

Research Article

# Sequence of phase transformations at the formation of the strontium chrome-molybdate compound

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#### **Abstract**

The sequence of phase transformations in the process of crystallization of the Sr, CrMoO<sub>6</sub> by the solid-phase technique from a stoichiometric mixture of simple oxides SrCO<sub>3</sub> + 0.5Cr<sub>2</sub>O<sub>3</sub> + MoO<sub>2</sub>, has been investigated. It was determined that the synthesis of the strontium chrome-molybdate proceeds through a series of sequential-parallel stages. By means of the differential thermal analysis and thermogravimetric analysis data, it has been established that five clearly expressed endothermal effects were observed in the temperature range 300-1300 K. It was found that during the studies of the phase transformations sequence in the process of the double perovskite synthesis, SrCrO<sub>4</sub>, SrMoO<sub>4</sub> and Sr,CrO<sub>4</sub> are the main concomitant compounds. Herewith, it has been observed that with the annealing temperature increase from 300 to 1270 K, the complex compounds SrCrO<sub>4</sub>, SrCrO<sub>3</sub> (350-550 K) and SrMoO<sub>4</sub>, Sr, CrO<sub>4</sub> (600-750 K) are emerging initially and practically simultaneously. It has been revealed with a subsequent temperature increase that in the temperature range 940-1100 K, the SrMoO<sub>4</sub>, Sr,CrO<sub>4</sub> and SrCrO<sub>3</sub> phase concentration dramatically drops with the emerging and growth of the Sr,CrMoO<sub>6.5</sub> double perovskite. With that in the range up to 1120–1190 K, the main XRD reflexes intensity for the SrCrO<sub>3</sub> and SrMoO<sub>4</sub> lowers substantially, and their content in the samples at 1170 K is no more than 7.9%. During a consideration of the derivative of the SrCrO<sub>3</sub>, SrMoO<sub>4</sub> and Sr,CrO<sub>4</sub> phase transformation degree ( $|(d\alpha/dt)|_{max}$ ), at which their crystallization rates are maximal, it has been determined that |(d\alpha/dt)|\_max for the Sr<sub>2</sub>CrO<sub>4</sub> corresponds to the maximal temperature 1045 K, which indicates the presence of considerable kinetic difficulties at the formation of the Sr<sub>2</sub>CrO<sub>4</sub> phase. Thereafter this phase does not disappear and at its appearance the slowing down of the double perovskite growth takes place. On the base of investigations of the phase transformations dynamics for the obtaining of the single-phase Sr<sub>2</sub>CrMoO<sub>6,8</sub> compound with the superstructural ordering of the Cr/Mo cations and improved magnetic characteristics, the SrCrO<sub>2</sub> and SrMoO<sub>4</sub> precursors were used with combined heating modes.

# Keywords

double perovskite; differential thermal analysis; thermogravimetric analysis; sequence of phase transformations; crystallization rate

### 1. Introduction

Complex oxides with the double perovskite structure are the unique class of materials, having a number of exotic properties, such as ferrimagnetism with high values of Curie temperature  $(T_C)$  and the half-metal nature [1–3]. These materials are prospective from the point of view of the spintronic applications [4–6]. Materials with a large Curie temperature values are required for a creation of devices functioning at room temperature. At present, the most investigated system of this kind is the ferromagnetic  $\mathrm{Sr_2FeMoO_{6-8}}$  with  $T_C \sim 420~\mathrm{K}$ , being caused by the indirect interaction  $\mathrm{Fe}(t_{2\mathrm{g}})\mathrm{-O-Mo}(t_{2\mathrm{g}})$  [7–9]. A similar  $T_C$  value has been determined by Auth et al for the  $\mathrm{Sr_2FeReO_6}$  on the base of neutronographic investigations [10]. Philipp et al. have informed about the  $T_C$  = 458 K for  $\mathrm{Sr_2CrWO_6}$  [11].

The strontium chrome-molybdate,  $Sr_2CrMoO_6$ , is one of the most interesting compounds with the ordered double perovskite structure [12]. This is a magnetic oxide which is crystallized in a cubic structure with the Fm3m space group. Being based on the X-ray absorption spectroscopy data, it has been determined that as distinct from the double perovskites on the base of Fe, no valent compensation can take place between the  $Cr^{3+}$  and  $Mo^{5+}$  cations in the ordered  $Sr_2CrMoO_6$ , as  $Cr^{3+}$  can be only in the 3+ state [13–16]. Due to a big difference in the charge and ion radii between the  $Cr^{3+}$  (3d³, S=3/2) and  $Mo^{5+}$  (4d¹, S=1/2), regular placement of the alternating  $CrO_6$  and  $MoO_6$  octahedra leads to the emergence of  $Cr^{3+}$  and  $Mo^{5+}$  antiferromagnetic ion pairs. This leads to the ferromagnetic ordering with the transition temperature  $T_C \sim 470 \text{ K}$  [16].

In spite of a realization of a number of investigations devoted to the studies of physical-chemical properties of the  $Sr_2MMoO_c$  (M = Cr, Mn, Fe, and Co) rate [16–18], presently a little information is available concerning the Sr-, CrMoO<sub>6</sub>, due to a complexity of its obtaining. Some research papers present the information on the obtaining of the strontium chrome-molybdate by means of the solid-phase reactions with a subsequent employment of the high-temperature synthesis in a reducing gas environment [12-14, 19]. As a result of the analysis of the accumulated data, which has been carried out by a number of researchers, the multistage nature of the Sr<sub>2</sub>CrMoO<sub>6</sub> crystallization process was determined [12, 19, 20]. This is caused by a complex character of the phase transformations. It is rather problematic to obtain the single-phase compound with a pre-determined anion and cation deficiency. Therefore, properties of the Sr<sub>2</sub>CrMoO<sub>6</sub> compound obtained by various researchers are different [12, 19–21]. This fact demonstrates the nonreproducibility of the ferrimagnetic properties, which is caused by the uncontrollability of the defect formation processes in the double perovskite structure [22–24]. It has been determined on the base of analysis of the research results [12, 19, 20, 22, 24] that it is quite problematic to obtain the single-phase Sr<sub>2</sub>CrMoO<sub>6</sub> compound, due to the presence of the secondary phases, such as SrMoO<sub>4</sub>, SrCrO<sub>3</sub>, and it is practically impossible to remove the SrMoO<sub>4</sub> compound.

Moreover, the presence of secondary phases influence the general magnetization picture, which leads to the incorrect interpretation of the Sr<sub>2</sub>CrMoO<sub>6</sub> powders magnetic characteristics [12–15, 19, 21].

At the same time, strict correlations, connecting the functional characteristics of materials with the conditions of their obtaining, are practically absent in the realized investigations. In this case, a formation of the single-phase Sr<sub>2</sub>CrMoO<sub>6</sub> compound under conditions of control over the defect formation processes and, accordingly, the compound with reproducible physico-chemical properties needs analysis of the phase transformations occurring in the batch as well as studies of the kinetics of the degree of conversion of double perovskite during its crystallization. Therefore, recently the attention of researchers has been drawn to deeper and more detailed approaches to the synthesis of double perovskites associated with the study of the sequence of phase transformations during their crystallization. On this regard, investigations aimed at studying high-temperature phase transformations and determining the composition of intermediate crystalline phases in the process of Sr<sub>2</sub>CrMoO<sub>6</sub> synthesis are of particular importance. The present article is dedicated to establish a correlation between the rate of phase transformations and the degree of phase transformation of strontium chrome-molybdate, which will allow for a controlled change in the phase composition of the synthesized ceramic with reproducible physico-chemical properties.

# 2. Experimental

SrCO $_3$ , Cr $_2$ O $_3$  and MoO $_3$  were used as initial reagents for studying the sequence of phase transformations in compounds of variable composition Sr $_2$ CrMoO $_{6-\delta}$ . Mixing and grinding of the stoichiometric mixture of the starting reagents was carried out in a ball mill "PM 100" Retsch GmbH in ethanol for 15 hours. Annealings of the material was carried out in polythermal mode at temperatures in the range 300–1200 °C in the 5%  $H_2$ /Ar flow, followed by quenching at room temperature.

The in situ experiment on the X-ray diffraction analysis (XRD) for the monitoring of appearance and disappearance of crystal phases in the process of the double perovskite synthesis from the initial mixture (SrCO<sub>3</sub>, MoO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>) was carried out on the "PANalytical Empyrean" diffractometer using the  $CuK_a$  radiation. The argon-hydrogen atmosphere was created by means of the argon-hydrogen mixture constant flow through the high-temperature camera "Anton Paar HTK 1200N". The experiments were carried out in the temperature range 290-1270 K with the heating rate 10 deg/min. With that, every point has been measured consistently 4 times at the obtaining of the pre-determined temperature (exposition time was 2.5 minutes). Quantitatively, the phase composition of solid-phase synthesis products was determined on the basis of XRD data using the POWDERCELL [25] and FullProf [26] software products with an employment of the Rietveld technique.

The thermogravimetric analysis (**TGA**) has been carried out using the TG 209 F1 Libra (Netzsch) measuring setup. The differential thermal analysis (**DTA**) of the samples was carried out by means of the SetaramLabsys TG – DSC16 set up in the temperature 300–1270 K at a heating rate of 1.4 deg/min in an argon stream.

Magnetic properties of the samples were investigated on the "Cryogenic Limited" universal setup in the temperature range 4.2–300 K in the magnetic field up to 8 T.

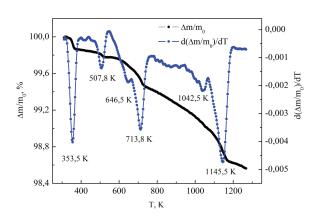
#### 3. Results and discussion

It has been determined according to the TGA and DTA results that practically no changes occur when the sample consisting of the starting reagents in the stoichiometric ratio  $SrCO_3 + 0.5Cr_2O_3 + MoO_3$  is heated from 300 to 510 K. According to the TGA data, a slight decrease in its mass is observed ( $\Delta m/m_0 < 2\%$ ), which can be explained by the chemical processes taking place in the batch and associated evolution of gaseous reaction products (Fig. 1).

When heated to the higher temperatures, thermal processes intensify and five well pronounced endothermic effects are observed in the temperature range 300–1300 K (Fig. 2).

The first endothermic effect, starting at a temperature of 320 K and reaching a minimum at T=353.5 K, is accompanied by a decrease in the mass of the sample ( $\Delta m/m_0 \sim 0.13\%$ ), which is most likely due to the evolution of gaseous reaction products  $\rm CO_2$  by means of a decomposition of the strontium carbonate (Figs 1, 2). So, in the temperature range corresponding to the first endothermic effect, crystallization of the SrCrO<sub>3</sub> compound in the SrCO<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> system is observed, proceeding with the release of carbon dioxide and oxygen adrosption, according to the reaction equation:

$$SrCO_3 + 0.5Cr_2O_3 + 0.25O_2 \downarrow = SrCrO_3 + CO_2 \uparrow \qquad (1)$$



**Figure 1.** TGA dependences of the change rate of the normalized mass of the  $SrCO_3 + 0.5Cr_2O_3 + MoO_3$  powder mixture annealed in a continuous 5% H<sub>2</sub>/Ar flow at a heating rate of 1.4 deg/min in the temperature range 300–1300 K

The second, smaller by the value, endothermic effect in the mixture of the starting reagents  $SrCO_3 + 0.5Cr_2O_3 + MoO_3$  with a minimum at T = 507.8 K is accompanied by a smaller change in the mass of the batch ( $\Delta m/m_0 \sim 0.07\%$ ) than that for the first effect and, accordingly, it is caused by the release of gaseous reaction products. According to the XRD data the emergence and growth of the  $SrCrO_4$  have been detected (Fig.3):

$$SrCO_3 + 0.5Cr_2O_3 + 0.75O_2 \downarrow = SrCrO_4 + CO_2 \uparrow$$
 (2)

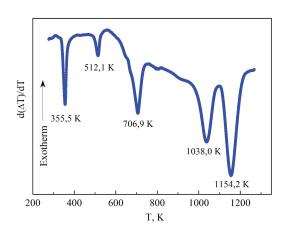
The smaller second TGA and DTA peaks are caused by a large amount of the adsorbed oxygen. According to the TGA data, at the further temperature increase, in the range of 600-750 K, a sharp rise of the temperature increase rate and the amplitude of the sample mass decrease, which reaches the extremum at  $T = 713.8 \text{ K} (\Delta m/m_0 \sim 0.31\%)$ (Fig. 1). At that, one should indicate a presence of the satellite peak with a minimum at T = 645.5 K, indicating the parallel chemical processes having different amount of evolving and adsorbing gaseous reaction products. Nevertheless, according to the DTA results, the third clearly expressed extremum, observed at T = 706.9 K is a solitary one (Fig. 2). According to the XRD data, a heating of the compounds mixture in the temperature range 600-750 K leads to the decrease of the SrCO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> phases amount, together with a simultaneous emergence and growth of the Sr<sub>2</sub>CrO<sub>4</sub> and SrMoO<sub>4</sub> compounds:

$$SrCO_3 + MoO_3 = SrMoO_4 + CO_2 \uparrow$$
 (3)

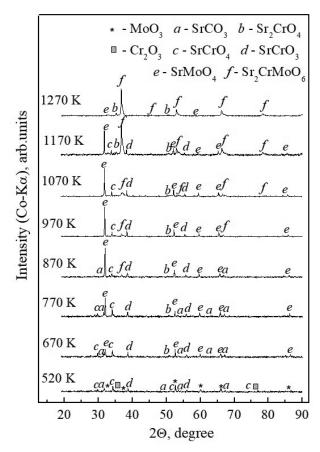
$$2SrCO_3 + 0.5Cr_2O_3 + 0.25O_2 \downarrow = Sr_2CrO_4 + 2CO_2 \uparrow (4)$$

These chemical processes are taking place with a simultaneous release of the carbon dioxide ((3)-(4)).

In the temperature range 940–1100 K corresponding to the fourth endothermic effect in the mixture of the starting reagents SrCO<sub>3</sub> + 0.5Cr<sub>2</sub>O<sub>3</sub> + MoO<sub>3</sub> with a minimum



**Figure 2.** DTA dependences of the change of the normalized mass of the  $SrCO_3 + 0.5Cr_2O_3 + MoO_3$  powder mixture annealed in a continuous 5% H<sub>2</sub>/Ar flow at a heating rate of 1.4 deg/min in the temperature range 300–1300 K



**Figure 3.** XRD patterns of the  $SrCO_3+0.5Cr_2O_3+MoO_3$  mixture, taken *in situ* in the  $Ar/H_2$  medium at a heating rate of 10 deg / min, presented at the temperature range 520–1270 K

at T=1038 K, an insignificant increase in the mass loss of the sample, achieving  $(\Delta m/m_0 \sim 0.30\%)$  at T=1042.5 K is observed (Figs 1, 2). The emergence of the Sr<sub>2</sub>Cr-MoO<sub>6.8</sub> solid solution has been revealed during the investigation of the phase composition (Fig. 3). In this case, a chemical reaction with the formation of the strontium chrome-molybdate is realized according to the following chemical reactions:

$$SrCrO_4 + SrMoO_4 = Sr_2CrMoO_{6-\delta} + (1+\delta/2)O_2 \uparrow \qquad (5)$$

$$SrCrO_3 + SrMoO_4 = Sr_2CrMoO_{6-\delta} + (0.5 + \delta/2)O_2 \uparrow (6)$$

At that, an amount of the double perovskite increases, and the  $SrCrO_4$  and  $SrCrO_3$  phases concentration decreases. One can suppose that the  $SrCrO_4$  and  $SrCrO_3$  phases surfaces act as the active centers for the appearance of nuclei of the new  $Sr_2CrMoO_{6-\delta}$  phase, on which the dissociation process takes place, accompanied by the disappearance of the  $SrCrO_4$  and  $SrCrO_3$  phases during the  $Sr_2CrMoO_{6-\delta}$  growth.

With an increase in temperature to  $T=1154.2~{\rm K}$  in the region where the fifth endothermic effect was recorded, the main reflections of the SrCrO<sub>4</sub> phase are decreasing insignificantly, whereas the SrCrO<sub>4</sub> and SrCrO<sub>3</sub> phases amount is considerably larger, and their content in the sample at 1170 K was no more than 7.9% (Figs 2, 3).

$$SrCrO_3 + Sr_2CrO_4 + 2SrMoO_4 =$$

$$= 2Sr_2CrMoO_{6-\delta} + SrO + (1+\delta)O_2 \uparrow$$
(7)

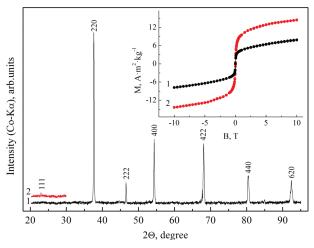
At that the main XRD reflexes of the SrO phase were absent, and the reflexes of the Sr<sub>2</sub>CrO<sub>4</sub> phase practically did not decrease. One can suppose, that the formed strontium oxide swiftly reacts with the chrome-strontium oxide according to the following reaction:

$$SrCrO_3 + SrO = Sr_2CrO_4$$
 (8)

Samples heated to temperatures of 1200 and 1270 K according to the XRD data are qualitatively identical and differ only in their quantitative composition. So, the composition of the sample heated up to T=1200 K has a quantitative phase ratio:  $\mathrm{Sr_2CrMoO_{6-\delta}}-47.2\%$ ,  $\mathrm{Sr_2CrO_4}-23.6\%$ , and  $\mathrm{SrMoO_4}-29.2\%$ . With a further increase in temperature up to 1270 K, the composition changes in the direction of increasing the content of double perovskite to  $\mathrm{Sr_2CrMoO_{6-\delta}}$  of 73.8% and decreasing the phases of  $\mathrm{Sr_2CrO_4}-15.3\%$  and  $\mathrm{SrMoO_4}-10.9\%$ .

In the temperature range 1200–1270 K, the sample mass practically does not change, while the thermal effect is present and the sample remains multiphase. This indicates the difficulty of solid-state reactions with the formation of the  $\mathrm{Sr_2CrMoO}_{6-\delta}$  solid solution. It was possible to synthesize the single-phase strontium chrome-molybdate without the cations superstructural ordering at T=1470 K in the 5% H<sub>2</sub>/Ar flow during 24 hours (Fig. 4, curve 1). Herewith, the saturation magnetization value ( $M_{\mathrm{sat}}$ ) is 7.8 A×m²×kg¹ at T=7 K in a magnetic field with the induction  $B \geq 6$  T (Fig. 4, inset).

Being based on the fact that at the annealing of the initial batch the SrCrO<sub>3</sub>, SrMoO<sub>4</sub> and Sr<sub>2</sub>CrO<sub>4</sub> complex oxides are the concomitant ones practically in the entire temperature range of the strontium chrome-molybdate and they are badly dissolved, for their removal one



**Figure 4.** XRD patterns of the single-phase  $Sr_2CrMoO_{6-\delta}$  samples: synthesized at T=1470 K in the 5%  $H_2/Ar$  flow during 24 hours (1); synthesized at combined modes (2). Insert: field dependences of the magnetization of the single-phase  $Sr_2CrMoO_{6-\delta}$  samples

needs to investigate the dynamics of their transformation degree ( $\alpha(T)$ ) (Fig. 5, a and b). On the base of obtained data it was important to develop the synthesis modes of the single-phase compound, at which the maximally fast dissolution of  $SrCrO_3$  and  $SrMoO_4$  without a formation of  $Sr_2CrO_4$ , with the emergence and growth on the single-phase strontium chrome-molybdate with the Cr/Mo superstructural ordering.

It has been determined as a result of investigations of  $d\alpha/dt = f(T)$  that amplitude values of the derivative of the degree of conversion of the phases  $SrCrO_3$ ,  $SrMoO_4$  and  $Sr_2CrO_4$  correspond to the temperatures  $T_1 = 920$  K,  $T_2 = 990$  K and  $T_3 = 1045$  K, correspondingly, at which their crystallization rates are maximal (Fig. 5, b). In view of the fact that  $T_3 > T_2 > T_1$ , this indicates the presence of more significant kinetic difficulties at the formation of  $Sr_2CrO_4$  phase, which further does not disappear, and at its emergence the double perovskite growth retardation is observed.

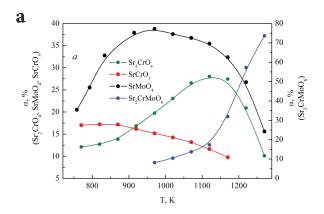
Based on the above data, it follows that in order to reduce the phase formation processes and increase the decomposition rate of intermediate products of the SrCrO, and SrMoO<sub>4</sub> reaction, in order to protect the formation of the Sr, CrO<sub>4</sub> during crystallization of the Sr, CrMoO<sub>6-8</sub> solid solution, the dynamics of phase transformations should be taken into account and combined heating conditions should be applied. According to the analysis of  $\alpha = f(T)$ , it was found that with an increase in the rate of temperature rise, the Sr<sub>2</sub>CrMoO<sub>6-8</sub> rises and it reaches the maximum values at T = 1070 K. In this case, for temperatures above 1200 K, a slowdown in the growth rate of the double perovskite is observed. The detected stepping change in the growth rate of  $Sr_2CrMoO_{6-\delta}$  with the presence of an extremum of the  $(d\alpha/dt)_{max} = 0.07$  at T = 1070 K, is caused by a formation of the intermediate reaction products, decreasing the coefficients of chemical diffusion of reagents into the reaction zone. Based on the fact that we are dealing with series-parallel reactions occurring simultaneously with the formation of various products and, above all, SrCrO<sub>3</sub>, SrMoO<sub>4</sub> and Sr<sub>2</sub>CrO<sub>4</sub>, the rate of the processes will be determined by a slower stage. One can

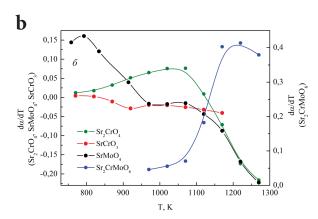
suppose that the dissolution of the  $Sr_2CrO_4$  phase could act as a limiting stage at the  $Sr_2CrMoO_{6-\delta}$  crystallization in the high-temperature region  $T \geq 1070$  K. Therefore, to increase the growth rate of  $Sr_2CrMoO_{6-\delta}$ , it is necessary to reduce the diffusion path of the starting reagents to the reaction zone by the eliminating intermediate reaction products during a crystallization of the double perovskite.

On the base of the obtained data, in order to obtain the single-phase solid solution with the Cr/Mo cations super-structural ordering, the synthesis was realized from the SrCrO<sub>3</sub> and SrMoO<sub>4</sub> using combined heating modes:

- at the first stage, preliminary synthesis was performed at T = 1070 K for 15 hours. This temperature was chosen due to the fact that at this value, according to the equation (6), the value |dα/dt = f(T)|<sub>max</sub> = 0.07 for the Sr<sub>2</sub>CrMoO<sub>6-δ</sub> solid solution was observed;
- at the second stage, to increase the reactivity of the mixture and the diffusion mobility of the reactants, the formed layer of the reaction product was crushed, homogenized, and the mixture was highly dispersed by thin vibro-grinding in alcohol for 2 hours;
- at the third stage, in order to decompose the SrMoO<sub>4</sub> and SrCrO<sub>3</sub> precursors as quickly as possible and achieve the degree of conversion value α = 100% for Sr<sub>2</sub>CrMoO<sub>6-8</sub>, as well as to prevent the Sr<sub>2</sub>CrO<sub>4</sub> phase formation, the synthesis was carried out at T = 1170 K for 15 hours, followed by heating up to T = 1200 K, since at these conditions the maximum values of the degree of the double perovskite conversion were achieved.

As a results of the use of combined synthesis modes, we have succeeded to obtain the  $Sr_2CrMoO_{6-\delta}$  single-phase compound with the superstructural ordering of iron and molybdenum cations (Fig. 4, curve 2). Herewith the saturation magnetization value is 14.4 A×m²×kg¹ at T = 7 K, in the magnetic field with the induction  $B \ge 6$  T (Fig. 4, inset).





**Figure 5.** Temperature dependences of the degree of conversion,  $\alpha(a)$  and their derivatives,  $d\alpha/dT(b)$ , for  $SrCrO_3$ ,  $SrMoO_4$ ,  $Sr_2CrO_4$  and  $Sr_2CrMoO_6$  compounds

### 4. Conclusion

It was determined during the investigation of the sequence of phase transformations during a crystallization of the strontium chrome-molybdate, that SrCrO<sub>2</sub>, SrMoO<sub>4</sub> and Sr<sub>2</sub>CrO<sub>4</sub> are the main concomitant compounds. Herewith it has been noticed that with an increase of annealing temperature from 300 K to 1270 K, SrCrO<sub>4</sub>, SrCrO<sub>3</sub> (350–550 K), and then SrMoO<sub>4</sub>, Sr<sub>2</sub>CrO<sub>4</sub> (600-750 K) complex compounds are appearing in the starting mixture initially and practically simultaneously. It was found at the subsequent temperature increase, that in the temperature range 940–1100 K that the SrMoO<sub>4</sub>, Sr<sub>2</sub>CrO<sub>4</sub> and SrCrO<sub>3</sub> phase concentration sharply decreases with the emergence and increase of the  $Sr_2CrMoO_{6-\delta}$  double perovskite. It has been determined as a result of investigations of  $d\alpha/dt =$ f(T), that amplitude values of the derivative of the degree of conversion of the phases SrCrO<sub>3</sub>, SrMoO<sub>4</sub> and Sr<sub>2</sub>CrO<sub>4</sub> correspond to the temperatures 920, 990 and 1045 K, correspondingly, when their crystallization rates are maximal. The largest crystallization temperature is characteristic for the Sr<sub>2</sub>CrO<sub>4</sub> phase. This indicates the presence of considerable kinetic difficulties at the formation of this phase, which further on does not disappear and retards the double perovskite growth. On the base of investigations of the phase transformations dynamics for the obtaining of the single-phase Sr<sub>2</sub>CrMoO<sub>6-δ</sub> compound with the superstructural ordering of the Cr/Mo cations and improved magnetic characteristics, the SrCrO<sub>3</sub> and SrMoO<sub>4</sub> precursors were used with combined heating modes.

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### References

- Serrate D., De Teresa J.M., Ibarra M.R. Double perovskites with ferromagnetism above room temperature. *J. Phys.: Condens. Matter*, 2007; 19(2): 023201. https://doi.org/10.1088/0953-8984/19/2/023201
- Rubi D., Frontera C., Roig A., Nogués J., Muñoz J.S., Fontcuberta J. A new approach to increase the Curie temperature of Fe–Mo double perovskites. *Materials Science and Engineering: B*, 2006; 126(2–3): 139–142. https://doi.org/10.1016/j.mseb.2005.09.013
- 3. Topwal D., Sarma D.D., Kato H., Tokura Y., Avignon M. Structural and magnetic properties of  $\mathrm{Sr_2Fe_{1+x}Mo_{1-x}O_6}$  (-1 $\leq$ x $\leq$ 0.25). *Phys. Rev. B*, 2006; 73(9): 0944191-1–0944191-1. https://doi.org/10.1103/PhysRevB.73.094419
- Kovalev L.V., Yarmolich M.V., Petrova M.L., Ustarroz J., Terryn H.A., Kalanda N.A., Zheludkevich M.L. Double perovskite Sr<sub>2</sub>FeMoO<sub>6</sub> films prepared by electrophoretic deposition. ACS Appl. Mater. Interfaces, 2014; 6(21): 19201–19206. https://doi.org/10.1021/am5052125
- Fontcuberta J., Balcells L., Bibes M., Navarro J., Frontera C., Santiso J., Fraxedas J., Martínez B., Nadolski S., Wojcik M., Jedryka E., Casanove M.J. Magnetoresistive oxides: new developments and applications. *J. Magn. Magn. Mat.*, 2002; 242–245(1): 98–104. https://doi.org/10.1016/S0304-8853(01)01208-2
- Balcells L., Calvo E., Fontcuberta J. Room-temperature anisotropic magnetoresistive sensor based on manganese perovskite thick films. *J. Magn. Mat.*, 2002; 242–245(2): 1166–1168. https://doi. org/10.1016/S0304-8853(01)01292-6
- Sarma D.D., Mahadevan P., Saha-Dasgupta T., Ray S., Kumar A. Electronic Structure of Sr<sub>2</sub>FeMoO<sub>6</sub>. *Phys. Rev. Lett.*, 2000; 85(12): 2549–2552. https://doi.org/10.1103/PhysRevLett.85.2549
- Kalanda N.A., Kovalev L.V., Waerenborgh J.C., Soares M.R., Zheludkevich M.L., Yarmolich M.V., Sobolev N.A. Interplay of superstructural ordering and magnetic properties of the Sr<sub>2</sub>FeMoO<sub>6-8</sub>

- double perovskite. Science Advanced Materials, 2015; 7(3): 446–454. https://doi.org/10.1166/sam.2015.2134
- Kalanda N., Turchenko V., Karpinsky D., Demyanov S., Yarmolich M., Balasoiu M., Lupu N., Tyutyunnikov S., Sobolev N. The role of the Fe/Mo cations ordering degree and oxygen non-stoichiometry on the formation of the crystalline and magnetic structure of Sr<sub>2</sub>FeMoO<sub>6-8</sub>. *Phys. Status Solidi B*, 2019; 256(5): 1800278-1–1800278-7. https://doi.org/10.1002/pssb.201800278
- 10. Auth N., Jakob G., Westerburg W., Ritter C., Bonn I., Felser C., Tremel W. Crystal structure and magnetism of the double perovskites A<sub>2</sub>FeReO<sub>6</sub> (A = Ca, Sr, Ba). *J. Magn. Magn. Mat.*, 2004; 272–276: E607–E608. https://doi.org/10.1016/j.jmmm.2003.12.484
- 11. Philipp J.B., Majewski P., Alff L., Erb A., Gross R., Graf T., Brandt M.S., Simon J., Walther T., Mader W., Topwal D., Sarma D.D. Structural and doping effects in the half-metallic double perovskite A<sub>2</sub>CrWO<sub>6</sub> (A = Sr, Ba, and Ca). *Phys. Rev. B.*, 2003; 68(14): 144431. https://doi.org/10.1103/PhysRevB.68.144431
- Zeng Z., Fawcett I.D., Greenblatt M., Croft M. Large magnetore-sistance in double perovskite Sr<sub>2</sub>Cr<sub>1.2</sub>Mo<sub>0.8</sub>O<sub>6.8</sub>. *Materials Research Bulletin*, 2001; 36(3–4): 705–715. https://doi.org/10.1016/S0025-5408(01)00520-7
- Seung-Iel Park, Hong Joo Ryu, Sung Baek Kim, Bo Wha Lee, Chul Sung Kim. Neutron diffraction and magnetic properties of Sr-<sub>2</sub>Fe<sub>0.9</sub>Cr<sub>0.1</sub>MoO<sub>6</sub>. Phys. B: Condens. Matter, 2004; 345(1–4): 99–102. https://doi.org/10.1016/j.physb.2003.11.032
- Wang J., Liu G., Zhong W., Du Y. Magnetic inhomogeneity and valence state in Sr<sub>2</sub>CrWO<sub>6</sub> double perovskite. *J. Appl. Phys.*, 2003; 93(1): 471–474. https://doi.org/10.1063/1.1524710
- Ngantso G.D., Benyoussef A., El Kenz A., Naji S. Study of the magnetic properties and phase transitions of Sr<sub>2</sub>CrMoO<sub>6</sub> by mean-field approximation. *J. Supercond. Nov. Magn.*, 2015; 28(8): 2589–2596. https://doi.org/10.1007/s10948-015-3077-7

- Patterson F.K., Moeller C.W., Ward R. Magnetic oxides of molybdenum (V) and tungsten (V) with the ordered perovskite structure. *Inorg. Chem.*, 1963; 2(1): 196–198. https://doi.org/10.1021/ic50005a050
- 17. Chan T.S., Liu R.S., Hu S.F., Lin J.G. Structure and physical properties of double perovskite compounds Sr<sub>2</sub>FeMO<sub>6</sub> (M = Mo, W). *Materials Chemistry and Physics*, 2005; 93(2–3): 314–319. https://doi.org/10.1016/j.matchemphys.2005.03.060
- Moritomo Y., Xu Sh., Machida A., Akimoto T., Nishibori E., Takata M., Sakata M. Electronic structure of double-perovskite transition-metal oxides. *Phys. Rev. B*, 2000; 61(12): R7827. https://doi.org/10.1103/PhysRevB.61.R7827
- Arulraj A., Ramesha K., Gopalakrishnan J., Rao C.N.R. Magnetoresistance in the double perovskite Sr<sub>2</sub>CrMoO<sub>6</sub>. *J. Solid State Chemis*try, 2000; 155(1): 233–237. https://doi.org/10.1006/jssc.2000.8939
- Philipp J.B., Reisinger D., Schonecke M., Marx A., Erb A., Alff L., Gross R., Klein J. Spin-dependent transport in the double-perovskite Sr<sub>2</sub>CrWO<sub>6</sub>. Appl. Phys. Lett., 2001; 79(22): 3654–3656. https://doi. org/10.1063/1.1421227
- 21. Li Q. F., Zhu X. F., Chen L. F. First-principles investigations of disorder effects on electronic structure and magnetic properties in

- Sr<sub>2</sub>CrMoO<sub>6</sub>. *J. Phys.: Condens. Matter*, 2008; 20(25): 255230. https://doi.org/10.1088/0953-8984/20/25/255230
- 22. Geprägs S., Czeschka F.D., Opel M., Goennenwein S.T.B., Yu W., Mader W., Gross R. Epitaxial growth and magnetic properties of r<sub>2</sub>CrReO<sub>6</sub> thin films. *J. Magn. Magn. Mat.*, 2009; 321(13): 2001– 2004. https://doi.org/10.1016/j.jmmm.2008.12.029
- 23. Yarmolich M., Kalanda N., Demyanov S., Fedotova Ju., Bayev V., Sobolev N. Charge ordering and magnetic properties in nanosized Sr<sub>2</sub>FeMoO<sub>6-δ</sub> powders. *Phys. Status Solidi B*, 2016; 253(11): 2160– 2166. https://doi.org/10.1002/pssb.201600527
- 24. Ritter C., Blasco J., De Teresa J.M., Serrate D., Morellon L., Garcia J., Ibarra M.R. Structural and magnetic details of 3d-element doped Sr<sub>2</sub>Fe<sub>0.75</sub>T<sub>0.25</sub>MoO<sub>6</sub>. Solid State Sciences, 2004; 6(5): 419–431. https://doi.org/10.1016/j.solidstatesciences.2004.02.007
- 25. Kraus W., Nolze G. POWDER CELL a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *J. Appl. Cryst.*, 1996; 29(3): 301–303. https://doi.org/10.1107/S0021889895014920
- Rodríguez-Carvajal J. Recent developments of the program FULL-PROF. In: Commission on powder diffraction (IUCr). Newsletter, 2001: 26: 12–19. https://www.fkf.mpg.de/4112052/cpd26.pdf