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Thermal Behaviour of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ Probed by X-ray Synchrotron Powder Diffraction and Impedance Spectroscopy Measurements

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Crystal structure and transport properties of the mixed praseodymium cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ have been studied in the temperature range of 298–1173 K by a combination of *in situ* X-ray synchrotron powder diffraction and temperature dependent impedance spectroscopy measurements. *In situ* high temperature powder diffraction examination of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series revealed considerable anomalies in the lattice expansion which are especially pronounced for the cobalt-rich specimens. These anomalies, which are reflected in a sigmoidal dependence of the unit cell dimensions and in the considerable increase of the thermal expansion coefficients, are obviously associated with transitions of Co^{3+} ions from low spin to the higher spin states and the coupled metal–insulator transitions, occurring in rare earth cobaltites at the elevated temperatures. Indeed, the temperature-dependent impedance measurements clearly prove the change of conductivity type from dielectric to the metallic behaviour in the mixed cobaltite-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ at the elevated temperatures.

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1. Introduction

The interest in the rare earth perovskite cobaltites RCoO_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 attractive fundamental physical properties, such as temperature induced metal–insulator 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 [1–3]. Stabilization 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.

2. Experimental

Mixed praseodymium cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1, 0.2 \dots 0.8, 0.9$), as well as the “pure” PrCoO_3 and PrFeO_3 compounds were obtained from the oxides Pr_6O_{11} , Co_3O_4 , and Fe_2O_3 by solid-state reactions in air at the temperature of 1573 K. X-ray phase and structural characterization of the samples at room temperature was performed by using

Huber imaging plate Guinier camera G670 ($\text{Cu } K_{\alpha 1}$ radiation, $\lambda = 1.54056 \text{ \AA}$). Temperature evolution of the crystal structure has been studied *in situ* in the temperature range of 298–1173 K by means of X-ray powder diffraction applying synchrotron radiation. The experiments were performed at the powder diffractometer at beamline B2 of HASYLAB@DESY [4, 5] during beamtimes allocated to the HASYLAB projects I-20110214 and I-20110837. Analysis of the diffraction data was carried out using the WinCSD program package [6]. The investigation of the electrical conductivity was performed at the Clausthal University of Technology by AC impedance measurements in the frequency range from 1 Hz to 1 MHz using the impedance/gain-phase analyzer (Solartron 1260).

3. Results and discussion

X-ray powder diffraction examination revealed that all samples synthesised possess orthorhombic perovskite structure isotypic with GdFeO_3 . Full profile Rietveld refinement, performed in space group $Pbnm$, confirms isostructurality of the mixed cobaltites-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ with the parent compounds PrCoO_3 and PrFeO_3 . Peculiarity of the PrCoO_3 – PrFeO_3 system is a lattice parameter crossover [7], which results in four regions of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ solid solution with different relations of the cell dimensions (Fig. 1, top part). The reason for this phenomenon, which was also observed in the related $\text{NdCo}_{1-x}\text{Fe}_x\text{O}_3$ system [8], as well as in some mixed aluminates $\text{Sm}_{1-x}\text{R}_x\text{AlO}_3$ and gallates $\text{La}_{1-x}\text{R}_x\text{GaO}_3$ [9–12], is that the isotypic end members

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of the corresponding systems display different cell parameters ratio within the same GdFeO_3 type of structure. In spite of formation of dimensionally cubic lattice at certain compositions of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ solid solution (Fig. 1), the symmetry of the structure remains orthorhombic. This is confirmed by an analysis of concentration dependences of the selected interatomic distances which show a divergent behaviour, indicating systematic increase of orthorhombic perovskite deformation in the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series (Fig. 1, bottom part).

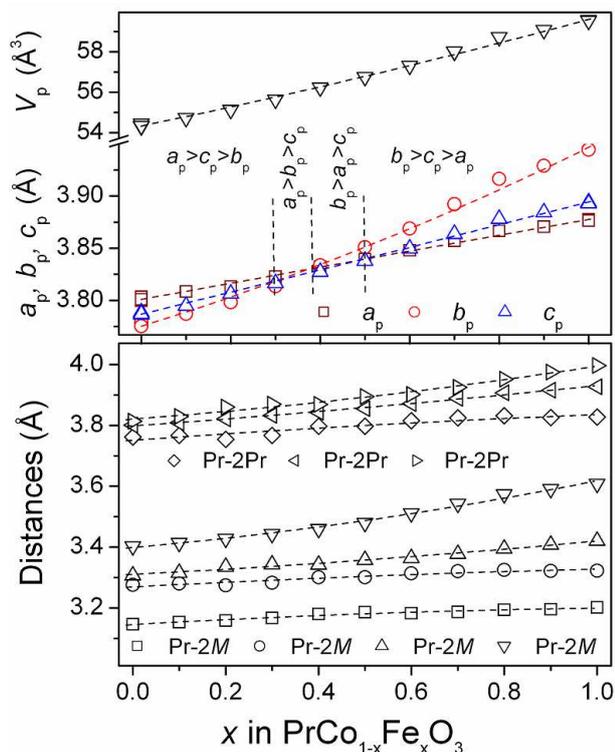


Fig. 1. Concentration dependences of the normalized unit cell dimensions (top part) and the selected interatomic distances Pr-Pr and Pr-M ($M = \text{Co}_{1-x}\text{Fe}_x$, bottom part) in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ solid solution. The orthorhombic lattice parameters are normalized to the perovskite cell as follows: $a_p = a_0/\sqrt{2}$, $b_p = b_0/\sqrt{2}$, $c_p = c_0/2$, $V_p = V_0/4$.

In situ high-temperature X-ray synchrotron powder diffraction investigation revealed that all $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ samples remain orthorhombic in the temperature range of 298–1173 K. No structural phase transitions were detected. As an example, Fig. 2 demonstrates graphical results of full profile Rietveld refinement of $\text{PrCo}_{0.3}\text{Fe}_{0.7}\text{O}_3$ structure at 1173 K. Crystal structure parameters of two representatives of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series at room temperature and 1173 K derived from high-resolution X-ray synchrotron powder diffraction data are collected in Table I.

Analysis of the temperature dependence of unit cell dimensions of all $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ samples synthesized revealed considerable anomalies in the lattice expansion, which are especially pronounced for the cobalt-rich spec-

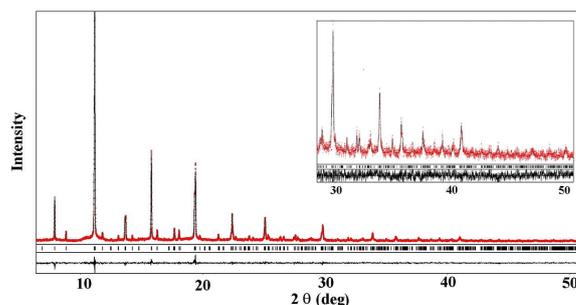


Fig. 2. X-ray synchrotron powder diffraction pattern of $\text{PrCo}_{0.3}\text{Fe}_{0.7}\text{O}_3$ ($\lambda = 0.53833 \text{ \AA}$) recorded at 1173 K, in comparison with calculated pattern. Difference curve between measured and calculated profiles is shown below the diagrams, reflection positions are indicated by ticks.

imens. The observed anomalies in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series, which are reflected in a sigmoidal dependence of the unit cell dimensions and in the considerable increase of the thermal expansion coefficients, TECs (Fig. 3), are obviously associated with the transition of Co^{3+} ions from low spin to the higher spin states and the coupled metal-insulator transitions, similar as it occurs in the “pure” praseodymium cobaltite at the elevated temperatures [1–3].

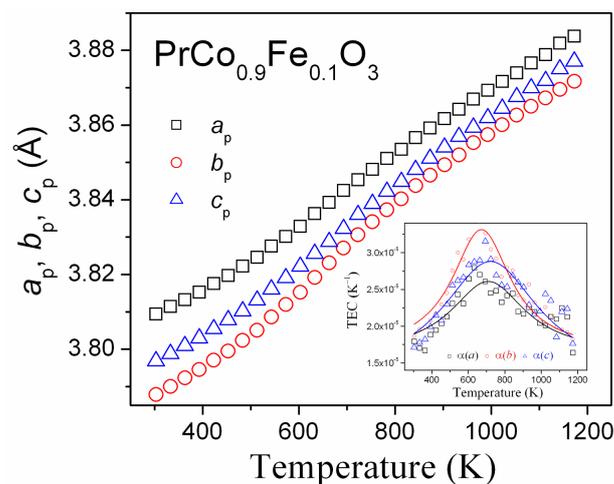


Fig. 3. Temperature dependence of the normalized lattice parameters of $\text{PrCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ and corresponding linear thermal expansion coefficients (inset).

Observed deviations in the lattice expansion in the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series become less pronounced with the decreasing cobalt content, but they are clearly detectable even in the iron-richest $\text{PrCo}_{0.1}\text{Fe}_{0.9}\text{O}_3$ specimen (Fig. 4).

The temperature-dependent impedance measurements clearly prove the change of conductivity type from dielectric to the metallic behaviour in the mixed cobaltite-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ at the elevated temperatures (Fig. 5). The temperature of insulator-metal transition

in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series increases from 723 K for $x = 0.4$ to 1100 K for $x = 0.8$ (Fig. 5, inset), which is in a good

agreement with the results obtained from the analysis of thermal expansion data.

Lattice parameters, coordinates and displacement parameters of atoms in $\text{PrCo}_{0.7}\text{Fe}_{0.3}\text{O}_3$ and $\text{PrCo}_{0.3}\text{Fe}_{0.7}\text{O}_3$ structures at 300 K and 1173 K.

TABLE I

| Lattice param. [Å] | Atoms [sites] | x | y | z | B_{iso} [Å ²] |
|---|---------------|-----------|-------------|------------|-----------------------------|
| $\text{PrCo}_{0.7}\text{Fe}_{0.3}\text{O}_3$, $T = 300$ K, $Pbnm$, $R_I = 0.066$, $R_P = 0.156$ | | | | | |
| $a = 5.4086(8)$ | Pr, 4a | 0.5073(3) | 0.0303(2) | 1/4 | 0.890(7) |
| $b = 5.4002(4)$ | Fe/Co, 4b | 0 | 0 | 1/2 | 0.47(2) |
| $c = 7.639(1)$ | O1, 4c | 0.070(5) | -0.015(2) | 1/4 | 0.8(4) |
| | O2, 8d | 0.295(3) | 0.219(4) | 0.525(3) | 0.9(2) |
| $\text{PrCo}_{0.7}\text{Fe}_{0.3}\text{O}_3$, $T = 1173$ K, $Pbnm$, $R_I = 0.081$, $R_P = 0.178$ | | | | | |
| $a = 5.5062(8)$ | Pr, 4a | 0.5146(3) | 0.0288(3) | 1/4 | 1.14(1) |
| $b = 5.5020(6)$ | Fe/Co, 4b | 0 | 0 | 1/2 | 0.98(5) |
| $c = 7.783(1)$ | O1, 4c | 0.086(8) | 0.014(4) | 1/4 | 2.4(5) |
| | O2, 8d | 0.252(6) | 0.201(5) | 0.504(4) | 2.4(5) |
| $\text{PrCo}_{0.3}\text{Fe}_{0.7}\text{O}_3$, $T = 300$ K, $Pbnm$, $R_I = 0.058$, $R_P = 0.130$ | | | | | |
| $a = 5.4551(2)$ | Pr, 4a | 0.5070(3) | 0.0384(1) | 1/4 | 0.881(9) |
| $b = 5.5036(2)$ | Fe/Co, 4b | 0.069(3) | 0 | 1/2 | 0.50(3) |
| $c = 7.7288(2)$ | O1, 4c | 0.285(2) | -0.0059(15) | 1/4 | 1.4(3) |
| | O2, 8d | 0.209(2) | 0.209(2) | 0.5336(13) | 0.48(15) |
| $\text{PrCo}_{0.3}\text{Fe}_{0.7}\text{O}_3$, $T = 1173$ K, $Pbnm$, $R_I = 0.067$, $R_P = 0.158$ | | | | | |
| $a = 5.5275(2)$ | Pr, 4a | 0.5041(7) | 0.0334(2) | 1/4 | 2.25(3) |
| $b = 5.5626(2)$ | Fe/Co, 4b | 0 | 0 | 1/2 | 0.99(4) |
| $c = 7.8333(3)$ | O1, 4c | 0.074(4) | -0.009(2) | 1/4 | 1.8(5) |
| | O2, 8d | 0.295(2) | 0.215(2) | 0.530(2) | 1.1(3) |

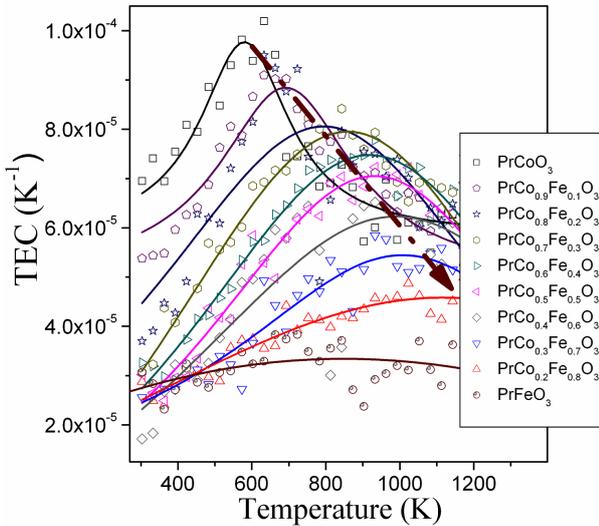


Fig. 4. Temperature dependence of the volumetric thermal expansion coefficients in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series.

Activation energy of electrical conductivity in the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series derived from the Arrhenius plots (Fig. 6) increases systematically with increasing iron content from 0.56 eV for $x = 0.4$ to 0.93 eV for $x = 0.8$ samples, being in good agreement with the literature data for the parent PrCoO_3 [13] and PrFeO_3 [14] compounds (Fig. 6, inset).

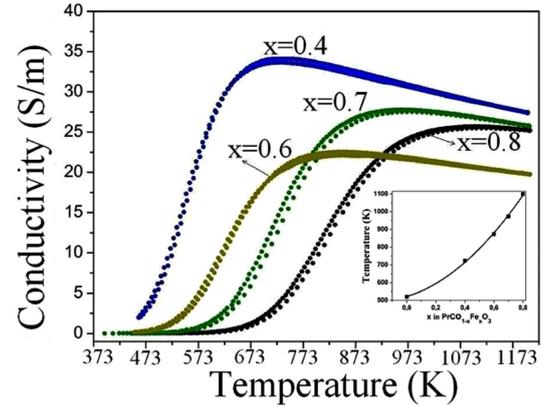


Fig. 5. Temperature dependences of electrical conductivity of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$. Inset shows concentration dependence of the I-M transition temperature in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series. The data for PrCoO_3 are taken from [2].

4. Conclusions

Series of microcrystalline powders of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ were obtained by solid-state reactions technique in air at 1473 K. Concentration dependence of the unit cell dimensions of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ proves a formation of continuous solid solution, peculiarity of which is the lattice parameters crossover. *In situ* high temperature powder diffraction examination of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series revealed

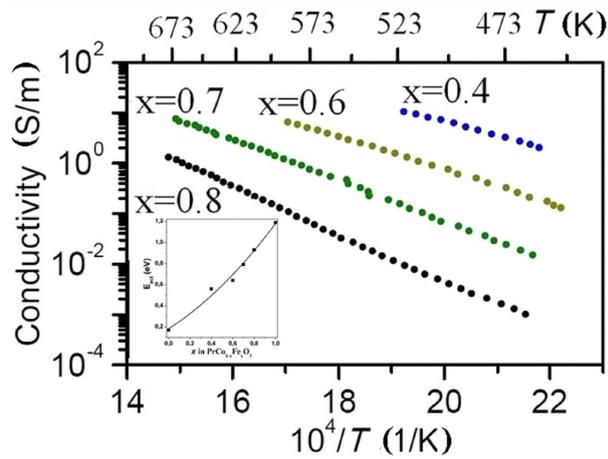


Fig. 6. Arrhenius plot of electrical conductivity of $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ samples. Inset shows concentration dependences of the activation energy in $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series.

considerable anomalies in the lattice expansion which are especially pronounced for the cobalt-rich specimens. The temperature-dependent impedance measurements clearly prove the change of conductivity type from dielectric to the metallic behaviour in the mixed cobaltite-ferrites $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ at the elevated temperatures. Activation energy of electrical conductivity in the $\text{PrCo}_{1-x}\text{Fe}_x\text{O}_3$ series derived from the Arrhenius plots increases systematically with increasing Fe content.

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