

Analysis of phase changes during synthesis of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ solid solution by the solid-phase reaction method

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Abstract

Phase transformations during crystallization of the magnetic metal-oxide compound $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ by the solid-phase reactions method from a mixture of simple reagents $2\text{SrCO}_3 + 0.6\text{Fe}_2\text{O}_3 + 0.8\text{MoO}_3$ have been analyzed. By means of differential-thermal and thermogravimetric analyses it was found that the synthesis of strontium ferromolybdate of the $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ composition proceeds through a series of successive-parallel stages. In this way, when considering the dynamics of phase transformations, it has been found that the main accompanying compounds during the crystallization of the solid solution of double perovskite $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ are Fe_2O_3 , SrCO_3 , SrMoO_4 and SrFeO_3 . When analyzing the phase composition of the batch consisting of a mixture of initial reagents of stoichiometric composition: $2\text{SrCO}_3 + 0.6\text{Fe}_2\text{O}_3 + 0.8\text{MoO}_3$, it was noted that with an increase in temperature, complex compounds SrMoO_4 , SrFeO_3 , and then $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ as well, appear almost simultaneously. This circumstance indicates that the compounds SrMoO_4 and SrFeO_3 are the structure-forming ones for the solid solution of ferromolybdate – strontium. With a subsequent increase in temperature to 1470 K, it was found that the dissolution of SrFeO_3 with the formation of double perovskite $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ occurs faster than the dissolution of strontium molybdate SrMoO_4 . The results of the analysis indicate the difficult nature of the dynamics of solid-phase reactions during the formation of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$.

Keywords

magnetic metal-oxide compound, differential-thermal analysis, thermogravimetric analysis, X-ray phase analysis, sequence and degree of phase transformations

1. Introduction

Currently, intensive research is being carried out to improve the methods of production of magnetic materials. These investigations are aimed at optimizing synthesis conditions to improve their physical and chemical characteristics, with the aim of their large-scale industrial use. In this regard, solid solutions of double perovskites with the general formula $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_{6-\delta}$, which have high chemical stability in reducing atmosphere, large values of Curie temperature (400–450 K), a significant degree of spin polarization of conduction electrons ($\sim 100\%$), as well as low values of control magnetic fields ($B < 0.5$ T) are of great interest to specialists in the field of spintronics [1–15]. It should be noted the good ability of strontium ferromolybdate solid solution for hydrogen storage and transportation, for example, in rechargeable batteries, which is one of the main directions of scientific and technological progress [12–15]. Such characteristics of $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_{6-\delta}$ solid solutions are very important when considering solid oxide fuel cells (SOFC) and hydrogen as a fuel for clean and environmentally friendly power generation [14, 15]. Another remarkable property of $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_{6-\delta}$ solid solutions having both ionic and electronic conductivity is their ability to convert the chemical energy of the fuel into electricity, which gives them a number of undeniable advantages over conventional power generation methods [15]. The development of SOFCs and power generation systems based on $\text{Sr}_2\text{Fe}_{1+x}\text{Mo}_{1-x}\text{O}_{6-\delta}$ solid solutions is indeed a promising direction. This technology offers efficient and environmentally friendly conversion of chemical energy of fuel into electricity.

Despite the fact that there is a great interest in such materials nevertheless and to date there is no optimization of the conditions for obtaining single-phase solid solutions of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ composition with reproducible physical and chemical properties. This leads to the fact that there is a difference in a number of important

characteristics from author to author, which seems to be related to the peculiarities of sample preparation techniques [16–18]. In this regard, the goal of this research is to identify the source of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ solid solutions properties, improve and adapt the synthesis methods for their use in various branches of the electronics industry.

2. Experimental

SrCO_3 , Fe_2O_3 , and MoO_3 were used as initial reagents to study the sequence of phase transformations in compounds of variable composition $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$. Mixing and grinding of stoichiometric mixture of initial reagents was carried out in a ball mill “PM 100” Retsch GmbH in alcohol for 3 h. The obtained powder was pressed into pellets of 10 mm diameter, 4–5 mm thickness. The annealings were carried out in polythermal mode in the temperature range of 300–1420 K in argon flow and at a heating rate of 5 deg/min followed by quenching at room temperature.

X-ray diffraction analysis (XRD) has been performed on a Bruker AXE D8 Focus diffractometer with a LynxEye detector using CuK_α radiation. The measurements were recorded at the standard rate of 1.5 $2\theta/\text{min}$. The phase composition of solid phase synthesis products has been quantitatively determined on the basis of XRD data using PowderCell and FullProf software by the Rietveld method [19, 20].

The thermal behavior of the samples was investigated using differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) with a differential scanning calorimeter (DSC): simultaneous thermal analyzer STA 449 F3 Jupiter (NETZSCH, Germany) in the argon flow at a heating rate of 5 deg/min.

3. Results and discussion

According to the DTA data it was established that at heating of the powder consisting of initial reactants in stoi-

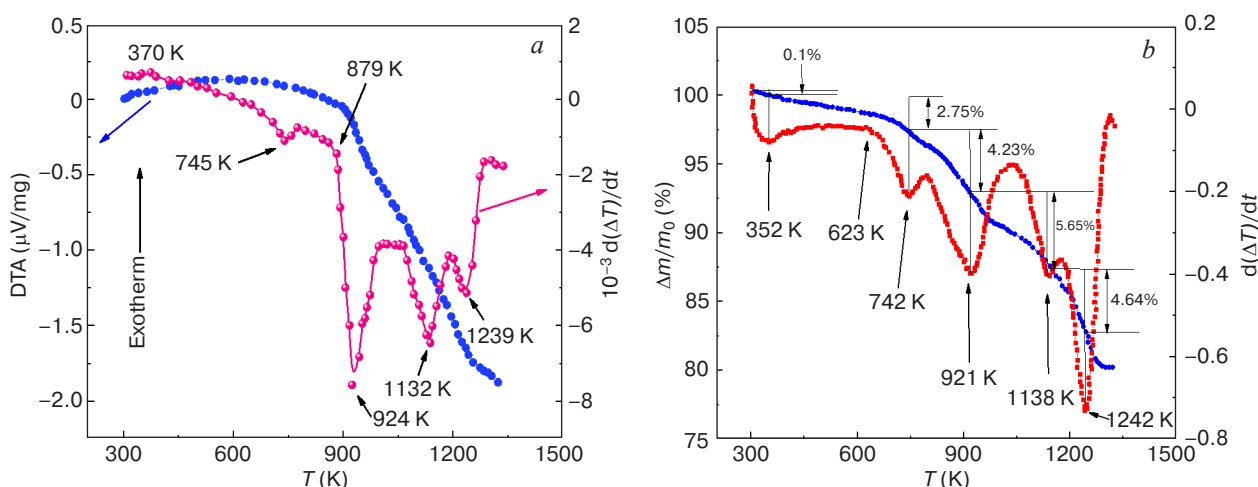


Figure 1. Temperature dependences of: (a) thermal effects and their derivative, (b) mass change and its derivative, of a mixture of powder $2\text{SrCO}_3 + 0.6\text{Fe}_2\text{O}_3 + 0.8\text{MoO}_3$, annealed in a continuous argon flow at a heating rate of 5 deg/min

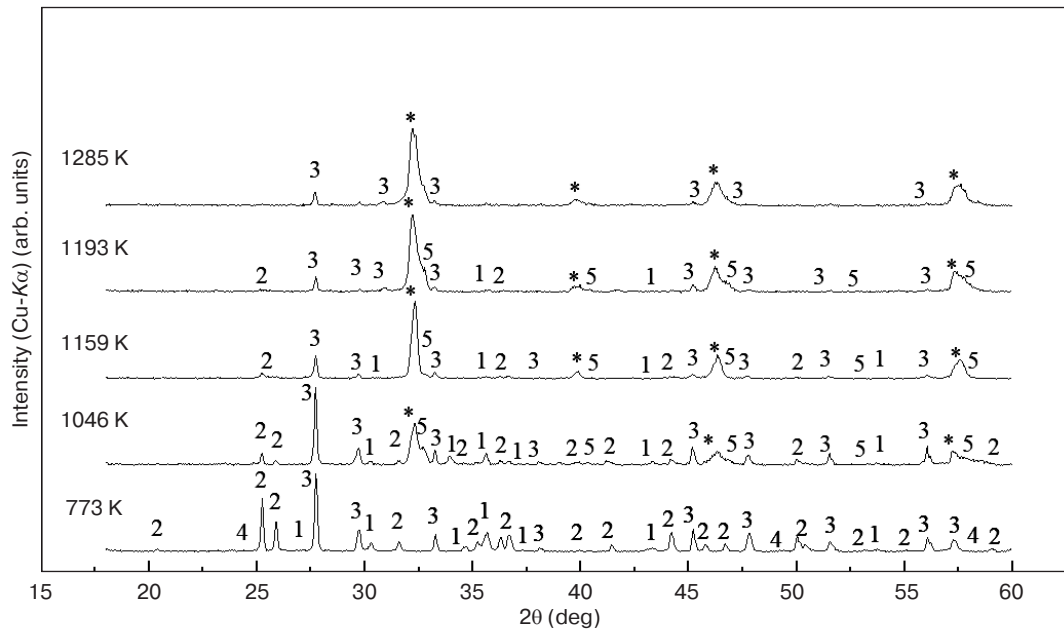
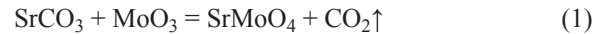


Figure 2. XRD patterns of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ samples synthesized in a continuous argon flow at a heating rate of 5 deg/min obtained by quenching at room temperature: (1) Fe_2O_3 ; (2) SrCO_3 ; (3) SrMoO_4 ; (4) MoO_3 ; (5) SrFeO_3 ; (*) SFMO

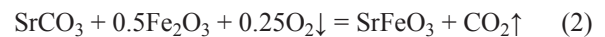
chiometric ratio $2\text{SrCO}_3 + 0.6\text{Fe}_2\text{O}_3 + 0.8\text{MoO}_3$ in the range from 300 to 500 K weakly expressed exothermic process with maximum at 370 K has been observed. At the same time, according to TGA data in the temperature range of 300–360 K a decrease in its mass ($m \sim 0.1\%$) is observed, which can be explained by the presence of surface desorption of gaseous reaction products H_2O , CO_2 and O_2 in the sample (Fig. 1).

At the heating to higher temperatures chemical processes intensify and in the temperature range of 500–880 K the first endothermic effect is observed at $T = 745$ K, accompanied, according to the TGA analysis, by $m \sim 2.87\%$ decrease in sample mass (see Fig. 1). So, according to the data of XRD and EDX analyses (Figs 2 and 3) in the

temperature range of existence of the first endothermic effect crystallization of SrMoO_4 compound in the system $\text{SrCO}_3\text{--MoO}_3$, is observed, proceeding with the release of carbon dioxide according to the chemical reaction:



With a further increase in temperature to 1000 K, the presence of an endothermic effect at $T = 924$ K with a decrease in the mass of the sample was noted, indicating the occurrence of chemical processes with the release of gaseous reaction products (see Fig. 1). When studying the phase and elemental composition of the quenched sample from 950 K to room temperature, the appearance of a strontium ferrite compound with a simultaneous decrease in the SrCO_3 and Fe_2O_3 phases has been detected. In this case, the chemical reaction with the formation of strontium ferrite occurs with the simultaneous absorption of oxygen and the release of carbon dioxide according to the equation:



In the temperature range of existence of the third endothermic effect in the mixture of the initial and already formed reagents SrCO_3 , Fe_2O_3 , MoO_3 , SrFeO_3 and SrMoO_4 with a minimum at $T = 1132$ K, an increase in the mass loss of the sample to 5.65% is observed. In this case, the amount of double perovskite increases, while the amount of strontium molybdate and strontium ferrite decreases (Fig. 4). Based on the fact that at $T > 1132$ K, according to the XRD data, the concentration of simple oxides and strontium carbonate in the mixture drops almost to zero, and the concentration of the solid solution increases $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$, it can be assumed that the

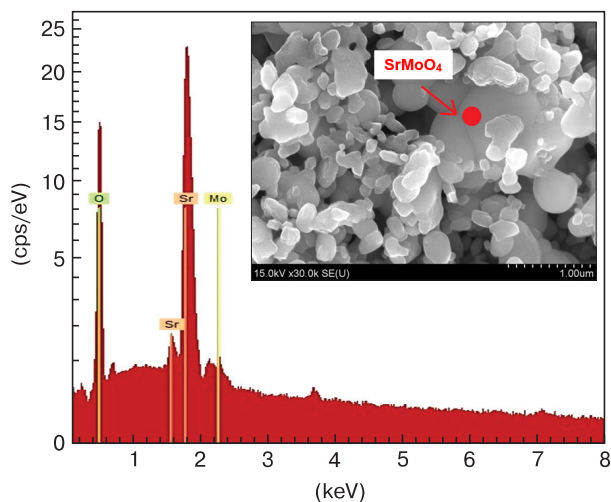
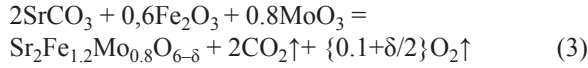


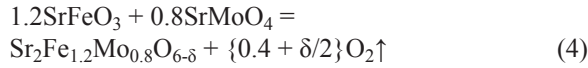
Figure 3. Elemental composition of the grain of the SrMoO_4 phase and the microstructure of a sample consisting of a stoichiometric mixture of $2\text{SrCO}_3 + 0.6\text{Fe}_2\text{O}_3 + 0.8\text{MoO}_3$ obtained by heating at a rate of 5 K/min in the argon flow to 750 K, followed by quenching at 300 K

endothermic effect and the greatest decrease in the mass of the sample are due to the following chemical reaction with the release of oxygen:



With further increase in temperature, an insignificant fourth endothermic effect is observed with a minimum at $T = 1239$ K, accompanied by a decrease in the sample mass by 4.64%. In this case, in the quenched sample at room temperature $T = 300$ K, an increase of the degree of phase transformation $\alpha(T)$ of the $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ phase and a decrease in $\alpha(T)$ of the content of the SrMoO_4 and SrFeO_3 phases are established (Fig. 5).

In this case, the degree of phase transformation for SrMoO_4 decreases to 11%, while for SrFeO_3 , $\alpha(T) \rightarrow 0$. Based on the above results, the reaction of the chemical process with the formation of a magnet can be represented as:



With a further increase in temperature to $T = 1370$ K, no significant thermal effects or changes in mass were detected. In this case, the main reflex of the SrMoO_4 phase decreases and its content in the sample is no more than 5%. In this case, the interface of the solid phases between which mutual diffusion of chemical elements occurs moves deep into the intermediate phase SrMoO_4 . In this case, a decrease in the growth rate of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ at conversion degrees of $\alpha \geq 94\%$ is due to an increase in the thickness of the interface of the solid phases. If the resulting product layer has low mobility of cations

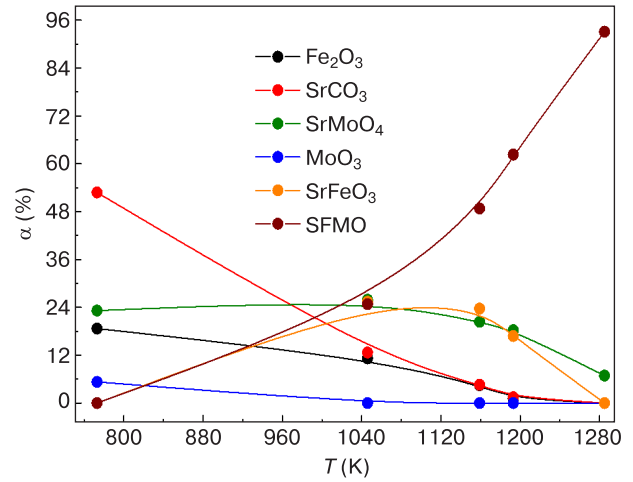


Figure 4. Temperature dependences of the degree of transformation ($\alpha(T)$) of the phases MoO_3 , Fe_2O_3 , SrCO_3 , SrMoO_4 , SrFeO_3 and $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ in samples synthesized from a mixture of reagents

and anions, then the heterogeneous reaction from the adsorption-chemical mode passes into the diffusion mode, which in turn is indicated by the above results. According to the XRD data, the samples heated to the temperatures of 1370 and 1473 K are qualitatively identical and differ only in their quantitative composition. Thus, the composition of the sample heated to $T = 1370$ K has the following quantitative phase ratio: 95% for $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ and 5% for SrMoO_4 . With a further increase in temperature to 1473 K, the composition changes towards an increase in the magnetic content to values of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta} - \alpha(T) = 97\%$ and a decrease in strontium molybdate content to 3% of SrMoO_4 . This indicates the difficulty of solid-phase reactions with the formation of a solid solution of the strontium ferromolybdate.

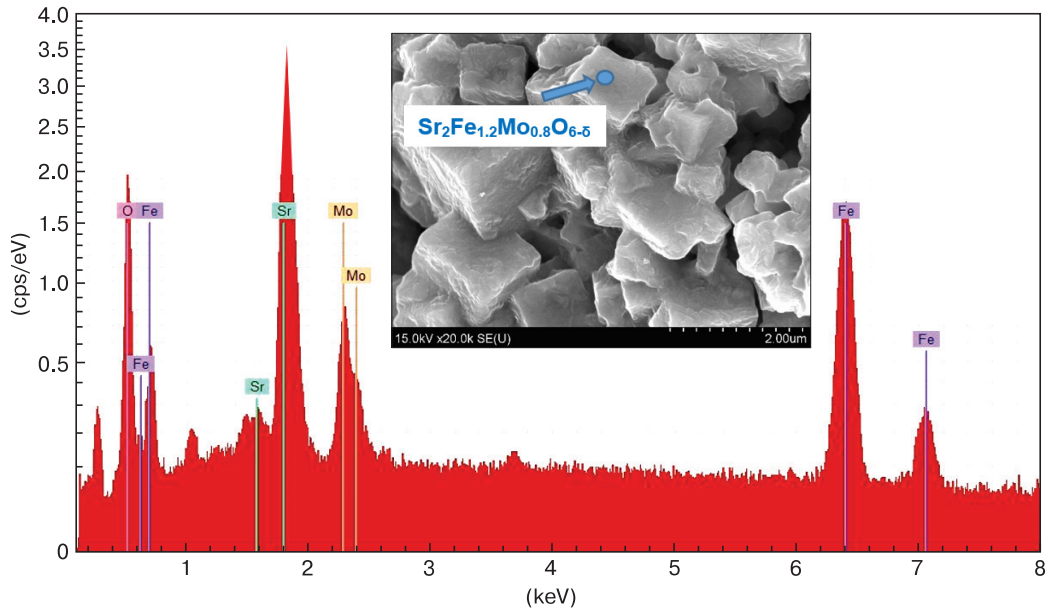


Figure 5. Elemental composition of the grain of the $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ phase and the microstructure of the sample obtained by heating at a rate of 5 deg/min a stoichiometric mixture of $\text{SrCO}_3 + 0.6\text{Fe}_2\text{O}_3 + 0.8\text{MoO}_3$ in an argon flow to 1240 K followed by quenching at 300 K

4. Conclusions

Thus, when considering the dynamics of phase transformations, it was found that the main accompanying compounds in the crystallization of solid solution of double perovskite $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ are Fe_2O_3 , SrCO_3 , SrMoO_4 and SrFeO_3 . When analyzing the phase composition of the charge consisting of a mixture of initial reagents of stoichiometric composition: $2\text{SrCO}_3 + 0.6\text{Fe}_2\text{O}_3 + 0.8\text{MoO}_3$ it has been noticed that with increasing temperature almost simultaneously appear complex compounds SrMoO_4 , SrFeO_3 and then $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$. This fact indicates that the compounds SrMoO_4 and SrFeO_3 , are structure-forming for the ferromolybdate-strontium solid solution. With

a subsequent increase in temperature to 1470 K, the dissolution of SrFeO_3 to form the $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ double perovskite is found to occur faster than the strontium molybdate SrMoO_4 . The results of the analysis indicate the complicated character of solid-phase reactions during the formation of $\text{Sr}_2\text{Fe}_{1.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$.

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