

New Mixed Perovskite $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$) as a Potential Thermoelectric and Sensory Material

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Abstract – The mixed earth rare cobaltites and chromites with general formula $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$) were obtained by solid state reaction in air at 1373 K. Based on high temperature X-ray synchrotron powder diffraction data in range temperature 298–1273 K abnormal thermal expansion of lattice dimensions was observed. Thermal expansion coefficient showed maxima, which point on insulator-metal transition. Abnormal behavior is associated with changes of spin state of Co^{3+} ions.

Key words – perovskite, thermal expansion, lattice parameters, insulator-metal transition, spin state, mixed cobaltites and chromites, spin transition.

I. Introduction

The rare earth (R) cobaltites and chromites with a perovskite structure are promising materials for SOFC, thermoelectric, catalysis and sensory materials [1–3] due to their high electrical conductivity, stability in reducing atmosphere and an electronic sensitivity against humidity and gases. $R\text{CoO}_3$ and $R\text{CrO}_3$ compounds are p -type semiconductors [2–3]. The electrical conductivity of cobaltites $R\text{CoO}_3$ increases with the increasing temperature while the Seebeck coefficient decreases indicating that holes are major conduction carries in these compounds [3].

The $R\text{CoO}_3$ -based materials show a few magnetic and electronic phase transitions, which are associated with changes of spin state of Co^{3+} ions in the octahedral coordination. Thus, their electrical and magnetic properties are dependent upon spin state of Co^{3+} ions, which can change with the increasing of temperature from low spin (LS, $t_{2g}^6 e_g^0$, $S=0$), to intermediate (IS, $t_{2g}^5 e_g^1$, $S=1$) and high spin configurations (HS, $t_{2g}^4 e_g^2$, $S=2$) [4, 5]. The spin transitions are manifested by observable changes of the crystal structure parameters: the increase of the ionic radius of Co^{3+} cation with the rise of the spin state expresses in the anomalies of the thermal expansion of crystal lattice.

In addition, $R\text{CrO}_3$ series also using as potential application in magnetic liquids, medical diagnostics and magnetic storage media. These compounds are multiferroic, because they exhibit complex magnetic

transitions at different temperatures due to magnetic spin interaction between two magnetic ions R^{3+} and Cr^{3+} [2].

II. Experimental and discursion

$R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$) series were obtained by solid state reactions technique. Precursor oxides $R_2\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$), Co_3O_4 and Cr_2O_3 were ball-milled in ethanol for 5h, dried, pressed into pellets and annealed in air at 1373 K for 20h. After regrinding as-obtained product was repeatedly ball-milled in ethanol for 2h, dried and annealed in air at 1373 K for 45 h with one intermediate re-grinding.

Laboratory X-ray powder diffraction at room temperature (Huber Imaging plate camera G670, $\text{CuK}\alpha_1$ radiation) confirmed orthorhombic perovskite structure isotypic with GdFeO_3 (space group $Pbnm$). The unit cell dimensions of $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ are in good agreement with the structural data of the parent $R\text{CoO}_3$ and $R\text{CrO}_3$ compounds, thus proving formation of the continuous solid solution in the $R\text{CoO}_3$ – $R\text{CrO}_3$ system

Thermal behaviour of the crystal structure of $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$) have been studied *in situ* by high-resolution X-ray synchrotron powder diffraction in the temperature range of 298–1273 K with the temperature step of 50 K. Corresponding measurements were performed at beamline ID22 of ESRF (Grenoble, France). Analysis of the diffraction data was carried out using the WinCSD program package.

The investigated samples adopt an orthorhombic perovskite structure in the whole investigated temperature range. 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 (Fig. 1) and in increase of the thermal expansion coefficients (TEC's) with a broad maximum near ~920 K for $\text{DyCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$ and $\text{HoCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$, ~870 K for $\text{ErCo}_{0.5}\text{Cr}_{0.5}\text{O}_3$ (Fig. 2).

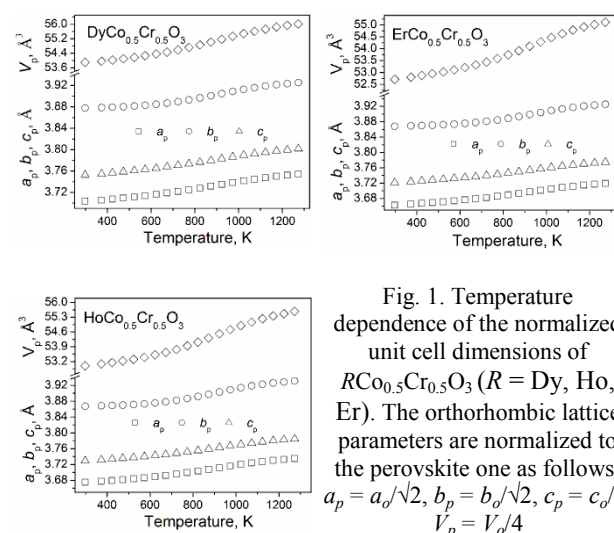


Fig. 1. Temperature dependence of the normalized unit cell dimensions of $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$). The orthorhombic lattice parameters are normalized to the perovskite one as follows: $a_p = a_o/\sqrt{2}$, $b_p = b_o/\sqrt{2}$, $c_p = c_o/2$, $V_p = V_o/4$

Observed structural anomalies in $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ at high temperature are associated with the magnetic and electronic phase transitions. Obviously, these anomalies

result by the excitation of Co^{3+} ions from the low spin to the higher spin states associated with an insulator-metal (I-M) transition. In particular, “pure” DyCoO_3 undergoes magnetic, spin-spin and metal-insulator transitions at 740 K, 785 K and 825 K [5]. According to the electronic phase diagram of $R\text{CoO}_3$ perovskites [6], ErCoO_3 and undergoes phase transitions from nonmagnetic dielectric to paramagnetic dielectric state at ~ 528 K and I-M transition at ~ 811 K. For HoCoO_3 those phase transitions are at ~ 505 K and ~ 790 K, respectively. As shown in Fig. 1 and 2 strong anomalies are most pronounced in b -direction.

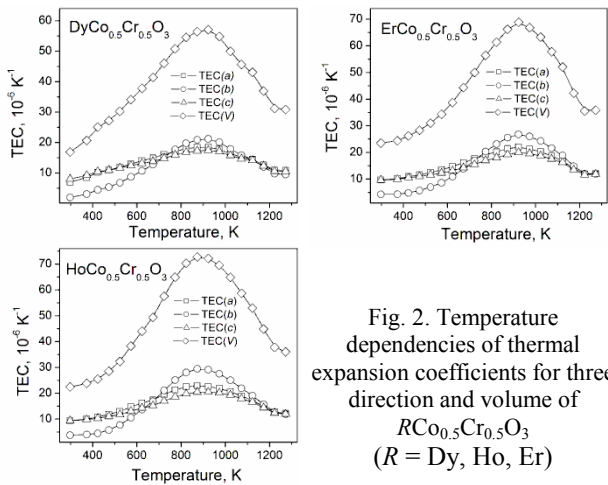


Fig. 2. Temperature dependencies of thermal expansion coefficients for three direction and volume of $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$)

Analysis of the selected bond lengths (Fig. 3) and octahedra tilt angles (Fig. 4) allows to detect extra structural anomalies, which are evidently associated with the electronic and magnetic phase transitions occurring in the end members of $R\text{CoO}_3$ – $R\text{CrO}_3$ system. 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.

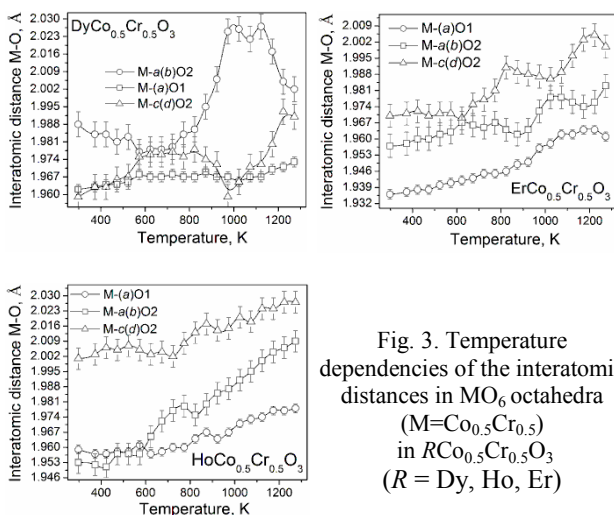


Fig. 3. Temperature dependencies of the interatomic distances in MO_6 octahedra ($M = \text{Co}_{0.5}\text{Cr}_{0.5}$) in $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$)

As shown in Fig. 3 largest distortion was observed in equatorial plane of octahedral MO_6 , which explained change of ionic radii of Co^{3+} . Therefore, corresponding

curves change their slope three or four time in depending from earth rare elements. Analysis of octahedra tilt angles revealed nonlinear changes of angles in MO_6 octahedral (Fig. 4, left panel) and between some MO_6 octahedral (Fig. 4, right panel).

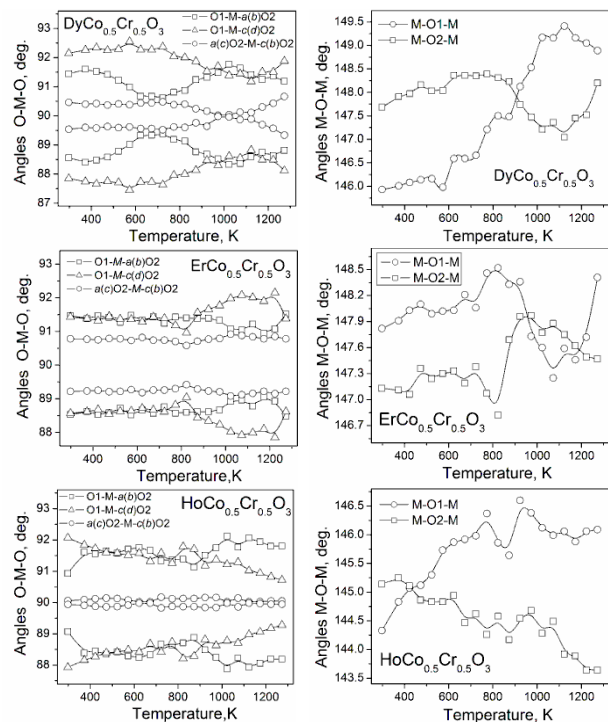


Fig. 4 Temperature dependencies of the O-M-O angles inside MO_6 octahedra and M-O-M angles between octahedra in the $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$) structure.

Conclusion

New mixed perovskites $R\text{Co}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($R = \text{Dy}, \text{Ho}, \text{Er}$) were obtained by solid state reactions technique. High-resolution X-ray synchrotron powder diffraction examination was performed. Abnormal thermal expansion of lattice dimensions and TEC's was observed, which are associated with changes spin state of Co^{3+} . Extra anomalies of structure also related with change of octahedra volume. Maxima of TEC are shifted to high temperature compared with “pure” earth rare cobaltites.

References

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