

Spin-State Transitions in New Mixed RE Cobaltites, Cobaltites-Chromites and Cobaltites-Ferrites probed by high-temperature lattice expansion

L. Vasylechko, O. Kharko, O. Myakush, A. Bell¹

Semiconductor Electronics Department, Lviv Polytechnic National University, 12 Bandera St., 79013 Lviv, Ukraine

¹ HASYLAB at DESY, Notkestraße 85, 22607 Hamburg, Germany

The interest in the rare earth (RE) perovskite cobaltites $R\text{CoO}_3$, chromites RCrO_3 and ferrites RFeO_3 is stimulated by their unique properties, such as high electrical conductivity, significant electrochemical and catalytic activity. Complementary cobaltites RCoO_3 possess fascinating fundamental physical properties, such as temperature induced metal-insulator (M-I) transitions and different types of magnetic ordering, which are strongly dependent on the spin state of Co^{3+} cations. The latter undergo a thermally driven transition from a low-spin (LS) to intermediate-spin (IS) and high-spin (HS) states. Stabilisation and purposeful tuning of the different spin states of Co^{3+} can be achieved by a mutual substitution of cations and they can be controlled by probing of thermal expansion, which is very sensitive to spin-state transitions and crystal-field excitations as well as their coupling to the lattice [1, 2]. The aim of the present work is the study of the phase relationship and high-temperature structural behaviour of new mixed RE cobaltites, cobaltites-chromites and cobaltites-ferrites formed in $\text{RCoO}_3\text{-R}'\text{CoO}_3$, $\text{RCoO}_3\text{-RCrO}_3$ and $\text{RCoO}_3\text{-RFeO}_3$ pseudo-binary systems in order to establish the influences of the “chemical pressure” on the possible structural, spin-state and electronic phase transitions.

Series of $\text{R}_{1-x}\text{R}'_x\text{CoO}_3$ ($\text{R}, \text{R}' = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$), $\text{RCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($\text{R} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}$) and $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ specimens have been prepared from stoichiometric amounts of the rare earth oxides, Co_3O_4 , Cr_2O_3 and Fe_2O_3 by solid-state reaction technique. The mixtures of starting components for a synthesis of RE cobaltites were pressed in the pellets and sintered in air at 1423–1473 K for 50–60 h, with one intermediate re-grinding of the products. For a synthesis of mixed cobaltites-chromites, the precursor powders were ball-milled in ethanol for 9 h, dried, pressed in the pellet and sintered in air at 1573 K for 12 h. After the cooling down to the room temperature, the pellets were re-ground, ball-milled for 2 h, pressed and fired at 1573 K for 13 h. Mixed cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ were obtained by solid state reaction in air at 1573 K for 30h. Phase identification and structural characterisation at ambient conditions was performed on the basis of laboratory X-ray powder diffraction data (Huber imaging plate Guinier camera G670, $\text{Cu } K_{\alpha 1}$ radiation). Thermal behaviour of the crystal structure has been studied *in situ* in the temperature range of 298–1173 K. Corresponding experiments were performed at the powder diffractometer at beamline B2, equipped with STOE capillary furnace and image plate detector OBI.

Two types of solid solutions $\text{La}_{1-x}\text{R}_x\text{CoO}_3$ with different kinds of distorted perovskite structure – orthorhombic and rhombohedral ones – are formed in the $\text{LaCoO}_3\text{-RCoO}_3$ systems with Pr, Nd, Sm, Eu, Gd and Tb. In contrast, continuous solid solutions with orthorhombic perovskite structure exist in the systems $\text{PrCoO}_3\text{-RCoO}_3$ ($\text{R} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$), $\text{NdCoO}_3\text{-RCoO}_3$ ($\text{R} = \text{Sm}, \text{Eu}, \text{Gd}$), and $\text{SmCoO}_3\text{-RCoO}_3$ ($\text{R} = \text{Eu}, \text{Gd}$). Peculiarity of the majority of PrCoO_3 - and NdCoO_3 -based systems is the lattice parameters cross-over, resulting in the appearance of metrically tetragonal or cubic lattices at certain compositions. The reason for this phenomenon, which is also observed in the related systems based on some rare earth aluminates and gallates [3], is that the isotypic end members of the corresponding systems display different cell parameters ratio within the same orthorhombic GdFeO_3 type of structure. Formation of continuous solid solutions with the orthorhombic perovskite structure is also typical for the mixed cobaltite-chromite systems $\text{RCoO}_3\text{-RCrO}_3$ ($\text{R} = \text{Pr}, \text{Sm}, \text{Eu}$ and Gd) and cobaltite-ferrite system $\text{PrCoO}_3\text{-RFeO}_3$. In the praseodymium based solid solutions $\text{PrCo}_{1-x}\text{Cr}_x\text{O}_3$ and $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ a lattice parameter cross-over results in a metrically cubic orthorhombic structure in the $\text{PrCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$ and $\text{PrCo}_{0.6}\text{Fe}_{0.4}\text{O}_3$ specimens.

In situ high-temperature powder diffraction examinations of the mixed RE cobaltites $\text{R}_{1-x}\text{R}'_x\text{CoO}_3$ revealed strong anomalies in the lattice expansion reflected in a sigmoidal dependence of the cell dimensions and in clear maxima in the thermal expansion coefficients, TEC (Fig. 1), which are

unambiguously related to the changes in the spin state of Co^{3+} ions. The increase of the cell volumes, evaluated by the comparison of the studied cobaltites with corresponding rare earth aluminates, corresponds to the increase of the Co^{3+} ionic radii at about 0.002 nm, which favour the low-spin – intermediate-spin scenario of the spin transition. Observed anomalies in the lattice expansion of the mixed cobaltites-chromites $\text{RCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$ and cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ are less pronounced. For instance, the increase of the cell volume in $\text{PrCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$ and $\text{EuCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$ is *ca.* 2 times smaller than in $\text{Pr}_{0.4}\text{Eu}_{0.6}\text{CoO}_3$ (Fig. 2). Moreover, the critical temperatures at the thermal expansion coefficients, obtained by derivation of the cell volumes of $\text{RCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$, are considerably higher than in corresponding rare-earth cobaltites (Fig. 1).

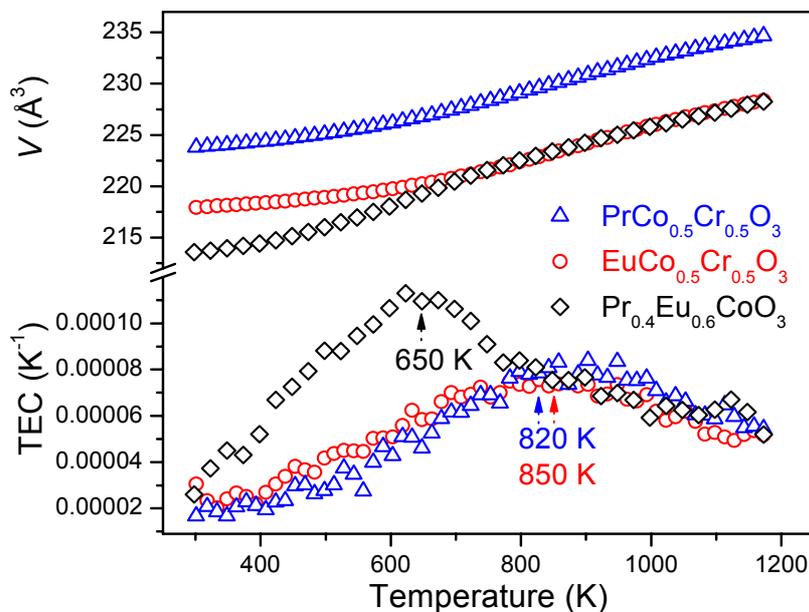


Figure 1: Temperature dependencies of the cell volumes and thermal expansion coefficients of Pr and Eu cobaltites-chromites in comparison with praseodymium-europium cobaltite $\text{Pr}_{0.4}\text{Eu}_{0.6}\text{CoO}_3$.

Based on experiential data on characteristic temperatures of thermal expansion coefficients (TEC_{max}) for the mixed RE cobaltites studied, as well as on the estimated existence ranges of two types of $\text{R}_x\text{R}'_{1-x}\text{CoO}_3$ solid solutions, a tentative phase diagram of rare earth cobaltites with perovskite structure have been constructed. Clear correlation between the temperatures of M-I transitions and R-cation radii have been found for $\text{R}_x\text{R}'_{1-x}\text{CoO}_3$ solid solutions and RCoO_3 compounds. It is shown that the critical temperatures of the thermal expansion coefficients reflect very well the temperatures of M-I transitions, proving that the analysis of thermal expansion is very useful tool for the study of such kind of transitions in the cobaltite-based systems. Especially this is important for the Pr- and Nd-containing compositions, where the spin-state transition is seen much better in the thermal expansion data than in the magnetic susceptibility due to the large contribution of the $4f$ moments of Pr and Nd ions on the magnetic properties.

Acknowledgements: The work was supported in parts by the Ukrainian Ministry of Education and Sciences (Project “Neos”) and ICDD Grant-in-Aid program.

References

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