Reappearance of Antiferromagnetic Order in Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ for $\delta > 0.51$

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The absence of the antiferromagnetic order in Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ has been found to remain unchanged by applying a hydrostatic pressure of 10 kbar. In magnetic studies of polycrystalline Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ ($\delta = 0.07$—0.69), we have found a reappearance of the antiferromagnetic phase, caused by an increase in oxygen index $\delta$ above 0.51 related to extra oxygen ions addition into the NdO$_2$ plane. For the samples with $\delta = 0.555$ and 0.59, a coexistence of well developed antiferromagnetic phase with ferrimagnetic one is evidenced.

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1. Introduction

The layered perovskites $RBaCo_2O_{5+\delta}$ ($R$ = lanthanide ion or $Y$, $\delta = 0.5$) are characterized by the sequence of complex magnetic and electronic phase transitions observed with increasing temperature: antiferromagnet-ferromagnet (AFM-FM, $T_N = 200$—250 K), ferromagnet-paramagnet ($T_C = 280$—310 K), and insulator-metal transition ($T_{MIT} = 330$—360 K), which can be tuned by a substitution at the $R$-, Ba-, and Co-sites or by a change of oxygen content $5 + \delta$ [1–6]. The perovskite-related structure [3] consists of aligned along the $c$-axis layers of $RO_2$-$CoO_2$-$BaO-Co$-$O_2$. Each Co ion is coordinated by 5 or 6 oxygen ions, forming pyramid or octahedron, depending on the oxygen index $\delta$. The variation of $\delta$ index leads to addition or removal of oxygen ions from the $RO_5$ planes, changing the ratio of the Co octahedral/pyramidal coordination, and altering charge doping of the Co$_2$O$_2$ planes. For $\delta = 0$, i.e., for the compound with no oxygen in $RO_5$ layer, all Co ions are pyramidal coordinated (Co$_5$O$_{18}$) and gradual increase of $\delta$ up to 1 leads to transition to octahedral coordination of all Co ions (Co$_6$O$_{19}$). For the compound with $\delta = 0.5$, there is an additional order of octahedrally and pyramidal coordinated planes along the $b$-axis. Variation of $\delta$ value leads to the changes in the formal valence of Co ions. For $\delta = 0.5$, only Co$^{3+}$ ions are present. A small shift from that value leads to hole-doping (Co$^{4+}$) or electron-doping (Co$^{2+}$). Taskin et al. [4] have shown very strong dependence of the ground state on oxygen content; i.e., on simultaneous changes of coordination and charge doping for $GbBaCo_2O_{5+\delta}$, from charge-ordered insulating antiferromagnet ($\delta = 0$), to optimally doped insulator ($\delta = 0.5$), and finally to metallic ferromagnet ($\delta = 0.7$). On the contrary, the heterovalent substitutions at $R$ and Ba-sites for the fixed oxygen content do not affect oxygen vacancy ordering but only alter charge doping of the Co$_2$O$_2$ planes.

Upon Ca$^{2+}$ substitution for Nd$^{3+}$ at the $R$-site the temperature of antiferro-ferrimagnetic phase transition is drastically suppressed. At 10% Ca content this magnetic transition is completely absent and antiferromagnetic order does not appear [5, 6]. In this work we show that the reappearance of antiferromagnetic phase is possible by variation of $\delta$ in Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$.

2. Experimental details

Polycrystalline samples of Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ with $\delta = 0.07$—0.69 have been obtained by using a standard solid-state synthesis method described in detail in Ref. [3]. Single-phase samples were annealed in argon or oxygen at various temperatures and the oxygen content was established by thermogravimetric measurements. X-ray diffraction experiments were performed in a Rigaku diffractometer. Magnetic measurements were carried out using a Magnetic Property Measurement System (Quantum Design) in the temperature range of 5–380 K in magnetic fields up to 50 kOe. An external hydrostatic pressure up to 10 kbar was applied, using an easyLab Technologies Mcell 10 pressure cell.

3. Results and discussion

X-ray diffraction patterns for the studied Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ samples are presented in Fig. 1. The evolution of the crystal structure with $\delta$ is similar to the one for undoped $RBaCo_2O_{5+\delta}$ [4]. For $\delta \leq 0.25$, this material adopts a tetragonal structure. In the range $0.40 \leq \delta \leq 0.55$, the vacancy-ordered orthorhombic structure is observed, in particular from the splitting of the 040 and 200 peaks between 46 and 47 deg. Further oxidation for $\delta \geq 0.59$ changes the structure into tetragonal one with smaller lattice parameters. Figure 2a presents the temperature dependence of magnetization for Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ with $\delta = 0.43$—0.69, measured

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using “field-cooling” procedure ($M_{\text{FC}}$) in a magnetic field of 1000 Oe. An antiferromagnetic phase is not present for the oxygen content $\delta$ varying from 0.5 down to 0.43. The $T_C$ decreases from 310 K for the sample with $\delta = 0.5$ [5] to 295 K for $\delta = 0.43$. For $\delta = 0.555$, we have observed a significant decrease of magnetization with a small cusp near 235 K (Fig. 2b). Below 235 K, the $M_{\text{FC}}$ decreases, but not to zero, which may be an indication of appearance of antiferromagnetic ordering in ferrimagnetic matrix. At around 140 K, a smooth plateau is well developed. From $M(T)$, we can estimate $T_N = 230$ K and $T_C = 245$ K, which is considerably lower than $T_C$ for the samples with $\delta \approx 0.5$. The Ca$^{2+}$ hole-doping results in mixed valence of Co$^{3+}$–Co$^{4+}$.

It was suggested [5] that interactions between Co$^{3+}$ and Co$^{4+}$ ions lead to ferrimagnetic ordering. An increase of $\delta$ up to 0.555 results in further hole-doping, which increases the number of Co$^{3+}$–Co$^{4+}$ pairs, but also disorders Co–O network by formation of larger number of CoO$_6$ octahedra at the expense of CoO$_5$ pyramids. It seems that disorder, induced by oxygen content change, is responsible mainly for a decrease of $T_C$ for Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ since the same tendency was reported by Taskin et al. [4] for GdBaCo$_2$O$_{5+\delta}$.

Further increase in oxygen content results in shift of a cusp in $M(T)$ dependence down to about 110 K for $\delta = 0.59$, correlated with an increase in magnetization value. One can observe a further decrease in $T_N$ and $T_C$ for higher oxygen contents, which confirms the important role of oxygen vacancy ordering in regulating of both $T_N$ (= 90 K) and $T_C$ (= 130 K). Then, the reappearance of the phase transition from antiferromagnetic to ferrimagnetic phase by degrading the oxygen vacancy ordering is possible. Further increase in oxygen content for $\delta$ above 0.6 results in a complete collapse of oxygen vacancy ordering, evidenced by a vast increase in magnetization. Here, the material adopts a tetragonally distorted perovskite structure with oxygen vacancies distributed randomly across the crystal lattice. Figure 2b presents the $M(T)$ dependence for Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ and for selected electron-doped compositions with $\delta \leq 0.4$, recorded in $M_{\text{ZFC}}$ and “field-cooling” mode. Taskin et al. [4] have shown a decrease in both $T_N$ and $T_C$ as a result of electron doping by oxygen removal from GdBaCo$_2$O$_{5+\delta}$. In our case, the situation is different. Starting from 295 K for $\delta = 0.43$, the $T_C$ increases to 340 K with a decrease in $\delta$ down to 0.34 (not shown in the figure), and again decreases to 295 K with a further decrease in $\delta$ to 0.25. In the case of removing the oxygen ions from RO$_6$, we have found a gradual decrease in magnetization, but the compositions remain ferrimagnetic without a noticeable decrease in $T_C$ for oxygen content lowered to $\delta = 0.07$, where a complete disappearance of spontaneous ordering for the whole investigated temperature range is noticed.

Figure 3a presents the field dependences of the magnetization recorded at 5 K for the samples with $\delta$ values of 0.5 and above. One can see the smallest value of $M$ at the highest applied field for the sample with $\delta = 0.555$, and the highest value of $M$ at the highest applied field for the one with $\delta = 0.69$. For $\delta > 0.555$ we observe a clear hysteretic behavior, characteristic of ferrimagnetic ordering, and a linear $M(H)$ dependence in the high-field region, characteristic of an antiferromagnetic contribution to the net magnetization. This is in line with conclusions based on the results of $M(T)$ measurements that some antiferromagnetic fraction exists at low temperatures for the samples with $\delta = 0.59$ and 0.69. For $\delta < 0.5$, the shape of $M(H)$ is different, indicating a competition of antiferromagnetic and ferrimagnetic interactions at low temperatures. The hysteretic behavior weakens for $\delta = 0.59$ in the ferrimagnetic region (Fig. 3b). For $\delta = 0.555$, we observe a completely different shape of the hysteresis loop recorded at 150 K, characteristic of domination of ferrimagnetic interactions, with an invar effect and the saturation of the magnetization for 50 kOe (Fig. 3c). The same shape of the $M(H)$ dependence is observed for the already ferrimagnetic sample with $\delta = 0.43$, in the full

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**Fig. 1.** X-ray diffraction spectra for Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$. The intensity data are presented in a logarithmic scale and shifted for clarity.

**Fig. 2.** The temperature dependence of magnetization recorded in magnetic field of 1000 Oe for Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ with $\delta \geq 0.43$ (a) and with $\delta = 0.07–0.555$ (b).
Figure 3 shows that under applied hydrostatic pressure up to 10 kbar it is not possible to induce an appearance of antiferromagnetic phase in Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$. Under a pressure of 10 kbar, one can see a sudden decrease in magnetization with increasing temperature at around 300 K and a transition to the paramagnetic state above $T_C$. Such a decrease in $T_C$ under applied pressure is in agreement with the results of $dT_C/dP$ obtained for the samples with lower Ca$^{2+}$ substitution levels, for which the pressure coefficient of $T_C$ was found to decrease with increasing $x$ and become negative at $x = 0.06$, contrary to that for undoped NdBaCo$_2$O$_{5.5}$ with positive $dT_C/dP$ [7].

4. Conclusions

We have shown a strong variation of magnetic properties with the oxygen content changed over wide range for Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5+\delta}$ ($\delta = 0.07–0.69$). We have found a reappearance of the antiferromagnetic phase, caused by an increase of the oxygen index $\delta$ above 0.51. Under applied hydrostatic pressure up to 10 kbar we did not observe an appearance of the antiferromagnetic phase for the optimally doped Nd$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5.5}$.

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References