Research Article

Synthesis, Single Crystal Growth, and Properties of Cobalt Deficient Double Perovskite EuBaCo$_{2-x}$O$_{6-\delta}$ ($x = 0$–0.1)

S. V. Telegin,[1,2] A. Yu. Zuev,[2] S. V. Naumov,[1] E. I. Patrakov,[1] and D. S. Tsvetkov[2]

[1]*Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia*
[2]*Department of Physical and Inorganic Chemistry, Ural Federal University, Ekaterinburg, Russia*

Correspondence should be addressed to D. S. Tsvetkov; dmitry.tsvetkov@urfu.ru

The cobalt deficient double perovskites EuBaCo$_{2-x}$O$_{6-\delta}$ with $x = 0$–0.1 were obtained both as powders and as single crystal. Formation of cobalt vacancies in their crystal lattice was shown to be accompanied by the formation of oxygen ones. Chemical lattice strain caused by this cooperative disordering of cobalt and oxygen sublattices was found to be isotropic contrary to that caused by the formation of oxygen vacancies only. Cobalt deficiency was also shown to lead to lowering overall conductivity and Seebeck coefficient of EuBaCo$_{2-x}$O$_{6-\delta}$ double perovskites as a result of simultaneous decrease of charge carriers' concentration and their mobility as well as number of sites available for electrons and holes transfer. Strong anisotropy of the overall conductivity of the single crystal double perovskites EuBaCo$_{2-x}$O$_{6-\delta}$ was found and explained on the basis of preferential location of oxygen vacancies in the rare-earth-oxygen- (REO-) planes.

1. Introduction

Double perovskites LnBaB$_2$O$_{6-\delta}$ (Ln = rare-earth element, B = 3d element) with layered structure, which consists of alternating perovskite layers containing either rare-earth elements or Ba [1–3], have already received great attention in past decades due to their fast oxide ion transport, high mixed ionic and electronic conductivity, and high catalytic activity with respect to the oxygen reduction [2–6]. The double cobaltites LnBaCo$_2$O$_{6-\delta}$ are of particular interest due to diverse physical properties of cobalt ions [4, 7–9], which may exist not only in different oxidation states: Co^{2+}, Co^{3+}, and Co^{4+}, but also in different spin states, and may have several coordination environments, such as tetrahedral, octahedral, square pyramidal, and trigonal pyramidal. As a consequence, double cobaltites LnBaCo$_2$O$_{6-\delta}$ have really wide homogeneity range with respect to oxygen. Their oxygen content, $6-\delta$, may change in the range from 6 to 5 upon lowering oxygen partial pressure (pO$_2$) in ambient atmosphere and, for some of them, may be even lower than 5 [10]. This large oxygen deficiency is accommodated mostly by the formation of oxygen vacancies in the layers containing rare-earth ions. Depending on pO$_2$ (oxygen content) and temperature an ordering of oxygen vacancies may occur and, consequently, different superstructures lowering the symmetry of the crystal lattice may be observed as well [1]. As an example, Figure 1 shows the unite cell of EuBaCo$_2$O$_{5.5}$ with the most typical ordering of oxygen vacancies when they are regularly alternating with occupied oxygen positions along the **b**-axis of the cell. As a result, cell parameter **b** is doubled as compared to disordered state. Thus the lattice of the oxide has orthorhombic symmetry with s.g. Pmmm when oxygen vacancies are ordered or tetragonal symmetry with s.g. P4/mmm when they are disordered [1].

It should be emphasized that, up to now, only influence of the oxygen deficiency on the crystal structure and properties of double perovskites was studied [1–4, 10] while both their cationic sublattices are assumed to be stoichiometric. However, according to our preliminary study double perovskites may accommodate significant (up to 0.1) cation understoichiometry in their lattice.

Therefore the priority purposes of this work were to be (i) synthesis of single phase EuBaCo$_{2-x}$O$_{6-\delta}$ powder, (ii) single crystal EuBaCo$_{2-x}$O$_{6-\delta}$ growth, and (iii) investigation
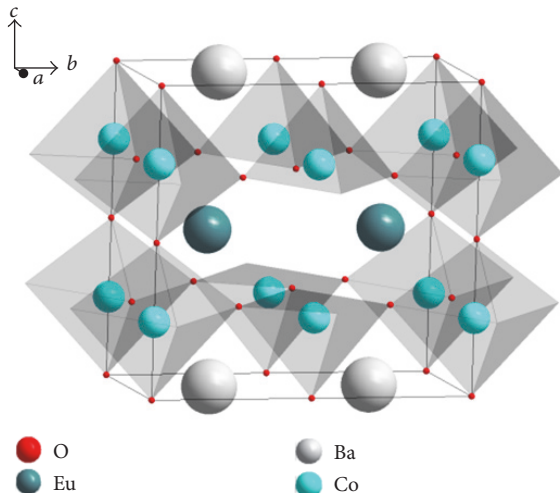
FIGURE 1: Unit cell of $EuBaCo_2O_{5.5}$ with orthorhombic symmetry, s.g. Pmmm.

of structural and electrical properties of the cation understoichiometric double perovskite $EuBaCo_{2-x}O_{6-\delta}$, where $x = 0–0.1$.

2. Materials and Methods

Powder samples of cation understoichiometric double perovskite $EuBaCo_{2-x}O_{6-\delta}$ ($x = 0$, 0.01, 0.05, 0.10) were synthesized by Pechini method [11]. Eu_2O_3 (purity 99.99%), Co (purity 99.9%), $BaCO_3$ (99.99%), HNO_3 (purity 99.99%), citric acid monohydrate (purity 99.8%), and ethylene glycol (purity 99.8%) were used as starting materials. Stoichiometric mixture of Eu_2O_3, Co, and $BaCO_3$ was dissolved in diluted (1 : 3) nitric acid. Equimolar amounts of citric acid and ethylene glycol were added to the as-obtained solution, which was then evaporated at 90°C for 5 hours under constant stirring. The obtained mixture was heated for 4 hours at 140°C in air for complete etherification and then resultant precursor was burned at 450°C for 2 hours. The as-prepared powder was further calcined at 1100°C and 1150°C for 20 hours in air with intermediate regrinding. After final calcination at 1150°C the powder samples were slowly (1°C/min) cooled in air to room temperature.

Phase purity of the samples prepared accordingly was studied by XRD in Cr Kα radiation using DRON-2 diffractometer (Bourevestnik, Russia). XRD showed no indication for the presence of a second phase in the as-prepared cobalt deficient samples $EuBaCo_{2-x}O_{6-\delta}$, where $x = 0–0.1$.

Powder samples for overall conductivity and Seebeck coefficient measurements were axially pressed into rectangular bars of $18 \times 3 \times 2\,mm^3$ at 50 MPa and sintered at 1150°C for 24 h in air. The relative density of the samples prepared accordingly was found to be 72% of the theoretical value.

Single crystal of $EuBaCo_{2-x}O_{6-\delta}$ with $x = 0.1$ was grown with 5 mm/hour rate in air atmosphere by floating zone technique using vertical optical floating zone furnace URN-2-3P (MEI, Russia).

TABLE 1: The results of the elemental analysis of the as-prepared powder samples of $EuBaCo_{2-x}O_{6-\delta}$ ($x = 0–0.10$).

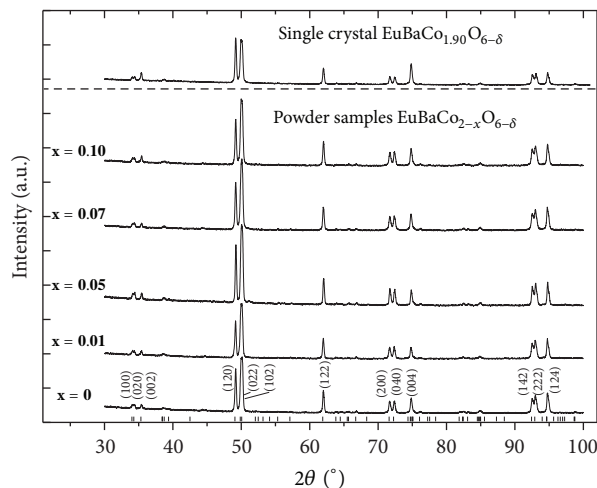| Cobalt deficiency, x	Cation, at.* %			Sample composition
	Co	Ba	Eu	
0	50.16	24.05	25.79	$Eu_{1.04}Ba_{0.96}Co_{2.01}O_{6-\delta}$
0.01	49.81	24.03	26.16	$Eu_{1.04}Ba_{0.96}Co_{1.99}O_{6-\delta}$
0.05	49.34	25.28	25.38	$Eu_{1.00}Ba_{1.00}Co_{1.95}O_{6-\delta}$
0.07	49.15	25.03	25.82	$Eu_{1.02}Ba_{0.98}Co_{1.93}O_{6-\delta}$
0.10	48.67	25.15	26.18	$Eu_{1.02}Ba_{0.98}Co_{1.90}O_{6-\delta}$

*Relative uncertainty ± 2%.

FIGURE 2: XRD patterns of the powder samples of double perovskites $EuBaCo_{2-x}O_{6-\delta}$ ($x = 0$, 0.01, 0.05, 0.10) and ground single crystal $EuBaCo_{1.90}O_{6-\delta}$.

The elemental composition of the obtained samples (both ceramic and single crystalline) was studied using Inspect F scanning electron microscope (FEI, USA) equipped with EDAX energy dispersive spectrometer. The oxygen content was measured by the samples direct reduction in hydrogen flow in the thermogravimetric setup STA409PC (Netzsch, Germany).

Overall conductivity and Seebeck coefficient were measured simultaneously by 4-probe dc-method using Zirconia-M setup (Research Technologies, Russia). The measured thermo-EMF was corrected for that of Pt-leads [12].

3. Results and Discussion

3.1. Chemical Composition, Crystal Structure, and Lattice Expansion. Figure 2 shows XRD patterns of the as-prepared double perovskite powders $EuBaCo_{2-x}O_{6-\delta}$ ($x = 0$, 0.01, 0.05, 0.10) and ground single crystal $EuBaCo_{1.90}O_{6-\delta}$. The averaged results of their elemental analysis are summarized in Table 1. Figure 3 shows distribution of elements along and across the cleavage surface of the as-grown single crystal $EuBaCo_{1.9}O_{6-\delta}$. The direction of crystal growth was determined by X-ray diffraction. Figure 4 shows indexed XRD patterns obtained from planes parallel and perpendicular to the
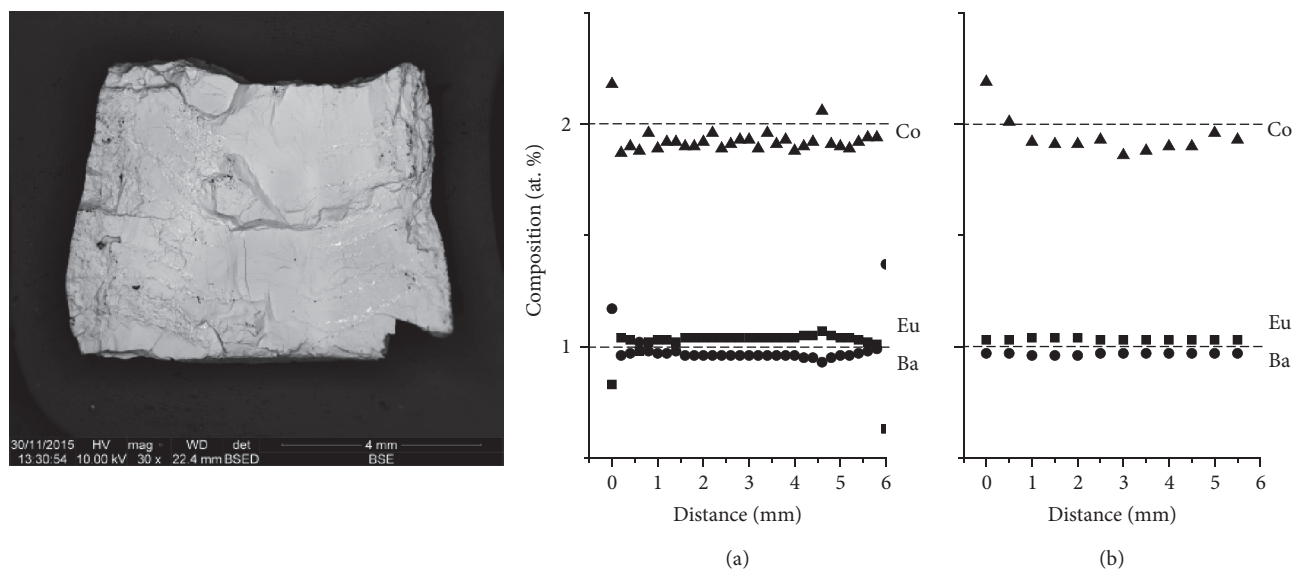
FIGURE 3: Photo of the [001] cleavage surface of the grown $EuBaCo_{1.90}O_{6-\delta}$ single crystal (on the left) and elements distribution (on the right): (a) across the sample, (b) along the sample.

TABLE 2: Cell parameters of double perovskites $EuBaCo_{2-x}O_{6-\delta}$ ($x = 0–0.1$).

Sample	a^*, Å	b^{**}, Å	c^{**}, Å	V^{**}, Å^3
$EuBaCo_{2.00}O_{6-\delta}$	3.8820	7.8271	7.5438	229.216
$EuBaCo_{1.99}O_{6-\delta}$	3.8824	7.8269	7.5443	229.247
$EuBaCo_{1.95}O_{6-\delta}$	3.8830	7.8290	7.5477	229.449
$EuBaCo_{1.93}O_{6-\delta}$	3.8849	7.8314	7.5514	229.743
$EuBaCo_{1.90}O_{6-\delta}$	3.8851	7.8331	7.5513	229.804
Single crystal $EuBaCo_{1.90}O_{6-\delta}$	3.8833	7.8332	7.5514	229.703

*Uncertainty ± 0.0005 Å. **Uncertainty ± 0.001 Å.
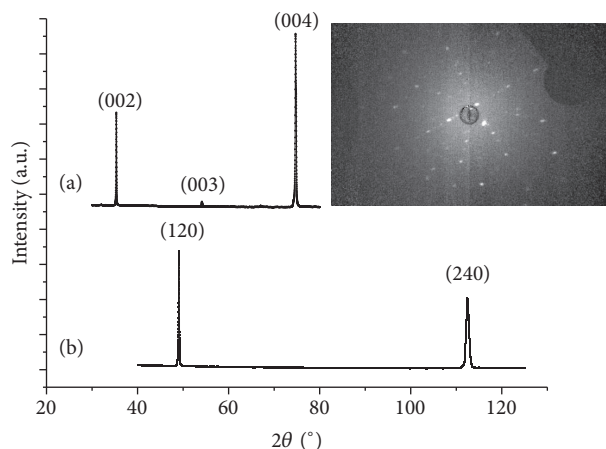

FIGURE 4: XRD patterns obtained from planes perpendicular (a) and parallel (b) to the growth direction of the $EuBaCo_{1.9}O_{6-\delta}$ single crystal. Inset shows the Lauegram taken perpendicular to the growth direction of the crystal.

growth direction as well as Lauegram taken perpendicular to the growth direction of the crystal. As seen $EuBaCo_{1.90}O_{6-\delta}$ single crystal growth occurred along the [120] direction.

Lauegram shows well-defined reflexes ensuring good quality of the as-grown crystal and the absence of the crystal twinning.

As seen all the samples obtained are single phase with composition very close to the nominal one with slight overstoichiometry in Eu and understoichiometry in Ba. Their XRD patterns were indexed with the Pmmm space group. The refined lattice parameters are given in Table 2 and their normalized change is shown in Figure 5 as a function of cobalt deficiency.

As it follows from Figure 5 cobalt deficiency leads to lattice expansion of the double perovskite $EuBaCo_{2-x}O_{6-\delta}$. Moreover, as seen in Figure 5 this expansion is isotropic. Indeed, normalized expansion along the three axes has almost the same value, $(0.9\pm0.1)\%$ per 1 mole of cobalt vacancies in 1 mole of oxide. The total volume expansion, therefore, is three times as large.

Interestingly, chemical lattice strain caused solely by oxygen vacancies formation was found to be anisotropic in double perovskites [5, 6] with expansion in **ab**-plane due to decrease of cobalt oxidation state [5, 6] and contraction along **c**-axis due to the high concentration of oxygen vacancies localized in rare-earth-oxygen- (REO-) plane, which prompts shifts in Co and O positions towards the REO-plane [6].
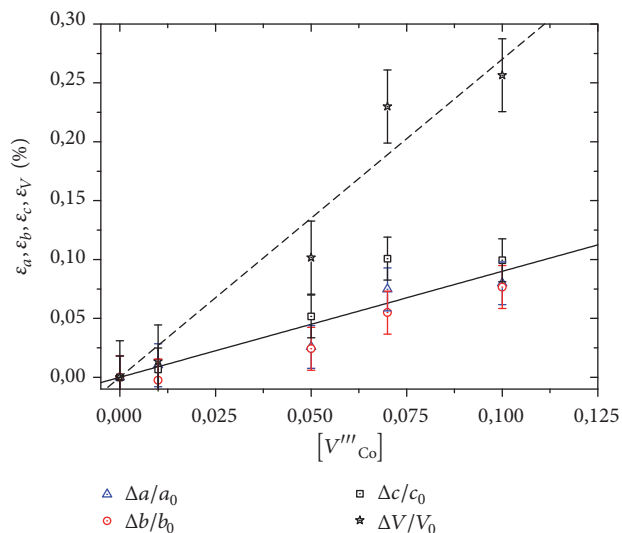
FIGURE 5: Normalized change of the lattice parameters of polycrystalline samples of $EuBaCo_{2-x}O_{6-\delta}$ ($x = 0-0.1$) at room temperature in air as a function of cobalt deficiency.
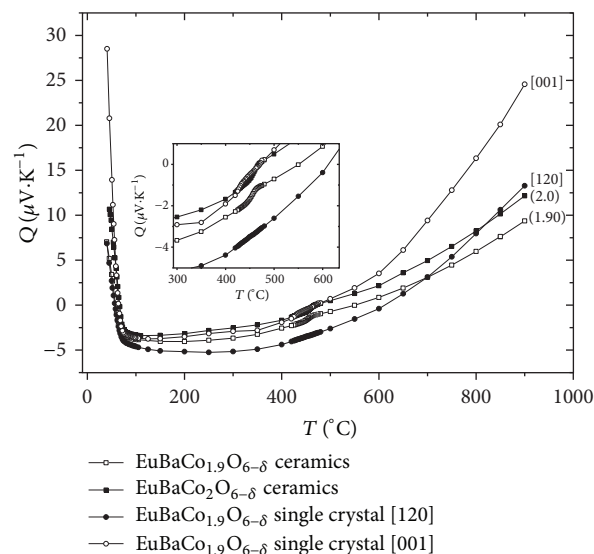

FIGURE 6: Thermo-EMF coefficient as a function of temperature in air for polycrystalline (ceramic) samples $EuBaCo_{2.0}O_{6-\delta}$ and $EuBaCo_{1.90}O_{6-\delta}$ and single crystalline $EuBaCo_{1.90}O_{6-\delta}$ measured along the ab-plane ([120]) and along the c-axis ([001]).

In the case of cobalt deficient double perovskite $EuBaCo_{2-x}O_{6-\delta}$, however, it seems that cobalt oxidation state, and, as a consequence, its mean size (radius), remains unchanged due to cobalt vacancies formation. Indeed, TG measurements showed oxygen content 5.50 in the cation stoichiometric $EuBaCo_{2-x}O_{6-\delta}$ sample ($x = 0$) slowly (100°C/hour) cooled in air to room temperature and 5.35 in cation deficient one with $x = 0.1$. Obviously this oxygen content corresponds to cobalt average oxidation state 3.0 in both oxides. Hence, formation of cobalt vacancies seems to be fully compensated by the oxygen release from the oxide lattice and thus it may be considered, to some extent, as a removal of cobalt polyhedrons from the double perovskite lattice. Aforementioned observation gives rise to drawing a conclusion that a mechanism of the lattice expansion caused by cation vacancies formation is quite different from that of expansion caused only by oxygen vacancies formation.

3.2. Electrical Properties. Figure 6 shows thermo-EMF coefficient measured in air as a function of temperature for polycrystalline (ceramic) $EuBaCo_2O_{6-\delta}$ and $EuBaCo_{1.9}O_{6-\delta}$ samples. Thermo-EMF coefficient of single crystal $EuBaCo_{1.9}O_{6-\delta}$ measured parallel ([120]) and perpendicular ([001]) to the growth direction is given *ibidem*. Abrupt drop of the Seebeck coefficient caused, most likely, by the metal-insulator transition is clearly seen in the vicinity of 70–75°C [1]. As seen in the insert of Figure 6, there is also some inflection in the temperature range 450–460°C corresponding to Pmmm-P4/mmm phase transition [7, 8]. Figure 6 also shows that cobalt deficiency leads to somewhat decrease of the thermo-EMF coefficient most likely due to the decrease of the number of sites for electrons and holes transfer as follows from Heikes equation [13].

Overall conductivity of polycrystalline (ceramic) $EuBaCo_2O_{6-\delta}$ and $EuBaCo_{1.9}O_{6-\delta}$ samples and single crystal

$EuBaCo_{1.9}O_{6-\delta}$ measured parallel ([120]) and perpendicular ([001]) to the growth direction is shown in Figure 7 as a function of temperature in air.

The manifestation of the metal-insulator (around 80°C) as well as Pmmm-P4/mmm transition (around 450°C) is clearly seen on the temperature dependencies given in Figure 7. It is also obvious from Figure 7(a) that cobalt deficiency decreases total conductivity due to both decreasing concentration of the charge carriers and lowering their mobility as a result of the break of conducting Co-O-Co chains. It is worth noting that total conductivity is strongly anisotropic in $EuBaCo_2O_{6-\delta}$ as shown in Figure 7(b). This seems to be attributed to the localization of oxygen vacancies mostly in REO-planes, which causes break of conducting Co-O-Co chains along the c-axis and hampers electrons and holes movement along the c-axis as compared to that in the ab-plane where Co-O-Co chains remain unchanged, at least, until the oxygen content in $EuBaCo_{2-x}O_{6-\delta}$ reaches 5.0; afterwards oxygen vacancies are formed randomly in oxygen polyhedrons as we showed recently for $GdBaCo_2O_{6-\delta}$ [10].

4. Conclusion

The polycrystalline and single crystalline double perovskites $EuBaCo_{2-x}O_{6-\delta}$ with both stoichiometric and understoichiometric composition with respect to cobalt were obtained and investigated. As a result, the influence of cobalt deficiency on crystal structure and properties of double perovskites $EuBaCo_{2-x}O_{6-\delta}$ was established. Formation of cobalt vacancies was shown to be accompanied by the release of equivalent amount of oxygen from the oxide lattice. Chemical lattice expansion caused by this cooperative disordering of cobalt and oxygen sublattices was shown to be isotropic contrary to that caused by the formation of oxygen vacancies only.
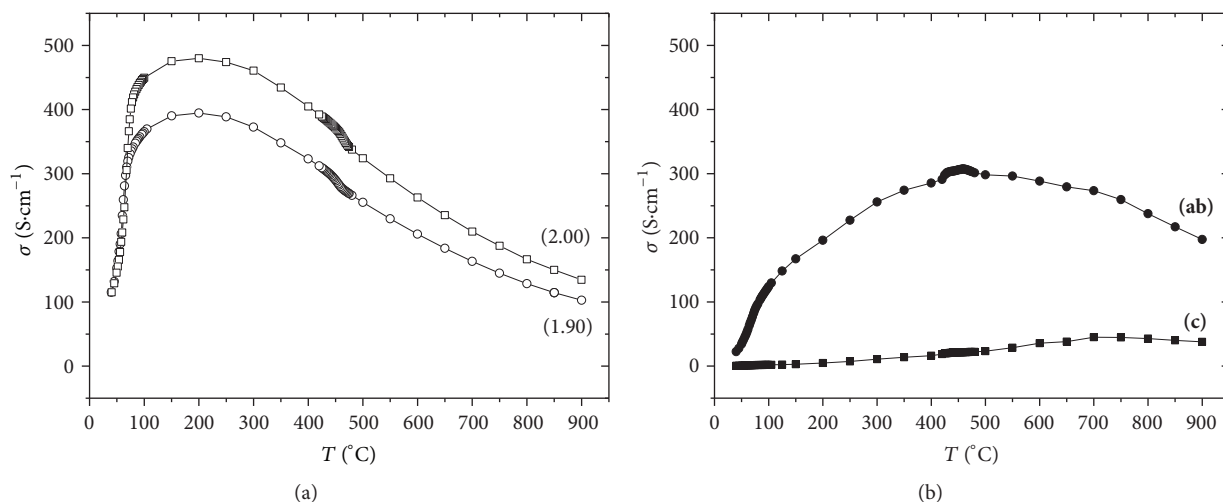
FIGURE 7: Overall conductivity as a function of temperature in air for (a) polycrystalline (ceramic) $EuBaCo_2O_{6-\delta}$—(2.00) and $EuBaCo_{1.9}O_{6-\delta}$—(1.90) samples and (b) single crystal $EuBaCo_{1.9}O_{6-\delta}$ sample measured parallel ([120])—(**ab**) and perpendicular ([001])—(**c**) to the growth direction.

Cobalt deficiency was found to decrease the overall conductivity and Seebeck coefficient of $EuBaCo_{2-x}O_{6-\delta}$ double perovskites as a result of decreasing charge carriers concentration and simultaneously lowering their mobility as well as number of sites available for electrons and holes transfer.

Overall conductivity of double perovskites $EuBaCo_{2-x}O_{6-\delta}$ was shown to be strongly anisotropic due to preferential location of oxygen vacancies in REO-planes. As a result charge transfer along the **c**-axis is hampered as compared to that in the **ab**-plane.
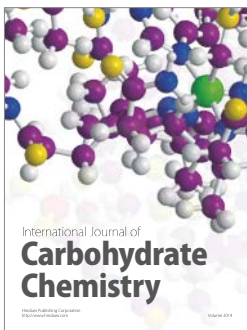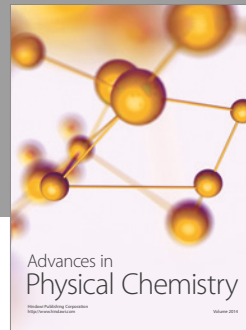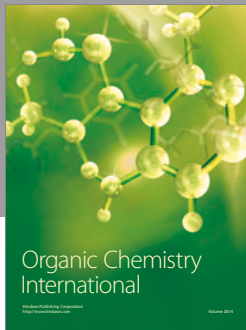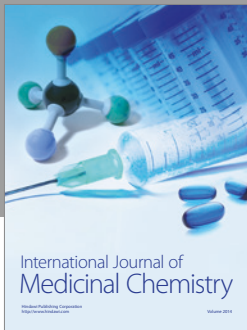
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

References

[1] A. Maignan, C. Martin, D. Pelloquin, N. Nguyen, and B. Raveau, "Structural and magnetic studies of ordered oxygen-deficient PerovskitesLnBaCo$_2$O$_{5+\delta}$ closely related to the "112" structure," *Journal of Solid State Chemistry*, vol. 142, no. 2, pp. 247–260, 1999.

[2] I. L. Ivanov, D. A. Malyshkin, N. S. Tsvetkova et al., "Oxygen content and thermodynamics of formation of double perovskites REBaCo$_2$O$_{6-\delta}$ (RE = Gd, Pr)," *Thermochimica Acta*, vol. 578, pp. 28–32, 2014.

[3] B. Raveau, M. D. Motin Seikh, V. Pralong, and V. Caignaert, "Ordered oxygen deficient '112' perovskites, LnBaCo$_2$O$_{5.50+\delta}$: complex magnetism and transport properties," *Bulletin of Materials Science*, vol. 32, no. 3, pp. 305–312, 2009.

[4] A. A. Taskin, A. N. Lavrov, and Y. Ando, "Transport and magnetic properties of GdBa Co$_2$O$_{5+x}$ single crystals: a cobalt oxide with square-lattice Co O$_2$ planes over a wide range of electron and hole doping," *Physical Review B-Condensed Matter and Materials Physics*, vol. 71, no. 13, Article ID 134414, 2005.

[5] D. S. Tsvetkov, I. L. Ivanov, D. Malyshkin, V. V. Sereda, and A. Y. Zuev, "Mechano-chemical coupling in double perovskites as energy related materials," *ECS Transactions*, vol. 72, no. 24, pp. 21–35, 2016.

[6] R. A. Cox-Galhotra, A. Huq, J. P. Hodges et al., "An in-situ neutron diffraction study of the crystal structure of PrBaCo$_2$O$_{5+\delta}$ at high temperature and controlled oxygen partial pressure," *Solid State Ionics*, vol. 249-250, pp. 34–40, 2013.

[7] S. V. Naumov, S. V. Telegin, D. S. Tsvetkov, E. I. Patrakov, O. G. Reznitskikh, and V. S. Gaviko, "Phase transitions in cobalt deficient single crystal GdBaCo$_{2-x}$O$_{5+\delta}$," *Bulletin of the Russian Academy of Sciences*, vol. 77, p. 1513, 2013.

[8] S. V. Telegin, S. V. Naumov, O. G. Reznitskikh, and E. I. Patrakov, "Effect of cobalt deficiency on the structural phase transition in O$_{6-\delta}$," *Physics of the Solid State*, vol. 57, no. 11, pp. 2290–2296, 2015.

[9] B. Raveau and M. M. Seikh, *Cobalt Oxides: From Crystal Chemistry to Physics*, Wiley-VCH, Weinheim, Germany, 2012.

[10] D. S. Tsvetkov, V. V. Sereda, and A. Y. Zuev, "Oxygen non-stoichiometry and defect structure of the double perovskite GdBaCo$_2$O$_{6-\delta}$," *Solid State Ionics*, vol. 180, no. 40, pp. 1620–1625, 2010.

[11] M. P. Pechini, *Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor*, US Patent, 1967.

[12] R. B. Roberts Csiro, "The absolute scale of thermoelectricity II," *Philosophical Magazine B: Physics of Condensed Matter; Statistical Mechanics, Electronic, Optical and Magnetic Properties*, vol. 43, no. 6, pp. 1125–1135, 1981.

[13] R. R. Heikes, *Thermoelectricity: Science and Engineering*, Ure RW Interscience, New York, NY, USA, 1961.