STRUCTURAL PHASE TRANSITIONS AND THERMODYNAMIC STABILITY OF THE RUDDLESDEN-POPPER NICKELATE $La_3PrNi_3O_{10-\delta}$

Tsvetkova N.S., *Ivanov I.L.*, *Malyshkin D.A.*
Ural Federal University
620002, Ekaterinburg, Mira st., 19

The Ruddlesden-Popper (R-P) nickelates $Ln_{n+1}Ni_nO_{3n+1}$ (Ln = La, Pr, Nd) belong to the class of materials promising for application as cathode materials for intermediate temperature solid oxide fuel cells. The alternation of n perovskite ($LaNiO_3$) and rock salt (LaO) layers along the c-axis is the unique feature of R-P oxides crystal structure. The increase of n in the series $Ln_{n+1}Ni_nO_{3n+1}$ enhances the thermal stability, electronic transport and electrochemical performance. Presently, there is no consensus concerning the crystal structure of higher-order (n = 3) nickelates. The results of numerous room temperature structure studies disagree with each other. The same applies to the details of the structural phase transitions observed in these oxides upon temperature change.

In the present work the detailed investigation of the crystal structure of $La_3PrNi_3O_{10-\delta}$ R-P nickelate was performed by combination of instrumental techniques, analysis of the available literature data and considering the group-subgroup relations.

Variation of $La_3PrNi_3O_{10-\delta}$ crystal structure with temperature was studied by in situ high-temperature X-ray diffraction (HT-XRD) with XRD 7000 diffractometer (Shimadzu, Japan) at 25–1000 °C in air. The crystal structure refinement was carried out by Rietveld method using the Rietica 4.0 software. The isobaric heat capacity (C_p) was measured by differential scanning calorimetry (DSC) with MHTC 96 (Setaram, France) calorimeter in the temperature range 25–900 °C in air. The resulting C_p temperature dependence possesses complex shape with three anomalies indicating the second order phase transitions and supporting the results of in situ HT-XRD. Accordingly, the HT-XRD patterns were analyzed based on group-subgroup relations using the software SUBGROUPGRAPH and WYCKSPLIT of Bilbao Crystallographic Server. During the analysis the structural data (atomic coordinates and Wyckoff positions) for related oxides available in the literature were used as an independent source of crystallographic information. As a result, the following sequence of the second order phase transitions in the temperature range from 1000 to 25 °C in air was proposed:

*I*4/*mmm* (No. 139) > *Fmmm* (No. 69) > *C*2/*m* (No. 12) > $P2_1/a$ (No. 14).

The thermodynamic stability limits of $La_3PrNi_3O_{10-\delta}$ depending on temperature and oxygen partial were determined by thermogravimetric analysis (TGA) and coulometric titration technique. TGA was performed using STA409PC (Netzsch GmbH, Germany) thermobalance in the temperature range 25–1200 °C in air. Coulometric titration was carried out in the original home-built setup in the ranges of temperature and oxygen partial pressure 800–950 °C and 10^{-5}–1 atm, respectively. The products of phase decomposition reactions were identified by equilibrating the $La_3PrNi_3O_{10-\delta}$ under required conditions followed by quenching with subsequent XRD analysis.

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (theme № FEUZ-2026-0011).