Crystal structure and thermal behaviour of solid solutions in the LaAlO$_3$–TbAlO$_3$ system

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At room temperature LaAlO$_3$ has the rhombohedral crystal structure (space group (S.G.) $R\bar{3}c$), which transforms into ideal perovskite cubic structure (S.G. $Pm\bar{3}m$) at 820 K. TbAlO$_3$ possesses orthorhombic symmetry (S.G. $Pbnm$) in a wide temperature range of 12–1173 K [1].

In order to study the phase and structural behaviour in the LaAlO$_3$–TbAlO$_3$ pseudo-binary system a series of La$_{1-x}$Tb$_x$AlO$_3$ samples with $x$ in the range of 0.1–0.9 were prepared from the oxides La$_2$O$_3$, Tb$_4$O$_7$, and Al$_2$O$_3$ by a combination of solid state reaction and arc melting in Ar atmosphere. The crystal structures of the solid solutions La$_{1-x}$Tb$_x$AlO$_3$ and their thermal behaviour in a wide temperature range of 12–1173K have been investigated by using high-resolution powder diffraction applying synchrotron radiation (beamline B2, HASYLAB at DESY) and differential thermal analysis (DTA) methods. All crystallographic calculations (refinements of the lattice parameters as well as full profile structure refinements) were performed by means of the Windows version of the Crystal Structure Determination program package WinCSD [2].

From the results of the XRD phase and crystal structural analysis it was established that two kinds of solid solutions La$_{1-x}$Tb$_x$AlO$_3$ one with rhombohedral ($x \leq 0.18$) and one with orthorhombic ($x \geq 0.42$) crystal structure exist at ambient temperature. A wide immiscibility gap exists between these two perovskite-type phases. All lattice parameters decrease monotonically with increasing Tb content in La$_{1-x}$Tb$_x$AlO$_3$ and a strong anisotropy in the lattice contraction is observed for the rhombohedral and orthorhombic phase. However, the normalized volume decreases almost linear with increasing Tb content.

At elevated temperatures, continuous phase transitions from rhombohedral to cubic structures were observed in the La$_{1-x}$Tb$_x$AlO$_3$ samples with $x < 0.4$. In the sample with the composition La$_{0.9}$Tb$_{0.1}$AlO$_3$, this transformation was detected at 1175 K (Fig. 2, a). Onset of another type of phase transition was detected in the La$_{0.4}$Tb$_{0.6}$AlO$_3$ and La$_{0.5}$Tb$_{0.5}$AlO$_3$. This phase transition was defined as a first-order transformation from the orthorhombic to a rhombohedral structure, similar
to other pseudo-binary systems based on LaAlO_3 [3]. The limitation of the equipment used did not allow us to detect the completion of orthorhombic-to-rhombohedral phase transition (Fig. 2, b).

Based on the results of in situ synchrotron powder diffraction examinations and DTA measurements as well as available literature data, the phase diagram of the pseudo-binary system LaAlO_3–TbAlO_3 has been constructed (Fig. 3).

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References

