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Impact of charge doping, oxygen disorder and hydrostatic pressure on thermoelectric and magnetic properties of $NdBa_{0.94}La_{0.06}Co_2O_{5+\delta}$

Jaroslaw Pietosa [a],*, Kazimierz Piotrowski [a], Roman Puzniak [a], Andrzej Wisniewski [a], Stanislaw Kolesnik [b], Bogdan Dabrowski [b]

[a] *Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46, PL-02-668 Warsaw, Poland*
[b] *Department of Physics, Northern Illinois University, De Kalb, IL 60115, USA*

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ABSTRACT

Structural, thermoelectric and magnetic properties of $NdBa^{2+}_{1-y}La^{3+}{}_{y}Co_2O_{5+\delta}$ ($y = 0.06$) were investigated over a wide range of oxygen content $0.26 < \delta < 0.90$. The single-phase orthorhombic samples with ordered planes of the 5- and 6-coordinated to oxygen cobalt ions were obtained and studied for $0.45 < \delta < 0.55$. It was found that the Seebeck coefficient in the studied samples is magnetic field insensitive and shows that the doping with cation and oxygen is well described below metal–insulator transition at T_{MIT} by the Heikes formula with the effective charge doping $c = -y/2 + \delta - 0.5$. Thermal conductivity exhibits characteristic decrease at T_{MIT} due to removal of the electronic contribution and is well correlated with suppression of the Seebeck coefficient. The T_{MIT} and the Neel temperature T_N reach maximum values for slightly electron doped sample $c = -0.03$ with a perfect oxygen ordering $\delta = 0.5$ while the Curie temperature T_C shows continuous decrease with the increase of δ. Comparison of magnetic ac and dc measurements with those for the $GdBaCo_2O_{5+\delta}$ (Taskin et al., 2005) and Ca substituted $NdBaCo_2O_{5.5}$ (Kolesnik et al., 2012) systems shows that perfection of the oxygen ordering is more important in controlling the magnetic properties than the overall charge doping. The hydrostatic pressure was observed to stabilize the antiferromagnetic phase for $NdBa_{0.94}La_{0.06}Co_2O_{5.5}$.

1. Introduction

The layered perovskites $RBaCo_2O_{5+\delta}$ (R = lanthanide ion or Y, $\delta = 0.5$) are characterized by a sequence of complex magnetic and electronic phase transitions observed with increasing temperature: antiferromagnet–ferromagnet (T_N = 200–250 K), ferromagnet–paramagnet (T_C = 280–310 K), and insulator–metal (T_{MIT} = 330–360 K), which can be tuned by a substitution at the R-, Ba- and Co-sites or by a change of oxygen content $5+\delta$ (δ-doping) [1–5]. The perovskite-related structure [3] consists of the layers of RO_δ–CoO_2–BaO–CoO_2 aligned along the c-axis. The Co ions are coordinated by 5 or 6 oxygen ions, forming pyramids or octahedrons, depending on the oxygen content δ. The addition or removal of oxygen ions to/from the RO_δ planes changes the ratio of the Co octahedral to pyramidal coordination and alters charge doping of the CoO_2 planes. For $\delta = 0$, i.e., for the compound with no oxygen in the RO_δ layer, all $Co^{2.5+}$ ions are pyramidally coordinated (CoO_5). An increase of δ to 1 leads to a transition to octahedral coordination of all $Co^{3.5+}$ ions (CoO_6). For the compound with $\delta = 0.5$, there is an additional order of octahedrally and pyramidally coordinated planes along the b-axis, and the Co^{3+} ions are present for both coordinations. Variation of δ from 0.5 leads to the changes in the formal valence ($c = \delta - 0.5$) of cobalt ions to hole-doping ($\delta > 0.5$) or electron-doping ($\delta < 0.5$), and in addition, to a disorder of the oxygen vacancy ordering by changing the ratio of the Co octahedral to pyramidal coordination. Taskin et al. [4] have shown that any deviation from perfect oxygen vacancy ordering and optimal charge doping by δ-doping leads to a decrease of critical temperatures of all phase transitions. Specifically, the T_{MIT} is very slightly suppressed on the electron-doped side ($c < 0$) and little more on the hole-doped side ($c > 0$), and the T_C and T_N show symmetric small and large suppression, respectively, on both sides. Moreover, magnetic and transport properties point to the phase separation into two insulating phases in the electron-doped region and into insulating and metallic phase in the hole-doped region when δ is below 0.45 and above 0.55, respectively. These oxygen contents define the lower and upper limits, respectively, of the single-phase region of the oxygen vacancy ordered orthorhombic phase [4].

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* Corresponding author.
E-mail address: pietosa@ifpan.edu.pl (J. Pietosa).

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Pure charge doping was studied by heterovalent substitutions at the *R*-site for compounds with $\delta = 0.5$, which maintained the oxygen vacancy ordering, i.e., it did not affect the ratio of the pyramidal and octahedral coordinations of cobalt [5]. Rather different phase diagram of electronic and magnetic transitions was established by using cation substitutions than by δ-doping. For example, in the case of the $Nd^{3+}_{1-x}Ca^{2+}{}_xBaCo^{(3+x/2)+}{}_2O_{5.5}$ system for which a wide single-phase hole doping range $c = x/2 = 0–0.1$ was achieved, the T_{MIT} was only slightly and linearly suppressed from 345 to 340 K [5]. The T_C showed linear *increase* from 260 to 340 K for $c = 0–0.08$ ($x = 0.16$) where it merged with the T_{MIT}. The T_N was rapidly suppressed and for the compounds with $c \geqslant 0.05$ ($x \geqslant 0.1$) the antiferromagnetic phase disappeared [5]. Isoelectronic Ca for Ba substitution in $YBa_{1-x}Ca_xCo_2O_{5.5}$ ($x = 0–0.1$) was investigated by Aurelio et al. [6]. They found a gradual diminishment of AFM long range order with an increase of *x* up to complete disappearance for $x = 0.1$. Studies of various substituted and oxygen nonstoichiometric [7,8] compounds indicated that the changes in electronic structure induced by substitutions and/or oxygen defects govern the values of T_N, T_C and T_{MIT}. Magnetic and neutron diffraction studies of complex Co-substituted and oxygen deficient $TbBaCo_{1.9}Fe_{0.1}O_{5.43}$ were performed by Troyanchuk et al. [9]. They showed that in this compound spontaneous magnetization develops at $T_N = 305$ K and decreases abruptly below 200 K. They showed that extra oxygen vacancies are located mainly in the pyramidal sublattice leading to tetrahedral coordination. According to their studies the ferromagnetic and the G-type antiferromagnetic phases co-exist in high-temperature. The ferromagnetic component appears due to canting of Co^{3+} ions magnetic moments. They suggest that non-collinear magnetic structure arises from competition between positive and negative exchange interactions as well as from magnetocrystalline anisotropy in the pyramidal sublattice. Studies of oxygen loaded $PrBaCo_2O_6$ with all octahedral coordinated Co showed [10] that this ferromagnetic compound exhibits the $T_C = 210$ K, i.e., larger than those of $LaBaCo_2O_6$ ($T_C \approx 175$ K) and of $NdBaCo_2O_6$ ($T_C \approx 200$ K), what suggests that the size of the lanthanide may influence slightly the double exchange mechanism, i.e., the Co–O–Co bond angle. On the other hand, the creation of oxygen vacancies in $PrBaCo_2O_{5+\delta}$ ($0.80 < \delta < 1$) leads to a strong competition between ferromagnetism and antiferromagnetism due to the appearance of superexchange $Co^{3+}–O–Co^{3+}$ antiferromagnetic interactions.

Comparison of the δ-doped and cation-substituted $RBaCo_2O_{5.5}$ systems indicated that a disruption of the oxygen vacancy ordering thru change of the ratio of the pyramidal and octahedral coordinations of cobalt affects physical properties as much as the charge doping.

The thermoelectric measurements have been previously done for the δ-doped [4] and the Ca for Nd substituted [5] $NdBaCo_2O_{5.5}$. Taskin et al. [4] have observed in $GdBaCo_2O_{5+\delta}$ below the T_{MIT} a spectacular divergence of the Seebeck coefficient α when oxygen content approached the value of $\delta = 0.5$ ($c = 0$). At $T = 100$ K, the value of α changed sign from -700 to $+800$ μV/K for oxygen content $\delta = 0.497$ ($c = -0.03$) and 0.501 ($c = 0.001$), respectively. On further δ-doping a characteristic rapid decrease of $|\alpha|$ was observed. Kolesnik et al. [5] have observed similar decrease of the positive α with increasing hole doping in $Nd^{3+}_{1-x}Ca^{2+}{}_xBaCo^{(3+x/2)+}{}_2O_{5.5}$ below the T_{MIT} (100–300 K). Both these experiments indicated that α below the T_{MIT} is approximately described by the Heikes formula $\alpha = -(k_B/e)\ln[c/(c-1)]$ [11] with the effective charge doping given by $c = x/2 + \delta - 0.5$.

The main aim of our current investigation was study of the compounds with a wide range of the effective charge doping $c = x/2 - y/2 + \delta - 0.5$ to probe separately the effects of disruption of the oxygen vacancy ordering and the charge doping. The heterovalent La for Ba-substituted compound $Nd^{3+}Ba^{2+}_{1-y}La^{3+}{}_y Co_2O_{5+\delta}$ ($y = 0.06$) obtained here for the first time and studied with widely varying oxygen contents allows to achieve this goal. Investigation of the thermoelectric and magnetic properties permitted separation of the charge doping and oxygen disorder effects [4,5]. The low-temperature values of α were found to correlate well with the effective charge doping level for the single phase orthorhombic samples with $\delta = 0.48$, 0.5 and 0.55. In this work, the magnetic properties under hydrostatic pressure were investigated as well, in order to make a comparison of changes of T_N, T_C, and T_{MIT} between the cation hole-doped $Nd_{0.94}Ca_{0.06}BaCo_2O_{5+\delta}$ [5] and electron-doped $NdBa_{0.94}La_{0.06}Co_2O_{5+\delta}$ systems.

2. Experimental details

Polycrystalline samples of $NdBa_{0.94}La_{0.06}Co_2O_{5+\delta}$ have been obtained by using a standard solid-state synthesis method described in detail in Ref. 5. Single-phase samples as confirmed by X-ray diffraction (using a Rigaku D/MAX powder diffractometer) were prepared by annealing in argon or oxygen at various temperatures, and the oxygen content $\delta = 0.26–0.90$ was determined by thermogravimetric measurements. Exploration of compositions with higher amounts of La substitution levels showed that the solubility limit of layered perovskite structure is near $y = 0.1$ beyond which impurity of the simple perovskite structure appears.

Magnetic measurements were carried out using a Magnetic Property Measurement System (MPMS of the Quantum Design). The measurements of the ac susceptibility at ambient pressure, for various frequencies ($f = 10$, 10^2, 10^3, and 10^4 Hz) were performed with the AC susceptibility and DC magnetization option (ACMS) of the Quantum Design Physical Property Measurement System (PPMS). Thermal conductivity and the Seebeck coefficient were measured using PPMS Thermal Transport Option. Hydrostatic pressure was applied, using an easyLab Technologies MCell10 pressure cell with Daphne 7373 oil [12], which is considered as one of the best pressure mediums from the point of view of the smallest decrease of pressure with decreasing temperature in the pressure range above 7 kbar [13]. A high-purity Sn wire (0.25 mm in diameter) was employed as an *in situ* manometer.

3. Results and discussion

Structural refinements of $NdBa_{0.94}La_{0.06}Co_2O_{5+\delta}$ were performed by the Rietveld method with the GSAS/EXPGUI suite. The lattice parameters determined for these refinements are presented in Fig. 1. For the samples with oxygen content in the range $\delta = 0.4–0.6$, the crystal structure is orthorhombic "122-type" in the *Pmmm* space group, characterized by the doubled *b* and *c* axes and oxygen vacancy ordering. Outside of the above range of oxygen content, the crystal structure can be refined within the tetragonal *P4/mmm* space group, which shows the doubling of the *c* axis and $a = b$. The samples on the boundary between the orthorhombic and tetragonal phase ranges (e.g., with $\delta = 0.6$), for which two sets of lattice parameters are presented in Fig. 1, can be refined as any of the two phases with similar quality. This indicates possible coexistence of both phases in the transitional range of oxygen contents. Qualitatively, the presence of the two phases is similar to

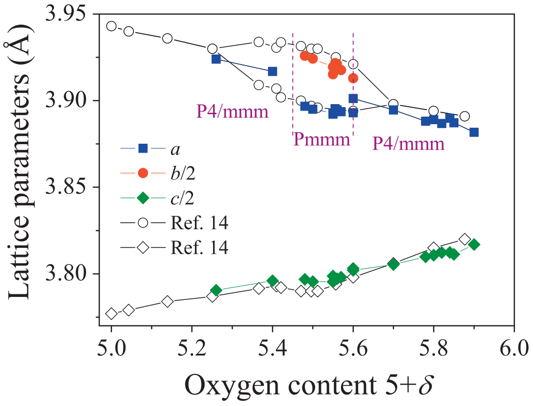

Fig. 1. Structural parameters for $NdBa_{0.94}Ca_{0.06}Co_2O_{5+\delta}$ as a function of oxygen content.