$ is further assumed as $(1-\alpha)^{\mathrm{n}}$, the intercept, I, of Equation 2 can be rewritten as

$$I = \ln[A(1-\alpha)^{\mathrm{n}}]. \tag{3}$$

Rearranging Equation 3, we obtain

$$I = \ln A + n \ln(1-\alpha). \tag{4}$$

Thus, if we plot I vs. $\ln(1-\alpha)$, we will obtain a straight line whose slope is n and whose intercept is ln A. As observed in Fig. 3, only one linear region is obtained, which is different from the SBN ceramics [17]. The values of n and A obtained from Fig. 3, are 3.08 and 6.27×10^8, respectively. And the rate constant k can be calculated via the evaluated values of the activation energy Q and frequency factor A. Furthermore, based on the equation of $\beta(d\alpha/dT) = kf(\alpha)$, we can further verify the validity of the present empirical model by evaluating the values of the left-hand side of this equation, $\beta(d\alpha/dT)$, based on the experimental data and those of the right-hand side of this equation, $kf(\alpha)$, from the evaluated data. As observed in Fig. 4, the experimental and evaluated data are in good agreement, which not only justifies the validity of the proposed nonisothermal model but also further supports the suggestion related to formation mechanism of SFMO.

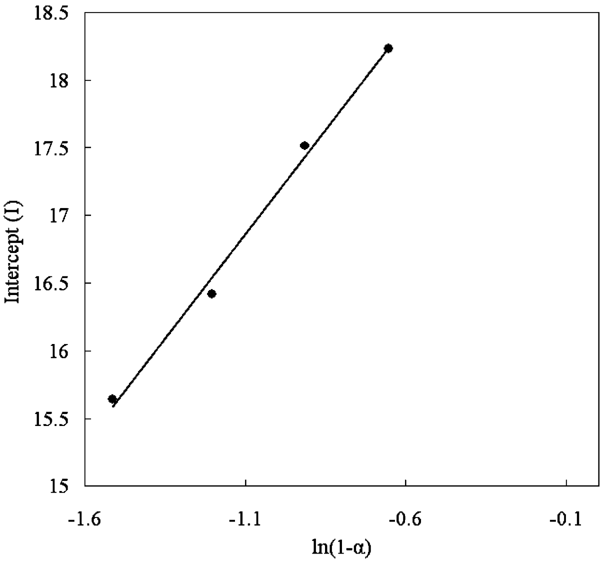

Figure 3 Plot of the intercept I versus ln(1-α) of SFMO, showing one linear region.

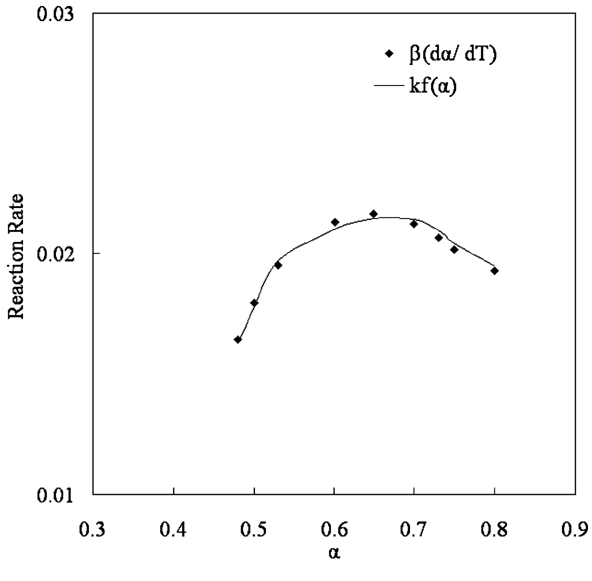

Figure 4 Comparison of the values of $\beta(d\alpha/dT)$, based on the experimental data, and $kf(\alpha)$, obtained from the theoretical data at different α values for SFMO.

4. Conclusions

The empirical kinetic model developed in the previous work [17] not only is proved to be valid to analyze the nonisothermal kinetics of the solid-state reaction during forming SFMO but also further supports the suggestion related to formation mechanism of SFMO. The activation energy of the formation reaction calculated from this model is about 185 kJ/mol. This value is low and can be attributed to the lower structure distortion during the formation of SFMO.

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