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The impact of Nd^{3+}/La^{3+} substitution on the cation distribution and phase diagram in the $La_2SrAl_2O_7$-$Nd_2SrAl_2O_7$ system

The effect of isovalent cation substitution of lanthanum atoms in the structure of $La_2SrAl_2O_7$ oxide, and phase equilibria (solidus-liquidus curves) in the binary system $La_2SrAl_2O_7$-$Nd_2SrAl_2O_7$ were studied. It was found that Nd^{3+} substitution for La^{3+} has effect on the structure of $La_2SrAl_2O_7$ in respect of the character of cation distribution in the solid solution $La_{2-x}Nd_xSrAl_2O_7$ from statistically disordered to the ordered one where strontium cations predominantly occupied the rock-salt layers, as reflected by the solidus-liquidus lines.

Keywords: perovskites, transition metal oxides, solid solutions, layered compounds, phase diagram

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Introduction

The elements that occupy A-sites in the perovskite-related oxides play a significant role in both crystallographic and physical properties. A well-known fact is related to the heterovalent substitutions of large A^{p+} cations which can trigger mixed valence state of B transition elements and induced superconductivity in cuprates or giant magnetoresistance in manganites. It is also generally acknowledged that electrical properties of a perovskite-like solid solution depend significantly on the mean size of cations located in the A-site positions, and even more – on the size mismatch between them.

The isovalent substitution of Ca^{2+} for Sr^{2+} was studied intensively in the superconducting cuprates $La_{2-x}Sr(Ca)_xCu_2O_{6-\delta}$ [1] and in the magnetoresistant manganites $Ln_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr) [2]. The crystal chemistry of such cationic substitution in the perovskite-like aluminates is quite similar, as exemplified by the results obtained for two structural types of layered aluminates – $LaSr(Ca)AlO_4$ and $La_2Sr_{1-x}Ca_xAl_2O_7$ [3, 4]. The most striking result is the evidence for the high destabilizing role of Ca^{2+}. It is confirmed by the fact that $LaCaAlO_4$ is thermodynamically unstable, it has demixed to $LaAlO_3$ and

CaO instead of complex crystallographic transformation, which is originated in local ordering of Ca^{2+} and La^{3+} ions [5, 6]. The substitution of Ca^{2+} for Sr^{2+} in $La_2SrAl_2O_7$ is more crucial for the layered structure, and brings progressive instability when the amount of Ca becomes more than $x = 0.5$ because of the positional ordering phenomena [4].

To clarify the different rare-earth (RE) cations' presence in layered perovskite type oxides, it is important to understand their crystal chemistry and stability of the intergrowth structure that influences their properties and potential applications. The size of RE cation, as well as partial RE and Sr cation ordering, play a prominent role in the actual magnetotransport properties. This is the reason why it is worthwile to investigate the cation ordering and the stability of structure in the system where the redox processes for the transition metal are eliminated, as in the case of the isostructural aluminates.

We herein report on the structure analysis for the series of solid solutions $La_{1-x}Nd_x)_2SrAl_2O_7$ and the investigation of solidus-liquidus equilibria in system $La_2SrAl_2O_7$-$Nd_2SrAl_2O_7$. Both RE strontium aluminates $Ln_2SrAl_2O_7$ (Ln = La, Nd) belong to the $n = 2$ member of so-called Ruddlesden-Popper phases ($A_{n+1}B_nO_{3n+1}$) [7], in which double perovskite slabs (P_2) alternate with the rocksalt layers (RS). The stability of the structure represented as (P_2/RS) intergrowth for the studied aluminates and their solid solutions at high temperatuteres are considered in the view of the RE–Sr cation ordering.

Experimental

Solid solutions $(La_{1-x}Nd_x)_2SrAl_2O_7$ were prepared by a solid state reaction of the stoichiometric amounts of RE_2O_3 (RE = La, Nd), Al_2O_3, and $SrCO_3$ according to the following equation:

$$(1-x)La_2O_3 + xNd_2O_3 + SrCO_3 + Al_2O_3 \rightarrow$$
$$\rightarrow (La_{1-x}Nd_x)_2SrAl_2O_7 + CO_2.$$

The mixtures were preheated at 900 °C in air, then grinded, pelletized and annealed at 1450 °C for 100 hours (140 hours for RE = La), and cooled in air.

The as-prepared compounds were characterized by the X-ray powder diffraction (XRPD) using a Philips PW3020 diffractometer, in Cu Kα radiation. The structural analysis of the aluminates was made using the results collected in the angular range $2\theta = 5$–$120°$, with the step of 0.04° in 2θ and exposure time of 12 s. The structural parameters were refined by the Rietveld method using the FullProf software.

The melting points for the samples were determined by the differential thermal analysis (DTA) using a VTA-982 high-temperature thermal analyzer in helium atmosphere with heating rate of 10 K/min.

Results and discussion

The results of X-ray diffraction (XRD) analysis show that the continuous series of solid solutions $(La_{1-x}Nd_x)_2SrAl_2O_7$ ($0 \leq x \leq 1$), crystallizing in the $Sr_3Ti_2O_7$ structural type, were obtained as single phases. The indexing of the XRPD patterns were performed within the conventional for the P_2/RS intergrowth structure tetragonal unit cell (space group (S.G.) *I*4/*mmm*). The values of unit cell parameters (Fig. 1) decrease monotonically with the increase of Nd content in accordance with the difference in their ionic radii $r(RE^{3+})$. Observed deviation from the Vegard's law might indicate the nonrandom distribution of neodymium atoms in the $La_2SrAl_2O_7$ structure. It is worth to note that, contrary to the $Ca^{2+} \rightarrow Sr^{2+}$substitution, the substitution of $Nd^{3+} \rightarrow La^{3+}$ does not limit the homogeneity range of the $(La_{1-x}Nd_x)_2SrAl_2O_7$ solid solutions.

It was shown earlier [8] that the distribution of Ln^{3+} and Sr^{2+}atoms over two non-equivalent structural positions, namely 12-coordinated AO_{12} and 9-coordinated AO_9, is different in $La_2SrAl_2O_7$ and $Nd_2SrAl_2O_7$. The distribution of La^{3+} and Sr^{2+} in $La_2SrAl_2O_7$ appears to be generally random, however, with some preferable La occupation of AO_{12} polyhedra in the perovskite layers. On the contrary, the visible deviation from the random distribution towards to the positional ordering of Nd^{3+} ions in rock-salt layers is observed in $Nd_2SrAl_2O_7$.

The situation is more complicated in $(La_{1-x}Nd_x)_2SrAl_2O_7$ solid solutions where AO_{12} and AO_9 polyhedra are occupied by the three types of ions: La^{3+}, Nd^{3+} and Sr^{2+}. In the case of the $Nd^{3+} \rightarrow La^{3+}$ substitution, the determination of the sites' occupation by the Rietveld refinement is more difficult, as compared to the case of the $Ca^{2+} \rightarrow Sr^{2+}$ substitution, because of the smaller difference in the number of electrons between La^{3+} and Nd^{3+} (three f-electrons). Therefore, the full-profile X-ray diffraction analysis of solid solutions $(La_{1-x}Nd_x)_2SrAl_2O_7$ provides only the information about the redistribution of Sr atoms over two sites with the change in the neodymium content. Although La^{3+} and Nd^{3+} could not be distinguished by the Rietveld refinement, one can take into account the general tendency obtained for the whole series of $Ln_2SrAl_2O_7$ oxides (Ln = La-Ho) [8], which showed the evidence of favorable occupancy of AO_9 polyhedra by the atoms with smaller atomic radii. Nevertheless, the structure of $(La_{1-x}Nd_x)_2SrAl_2O_7$ solid solutions was refined by means of the Rietveld method.

The occupancy values for the non-equivalent sites calculated for the random distribution of cations and obtained from the XRPD results for two solid solutions $(La_{1-x}Nd_x)_2SrAl_2O_7$ and parent oxides $La_2SrAl_2O_7$ and $Nd_2SrAl_2O_7$ are shown in Table 1. It should be emphasized that the Rietveld refinement gives only the occupancy for Sr atoms. The distribution of La and Nd atoms is undefinable; it could be assumed under consideration that redistribution of strontium from the rock-salt layers (AO_9 polyhedra) into the perovskite layers (AO_{12} polyhedra) is compensated specifically by the transfer of Nd to the rock-salt layers. It should be noted that deviation from the random distribution of cations is observed independently of the distribution of RE atoms when neodymium content is $x \geq 0.6$. No deviations for the random cation distribution were observed in the concentration range $x \leq 0.5$.

To summarize the aforementioned results one can conclude that the transition from random distribution of A-site cations (RE^{3+} and Sr^{2+}) between non-equivalent positions to the ordered one with certain

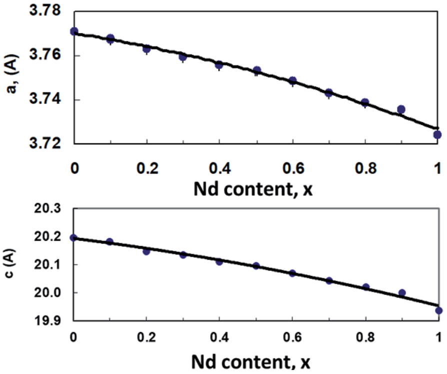

Fig. 1. The unit cell parameters for the $(La_{1-x}Nd_x)_2SrAl_2O_7$ solid solutions versus Nd content (x)

preferred occupancy of perovskite layers by Sr^{2+} ions with the Nd content increase takes place in vicinity of $x = 0.6$. Therefore, the distribution of La^{3+}, Nd^{3+}, Sr^{2+} cations between two non-equivalent sites (AO_9 and AO_{12}) could be presented by the structural diagram shown in Fig. 2.

Bearing in mind that the positional ordering when lanthanide atoms preferably located in the rock-salt layers sites stabilizes the layered P_2/RS type structure, one can conclude that solid solution $(La_{2-x}Nd_x)_2SrAl_2O_7$ should be more stable than lanthanum strontium aluminate $La_2SrAl_2O_7$, but less stable than neodymium-containing analog $Nd_2SrAl_2O_7$. The influence of cation ordering in the continuous series of solid solutions on the phase diagrams, which, in particular, can be observed on a shape of liquidus and solidus lines, was the issue of our further experimental study. We applied the ceramic technique followed by the XRPD analysis in order to examine the phase equilibria in the pseudo-binary system $La_2SrAl_2O_7$–$Nd_2SrAl_2O_7$ within the entire concentration range. Melting points were detected by means of a differential thermal analysis.

The phase diagram (Fig. 3) was constructed taking into account the particularities of the $Ln_2SrAl_2O_7$ melting mechanism [9]. It was found that both $La_2SrAl_2O_7$ and $Nd_2SrAl_2O_7$ melt incongruently:

$$Ln_2SrAl_2O_7 \rightarrow \text{Liquid} + LnAlO_3, \quad (Ln = La, Nd).$$

As a result, two types of double-phase fields where liquid phase coexists with the solid, namely, $(La_{2-x}Nd_x)_2SrAl_2O_7)$ + liquid and $(La_{1-x}Nd_xAlO_3)$ + liquid, appear on the phase diagram.

The main feature of phase equilibria in the $La_2SrAl_2O_7$–$Nd_2SrAl_2O_7$ system is the existence of the minimum on the solidus line. Considering the phase equilibria in the pseudo-binary $La_2SrAl_2O_7$–$Nd_2SrAl_2O_7$ system in combination with the structural transformations of cation coordination during the formation of the

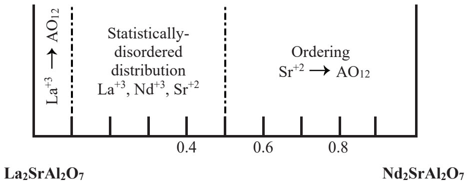

Fig. 2. The structural diagram for the pseudo-binary $La_2SrAl_2O_7$–$Nd_2SrAl_2O_7$ system

Table 1

The occupancy for A-site cations in the AO_{12} and AO_9 polyhedra in $La_2SrAl_2O_7$, $Nd_2SrAl_2O_7$ and $(La_{1-x}Nd_x)_2SrAl_2O_7$ solid solutions (x = 0.6 and 0.8)

P_2/RS		AO_{12}			AO_9		
		La^{+3}	Nd^{+3}	Sr^{+2}	La^{+3}	Nd^{+3}	Sr^{+2}
$Ln_2SrAl_2O_7$	random	0.67	–	0.33	1.33	–	0.67
	calculated	0.73	–	0.27	1.27	–	0.73
$(La_{0.4}Nd_{0.6})_2SrAl_2O_7$	random	0.26	0.41	0.33	0.52	0.80	0.67
	calculated	0.26	0.36	0.38	0.52	0.86	0.62
$(La_{0.2}Nd_{0.8})_2SrAl_2O_7$	random	0.13	0.54	0.33	0.27	1.06	0.67
	calculated	0.13	0.47	0.40	0.27	1.13	0.60
$Nd_2SrAl_2O_7$	random	–	0.67	0.33	–	1.33	0.67
	calculated	–	0.54	0.46	–	1.46	0.54

$(La_{2-x}Nd_x)_2SrAl_2O_7$ solid solution, it is noticeable that the minimum on the solidus line correlates with the disordering-ordering transition domain for La^{3+}, Nd^{3+}, Sr^{2+} distribution. The existence of minimum on the melting point plot may be related to the decrease of enthalpy of the solid solutions formation, which actually reflects the decrease in their stability. Certainly, the studied solid solutions cannot be described in terms of regular solution model, since the entropy contribution to the Gibbs energy of solid solutions formation, accompanied by the cation redistribution between the non-equivalent 12-coordinated (cuboctahedron AO_{12}) and 9-coordinated (antiprism AO_9) sites, should not be neglected.

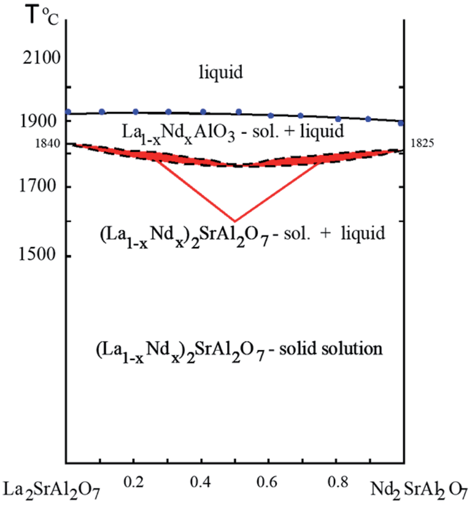

Fig. 3. Phase equilibria in the pseudo-binary $La_2SrAl_2O_7$–$Nd_2SrAl_2O_7$ system

Conclusions

It was shown that $Nd^{3+} \rightarrow La^{3+}$ cation substitution in the crystal structure of $La_2SrAl_2O_7$ allows to obtain continuous series of solid solutions $(La_{1-x}Nd_x)_2SrAl_2O_7$ $(0 \leq x \leq 1)$. Introduction of Nd^{3+} instead of La^{3+} changes the character of cation distribution in the $La_{2-x}Nd_xSrAl_2O_7$ solid solutions from a statistically disordered to the ordered with respect to the strontium cations in the rock-salt layers. The latter causes the particularities in the phase diagram for the pseudo-binary $La_2SrAl_2O_7$-$Nd_2SrAl_2O_7$ system. The minimum on the solidus line correlates with the cation disordering-ordering transition in respect of the Nd content.

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