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In situ X-ray Powder Diffraction Study of $R_{1-x}Nd_xAlO_3$ (R = La, Pr). Tetyana Basyuk^a, Leonid Vasylechko^a, Sergiy Fedeev^a, Vasyl Berezovets^b, Dmytro Trots^c, Rainer Niewa^d. ^aLviv Polytechnic National University, Semiconductor Electronics Department, Lviv, Ukraine. ^bKarpenko Physico-Mechanical Institute, Lviv, Ukraine. ^cDarmstadt University of Technology, Institute for Materials Science, Darmstadt, Germany. ^dTechnische Universität München, Department Chemie, Garching, Germany. E-mail: tanya.basyuk@gmail.com

At room temperature (RT) compounds $RAIO_3$ of the early rare-earth metals with R = La, Pr, Nd adopt rhombohedral structures ($R\bar{3}c$), which transform into the cubic perovskite structure at elevated temperatures. On cooling lanthanum and neodymium aluminates remain rhombohedral down to the lowest temperatures of 5 – 10 K, whereas $PrAlO_3$ undergoes a sequence of low-temperature (LT) phase transformations [1, 2].

In order to study the phase and structural behaviour in the $RAIO_3-NdAlO_3$ (R = La, Pr) pseudo-binary systems, a series of $R_{1-x}Nd_xAlO_3$ samples has been prepared by a combination of solid state reactions in air and arc-melting in Ar atmosphere. Crystal structures and thermal behaviour of the samples have been studied in a wide temperature range of 12 – 1173 K by means of a high-resolution powder diffraction technique applying synchrotron radiation (beamline B2, HASYLAB at DESY), thermal analysis and magnetic susceptibility measurements.

It was established, that continuous solid solutions with rhombohedral structure exist in the $RAIO_3-NdAlO_3$ systems at RT. Lattice parameters and cell volumes increase monotonically with increasing Nd content. At elevated temperatures, the $Pr_{1-x}Nd_xAlO_3$ and $La_{1-x}Nd_xAlO_3$ solid solutions undergo continuous phase transitions from rhombohedral to cubic structures. The phase transition temperatures rise with Nd concentration. Besides a high-temperature (HT) phase transition, a series of LT phase transformations were observed in the $PrAlO_3-NdAlO_3$ system. Temperatures of LT transformation do not depend on the average radius of R-cation and decrease with decreasing Pr content. LT modifications of $Pr_{1-x}Nd_xAlO_3$ solid solutions display orthorhombic (*Imma*), monoclinic (*I2/m*) and (pseudo)-tetragonal (*I4/mcm*) structures. Unexpectedly, a rare triclinic perovskite structure has been found for a sample with composition $Pr_{0.44}Nd_{0.56}AlO_3$ below 70 K.

Structural parameters of all modifications in the $R_{1-x}La_xAlO_3$ systems at different compositions and temperatures were refined.

Based on the results of *in situ* synchrotron powder diffraction examinations, DTA/DSC measurement and available literature data, the phase diagrams of the $PrAlO_3-NdAlO_3$ and $LaAlO_3-NdAlO_3$ pseudo-binary systems have been constructed.

[1] Moussa, S.M., Kennedy, B.J., Hunter, B.A., Howard, C.J., Vogt, T., *J. Phys.: Condens. Matter*, **2001**, 13, L203. [2] Vasylechko,

L.; Senyshyn, A.; Bismayer, U.; *Handbook on the Physics and Chemistry of Rare Earths*. **2009**, 39, 113.

Keywords: perovskites; phase transition and structure; phase diagram

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Single-Crystal-to-Single-Crystal Photoinduced Orton Rearrangement of Substituted *N*-chloroanilides: A New Efficient, Selective, Solventless Method for Aromatic Chlorination. Yildiray Topcu^{a,b}, Panče Naumov^{a,c,d}. ^aGraduate School of Engineering, Osaka University, 2-1 Yamada-oka, Osaka, 565-0871 Suita, Japan. ^bNevsehir University, Arts and Sciences Faculty, Chemistry Department, Avanos Yolu, TR-50300 Nevsehir, Turkey. ^cInstitute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, MK-1000 Skopje, Macedonia. E-mail: ytopcu@gmail.com

With four newly synthesized and characterized compounds (*N*-chlorobenzanilide and three methyl-substituted *N*-chloroacetanilides; Fig. 1b) we expanded our previous study^[1] of a new solid-state photochemical reaction, analogous to the acid-catalyzed Orton rearrangement in solution, by which an *N*-chlorine atom from the side amino group is transferred to the phenyl ring (Fig. 1a). The reaction mechanism and the products were studied with a combination of physico-chemical methods: steady-state X-ray photodiffraction, IR spectroscopy and HPLC analysis. The rearrangement proceeds rapidly, and is highly selective – properties which put this reaction in favor as a convenient, inexpensive, solventless, green method for aromatic chlorination.

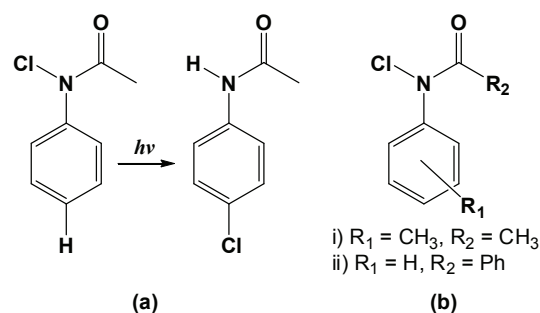


Fig. 1. (a) Schematic representation of the photoinduced Orton rearrangement of *N*-chloroacetanilide, and (b) structures of the studied substituted *N*-chloroanilide molecules.

[1] Naumov *et al.*, *J. Phys. Chem. B* **111**, **2007**, 10373–10378.

Keywords: reactive intermediates; single-crystal X-ray diffraction; solid-state photochemistry.