Concentration- and Temperature-Induced Phase Transitions in PrAlO$_3$–SrTiO$_3$ System

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Abstract

Single-phase mixed aluminate-titanate Pr$_{1-x}$Sr$_x$Al$_{1-x}$Ti$_x$O$_3$ ($x = 0.1, 0.2, 0.3, 0.5, 0.7$) with rhombohedral perovskite structure were prepared by solid-state reaction technique at 1823–1873 K. Morphotropic rhombohedral-to-cubic phase transition in Pr$_{1-x}$Sr$_x$Al$_{1-x}$Ti$_x$O$_3$ series is predicted to occur at $x = 0.88$. The temperature-induced structural phase transition $R\bar{3}c$–$Pm\bar{3}m$ in Pr$_{0.5}$Sr$_{0.5}$Al$_{0.5}$Ti$_{0.5}$O$_3$, detected at 930 K by in situ high-temperature X-ray synchrotron powder diffraction, occurs at considerably lower temperature as the corresponding transformation in the parent compound PrAlO$_3$ (1770 K). Such remarkable drop of the transition temperature is explained by gradual decrease of the perovskite structure deformation in the Pr$_{1-x}$Sr$_x$Al$_{1-x}$Ti$_x$O$_3$ series with increasing Sr and Ti contents as a consequence of the increasing Goldschmidt tolerance factor. For Pr$_{0.3}$Sr$_{0.7}$Al$_{0.3}$Ti$_{0.7}$O$_3$ phase, a sequence of the low-temperature phase transformation $R\bar{3}c$–$Immm(C2/m)$–$I4/mcm$ was detected.

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

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Background

Rare earth aluminates RAIO$_3$ with perovskite structure and SrTiO$_3$-based materials show diverse technological application. In particular, they are used as solid electrolytes and anode materials in solid oxide fuel cells, as substrates for thin film epitaxy, materials for laser hosts, scintillates and phosphors, high-temperature ceramics and refractory materials ([1–5] and references herein). Due to the opposite signs of the temperature coefficient of the resonant frequency ($\tau_f$) of the RAIO$_3$ and SrTiO$_3$ compounds, mixed aluminate-titanates formed in the RAIO$_3$–SrTiO$_3$ systems are considered as prospective microwave materials with a high dielectric constant, moderate quality factor and a near zero value of $\tau_f$ [5–7].

During the last decade, RAIO$_3$–SrTiO$_3$ systems are of considerable interest in the physics of materials used in modern engineering. The two-dimensional electron gas at the interface between two insulators LaAlO$_3$ and SrTiO$_3$ [8] has been an active research area in the field-tunable metal-insulator transition, 2D superconductivity, coexistence of superconductivity and ferromagnetism, etc. [9–11]. Just recently, a similar effect was reported on the interfaces of SrTiO$_3$ and RAIO$_3$ ($R = \text{La, Pr, Nd}$) and RGaO$_3$ compounds ($R = \text{La, Nd}$) in both crystalline and amorphous forms [12].

The aim of the present work is the study of the phase and structural behaviour of the mixed aluminate-titanates formed in the PrAlO$_3$–SrTiO$_3$ pseudo-binary system. At room temperature, the end members of the system—PrAlO$_3$ and SrTiO$_3$—adopt different variants of perovskite structure—rhombohedral $R\bar{3}c$ and cubic $Pm\bar{3}m$, respectively. Rhombohedral PrAlO$_3$ transforms into the cubic perovskite structure at about 1770 K ([4], and references herein). In addition, PrAlO$_3$ undergoes a sequence of low-temperature (LT) structural phase transformations from the rhombohedral to an orthorhombic $Imma$ structure at 205 K and from orthorhombic to a monoclinic $C2/m$ structure at 151 K ([4], and references herein). Strontium titanate SrTiO$_3$ undergoes a low-temperature structural phase transition from the cubic to the tetragonal $I4/mcm$ perovskite structure below 105 K [13, 14]. Owing to the abovementioned peculiarities of the crystal structures PrAlO$_3$ and SrTiO$_3$ and their structural instabilities, extremely complex phase and structural behaviour are expected in the mixed praseodymium-strontium aluminate-titanate system.
Methods

Mixed aluminates-titanates $\text{Pr}_1-x\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3, 0.5, 0.7$) were prepared from stoichiometric amounts of the constituent oxides $\text{Pr}_6\text{O}_{11}$, $\text{Al}_2\text{O}_3$, $\text{TiO}_2$ and strontium carbonate $\text{SrCO}_3$ by solid-state reaction technique. The precursor powders were ball milled in ethanol for 3–6 h, dried, pressed in the pellets and sintered in air at $1673–1773$ K for 18 h (the samples with $x = 0.1$ and 0.2) and at $1593$ K for 24 h (the samples with $x = 0.3, 0.5$ and 0.7). After regrinding and powdering, the obtained products were pressed in the pellets and repeatedly fired in air at $1873$ K ($x = 0.1$ and 0.2) and $1823$ K ($x = 0.3, 0.5$ and 0.7) for 10 h.

X-ray powder diffraction technique (Huber imaging plate Guinier camera G670, Cu $K\alpha_1$ radiation) was used for the phase and structural characterization of the samples at room temperature. Thermal behaviour of the mixed aluminates-titanates has been studied exemplarily on $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_3$ and $\text{Pr}_{0.5}\text{Sr}_{0.7}\text{Al}_{0.3}\text{Ti}_{0.7}\text{O}_3$ samples in the temperature ranges of 298–1173 K and 20–298 K, respectively. Corresponding in situ high-resolution X-ray synchrotron powder diffraction experiments were performed at beamlines B2 at HASYLAB/DESY (Hamburg, Germany) and ID22 at ESRF (Grenoble, France) during beamtimes allocated to the experiments I-20110214 and hc2044, respectively.

All crystallographic calculations including full-profile Rietveld refinement were performed by using WinCSD program package [15].

Results and Discussion

Examination of X-ray powder diffraction patterns revealed a formation of the single-phase perovskite structures in all samples synthesised (Fig. 1). No traces of parasitic phases were detected. An analysis of the splitting of diffraction maxima in the $\text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3$ patterns with $x = 0.1, 0.2, 0.3$ and 0.5 proves rhombohedral deformation of the perovskite structure. The rhombohedral splitting decreases with the increase in the content of strontium and titanium in the $\text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3$ series, completely vanishing in the $\text{Pr}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.3}\text{Ti}_{0.7}\text{O}_3$ sample. However, the presence of a weak (113) reflection at the diffraction pattern of this sample (Fig. 1) indicates that its structure still remains rhombohedral.

From the experimental XRD patterns of $\text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3$ samples, the crystal structure parameters of the
mixed aluminates-titanates were derived. Full-profile Rietveld refinement performed in space group \( R 3 c \) resulted in excellent agreement between calculated and experimental profiles (see, for example, Fig. 2) and led to the final structural parameters and residuals presented in Table 1.

Comparison of the obtained structural parameters of the praseodymium-strontium mixed aluminates-titanates with the literature data for the "pure" \( \text{PrAlO}_3 \) and \( \text{SrTiO}_3 \) (Fig. 3) clearly proves the formation of the extended solid solution \( \text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3 \) with rhombohedral perovskite structure. A morphotropic phase transition from rhombohedral to the cubic perovskite structure in the \( \text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3 \) series can be expected at \( x = 0.88 \), as it follows from the analysis of the concentration dependence of the unit cell dimensions of the rhombohedral lattice (Fig. 3). In the related \( \text{LaAlO}_3-\text{SrTiO}_3 \) system, the rhombohedral solid solution exists up to 60 mole % of \( \text{LaAlO}_3 \); after that, the transition to the cubic perovskite structure takes place [16].

\[ a, \text{Å} \quad 5.35081(8) \quad 5.37046 (4) \quad 5.38979 (4) \quad 5.42806 (5) \quad 5.4614 (3) \]
\[ c, \text{Å} \quad 13.0303 (3) \quad 13.0868 (2) \quad 13.1442 (2) \quad 13.2569 (2) \quad 13.378 (2) \]

| Atoms, sites | Parameters, residuals | \( x \) in \( \text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3 \) | \( 0.1 \) | \( 0.2 \) | \( 0.3 \) | \( 0.5 \) | \( 0.7 \) |
|-------------|-----------------------|---------------------------------|-------|-------|-------|-------|-------|
| \( \text{Pr/Sr}, 6c (0, 0, 1/4) \) | \( B_{iso} \text{ Å}^2 \) | \( x = 0.88 \) | \( 0.88 (2) \) | \( 0.69 (2) \) | \( 0.85 (1) \) | \( 0.95 (2) \) | \( 0.67 (2) \) |
| \( \text{Al/Ti}, 6b (0, 0, 0) \) | \( B_{iso} \text{ Å}^2 \) | \( x = 0.78 \) | \( 0.78 (7) \) | \( 0.70 (5) \) | \( 0.78 (3) \) | \( 0.67 (3) \) | \( 0.43 (3) \) |
| \( \text{O}, 18e (x, 0, 1/4) \) | \( x \) | \( 0.5485 (14) \) | \( 0.5429 (6) \) | \( 0.5364 (7) \) | \( 0.5333 (8) \) | \( 0.5333 (8) \) | \( 0.5239 (11) \) |
| \( R_I \) | \( 0.070 \) | \( 0.048 \) | \( 0.041 \) | \( 0.026 \) | \( 0.026 \) | \( 0.026 \) |
| \( R_P \) | \( 0.089 \) | \( 0.056 \) | \( 0.064 \) | \( 0.066 \) | \( 0.066 \) | \( 0.059 \) |

In situ high-temperature X-ray synchrotron powder diffraction investigation of the \( \text{Pr}_{0.5}\text{Sr}_{0.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_3 \) sample revealed a continuous phase transition from rhombohedral to the cubic perovskite structure at elevated temperatures. As it was established from the temperature-resolved X-ray synchrotron powder diffraction measurements, the rhombohedral lattice parameters \( a \) and \( c \) increase anisotropically with temperature and merge together at 930 K, when the transition to the ideal perovskite structure occurs (Fig. 4). In comparison with the parent \( \text{PrAlO}_3 \) compound, in which transformation to the cubic perovskite structure occurs around 1770 K [4], the \( R 3 c - Pm 3 m \) transition in \( \text{Pr}_{0.5}\text{Sr}_{0.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_3 \) takes place at considerably lower temperature of 930 K. Such remarkable drop of the phase transition temperature can be explained by gradual decrease of the perovskite structure deformation in the \( \text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3 \) series with...
increasing of Sr and Ti content. According to the phase diagram of the $\text{RAIO}_3$-based perovskite systems [4], the temperature of the $R\bar{3}c - Pm\bar{3}m$ phase transition decreases linearly with increasing radii of $R$ cation as a consequence of the increasing Goldschmidt tolerance factor.

Graphical results of Rietveld refinement of the high-temperature modifications of the $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_3$ structure and refined structural parameters at selected temperatures are presented in Fig. 5 and Table 2, respectively.

Spot-check examination of low-temperature structural behaviour of the $\text{Pr}_{1-x}\text{Sr}_x\text{Al}_{1-x}\text{Ti}_x\text{O}_3$ system was performed on the example of a $\text{Pr}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.3}\text{Ti}_{0.3}\text{O}_3$ sample at temperatures of 20, 80, 160 and 220 K. Extremely high resolution of the beamline ID22 at ESRF allows to detect subtle changes in the reflections splitting at different temperature measurements (Fig. 6), which clearly prove a sequence of LT phase transformations in this sample.

Crystal structures of $\text{Pr}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.3}\text{Ti}_{0.3}\text{O}_3$ at RT and at 220 K were refined in the space group $R\bar{3}c$, thus confirming the results derived from the convenient XRD data (Table 1). Taking into account the character of the reflection splitting, crystal structure parameters of the low-temperature modification of $\text{Pr}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.3}\text{Ti}_{0.3}\text{O}_3$ at 20 and 80 K were successfully refined in space group $I4/mcm$. X-ray synchrotron diffraction features of $\text{Pr}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.3}\text{Ti}_{0.3}\text{O}_3$ at 160 K could be successfully modelled either in the orthorhombic $I\text{mnb}$ or in the monoclinic $I2/m\text{(}C2/m\text{)}$ perovskite structure. Since in both cases during the refinement procedures, practically the same residuals were obtained, a preference should be given to the more symmetric orthorhombic structure. Taking into account that the end members of the system show different sequences of LT phase transformations $R\bar{3}c - I\text{mnb} - C2/m$ ($\text{PrAlO}_3$) and $Pm\bar{3}m$ –
I4/mcm (SrTiO₃), additional investigations are required in order to shade light on the complex phase and structural behaviour of the mixed aluminates-titanates below RT.

Conclusions
The formation of extended solid solution Pr₁₋ₓSrₓAl₁₋ₓTiₓO₃ with rhombohedral perovskite structure has been revealed in the PrAlO₃–SrTiO₃ pseudo-binary system based on X-ray powder diffraction data. An analysis of the obtained structural parameters in comparison with the data for the parent compounds PrAlO₃ and SrTiO₃ revealed a decrease of perovskite structure deformation in Pr₁₋ₓSrₓAl₁₋ₓTiₓO₃ series with increasing Sr and Ti content as a consequence of the increasing Goldschmidt tolerance factor. As a result, concentration-induced phase transition from a rhombohedral to the cubic perovskite structure takes place in the Pr₁₋ₓSrₓAl₁₋ₓTiₓO₃ system at x = 0.88. A decreasing structure deformation in Pr₁₋ₓSrₓAl₁₋ₓTiₓO₃ series leads to the significant decrease of the temperature-induced phase transition R 3 c – Pm 3 m from 1770 to 930 K in PrAlO₃ and Pr₀.₅Sr₀.₅Al₀.₅Ti₀.₅O₃, respectively. The sequence of the low-temperature phase transition R 3 c – Immm(12/m) – I4/mcm in Pr₀.₃Sr₀.₇Al₀.₃Ti₀.₃O₃ revealed during the spot-check X-ray synchrotron powder diffraction examination promises an extremely complex picture of the phase and structural relations in PrAlO₃–SrTiO₃ system below room temperature. Further structural and calorimetric investigations of the system are in progress.

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

Authors’ Contributions
LV synthesised the samples, performed the HT synchrotron powder diffraction measurements at HASYLAB and structural characterization of the samples and wrote the manuscript. RS contributed to the data evaluation, figure and table preparation and manuscript writing. YP and HR performed the laboratory X-ray and LT synchrotron diffraction measurements at ESRF. All authors read and approved the final manuscript.

Table 2
Refined structural parameters of rhombohedral and cubic modifications of Pr₀.₅Sr₀.₅Al₀.₅Ti₀.₅O₃

| Atoms, sites | Parameters, residuals | Temperature, space group | 373 K | 573 K | 823 K | 923 K | 1073 K | 1173 K |
|-------------|----------------------|-------------------------|-------|-------|-------|-------|--------|--------|
|             | a, Å                 | R 3 c                   | 5.4319 (2) | 5.4412 (2) | 5.4541 (5) | 3.8600 (2) | 3.8667 (2) | 3.8714 (2) |
|             | c, Å                 | R 3 c                   | 13.2708 (7) | 13.3041 (9) | 13.350 (2) | - | - | - |
|             | x                    | R 3 c                   | 0 | 0 | 0 | ½ | ½ | ½ |
|             | y                    | R 3 c                   | 0 | 0 | 0 | ½ | ½ | ½ |
|             | z                    | R 3 c                   | 1/4 | 1/4 | ½ | ½ | ½ | ½ |
|             | Biso Å²              | R 3 c                   | 1.15 (3) | 1.35 (3) | 1.69 (3) | 1.92 (5) | 2.01 (5) | 2.19 (5) |
|             | a                    | Pm 3 m                  | 0 | 0 | 0 | 0 | 0 | 0 |
|             | y                    | Pm 3 m                  | 0 | 0 | 0 | 0 | 0 | 0 |
|             | y                    | Pm 3 m                  | 0 | 0 | 0 | 0 | 0 | 0 |
|             | Biso Å²              | Pm 3 m                  | 0.72 (5) | 0.92 (6) | 0.95 (6) | 0.85 (8) | 1.19 (9) | 1.05 (9) |
|             | x                    | Pm 3 m                  | 0.530 (3) | 0.529 (3) | 0.506 (16) | ½ | ½ | ½ |
|             | y                    | Pm 3 m                  | 0 | 0 | 0 | 0 | 0 | 0 |
|             | z                    | Pm 3 m                  | 1/4 | 1/4 | ½ | ½ | ½ | ½ |
|             | Biso Å²              | Pm 3 m                  | 0.7 (2) | 0.8 (2) | 1.9 (2) | 2.9 (2) | 2.9 (2) | 3.5 (2) |
|             | R₁                   | Pm 3 m                  | 0.047 | 0.048 | 0.041 | 0.045 | 0.047 | 0.046 |
|             | Rp                   | Pm 3 m                  | 0.147 | 0.145 | 0.064 | 0.128 | 0.133 | 0.135 |

Fig. 6
Figures of LT synchrotron powder diffraction patterns of Pr₀.₅Sr₀.₅Al₀.₅Ti₀.₅O₃ (ESRF ID22 data, λ = 0.40003 Å). Splitting of (110), (200), and (211) reflections in rhombohedral (r) orthorhombic (o) and tetragonal (t) modifications of Pr₀.₃Sr₀.₇Al₀.₃Ti₀.₃O₃ is shown.
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