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Structural Behaviour of Solid Solutions in the NdAlO3-SrTiO3 System

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Abstract

Single-phase mixed aluminates-titanates $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ ($x = 0.3 \div 0.9$) were prepared from stoichiometric amounts of constituent oxides Nd_2O_3, Al_2O_3, TiO_2 and strontium carbonate $SrCO_3$ by solid-state reaction technique in air at 1773 K. Crystal structure parameters of $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ were refined by full-profile Rietveld refinement in space groups $R\,\bar{3}\,c$ ($x = 0.3$, 0.5, 0.7 and 0.8) and $Pm\,\bar{3}\,m$ ($x = 0.9$). Comparison of the obtained structural parameters with the literature data for the end members of the system $NdAlO_3$ and $SrTiO_3$ revealed formation of two kinds of solid solutions $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ with the cubic and rhombohedral perovskite structure. Morphotropic rhombohedral-to-cubic phase transition in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series occurs at $x = 0.84$. Based on the results obtained as well as the literature data for the parent compounds, the tentative phase diagram of the $NdAlO_3$–$SrTiO_3$ pseudo-binary system have been constructed.

Keywords: Perovskite aluminates and titanates, Crystal structure, Solid solution, Phase transition

Background

Mixed aluminates-titanates with perovskite structure formed in the $RAlO_3$–$ATiO_3$ pseudo-binary systems (R = rare earths, A = Sr, Ca) are prospective functional materials. In conjunction with alkaline-earth titanates, rare earth aluminates reveal excellent temperature-stable high-Q microwave dielectric properties and are widely used as radio-frequency ceramics in modern electronic devices ([1–6] and references herein). The highest Q-values among $RAlO_3$- and $ATiO_3$-based microwave ceramics were reported for $LaAlO_3$–$SrTiO_3$ system, which exhibits solid solubility across the entire compositional range. It was shown that dielectric properties of mixed aluminates-titanates ceramics do not significantly depend on the nature of the rare earth and the value of resonant frequency (t_f) can be tuned by changing the concentration of solid solution. Thus potentially useful ceramics with temperature-stable relative permittivity can be obtained in other $RAlO_3$–$ATiO_3$ perovskite series.

The interest to the $RAlO_3$–$SrTiO_3$ systems has been increased considerably during the last decade after discovering of the intrigue phenomena of two-dimensional electron gas at the interface between two insulators $LaAlO_3$ and $SrTiO_3$ [7]. The interface effects occurred in the $RAlO_3$–$SrTiO_3$ perovskite systems are in the focus of active research in the field of tunable metal-insulator transition, 2D superconductivity, coexistence of superconductivity and ferromagnetism, etc. [8–11].

The aim of the present work is the study of the phase and structural behaviour of the mixed aluminates-titanates formed in the $NdAlO_3$–$SrTiO_3$ pseudo-binary system. At room temperature, the end members of the system—$NdAlO_3$ and $SrTiO_3$—adopt different variants of the perovskite structure: rhombohedral $R\,\bar{3}\,c$ and cubic $Pm\,\bar{3}\,m$, respectively. Rhombohedral $NdAlO_3$ transforms into the cubic perovskite structure near 2100 K ([6] and references herein), whereas strontium titanate $SrTiO_3$ undergoes a low-temperature (LT) phase transition from the cubic to tetragonal $I4/mcm$ perovskite structure below 105 K [12, 13]. Owing to the abovementioned peculiarities of $NdAlO_3$ and $SrTiO_3$ crystal structures, complex phase and structural behaviour is expected in the mixed neodymium-strontium aluminate-titanate system.

Methods

Mixed aluminates-titanates of nominal compositions $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ ($x = 0.3$, 0.5, 0.7, 0.8, 0.9) were prepared by solid-state reaction technique. Stoichiometric

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amounts of the constituent oxides Nd_2O_3, Al_2O_3, TiO_2 and strontium carbonate $SrCO_3$ were ball-milled in ethanol for 5 h, dried, pressed into pellets and annealed in air at 1673 K for 9 h. After cooling the product, it was regrinded and repeatedly annealed at 1773 K for 9 h. X-ray powder diffraction technique (Huber imaging plate Guinier camera G670, Cu $K_{\alpha 1}$ radiation, $\lambda = 1.54056$ Å) was used for the phase and structural characterization of the samples at room temperature. All crystallographic calculations including full-profile Rietveld refinement were performed by using WinCSD program package [14].

Results and Discussion

Analysis of X-ray diffraction (XRD) data collected at room temperature (RT) showed that all samples synthesized adopt pure perovskite structure. No traces of foreign phases were detected (Fig. 1). Close examination of diffraction maxima revealed detectable rhombohedral deformation of the $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ samples with $x = 0.3$ and 0.5, whereas no visible reflections splitting or deformation was observed for the specimens with higher x values (Fig. 1, inset). However, a presence of minor superstructure (113) reflection, which is indicative for rhombohedral distortion of perovskite structure, testifies that the rhombohedral structure in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series persists at least up to $x = 0.8$.

Full-profile Rietveld refinement of $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ structures, performed in space groups $R\,\bar{3}\,c$ and $Pm\,\bar{3}\,m$ for the samples with $x \le 0.8$ and $x = 0.9$, respectively, entirely confirms suggested crystal structures of the specimens. Examples of graphical results of Rietveld refinement, showing excellent fits between experimental and calculated profiles of rhombohedral $Nd_{0.5}Sr_{0.5}Al_{0.5}Ti_{0.5}O_3$ and cubic $Nd_{0.1}Sr_{0.9}Al_{0.1}Ti_{0.9}O_3$ structures are presented on Fig. 2. Refined structural parameters of all synthesized $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ samples and corresponding residuals are presented in Table 1.

Concentration dependencies of the obtained lattice parameters and unit cell volumes of $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series in comparison with the literature data for $NdAlO_3$ [6] and $SrTiO_3$ [12] (Fig. 3) prove a formation of two kinds of solid solutions in the $NdAlO_3$–$SrTiO_3$ pseudo-binary system. Simultaneous aliovalent substitution of Sr^{2+} and Ti^{4+} species for Nd^{3+} and Al^{3+} sites reduces rhombohedral deformation in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series and led to morphotropic phase transition to the cubic perovskite structure at $x = 0.84$ (Fig. 3). In the related systems $LaAlO_3$–$SrTiO_3$ and $PrAlO_3$–$SrTiO_3$, the phase boundary between two perovskite structures takes place above $x = 0.8$ and at $x = 0.88$, respectively [15, 16].

A decreasing structural deformation in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series as a consequence of increasing Goldschmidt tolerance factor with increasing x should significantly effect on the temperature of structural phase transition $R\,\bar{3}\,c - Pm\,\bar{3}\,m$, which occurs in $NdAlO_3$ at about 2100 K [6]. According to structural phase diagram of the related $LaAlO_3$–$SrTiO_3$ system [15], the temperature of rhombohedra-to-cubic transition decreases almost linearly

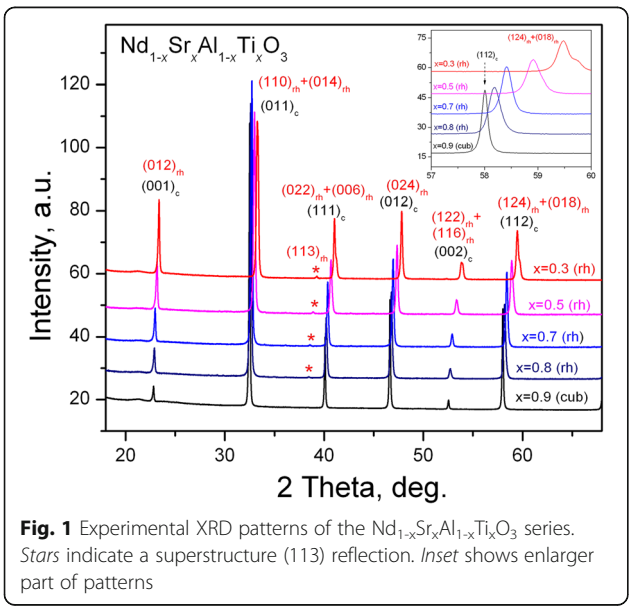

Fig. 1 Experimental XRD patterns of the $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series. *Stars* indicate a superstructure (113) reflection. *Inset* shows enlarger part of patterns

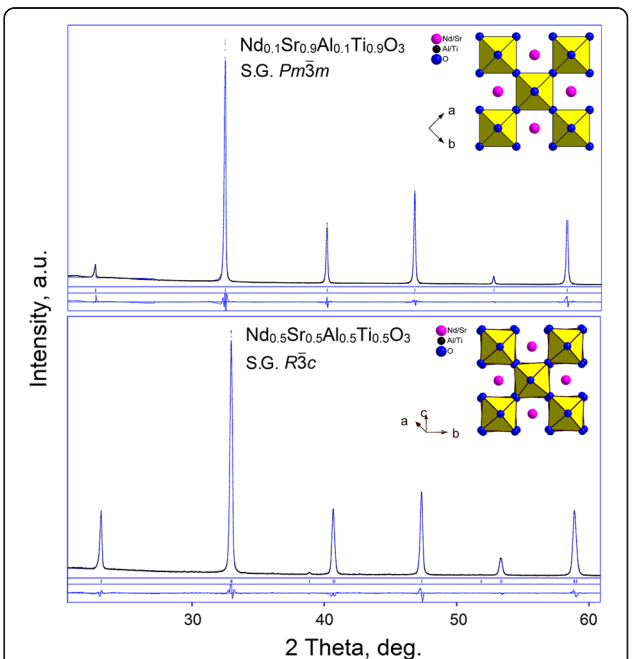

Fig. 2 Graphical results of Rietveld refinement of $Nd_{0.1}Sr_{0.9}Al_{0.1}Ti_{0.9}O_3$ and $Nd_{0.5}Sr_{0.5}Al_{0.5}Ti_{0.5}O_3$ structures. The experimental X-ray powder diffraction patterns (*dots*) are shown in comparison with the calculated patterns (*blue lines*). The difference curves between measured and calculated profiles are shown below the diagrams. *Inset* shows the view of the cubic and rhombohedral structures as corner-shared Al/TiO_6 octahedra with Nd/Sr species located between them

Table 1 Unit cell parameters, coordinates and isotropic displacement parameters of atoms in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ structures at RT

Atoms, sites	Parameter, residuals	*x* in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$, space group				
		0.3, $R\,\bar{3}\,c$	0.5, $R\,\bar{3}\,c$	0.7, $R\,\bar{3}\,c$	0.8, $R\,\bar{3}\,c$	0.9, $Pm\,\bar{3}\,m$
	a, Å	5.3836(4)	5.4281(4)	5.4674(5)	5.4849(8)	3.8911(1)
	c, Å	13.1180(2)	13.251(1)	13.368(2)	13.428(3)	–
Nd/Sr, 6*c* (0, 0, ¼)	B_{iso}, Å^2	0.73(2)	0.91(1)	0.67(2)	0.83(1)	0.90(4)
Al/Ti, 6*b* (0, 0, 0)	B_{iso}, Å^2	0.54(4)	0.41(2)	0.44(3)	0.53(2)	0.48(5)
O, 18*e* (*x*, 0, ¼)	*x*	0.5395(8)	0.5358(6)	0.5277(6)	0.5213(7)	–
	B_{iso}, Å^2	1.48(8)	1.25(5)	1.72(6)	1.57(5)	1.36(11)
	R_I	0.021	0.026	0.030	0.028	0.033
	R_P	0.076	0.091	0.083	0.086	0.092

from 850 K in "pure" $LaAlO_3$ to 350 K in the sample with nominal composition $La_{0.2}Sr_{0.8}Al_{0.2}Ti_{0.8}O_3$. Our recent in situ X-ray synchrotron powder diffraction investigations of the $PrAlO_3$–$SrTiO_3$ series [16] showed that the $R\,\bar{3}\,c$ – $Pm\,\bar{3}\,m$ transition temperature decreases gradually from 1770 K in $PrAlO_3$ to 930 K in $Pr_{0.5}Sr_{0.5}Al_{0.5}Ti_{0.5}O_3$ sample. Similar structure and phase behaviour at the elevated temperatures are also expected in the studied $NdAlO_3$–$SrTiO_3$ system, tentative phase diagram of which is shown on Fig. 4. However, extrapolation of the cubic phase boundary from high-temperature region to the higher $SrTiO_3$ concentrations would be speculative because of the different low-temperature structures of the parent compounds $NdAlO_3$ and $SrTiO_3$ ($R\,\bar{3}\,c$ and *I*4/*mcm*, respectively). Evidently, phase boundary between the $R\,\bar{3}\,c$ and *I*4/*mcm* structural modifications of $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ solid solution has to be present in the $SrTiO_3$-rich part of the phase diagram at low temperatures (Fig. 4). In addition, appearance of intermediate orthorhombic phase between rhombohedral $R\,\bar{3}\,c$ and tetragonal *I*4/*mcm* phase fields, as it occurs in the related $PrAlO_3$–$SrTiO_3$ [16] and $NdAlO_3$–$CeAlO_3$ [17] systems, could not be neglected.

Comprehensive analysis of *A*/*B*-cation substitution on the antiferrodistortive phase transition $Pm\,\bar{3}\,m$ – *I*4/*mcm* in $SrTiO_3$ recently performed in [18] revealed that transition temperature increases in nonlinear manner with decreasing tolerance factor, depending on substituent concentration. Based on this observation, one can

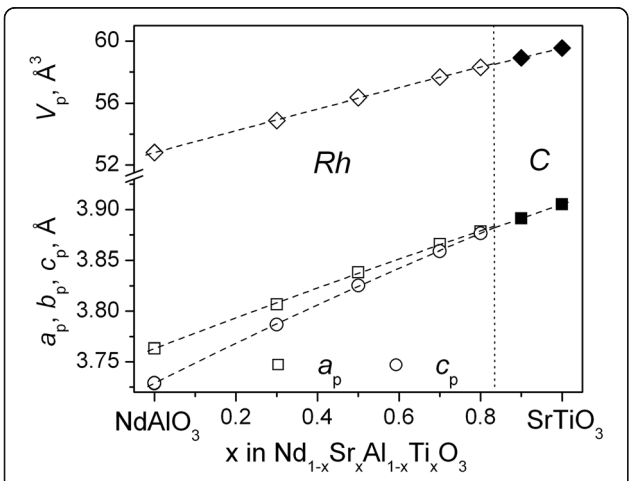

Fig. 3 Unit cell dimensions of $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series. The rhombohedral lattice parameters are normalized to the perovskite cell as follow: $a_p = a_r/\sqrt{2}, c_p = c_r/\sqrt{12}, V_p = V_r/6$. The *dotted line* marks the phase boundary between the *Rh* and the *C* phases

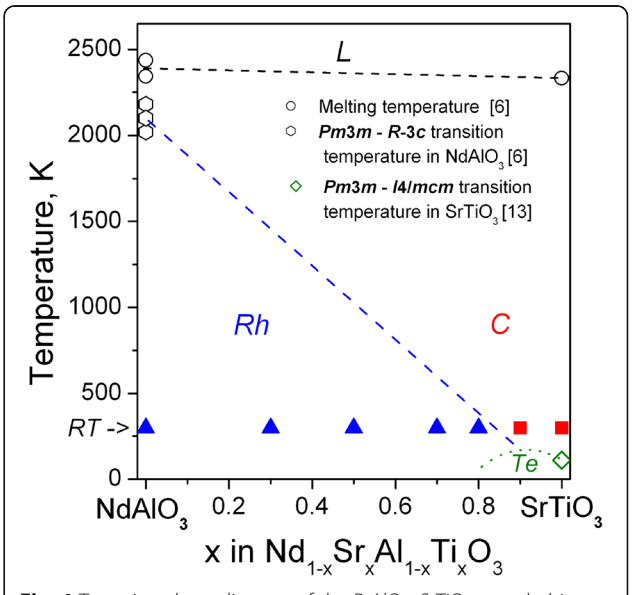

Fig. 4 Tentative phase diagram of the $PrAlO_3$–$SrTiO_3$ pseudo-binary system. The letters *L*, *C*, *Rh* and *Te* designate liquid, cubic, rhombohedral and tetragonal phase fields, respectively. The solid symbols designate the rhombohedral (*triangles*) and cubic (*squares*) perovskite structures experimentally observed in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series at RT

predict that $SrTiO_3$-richest samples in the $NdAlO_3$–$SrTiO_3$ system will transform to the tetragonal *I*4/*mcm* structure at the temperatures higher than the pure $SrTiO_3$ (105 K). To shad light on the low-temperature phase behaviour in the $NdAlO_3$–$SrTiO_3$ system, thorough structural, calorimetric and spectroscopic investigations are required.

Conclusions

Continuous solid solution $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ with perovskite structure is formed in the $NdAlO_3$–$SrTiO_3$ pseudo-binary system at 1773 K. Comparison of the obtained structural parameters with corresponding data for the parent compounds $NdAlO_3$ and $SrTiO_3$ proves a decrease of perovskite structure deformation as a consequence of increasing Goldschmidt tolerance factor with increasing x in $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series. As a result, concentration-induced phase transition from a rhombohedral $R\,\overline{3}\,c$ to the cubic perovskite structure occurs in the $Nd_{1-x}Sr_xAl_{1-x}Ti_xO_3$ system at $x = 0.84$. Experimental X-ray powder diffraction patterns and crystal structure parameters of rhombohedral $Nd_{0.7}Sr_{0.3}Al_{0.7}Ti_{0.3}O_3$ and cubic $Nd_{0.1}Sr_{0.9}Al_{0.1}Ti_{0.9}O_3$ phases are published by the International Centre of Diffraction Data (ICDD) in the last release of the Powder Diffraction Files (PDF cards NN 00-066-0395 and 00-066-0396, respectively) [19].

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Authors' Contributions
NO contributed to the data evaluation and manuscript writing. RS synthesized the samples and contributed to the data evaluation. KB contributed to the sample preparation and to the discussion of the results. LV performed structural characterization of the samples and contributed to the manuscript writing. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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