PHASE AND STRUCTURAL BEHAVIOUR OF THE $PrAlO_3$–$LaAlO_3$ PSEUDO-BINARY SYSTEM

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At room temperature, rare earth aluminates $RAlO_3$ were found to crystallize in rhombohedral $R\bar{3}c$ (R = La, Pr, Nd), orthorhombic *Pbmn* (R = Sm–Lu, Y) and tetragonal *I*4/*mcm* ($CeAlO_3$) structures. In general, two types of phase transformations are known for $RAlO_3$ perovskites. A continuous phase transition $Pm\bar{3}m$–$R\bar{3}c$ is typical for $RAlO_3$ compounds containing "light" rare-earth metals (R = La, Ce, Pr, Nd), whereas a first-order phase transformation $R\bar{3}c$–*Pbnm* is inherent for $SmAlO_3$, $GdAlO_3$ and $EuAlO_3$. The respective praseodymium aluminate shows an exceptional behaviour among the $RAlO_3$ compounds. Besides a high-temperature (HT) phase transition from rhombohedral to cubic perovskite structure, $PrAlO_3$ undergoes a sequence of low-temperature (LT) phase transformations, which is a solely exception among all AMO_3 compounds with perovskite structures [1]. A similar complex behaviour of the phase transformations has been observed for $CeAlO_3$-based perovskites [2].

In order to study the phase and structural behaviour in the $PrAlO_3$–$RAlO_3$ (R = La) pseudo-binary systems a series of $Pr_{1-x}R_xAlO_3$ samples (x = 0.1–0.9) was prepared by a combination of solid state reaction and arc melting in Ar atmosphere. Phase analyses of the samples were performed by X-ray powder diffraction. *In situ* LT and HT structural investigations have been performed by using a high-resolution powder diffraction technique applying synchrotron at beamline B2 of the synchrotron laboratory HASYLAB at DESY.

It was established, that a continuous solid solution $Pr_{1-x}La_xAlO_3$ with rhombohedral perovskite structure exists at ambient temperature. Lattice parameters and cell volumes increase monotonically with increasing La content.

At elevated temperatures, the solid solutions $Pr_{1-x}La_xAlO_3$ undergo continuous phase transitions from rhombohedral to cubic structures. Structural transformations $R\bar{3}c$–*Imma* and *Imma*–*C*2/*m* were observed in the majority of specimens below room temperature. The temperatures of both HT and LT phase transitions decrease with decreasing Pr content in $Pr_{1-x}La_xAlO_3$, but these transformations are different in nature. The HT transition is induced by a structural deformation and its temperature decreases with increasing R-cation radius and tolerance factor. The low temperature transitions in this system are caused by electronic effects and the temperatures decrease with decreasing Pr content. Structural parameters of all five modifications of the perovskite structure found for $Pr_{1-x}La_xAlO_3$ at different compositions and temperatures are refined.

Based on the results of *in situ* synchrotron powder diffraction examinations, DTA/DSC measurements and available literature data, the phase diagram of the $PrAlO_3$–$LaAlO_3$ pseudo-binary system has been constructed (Fig. 1).

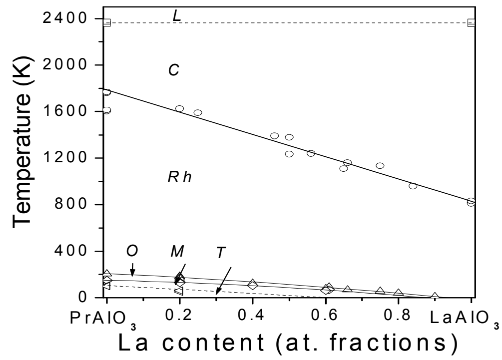

Figure 1. Phase diagram of the $PrAlO_3$–$RAlO_3$ pseudo-binary system. The symbols L, C, Rh, O, M and T indicate liquid, cubic, rhombohedral, orthorhombic, monoclinic and (pseudo)-tetragonal phase fields, respectively.

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