ESRF	**Experiment title:** Competitions of low temperature phase transitions in $Pr_{1-x}Sr_xAl_{1-x}Ti_xO_3$ system (x = 0.1−0.9)	**Experiment number**: hc2648
Beamline: ID22	**Date of experiment**: from: 07. December 2016 to: 12 December 2016	**Date of report**: 02 March 2021
Shifts: 9	**Local contact(s)**: Dr. Mauro Coduri	*Received at ESRF:*

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Report:

Abstract. The phase and structural behavior in the $Pr_{1-x}Sr_xAl_{1-x}Ti_xO_3$ series (x = 0.1÷0.9) were studied in the temperature range of 30–295 K. Four variants of the perovskite structure motif are unambiguously identified: cubic *Pm*$\bar{3}$*m*, rhombohedral *R*$\bar{3}$*c*, tetragonal *I*4/*mcm* and orthorhombic *Ibmm.* For monoclinic structure several models were developed and checked. For this purpose, in addition to the ESRF results, group-subgroup relationships, tendencies of the inclination of the coordination octahedra and electronic structure calculations were taken into account. Nevertheless, for the precise phase diagram, additional measurements with the smaller temperature steps are necessary.

A series of X-ray synchrotron powder diffraction experiment has been performed at the ID22 beamline in order to study of phases and structural behaviour of the mixed perovskites $Pr_{1-x}Sr_xAl_{1-x}Ti_xO_3$ (x = 0.1−0.9) in the temperature range of 30–295 K. High-resolution diffraction patterns were collected using incident photon beam with λ = 0.40001 Å. The diffraction experiments were performed in the Debye-Scherrer geometry (capillary Ø = 0.3 mm) by using liquid-helium-cooled cryostat and a nine crystal multi-analyser stage for high-resolution powder diffraction. Due to an excellent mechanical characteristics of the diffractometer and the high collimation of the beam, the typical full width at half maximum (FWHM) of reflections in this setup in the 2θ range of 5–45° was 0.008−0.037°, and their positions are accurate and reproducible to a few tenths of a millidegree. A total of 9 samples were investigated. A typical temperature step was 20 K for each sample. Structural parameters of all modifications of $Pr_{1-x}Sr_xAl_{1-x}Ti_xO_3$ solid solution were obtained by full profile Rietveld refinement by using WinCSD program package [1].

The analysis of the obtained diffraction patterns shows a rather complex behavior in the examined system. At least five variants of the perovskite structure motif are identified: cubic (space group *Pm*$\bar{3}$*m*, a = 3.89323(2) Å for x = 0.9 at RT, as example), rhombohedral (*R*$\bar{3}$*c*, a = 5.3742 Å, c = 13.0994 Å for x = 0.2 at RT), tetragonal (*I*4/*mcm* , a = 5.3354 Å, c = 7.6288 Å for x = 0.2 at 30 K), orthorhombic (*Ibmm*, a = 5.3776 Å, b = 5.3526 Å, c = 7.5621 Å, for x = 0.2 at 150 K) and monoclinic (the structure is not finaly established, s. below). The results of our experiment are provisionally summarized in the phase diagram, which reflects the presence of a particular modification as a function of temperature and composition. (Fig. 1).

The cubic modification is typical for the strontium-rich and high-temperature corner of the investigated phase diagram. The tetragonal structure is formed practically for all compositions up to 50−70 K and its temperature stability increases with increasing of strontium content (up to 210 K for x = 0.8). The rhombohedral arrangement is defined for the dominant part of the compositions (x = 0–0.6) and temperatures above 230 K. The orthorhombic structure is typically detected for intermediate compositions and temperatures (x = 0.2−0.6, T = 130−230 K).

The analysis of the crystal structure of the intermediate phase formed in the region between orthorhombic and tetragonal modifications, particularly in the praseodimium-rich compositions (designated as the "mon." field in Fig. 1), did not give an unambiguous solution. Fig. 2 represents exemplary (for x = 0.2 sample) an evolution of the reflections corresponding to 111 and 200 reflections in the cubic perovskite indicating successive phase transitions from rhombohedral through orthorhombic and monoclinic (?) to tetragonal structures during the cooling from room temperature to 30 K. The diffraction peaks measured at 70 K and 90 K are compatible with the monoclinic metric. Initially, two alternative scenarios for structural development in the 90K−30K region were considered. In the first (**1**) a structural model observed for the boder composition $PrAlO_3$ [2] was used for all temperatures (space group $I112/m$, a = 5.36124 Å, b = 5.36867 Å, c = 7.54518 Å, β = 90.63°, R_B = 0.014, R_P = 0.079 at 30 K). In the second (**2**) the same monoclinic $I112/m$ model was applied only for patterns at 70 K and 90 K. Low temperature patterns (50 K and 30 K) were instead succesfully refined with tetragonal structure: space group $I4/mcm$, a = 5.33539 Å, c = 7.62885 Å, R_B = 0.012, R_P = 0.098 at 30 K. Nevertheless, both scenarious have some contradictions. The presence of the monoclinic phase at low temperatures (scenario **1**) does not coincide with the presence of the tetragonal phase over a large interval, both in terms of composition and temperature (Fig. 1). Due to the large difference in the lattice parameters (especially the lattice parameter c), and absence of direct group-subgroup relations between $I112/m$ and $I4/mcm$ space groups this first order transition should be accompanied by two-phase regions, which were never observed. For the same reason, the continuous, temperature-dependent monoclinic-tetragonal phase transition is unlikely (scenario **2**). Therefore, several alternative models for diffraction patterns observed in "mon." field of Fig. 1 have been developed and tested. The most plausible structural model applied for 70 K and 90 K patterns is described in space group $I2/c11$ with a = 5.34039 Å, b = 5.34183 Å, c = 7.61961 Å, β = 90.17° (R_B = 0.019, R_P = 0.110 at 70 K). Advantages of this scenario (**3**): (*a*) the continuous second order temperature phase transition is plausible from the crystallographic point of view (direct group-subgroup relation between $I4/mcm$ and $I2/c11$ [3]); (b) the tilt of the coordination octahedra is more realistic ($a^-a^-c^-$ for $I2/c11$ and $a^0a^0c^-$ for $I4/mcm$). (c) moreover the $I2/c11$ model is favored compared to $I112/m$ according to the results of the electronic structure calculation, especially for the praseodimium rich compositions. To clarify this scenario (**3**) in more detail, definitely additional experiments with smaller temperature steps around "mon." field as well as neutron diffraction experiments are required.

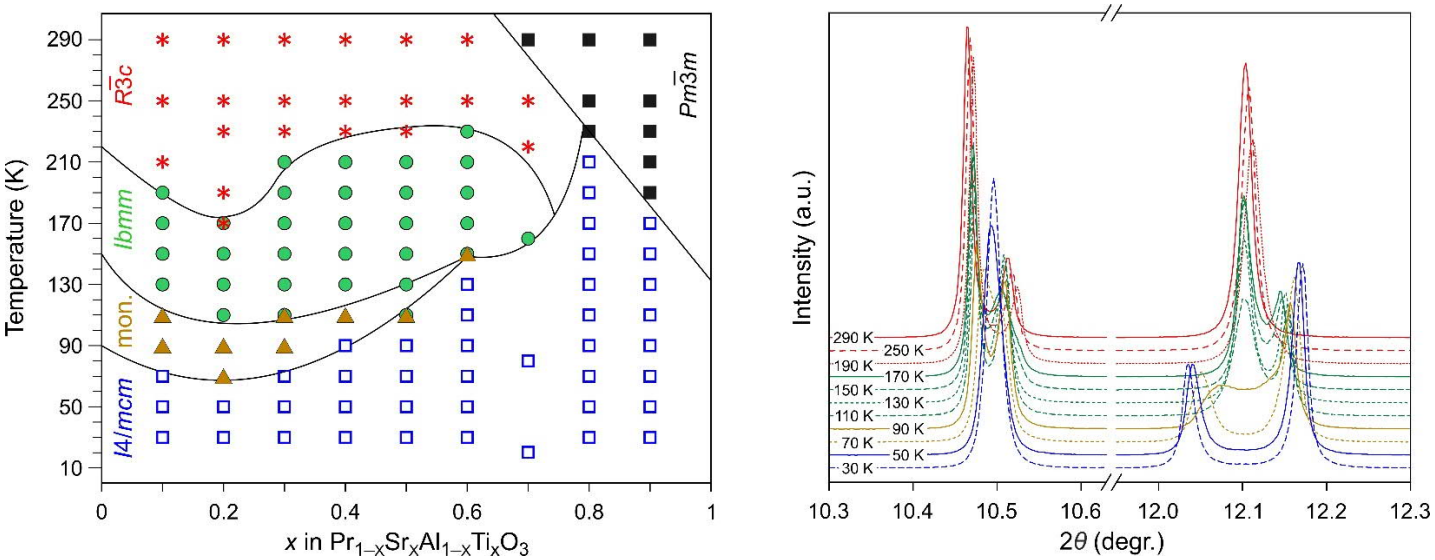

Fig. 1 (left). Temporary phase diagram of the $Pr_{1-x}Sr_xAl_{1-x}Ti_xO_3$ system as a function of temperature and composition.
Fig. 2 (right). Temperature evolution of the perovskite reflections corresponding to cubic 111 (left) and 200 (right) indicating successive phase transitions from rhombohedral (*R*-3*c*), through orthorhombic (*Ibmm*) and monoclinic (?) to tetragonal (*I4/mcm*) structures during the cooling from room temperature to 30 K.

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[3] O. Bock, U. Müller, *Acta Crystallogr.* B58 (2002) 594−606.