“Physico-chemical nanomaterials science”

Anomalous thermal behaviour of $TbCoO_3$ and $TbCo_{0.5}Cr_{0.5}O_3$ probed by X-ray synchrotron powder diffraction

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RCoO_3-based materials are of particular interest during the last decades, because their functional properties strongly depend on the electronic configuration of Co^{3+} ions, which can change from low-spin to the excited spin states upon the influence of the temperature and application of external or internal (chemical) pressure.

Single phase $TbCoO_3$ and $TbCo_{0.5}Cr_{0.5}O_3$ microcrystalline materials with the orthorhombic perovskite structure were obtained from the constituent oxides Tb_4O_4, Co_3O_4 and Cr_2O_3 by solid state reaction in air at 1473 K. Structural parameters of the mixed cobaltite-chromite $TbCo_{0.5}Cr_{0.5}O_3$ (space group *Pbnm*, a = 5.2478 Å, b = 5.4590 Å, c = 7.4991 Å) are in good agreement with the corresponding data for the parent $TbCoO_3$ and $TbCrO_3$ compounds, which testify a possible formation of continuous solid solution in the $TbCoO_3$–$TbCrO_3$ pseudo-binary system. *In situ* high-resolution X-ray synchrotron powder diffraction examination performed at the beamline B2 of HASYLAB@DESY in a broad temperature range of 298–1273 K, revealed remarkable deviations of the lattice parameters of $TbCoO_3$ and $TbCo_{0.5}Cr_{0.5}O_3$ from the “normal” behaviour. The observed thermal anomalies are reflected in a sigmoidal dependence of the unit cell dimensions and in abnormal increase of the coefficients of thermal expansion with well defined maxima at ~720 K ($TbCoO_3$) and ~890 K ($TbCo_{0.5}Cr_{0.5}O_3$). Obviously, these anomalies, as well as detectable discontinuities in the selected bond lengths and octahedra tilt angles are associated with the electronic and magnetic phase transitions occurred in the $TbCo_{1-x}Cr_xO_3$ system at the elevated temperatures. According to the electronic phase diagram of the *R*CoO_3 perovskites [1], $TbCoO_3$ undergoes the phase transition from nonmagnetic dielectric to paramagnetic dielectric state at ~450 K following with the insulator-metal transition at ~730 K. It is evident that the coupling of the electronic, magnetic and lattice degrees of freedom 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 *R*CoO_3 (*R* = rare earth): Heat capacity measurements // *Phys. Rev*. B -2008.-77.-P. 094402.