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The formation of the complex manganites $\text{LnSr}_2\text{Mn}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}$)

A.B. Missyul^{a,*}, I.A. Zvereva^a, T.T.M. Palstra^b

^a Department of Chemistry, Saint-Petersburg State University, Universitetsky pr., 26, 198504 St.-Petersburg, Russia

^b Solid State Chemistry Laboratory, Zernike Institute for Advanced Materials, University of Groningen, 9747AG Groningen, The Netherlands

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ABSTRACT

The process of formation of the Ruddlesden–Popper phases $\text{LnSr}_2\text{Mn}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}$) was investigated by means of X-ray diffraction, thermal analysis and microprobe analysis. Two parallel pathways were found for the reaction. The first one includes the formation of the intermediate K_2NiF_4 -type compound by interaction of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ and perovskite-type solid solution $(\text{Ln}, \text{Sr})\text{MnO}_3$, while in the second one the K_2NiF_4 -type intermediate is formed during the reaction of the same perovskite-type solid solution with the corresponding rare earth oxide. This result gives an explanation for the formation of two phases with slightly different cationic compositions. The kinetics of the reaction was investigated for both mechanisms resulting in determination of their relative contribution to the final composition. Pure $\text{NdSr}_2\text{Mn}_2\text{O}_7$ was obtained using a step-by-step process according to the first mechanism, and the magnetic properties of this phase were investigated.

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1. Introduction

The Ruddlesden–Popper phases $\text{Ln}_{1-2x}\text{Sr}_{2+2x}\text{Mn}_2\text{O}_7$ with a $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type structure (Fig. 1) are of significant interest due to the effect of colossal magnetoresistance. The properties of these compounds were studied intensively [1–7] but some issues remain unexplained. For example, structural investigations [8,9] had shown that some compounds were formed not as a single phase but as a mixture of two phases possessing a slightly different $\text{Ln}:\text{Sr}$ ratio. Also some of the data concerning their physical properties are controversial. Such a controversy was found for magnetic susceptibility of the $\text{NdSr}_2\text{Mn}_2\text{O}_7$. The temperature dependence given in [10] shows an unusual peak at 210 K while the authors of [11] present a curve that is typical for Ruddlesden–Popper manganites.

It was reported [12–14] that the formation of the $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type phases usually goes in a complex multistep way. In most cases the last step of such reactions is the interaction of the perovskite phase and the K_2NiF_4 -type Ruddlesden–Popper phase according to the equation $\text{ABO}_3 + \text{A}_2\text{BO}_4 = \text{A}_3\text{B}_2\text{O}_7$. The composition and stability of the intermediate phases might strongly affect the process of formation of the $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type phase. In the current article the process of formation of $\text{NdSr}_2\text{Mn}_2\text{O}_7$ is described and the possible explanation of the problems mentioned above are given based on the mechanism of the reaction.

2. Experimental

All materials were synthesized using a standard ceramic technique from stoichiometric quantities of Ln_2O_3 (Johnson Matthey, 99.9%), MnO_2 (Johnson Matthey, 99.9%), and SrCO_3 (Johnson Matthey, 99.99%). Initial compounds were ground in an agate mortar, pelletized and heated in a platinum crucible. The formation of the $\text{NdSr}_2\text{Mn}_2\text{O}_7$ from the Nd_2O_3 , SrCO_3 and MnO_2 was investigated at 1200 °C, heating time was 3–24 h. The conditions of syntheses of the pure compounds are summarized in Table 1.

The phase analysis was performed on a Philips Analytical X-Ray PW3020 diffractometer using $\text{Cu K}\alpha$ radiation in the range $2\theta = 20\text{--}60^\circ$ with 0.02° step. Step time was 4 s. The data for structure calculations were obtained with a Bruker D8 diffractometer. Rietveld refinement was performed with the GSAS suite of programs [10]. Powder diffraction pattern for the refinement was obtained in the range $2\theta = 10\text{--}135^\circ$ with 0.02° step. Step time was 9 s.

The DSC–TGA analysis of the reaction mixture was made using the TA SDT 2960 device. 37.243 mg of the sample were placed in the Pt pan and heated until 1300 °C in air with heating rate 20 °C/min. Corrections were made for the empty sample holder response.

The reaction mixture has been investigated by SEM (Carl Zeiss EVO 40EP). The microprobe analysis of the sample has been performed using the Oxford Instrument INCA 350 attachment.

The magnetic measurements were performed with a SQUID magnetometer MPMS 7 (Quantum Design) using a DC field 1000 Oe under both zero-field-cooled (ZFC) and field-cooled (FC) conditions in the temperature interval 5–350 K.

* Corresponding author. Tel.: +7 812 4284051; fax: +7 812 4286939.
E-mail address: lab2193@gmail.com (A.B. Missyul).

Fig. 1. Crystal structure of the $\text{LnSr}_2\text{Mn}_2\text{O}_7$ phases ($\text{Sr}_3\text{Ti}_2\text{O}_7$ structure type). ● – Ln, Sr; ◆ – MnO_6 octahedra.

3. Results and discussion

The qualitative phase analysis of the reaction mixture after 3 h heating at 1200 °C shows that the following phases are present: Nd_2O_3 , $\text{Sr}_7\text{Mn}_4\text{O}_{15}$, $\text{Nd}_x\text{Sr}_{1-x}\text{MnO}_3$ and $\text{Nd}_{1+x}\text{Sr}_{2-x}\text{Mn}_2\text{O}_7$ (Fig. 2). Using the analogy with the previously found mechanism of formation of the Ruddlesden–Popper phases $\text{Ln}_2\text{SrAl}_2\text{O}_7$ and $\text{Ln}_2\text{SrFe}_2\text{O}_7$ [12–15] the following mechanism had been proposed:

Table 1

Conditions of syntheses of different manganites.

Substance	Initial compounds	Heating temperature, °C	Time of heating, h
$\text{Nd}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$	Nd_2O_3 , SrCO_3 , MnO_2	1400	48
$\text{Nd}_{0.25}\text{Sr}_{1.75}\text{MnO}_4$	Nd_2O_3 , SrCO_3 , MnO_2	1300	48
$\text{Sr}_7\text{Mn}_4\text{O}_{15}$	SrCO_3 , MnO_2	1200	24
$\text{NdSr}_2\text{Mn}_2\text{O}_7$	Ln_2O_3 , SrCO_3 , MnO_2	1300	48
$\text{NdSr}_2\text{Mn}_2\text{O}_7$	$\text{Nd}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$, $\text{Nd}_{0.25}\text{Sr}_{1.75}\text{MnO}_4$	1400	48

Fig. 2. Powder diffraction pattern of the reaction mixture during the synthesis of $\text{NdSr}_2\text{Mn}_2\text{O}_7$ (1200 °C, 3 h). ◆ – Nd_2O_3 , ● – $\text{Sr}_7\text{Mn}_4\text{O}_{15}$, ★ – $\text{Nd}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$, ■ – $\text{Nd}_{1.75}\text{Sr}_{0.25}\text{Mn}_2\text{O}_7$.

Absence of the peaks of the $\text{Nd}_{0.25}\text{Sr}_{1.75}\text{MnO}_4$ phase on the powder pattern means that its formation is the slowest stage in the reaction while the last stage is much faster.

The fact that $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ appears in the reaction mixture instead of the K_2NiF_4 -type phase can be understood by analysis of the structure of SrMnO_3 . While possessing the same formula as perovskites, this compound has a different structure with face-sharing MnO_6 octahedra (Fig. 3a). This structural feature remains unchanged when the layered structure $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ is formed, leading to the different chemical composition (Fig. 3b).

The quantitative analysis of the reaction mixture shows that the proposed mechanism does not account for the reaction completely. The $\nu(\text{Sr}_7\text{Mn}_4\text{O}_{15}) : \nu(\text{Nd}_2\text{O}_3)$ molar ratio appears to be 0.77:1 instead of 2:1, as required by the proposed mechanism. In order to explain this fact it was proposed that the perovskite phase contains less Nd, while the excess of the Nd_2O_3 reacts with the perovskite in the same way as in case of the formation of the $\text{Gd}_2\text{SrFe}_2\text{O}_7$ [15]. This means that the perovskite phase reacts with Nd_2O_3 forming the K_2NiF_4 -type phase and this K_2NiF_4 -type phase reacts with the perovskite phase yielding the double-layered Ruddlesden–Popper phase. Again, the slowest stage of the reaction is the formation of the K_2NiF_4 -type phase.

The processes that take place in the system during heating were investigated by the DSC–TGA method (Fig. 4). Comparison with the data for the pure initial compounds and previously published results concerning the formation of the $\text{LnSr}_2\text{Al}_2\text{O}_7$ series [12] as well as X-ray phase analysis gives rise to the following explanation of the observed thermal effects. At 360 °C small amounts of water (about 0.5%) absorbed by Nd_2O_3 are released. At 650 °C MnO_2 decomposes yielding Mn_2O_3 . The broad peak at 950–1030 °C appears due to the series of processes: Mn_2O_3 decomposes yielding Mn_3O_4 , SrCO_3 undergoes a phase transition and the formation of the intermediate products starts. These processes result in a large decrease in mass (approximately 14%). At higher temperature the mass of the reaction mixture increases again because the formation of the intermediate compounds from Mn_3O_4 implies

Fig. 6. (a) The conversion degree for two mechanisms of the $\text{NdSr}_2\text{Mn}_2\text{O}_7$ formation at 1200°C . (b) Amount of the Ruddlesden–Popper phases formed by each of the reaction mechanisms (I and II) and total amount (Σ) of the Ruddlesden–Popper phases at 1200°C . (c) Kinetics of the formation of $\text{LaSr}_2\text{Mn}_2\text{O}_7$ (—●—) and $\text{GdSr}_2\text{Mn}_2\text{O}_7$ (—■—) at 1200°C .

The DSC–TGA data of the reaction mixture during the formation of $\text{LaSr}_2\text{Mn}_2\text{O}_7$ and $\text{GdSr}_2\text{Mn}_2\text{O}_7$ are qualitatively the same as for $\text{NdSr}_2\text{Mn}_2\text{O}_7$. This supports the conclusion that the formation process goes the same way for all lanthanides investigated.

The reaction mixture obtained during the formation of $\text{GdSr}_2\text{Mn}_2\text{O}_7$ has been investigated by SEM. The interacting particles have a size of 1–5 μm . The microprobe analysis of the sample has shown that the intermediate perovskite phase is $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, the composition being close to the one obtained for $\text{NdSr}_2\text{Mn}_2\text{O}_7$ by means of the X-ray diffraction data.

In order to obtain a single-phase $\text{NdSr}_2\text{Mn}_2\text{O}_7$ the step-by-step synthesis according to the mechanism (I) was performed. The single-phase product was obtained according to the X-ray diffraction data. The structure refinement of the $\text{NdSr}_2\text{Mn}_2\text{O}_7$

Fig. 7. Structure refinement of $\text{NdSr}_2\text{Mn}_2\text{O}_7$ obtained by the step-by-step synthesis. Inset: magnified peak at 45.5° .

Fig. 8. Magnetic susceptibility of $\text{NdSr}_2\text{Mn}_2\text{O}_7$ versus temperature. Inset: inverse magnetic susceptibility.

obtained by this method (see Table 2 and Fig. 7) gives the structure data close to that of the main phase in the mixture obtained by the one-step synthesis from the initial oxides [8]. The inset of Fig. 7 shows that the shape of the peak at $2\theta = 45.5^\circ$ is described nicely by taking into account α_1/α_2 stripping (see for comparison Fig. 2 in [8]). This result supports the conclusions of the kinetic studies, namely it shows that most of the $\text{NdSr}_2\text{Mn}_2\text{O}_7$ phase is formed by mechanism (I).

The magnetic susceptibility of the single-phase $\text{NdSr}_2\text{Mn}_2\text{O}_7$ was measured. The temperature dependence of the magnetic

Table 2
Structure of $\text{NdSr}_2\text{Mn}_2\text{O}_7$ obtained by the step-by-step synthesis.

	Ion	Position	x	y	z	U_{iso}	Occupancy
$\text{NdSr}_2\text{Mn}_2\text{O}_7$ $a = b = 3.84929(9)$ $c = 19.9566(6)$ $R_{\text{wp}} = 13.8\%$ $R_p = 10.2\%$	Nd^{3+}	2b	0	0	0.5	0.0092(7)	0.288(4)
	Sr^{2+}	2b	0	0	0.5	0.0092(7)	0.712(4)
	Nd^{3+}	4e	0	0	0.68290(7)	0.0117(5)	0.356(2)
	Sr^{2+}	4e	0	0	0.68290(7)	0.0117(5)	0.644(2)
	Mn^{3+}	4e	0	0	0.9018(2)	0.0024(5)	0.5
	Mn^{4+}	4e	0	0	0.9018(2)	0.0024(5)	0.5
	O^{2-}	2a	0	0	0	0.029(5)	1
	O^{2-}	4e	0	0	0.8026(6)	0.032(4)	1
	O^{2-}	8g	0	0.5	0.4025(4)	0.028(2)	1

susceptibility (Fig. 8) appeared to be almost the same as found by Zhang et al. [11] both qualitatively and quantitatively. This means that the anomaly observed by Battle et al. [10] is most likely due to phase separation. Two phase transitions are observed at low temperatures. According to [8], first of them (at 120 K) is due to the antiferromagnetic ordering of the Mn ions in the perovskite layers and the second one (at 30 K) is due to the antiferromagnetic ordering of the Nd ions. The deviation from the Curie–Weiss behavior at 280 K can be described as a result of the two-dimensional ferromagnetic interaction [17].

4. Conclusions

Investigation of the formation of manganites $\text{LnSr}_2\text{Mn}_2\text{O}_7$ (Ln = La, Nd, Gd) provides understanding of new aspects in nature of the phase separation in the double-layered Ruddlesden–Popper phases: namely the cationic composition in these compounds depends on the reaction pathway. The difference in the cationic composition of two phases obtained by the one-step synthesis is due to the difference in the mechanisms of formation.

Step-by-step synthesis of $\text{NdSr}_2\text{Mn}_2\text{O}_7$ according to one of the mechanisms (corresponding to the fastest reaction rate) yielded a single-phase product. The temperature dependence of the magnetic susceptibility is characteristic for single-phase Ruddlesden–Popper manganites.

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