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Model-free Kinetic Analysis of Sr₂FeMoO₆ Re-crystallization Process Used for Double-Perovskite Monocrystals Grown by Bridgman Method

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Abstract. The synthesis routes for polycrystalline bulk Sr₂FeMoO₆ (SFMO), offer various possibilities, but in all the cases it is difficult to obtain a single phase of this compound. A new challenge in the field is to achieve mono-crystals using different growing routes and the Bridgman method represents one of them. In order to establish the optimal conditions of mono-crystals growing process, a complex thermal investigation of bulk double perovskite has been performed. Differential thermal analysis investigation in argon inert atmosphere, starting from room temperature up to 1650°C provided information about melting and re-crystallization temperature range. Both, the activation energy of Sr₂FeMoO₆ re-crystallization process and the re-crystallization mechanism were comparatively analyzed by two free-model estimations (Friedman and Ozawa-Flynn-Wall analysis). The resulted data are very important in order to set up the heating program of Bridgman furnace.

INTRODUCTION

Sr₂FeMoO₆ (SFMO) has attracted a great attention in the last years due to their special properties such as half-metallic behavior, magnetic ordering below T_c=420 K, magnetoresistance at low field and possible application of spin polarized transport properties [1-3]. Over time, many synthesis methods have been used for obtaining this material, in most of the cases affording the cubic single phases. SFMO has a typically A₂B'B''O₆ double-perovskite structure with FeO₆ and MoO₆ octahedral alternating along to the three crystallographic axes. The most published papers have reported the fact that, due to the processing conditions it were obtained double-perovskites structures with antisite defects (AS), meaning that fraction of Mo atoms are located on the B'' site and an equivalent atoms of Fe tacking their place on the B' site [4-6]. The researches on these materials were enhanced from the desire to obtain compounds with ideal cubic structures and advanced properties. The Bridgman method represent one of the newest approach for the obtaining of SFMO mono-crystals, until now being reported only floating zone as feasible method for obtaining double perovskite single crystals [7]. This technique involves heating polycrystalline material in a container above its melting point and slowly cooling it from one end where a seed crystal is located. Single crystal material is progressively formed along the length of the container [8-9]. Considering these characteristics of the Bridgman furnace, it is necessary to know as much information about the thermal behavior of the polycrystalline materials that are to be processed by this method. The aim of this work is to highlight the thermal and thermo-kinetic parameters of the SFMO polycrystalline compounds in order to set and to optimize the Bridgman processing conditions.

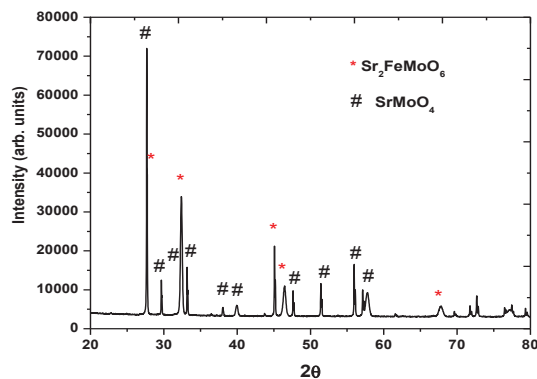
EXPERIMENTAL

Polycrystalline double perovskite Sr₂FeMoO₆ nanosized powders have been prepared using powder the metallurgy method. Different amounts of starting reagents, SrCO₃ 97% Riedel-de Haën, Fe₂O₃ 97% Fluka and

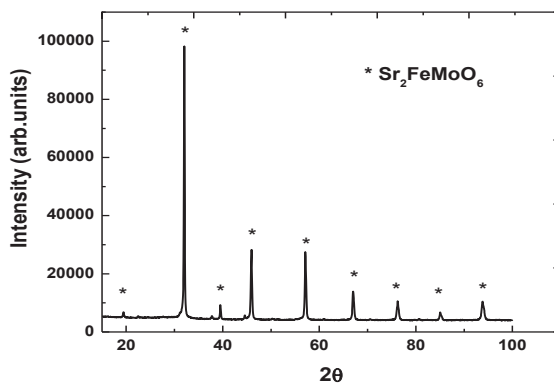
MoO₃ 99.5% Reactivil Bucharest, corresponding to Sr:Fe:Mo = 2:1:1 ratio, were mixed in a mortar for 1 hour. The resulted powder was introduced in an alumina crucible and calcined in air in a Nabertherm muffle furnace at 900°C for 2 hours. The resulted double perovskite precursor powder was pressed into pellets having 16 mm diameter and then sintered in H₂ (5%) / Ar (95%) reducing atmosphere at 1100°C for 4 hours in a Haereus quartz tube furnace. The formation of single phase Sr₂FeMoO₆ (particles size > 30 nm) has been confirmed by X-ray diffraction, performed on the sintered pellets with the help of a Brucker diffractometer equipped with CuK_α radiation. Differential thermal calorimetry analysis has been performed using a SETARAM SETSYS Evolution 18 instrument in a TG-DSC thermal analyzer mode. The accuracy of heat flow measurements was ± 0.001 mW, and the temperature precision of the ± 0.1 K. Equal amounts of sample (18 mg) were measured in argon inert atmosphere, starting from room temperature up to 1650°C at four different heating rates. Both, the activation energy of Sr₂FeMoO₆ re-crystallization process and the re-crystallization mechanism were comparatively analyzed by two free-model estimations (Friedman and Ozawa-Flynn-Wall analysis) using a specialized Thermo-kinetics software from NETZSCH.

RESULTS AND DISCUSSIONS

X-ray diffraction measurements performed in both cases: on the as calcined sample (fig. 1a), respectively, the sintered sample (fig. 1b) revealed the fact that, after calcination process a mixture of phases was obtained, Sr₂FeMoO₆ being the major one, but also SrMoO₄ can be distinguished as impurity.



(a)



(b)

FIGURE 1. X-ray diffraction performed on the calcined sample (a), and after the sintering treatment (b) respectively

After applying the sintering treatment, samples showed that all the diffraction peaks are in good agreement with the double perovskite phase having a tetragonal structure (space group I4/m) [10], and no second phase could be

detected. Differential thermal calorimetry (DSC) performed in argon inert atmosphere, starting from room temperature up to 1650°C provided information about SFMO double-perovskite oxide melting (fig. 2a) and re-crystallization (fig. 2b) temperature range.

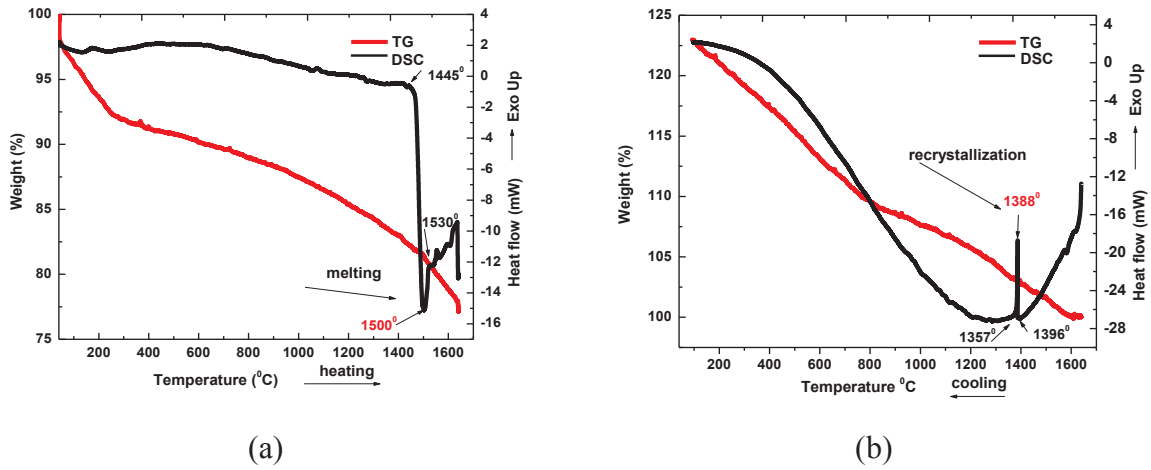


FIGURE 2. TG-DSC curves corresponding to a $\text{Sr}_2\text{FeMoO}_6$ heating (a), respectively, cooling (b) cycle in argon inert atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$

As can be observed from the two diagrams displayed above, $\text{Sr}_2\text{FeMoO}_6$ polycrystalline oxide begins to melt around 1445°C , the maximum of the melting peak being centered at 1500°C (fig. 2a). The SFMO re-crystallization process occurs around 1396°C , the maximum of this process appear at 1388°C (fig. 2b). This information is very important considering the fact that, there is no phase diagram specific to SFMO reported so far in literature and the information about melting and re-crystallization temperature of this compound are essential in order to set the parameters of the Bridgman furnace. The kinetic parameters of the re-crystallization process were comparatively determined using two free kinetic models: Friedman and Ozawa-Flynn-Wall. The first proposed model, Friedman, represents the most general of the derivative techniques and is based on the inter-comparison of the conversion rate, $\frac{dx}{dt}$, for a given degree of the conversion x determined when using different heating rates [11]. This method uses the following logarithmic differential equation:

$$\log \frac{dx}{dt} = \log x \frac{dx}{dT} - \log Af(x) - \frac{E}{4.575T} \quad (1)$$

with

$$\frac{dx}{dt} = kf(x) \quad (2)$$

expressing the conversion rate at a constant temperature T as function of the reactant concentration loss. $k(T)$ is always described by the Arrhenius equation [12-13]:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

A is the pre-exponential factor, E represent the activation energy and R is the general constant for gases.

$$f(x) = (1-x)^n \quad (4)$$

n being the reaction order.

This equation offers the possibility to obtain E values for a wide conversion range by plotting $\log \frac{dx}{dt}$ versus $\frac{1}{T}$ for a constant x value.

Ozawa-Flynn-Wall model is used to calculate the activation energy for certain given values of the conversion [14]. The characteristic equation to this model is the following:

$$\log \beta = \log \frac{AE}{g(x)R} - 2.315 - \frac{0.457E}{RT} \quad (5)$$

with

$$\beta = \frac{dT}{dt} \quad (6)$$

representing the heating rate, and $g(x)$ is the integral function of conversion:

$$g(x) = \int_{x_0}^{x_p} \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_0}^{T_p} e^{-E/RT} dT \quad (7)$$

T_0 is the initial temperature corresponding to a degree of conversion of x_0 and T_p is the inflection temperature, were $x = x_p$. The specificity of this model is that the activation energy for different conversion values can be determined

by applying a $\log\beta$ versus $\frac{1000}{T}$ plot. The pre-exponential factor is calculated as an average value over all dynamic heating rates. The re-crystallization peaks of the $\text{Sr}_2\text{FeMoO}_6$ double-perovskite obtained for the four chosen heating rates are presented in fig. 3.

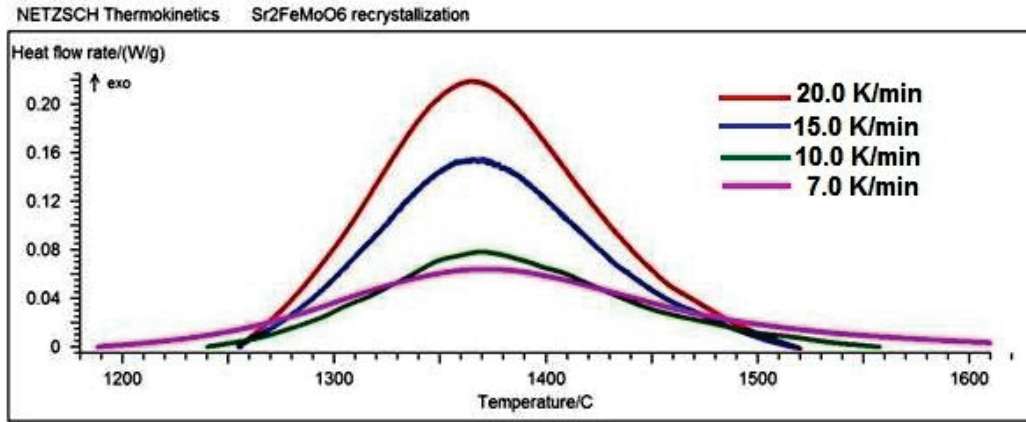


FIGURE 3. $\text{Sr}_2\text{FeMoO}_6$ re-crystallization peaks obtained at four heating rates: 7°C, 10°C, 15°C and 20°C per minute in argon inert atmosphere

The DSC curves displayed above analysis revealed the maximum of the re-crystallization process which appears in the [1350°C÷1400°C] temperature range; also it is noticed a systematic increase of these values with the increase of the heating rate. The figure 4 shows both Friedman (a), respectively, Ozawa-Flynn-Wall analysis (b) of the DSC data measured on $\text{Sr}_2\text{FeMoO}_6$ for all chosen heating rates.

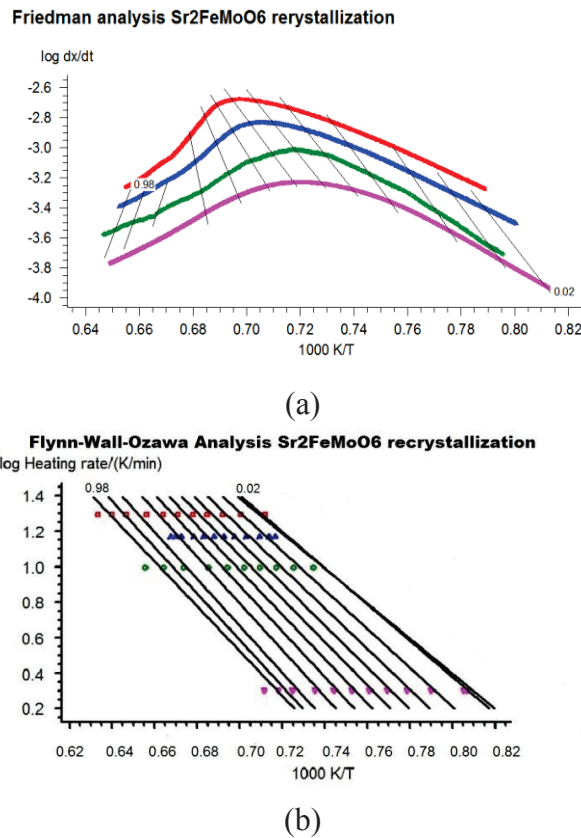


FIGURE 4. Kinetic model free-analysis on $\text{Sr}_2\text{FeMoO}_6$ re-crystallization process: (a) Friedman lines, respectively, Flynn-Wall-Ozawa lines (b)

The report of activation energies and pre-exponential factors as well resulted from both analyses is shown in Table 1.

TABLE 1. Tabular report of activation energies and pre-exponential factors for Sr₂FeMoO₆ re-crystallization evaluation process

Partial area (%)	E (KJ/mol) Friedman model	ln A (s ⁻¹) Friedman model	E (KJ/mol) Flynn-Wall-Ozawa model	ln A (s ⁻¹) Flynn-Wall-Ozawa model
10	554.80 ± 1.39	8.97	502.66 ± 7.01	11.75
20	546.09 ± 4.65	8.23	566.06 ± 3.87	9.88
30	481.07 ± 6.26	11.48	441.55 ± 2.24	8.65
40	452.66 ± 9.72	14.24	430.70 ± 3.51	8.11
50	466.19 ± 1.63	14.60	432.05 ± 4.80	8.17
60	538.74 ± 1.84	12.13	447.99 ± 5.94	8.92
70	579.02 ± 3.06	12.04	385.14 ± 9.73	10.65
80	363.67 ± 9.73	9.88	348.18 ± 1.67	13.53
90	280.52 ± 3.76	8.86	293.93 ± 3.91	11.00
100	262.58 ± 8.27	7.11	299.45 ± 3.65	6.70
Average	452.53 ± 5.03	10.75	414.77 ± 4.63	9.73

According to the kinetic evaluation, both parameters, the activation energies and pre-exponential factors reveal a clear dependence on the degree of conversion, showing a complex reaction path. On the whole, the energy of the Friedman and Ozawa-Flynn-Wall analysis agree very well with each other and the values are similar. In both situations it is noticed the presence of two maximum in activation energies, 554.80 ± 1.39 KJ/mol (Friedman) and 502.66 ± 7.01 KJ/mol (Ozawa-Flynn-Wall) at a conversion of 10%, respectively, 538.74 ± 1.84 (Friedman) and 447.99 ± 5.94 KJ/mol (Ozawa-Flynn-Wall) at a conversion of 60%. This fact sustains that, the SFMO re-crystallization process occurs in two stages. This behavior is perfectly justified considering the fact that, according to the literature, three standard models are employed to describe crystal growth from the melt: normal growth, screw dislocation and surface nucleation growth. The kinetics and morphology of the growth from the melt are determined by many factors such as: material transfer, the diffusion of material in melt, heat transfer, the removal of latent heat of crystallization from the growing crystal surface, the arrangement of atoms or ions species at the solid-liquid interface etc. [15-18]. In our case, the observed behavior of the activations energies calculated from the above mentioned methods confirm the existence of two underlying SFMO re-crystallization processes: nucleation and diffusion. The pre-exponential factor (known as the frequency factor) offer information about the number of nucleation site and has a similar trend in both analyses.

CONCLUSIONS

Sr₂FeMoO₆ re-crystallization process has been thermally investigated for the first time. DSC measurements revealed the temperature values corresponding to both melting and re-crystallization processes. Experimental data of the above-mentioned two methods: Friedman and Ozawa-Flynn-Wall analyses were used to evaluate the activation energies of the SFMO re-crystallization. Comparing the kinetic parameters by the two chosen free-models, for four heating rates, similar values are revealed. The two maximum of the re-crystallization activation energies obtained in both cases have confirmed the existence of a mechanism that takes place in two steps: nucleation and diffusion. Thus, besides the novelty of the approach, the obtained values will have an important contribution for setting the optimal parameters required to obtain single-crystals using the Bridgman method (first time used for Sr₂FeMoO₆ compounds).

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