At room temperature (RT) PrAlO$_3$ adopts rhombohedral structure ($R\bar{3}c$), which transform into the cubic perovskite structure at elevated temperatures. EuAlO$_3$ shows the orthorhombic GdFeO$_3$-type of structure at RT. A first-order phase transition to a rhombohedral structure in EuAlO$_3$ occurs at 1420 K. On cooling the europium aluminate remains orthorhombic down to 14 K, whereas PrAlO$_3$ undergoes a sequence of low-temperature (LT) phase transformations [1].

In order to study the phase and structural behaviour in the PrAlO$_3$–EuAlO$_3$ pseudo-binary system series of Pr$_{1-x}$Eu$_x$AlO$_3$ samples with $x$ in the range of 0.1 – 0.9 were prepared by a combination of solid state reaction and arc melting in Ar atmosphere. The crystal structures of the solid solutions Pr$_{1-x}$Eu$_x$AlO$_3$ and their thermal behaviour in a wide temperature range of 12–1173 K have been investigated by using in situ X-ray powder diffraction applying synchrotron radiation (beamline B2, HASYLAB) and DTA/DSC methods. Analysis of diffraction data was carried out by full-profile Rietveld refinements, using the WinCSD program package.

It was established that two kinds of solid solutions Pr$_{1-x}$Eu$_x$AlO$_3$ with rhombohedral ($R\bar{3}c$) and orthorhombic ($Pbnm$) structures exist at ambient temperature. An immiscibility gap between the two perovskite-type phases occurs around $x=0.3$. In an earlier study of the PrAlO$_3$–EuAlO$_3$ system performed by Brusset et al [2] reported an immiscibility gap between a pseudo-monoclinic and a rhombohedral symmetries phases in the range of 0.38<$x$<0.57. Lattice parameters and cell volumes decrease monotonically with decreasing Pr content (Fig. 1).

At elevated temperatures, a first-order transformation from the orthorhombic to a rhombohedral structure is observed in the Pr$_{1-x}$Eu$_x$AlO$_3$ samples with $x \geq 0.35$. We assume that the rhombohedral-to-cubic phase transition might occur considerably above the highest temperature (1700 K) reached in the experiments. Therefore, the temperatures of the $R\bar{3}c \leftrightarrow Pm\bar{3}m$ transition in the Pr$_{0.8}$Eu$_{0.2}$AlO$_3$ and Pr$_{0.5}$Eu$_{0.5}$AlO$_3$ samples were estimated from the extrapolation of the $c/a$ parameter ratios of the rhombohedral phase (Fig. 2).
Low-temperature (LT) examination revealed a sequence of phase transformations in the Pr$_{1-x}$Eu$_x$AlO$_3$ samples with $x<$0.3, whereas the solid solutions with $x\geq 0.35$ remain orthorhombic below RT. DTA/DSC experiment revealed phase transitions in the Pr$_{1-x}$Eu$_x$AlO$_3$ specimens with $x=0.1$, 0.2, 0.25 at 232 K, 245 K, 273 K, respectively. Crystal structure parameters of the LT modifications of Pr$_{0.8}$Eu$_{0.2}$AlO$_3$ were determined by using in situ synchrotron powder diffraction technique. A sequence of LT phase transformations $R\bar{3}c \leftrightarrow Imma \leftrightarrow C2/m$ has been found in this compound (Fig. 3).

Figure 2. Lattice parameters of rhombohedral Pr$_{0.8}$Eu$_{0.2}$AlO$_3$ in the temperature range of 300 – 1200 K and extrapolation to the expected phase transition to the cubic structure.

Figure 3. LT dependencies of perovskite lattice parameters and cell volumes of Pr$_{0.8}$Eu$_{0.2}$AlO$_3$.

Based on the results of in situ synchrotron powder diffraction examinations and DTA/DSC measurements as well as available literature data, the phase diagram of the pseudo-binary system PrAlO$_3$–EuAlO$_3$ has been constructed (Fig. 4). Five kinds of solid solutions with different perovskite-type crystal structures exist in the system, depending on composition and temperature. It was established that the temperatures of HT phase transitions in Pr$_{1-x}$Eu$_x$AlO$_3$ increase linearly with decreasing Pr content. The temperature of the $R\bar{3}c$–Imma phase transition increases with decreasing Pr content, whereas the temperature for the Imma$\leftrightarrow$C2/m transformation decreases. In contrast, in the recently investigated PrAlO$_3$–RAIO$_3$ systems with “large” rare-earth element La, Ce and Nd, the temperatures of both LT transitions drop with decreasing Pr content [3].

Figure 4. Phase diagram of the pseudo-binary system PrAlO$_3$–EuAlO$_3$. The letters L, C, Rh, O1, O2 and M designate liquid, cubic, rhombohedral, orthorhombic Imma, orthorhombic $Pbnm$ and monoclinic phase fields, respectively. The symbols * denote the data obtained from synchrotron experiments.

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References