CRYSTAL STRUCTURE AND THERMODYNAMIC STABILITY OF PHASES IN THE $(La,Pr,Nd)_2(Ni,Cu)O_4$

Sukhanov K.S., Gilev A.R., Kiselev E.A., Cherepanov V.A.
Ural Federal University
620002, Ekaterinburg, Mira st., 19

The Ruddlesden-Popper $Ln_2NiO_{4+\delta}$ (Ln=La, Nd, Pr) complex oxides are considered by researchers as promising materials for electrochemical devices, particularly, as cathodes for intermediate-temperature (600-800 °C) solid oxide fuel cells (IT-SOFCs). Insufficient thermodynamic stability at T<900 °C in air is their main disadvantage. Stability can be improved by partial replacing of praseodymium with lanthanum/neodymium and nickel with copper. The purpose of this work is to synthesize and to study the stability of $La_{2-x}(Pr,Nd)_xNi_{1-y}Cu_yO_{4+\delta}$ at 700 °C in air.

The $La_{2-x}(Pr,Nd)_xNi_{1-y}Cu_yO_{4+\delta}$ (x = 0,5; 1,0; 1,5; y = 0,4; 0,6; 0,8) complex oxides were synthesized via a citrate-nitrate process. The phase purity of the samples was confirmed by XRD analysis. The XRD results showed that $La_{2-x}(Pr,Nd)_xNi_{1-y}Cu_yO_{4+\delta}$ (x=0,5–1,0; y=0,4–0,6) and $La_{0.5}Pr_{1.5}Ni_{0.6}Cu_{0.4}O_{4+\delta}$ complex oxides were single-phase after annealing at 900 °C with the K_2NiF_4-type tetragonal structure. The $La_{1.5}Pr_{0.5}Ni_{0.2}Cu_{0.8}O_{4+\delta}$ and $La_{1.5}Nd_{0.5}Ni_{0.2}Cu_{0.8}O_{4+\delta}$ samples contained little amounts (< 0.6%) of PrO_x and Nd_2O_3. Impurities were found in the remaining samples, the content of which increased with increasing concentrations of praseodymium/neodymium and copper. For single-phase samples, *a* parameter decreases as the dopant concentration increases. The *c* parameter increases with copper doping and decreases with increasing concentration of praseodymium/neodymium. Structural stability with the addition of dopants can be described using the tolerance factor of the Paul Poix (t) for phases with the K_2NiF_4 type structure [1, 2]. Limiting value of t=0.85 could define single phase domains of the studied solutions satisfactorily. To study the thermodynamic stability in the intermediate-temperature range (600-800 °C), single-phase oxides obtained at 900 °C were kept at 700 °C in air for 30 days. The XRD results showed that all solid solutions$La_{2-x}Nd_xNi_{1-y}Cu_yO_{4+\delta}$ were stable after annealing at 700 °C in air. In the $La_{2-x}Pr_xNi_{1-y}Cu_yO_{4+\delta}$ system, compositions with x = 0.5 and y = 0.6; 0.8 were stable at 700 °C. Other studied solid solutions of $La_{2-x}Pr_xNi_{1-y}Cu_yO_{4+\delta}$ contained significant amounts (> 5%) of $La_{1-x}Pr_xNi_{1-y}Cu_yO_{3-\delta}$ and PrO_x impurity phases.

1. Poix P. Etude de la structure K_2NiF_4 par la methode des invariants, I. Cas des oxydes A_2BO_4 // J. Solid State Chem. – 1980. – V. 31. – P. 95–102. https://doi.org/10.1016/0022-4596(80)90011-0

2. Ganguly P., Rao C.N.R. Crystal Chemistry and Magnetic Properties of Layered Metal Oxides Possessing the K_2NiF_4 or Related Structures // J. Solid State Chem. – 1984. – V. 53. – P. 193–216. https://doi.org/10.1016/0022-4596(84)90094-X

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