Anomalous Thermal Expansion of $NdCo_{1-x}Ga_xO_3$

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New mixed cobaltites-gallates with nominal compositions $NdCo_{0.8}Ga_{0.2}O_3$ and $NdCo_{0.3}Ga_{0.7}O_3$ has been obtained from corresponding oxides by solid state reaction in air at 1373 K. X-ray powder diffraction revealed orthorhombic perovskite structure isotypic with $GdFeO_3$. The unit cell dimensions of the samples under investigation are in good agreement with the structural data of the parent $NdCoO_3$ and $NdGaO_3$ compounds, thus proving formation of continuous solid solution in the $NdCoO_3$–$NdGaO_3$ system. According to *in situ* high-temperature X-ray synchrotron powder diffraction examination performed at SNBL BM1A beamline of ESRF, both samples remain orthorhombic in a broad temperature range of 298–1100 K. No symmetry related structural changes were observed. However, comprehensive analysis of the obtained structural parameters of $NdCo_{0.8}Ga_{0.2}O_3$ and $NdCo_{0.3}Ga_{0.7}O_3$ revealed anomalous nonlinear lattice expansion, which is reflected in a sigmoidal dependence of the unit cell dimensions and in abnormally large values of thermal expansion coefficients (TEC) with broad maxima at around ~640 K and ~700 K, respectively. Evidently, similar to the "pure" rare earth cobaltites, these anomalies are caused by an excitation of Co^{3+} ions from low spin to the higher spin states and the coupled magnetic and insulator-metal (I-M) transition. In particular, corresponding transitions occurred in $NdCoO_3$ at 336 K and 635 K, respectively, are reflected in pronounced anomalies in the lattice expansion and clear maxima at the TEC curve at ~ 440 and 620 K [1]. In contrast, neodymium gallate $NdGaO_3$ does not display detectable lattice anomalies in high-temperature region and its unit cell dimension changes in a "normal" way [2].

The lattice anomalies in the mixed cobaltite-gallate series $NdCo_{1-x}Ga_xO_3$ become less pronounces with decreasing cobalt content and the characteristic maxima at the TEC curves are shifted to the higher temperature comparing with the "pure" $NdCoO_3$. Extra structural anomalies, which are evidently associated with the electronic and magnetic phase transitions occurred in $NdCo_{0.8}Ga_{0.2}O_3$ and $NdCo_{0.3}Ga_{0.7}O_3$, are detected in the temperature dependence of the selected bond lengths and octahedra tilt angles. The *M*–O–*M* angles in *RM*O_3 perovskites characterize the M^{3+}–O^{2-}–M^{3+} overlaps and determine their main magnetic and transport properties [3]. In the *R*CoO_3 series the increase of cooperative rotations of corner-shared CoO_6 octahedra leds to reduction of the bandwidth of Co(3*d*)–O(2*p*) interactions and increase of the spin-state transition temperature. The temperature dependence of the band width in the mixed cobaltites-gallates $NdCo_{0.8}Ga_{0.2}O_3$ and $NdCo_{0.3}Ga_{0.7}O_3$ shows clearly decreasing behaviour thus proving increasing population of the exited spin states of Co^{3+} ions with the temperature. It is evident that the coupling of the electronic and magnetic transitions combined with the lattice results in extremely complicated magnetic and electronic phase diagram of the mixed cobaltite-gallate systems.

Acknowledgements. The work was supported in parts by the Ukrainian Ministry of Education and Sciences under Project "RZE" and ICDD Grant-in-Aid program. The authors thank Yu.Prots and Yu. Dovgalyuk for the kind assistance with synchrotron powder diffraction measurements during beamtime allocated to the ESRF Experiment MA-2320.

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