Physico-chemical nanomaterials science

Anomalous thermal expansion of $HoCo_{0.5}Cr_{0.5}O_3$ probed by X-ray synchrotron powder diffraction

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The rare earth (*R*) cobaltites and chromites with perovskite-like structure are used as electrode materials for SOFC, thermoelectrics, catalysts and sensory materials due to their electrical and magnetic properties as well as significant electrochemical and catalytic activity. The $RCoO_3$-based materials are of particular interest, because their transport, magnetic and other properties are dependent upon the spin state of Co^{3+} ions.

New mixed dysprosium cobaltite-chromite $HoCo_{0.5}Cr_{0.5}O_3$ has been obtained for the first time from constituent oxides Ho_2O_3, Co_3O_4 and Cr_2O_3 by solid state reaction in air at 1373 K. X-ray powder diffraction examination revealed orthorhombic perovskite structure isotypic with $GdFeO_3$. The unit cell dimensions of $HoCo_{0.5}Cr_{0.5}O_3$ (a = 5.19707 Å, b = 5.46922 Å, c = 7.4578 Å) are in good agreement with the structural data of the parent $HoCoO_3$ and $HoCrO_3$ compounds, thus proving formation of the continuous solid solution in the $HoCoO_3$–$HoCrO_3$ system. According to the *in situ* high-resolution X-ray synchrotron powder diffraction examination performed at beamline ID22 of ESRF, $HoCo_{0.5}Cr_{0.5}O_3$ remains orthorhombic in a broad temperature range of 298–1273 K. No symmetry related structural changes were observed. However, an anomalous behaviour of the crystal lattice was observed, which is reflected in a sigmoidal temperature dependence of the unit cell parameters and in increase of the thermal expansion coefficients with a broad maxima near 870 K. Analysis of the selected bond lengths and octahedra tilt angles allows to detect extra structural anomalies, which are evidently associated with the electronic and magnetic phase transitions occurred in the $RCo_{1-x}Cr_xO_3$ system. In particular, $HoCoO_3$ undergoes spin state transition at 486 K and following insulator-metal transition at 782 K [1]. It is evident that the coupling of the electronic and magnetic transitions combined with the anomaly of the lattice behaviour will result in extremely complicated magnetic and electronic phase diagram of the mixed cobaltite-chromite systems.

1. *Tachibana M. et al.* Evolution of electronic states in $RCoO_3$ (R = rare earth): Heat capacity measurements // *Phys. Rev*. B -2008.-**77**.-094402.