Concentration and Temperature-Driven Phase Transitions in the NdAlO₃ – EuAlO₃ system

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Rare earth aluminates with perovskite structure and solid solutions based of them found the wide applications in the various fields of science and technique because of their unique properties. RAlO₃-based perovskite materials are widely used as substrates for the epitaxy of HTSC and CMR films, as components of solid oxide fuel cells, as active and passive laser media, scintillators and microwave dielectric materials. The physical and chemical properties of the perovskite crystals are closely linked to their variable phase composition and crystallography. The crystal structure can be highly affected by iso/aliovalent substitutions in cation sites or by varying temperature and/or pressure. Thus, the physical properties of perovskite materials can be tuned by modifying their crystal structure, until a material with the desired properties is obtained.

In this work we present the results of the phase and structural characterisation of the pseudo-binary system NdAlO₃–EuAlO₃ by a combination of X-ray phase and structural analysis and in situ high-temperature X-ray synchrotron powder diffraction technique. The Nd₁₋ₓEuₓAlO₃ samples were prepared by a combination of solid state reaction and arc melting in Ar atmosphere. X-ray phase and structural characterisation of the samples at room temperature (RT) was performed by laboratory Huber imaging plate Guinier camera G670 (Cu Kα₁ radiation, λ = 1.54056 Å). In situ high-temperature crystal structure investigations were carried out at beamline B2 at synchrotron laboratory HASYLAB/DESY (Hamburg, Germany). The diffraction experiments were performed in Debye-Scherrer capillary vertical geometry at the powder diffractometer equipped with a STOE furnace and on-site readable imaging plate detector OBI. Data analysis was carried out by the Rietveld method using the WinCSD program package.

The analysis of X-ray diffraction data collected at RT showed an orthorhombic Pbnm structure for Nd₁₋ₓEuₓAlO₃ specimens with x≥0.25 and rhombohedral R3c structure for the samples with x<0.15. The sample with nominal composition Nd₀.₈₆Eu₀.₁₄AlO₃ contains both rhombohedral (58.3 wt. %) and orthorhombic (41.7 wt. %) phases, as derived from a full-profile Rietveld refinement. In the Nd₀.₅₃Eu₀.₄₇AlO₃ specimen content of both rhombohedral R3c (78.92 wt. %) and orthorhombic Pbnm phase (21.08 wt. %) was revealed by the high-resolution synchrotron powder diffraction method, whereas by usual X-ray diffraction method only rhombohedral R3c phase was detected. Accordingly, the refinement of Nd₁₋ₓEuₓAlO₃ structures was performed in space groups R3c (x = 0.1) and Pbnm (x ≥ 0.20). Comparison of the obtained values of the lattice parameters of Nd₁₋ₓEuₓAlO₃ specimens with the literature data for the “pure” NdAlO₃ and EuAlO₃ [1] (Fig. 1) clearly prove on the formation of two kinds of solid solutions in the NdAlO₃–EuAlO₃ system. The results obtained are in good agreement with the data of Ref. [2], in with two kinds of Nd₁₋ₓEuₓAlO₃ solid solutions with rhombohedral and pseudo-monoclinic structures are mentioned to exist in the NdAlO₃–EuAlO₃ system at x<0.18 and x>0.25, respectively. The unit cell volume of orthorhombic solid solution Nd₁₋ₓEuₓAlO₃ decreases almost linearly in accordance with decreasing radii of rare-earth cations. A minor negative deviation from the Vegard’s law is observed in rhombohedral R3c phase. For certain compositions, the dimensions of the unit cells are very close to tetragonal or cubic; however, the symmetry of these structures remains orthorhombic.
In situ high-temperature examinations of the Nd$_{1-x}$Eu$_x$AlO$_3$ specimens revealed the presence of structural phase transitions from the orthorhombic Pbnm to rhombohedral R 3 c structure. In Nd$_{0.6}$Eu$_{0.4}$AlO$_3$ such transition occurs in the temperature range 573–673 K. The analysis of the diffraction patterns in the vicinities of the transition temperature revealed coexistence of both LT orthorhombic and HT rhombohedral phases, which proves the 1st-order discontinuous character of the phase transition. The thermal evolution of the lattice parameters of the Nd$_{0.6}$Eu$_{0.4}$AlO$_3$ sample illustrating the 1st-order phase transition from the orthorhombic to rhombohedral structure is presented in Fig. 2.

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 NdAlO$_3$–EuAlO$_3$ has been constructed.

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References
