**New A-site Ordered Perovskite Cobaltite LaBaCo$_2$O$_6$: Synthesis, Structure, Physical Property and Cation Order–Disorder Effect**

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By means of annealing LaBaCo$_2$O$_5$ under high pressure oxygen, we have successfully synthesized a new A-site ordered perovskite cobaltite, LaBaCo$_2$O$_6$. The structure and electromagnetic properties of LaBaCo$_2$O$_5$ have been investigated and compared to those of the ordinary A-site disordered La$_{0.5}$Ba$_{0.5}$Co$_3$O$_5$. Both LaBaCo$_2$O$_5$ and La$_{0.5}$Ba$_{0.5}$Co$_3$O$_5$ have mixed states of low-spin and intermediate-spin states and show metallic behaviors generated by double exchange interaction. LaBaCo$_2$O$_6$ has a ferromagnetic transition at $T_C = 175$ K, which is lower by $15$ K than $T_C$ of La$_{0.5}$Ba$_{0.5}$Co$_3$O$_5$. At around $140$ K, some structural changes are observed in both compounds and below the temperature they exhibit magnetic glassy (cluster glass) behaviors, accompanied by the gradual change to insulating or semiconductive behaviors. The refined structural data and magnetic and electrical properties suggest a partial $d_{z^2}$ orbital ordering for LaBaCo$_2$O$_5$ below $140$ K, in contrast to a partial $d_{x^2}$ orbital ordering for La$_{0.5}$Ba$_{0.5}$Co$_3$O$_5$.

KEYWORDS: A-site ordered/disordered perovskite cobaltites, Low spin and intermediate spin states, ferromagnetic metal, structural change, partial orbital ordering

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1. Introduction

In the last decade, perovskite cobaltites with the general formula $(R_1,A)^{3+}_1A^{2+}_x$Co$_3$O$_9$ ($R =$ rare earth elements and $A$ = alkaline earth elements) have received much attention because of their enchanting physical properties such as metal–insulator (MI) transition and spin configuration change. The spin configuration change is one of the remarkable phenomena characteristic of cobalt oxides. LaCo$_3$O$_9$ which is a good illustration has nonmagnetic Co$^{3+}$ ($3d^7$) ions with the low-spin (LS) state configuration ($t_{2g}^6$, $S = 0$) below $100$ K, and then the LS state gradually change to the intermediate-spin (IS) state ($t_{2g}^4e_g^2$, $S = 1$) with increase of temperature. Finally, it changes to the high-spin (HS) state ($t_{2g}^4e_g^2$, $S = 2$) above $550$ K. This is caused by the competition between the crystal field splitting $\Delta_C$ and the exchange energy $\Delta_E$ for $3d$ electrons and the occupied orbitals in Co$_3$O$_9$ octahedron. The $\Delta_C$ and $\Delta_E$ are controlled by choosing the combination of A-site cations, $R^{3+}$ and $A^{2+}$ with various ionic radii.

It is well known that the A-site cation modification in the perovskite oxides plays a very important role for the control of their physical properties. Very recently, we have verified the A-site randomness effect on perovskite manganites from the comparison of structural and physical properties between the A-site disordered R$_{0.3}$Ba$_{0.7}$Mn$_2$O$_{4.9}$ and ordered RBaMn$_2$O$_6$. It has been revealed that not only A-site randomness but also structural two-dimensionality produced by the layer ordering of A-site cations significantly influence physical properties of perovskite manganites; the exclusion of structural randomness particularly enhances charge-orbital order and magnetic long-range ordering, and moreover the structural two-dimensionality stabilizes the layer type $d_{z^2}$ orbital ordering in PrBaMn$_2$O$_6$ and NdBaMn$_2$O$_6$. This indicates that the order-disorder of A-site cations is one of reliable factors to control physical properties. Fortunately, perovskite cobaltites also have the A-site layer-type ordered compound, RBaCo$_2$O$_6$. These A-site ordered cobalt oxides are oxygen deficient perovskite compounds with a wide range of oxygen non-stoichiometry and various oxygen-vacancy ordering. In order to make randomness effect clear, it is crucial to obtain the stoichiometric compound, RBaCo$_2$O$_6$. However there has been no report of the fully oxidized A-site ordered cobaltites.

In this work, we have successfully synthesized a new A-site layer-type ordered LaBaCo$_2$O$_6$ and the ordinary disordered La$_{0.3}$Ba$_{0.7}$Co$_3$O$_5$. In the present paper, the structures and electromagnetic properties of LaBaCo$_2$O$_6$ are reported and compared to those of La$_{0.3}$Ba$_{0.7}$Co$_3$O$_5$. We also discuss how the A-site order–disorder affects the structural and physical properties of perovskite cobaltites.

2. Experimental

Polycrystalline sample of the A-site ordered LaBaCo$_2$O$_6$ was prepared by a similar synthesis procedure of the A-site ordered manganites. Mixed powder of starting materials, La$_{0.3}$O$_{1.9}$, BaCO$_3$ and CoO, in an appropriate molar ratio was ground, pressed into a pellet and heated at 1173–1423 K in Ar gas for 48 h, which yielded the A-site ordered and oxygen-deficient LaBaCo$_2$O$_{6-x}$ (x ~ 1.0). For the full oxidation, x = 0.0, the obtained sample was annealed at low temperature of 623 K in high-pressure O$_2$ gas (P = 200 atm) for 6 h. Thermogravimetric analysis by the reduction in H$_2$ confirmed the stoichiometric oxygen content of LaBaCo$_2$O$_{6.00}$. A slight oxygen-deficiency remained without the high-pressure oxygen annealing, and the annealing of LaBaCo$_2$O$_6$ under O$_2$ gas at high temperatures resulted in the disorder of La/Ba cations. Except LaBaCo$_2$O$_6$, we could not obtain the fully oxidized A-site ordered cobaltites.

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$\text{RBaCo}_2\text{O}_6$ ($R$ = rare earth elements) in the same condition of 200 atm oxygen pressure. The A-site disordered La$_{0.5}$Ba$_{0.5}$CoO$_3$ was synthesized by literature methods.$^{4,13}$ The crystal structures were refined by the Rietveld analysis of powder neutron diffraction using RIETAN2000.$^{14}$ The neutron powder diffraction experiments were conducted for $T = 20$–300 K using the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, at Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai, Japan. Neutrons with a wavelength of 1.8207 Å were obtained by the 331 reflection of the Ge monochromator. The 12$^*$-blank-sample-18$^*$ collimation was employed. The magnetic properties were studied using a SQUID magnetometer in a temperature range $T = 2$–400 K. The electric resistivity of a sintered pellet was measured for $T = 2$–400 K by a conventional four-probe technique.

3. Results and Discussion

Figure 1 shows neutron powder diffraction patterns of (a) LaBaCo$_2$O$_6$ and (b) La$_{0.5}$Ba$_{0.5}$CoO$_3$ at 300 K. In LaBaCo$_2$O$_6$, the 001 reflection around $2\theta = 13^*$ indicates a layer-type ordering of La/Ba cations (the inset of Fig. 1), and all of the observed diffraction peaks can be indexed in the space group $P4/mmm$ with the lattice parameters $a = 3.89984(7)$ Å, $c = 7.7145(2)$ Å, $V = 117.329(4)$ Å$^3$. The electron diffraction of LaBaCo$_2$O$_6$ shown in Fig. 2 also clearly shows the doubling of the $c$-axis and a tetragonal symmetry with $a_p \times a_p \times 2c_p$ cell, where $a_p$ and $c_p$ represent lattice parameters for the simple perovskite structure. Table I(a) shows the refined structural data of LaBaCo$_2$O$_6$ at 300 K. The $a$ is much longer than the $c/2$. Moreover, the CoO$_6$ octahedra have asymmetric (noncentrosymmetric) distortion [see the inset of Fig. 3(a)] as seen in the A-site ordered manganites.$^{8,15,16}$ Namely the CoO$_6$ octahedra have apically compressed CoO$_6$ octahedra at room temperature, although the shape is asymmetric along the $c$-axis. Figure 3(a) shows lattice parameters, bond distances and bond angle of LaBaCo$_2$O$_6$ as a function of temperature. On cooling, both $a$ and $c/2$ monotonically shrink down to 140 K and below the temperature the degree of the shrinkage become less. Between the two apical Co–O distances, the longer Co–O3 distance
measured under 0.1 T for (a) LaBaCo$_2$O$_6$ and (b) La$_3$Ba$_2$Co$_3$O$_{10}$. 13) Below around 140 K, agreeing with the previous work. 13) Below 180 K, accompanied by a Jahn–Teller (JT) distortion of lattice parameters for La$_{0.5}$Ba$_{0.5}$CoO$_3$. Concerning the low temperature structure of La$_{0.5}$Ba$_{0.5}$CoO$_3$, Fauth et al. reported the transition to a tetragonal phase below 180 K, accompanied by a Jahn–Teller (JT) distortion of CoO$_6$ octahedra. 13) Figure 3(b) shows the temperature dependence of lattice parameters for La$_{0.5}$Ba$_{0.5}$CoO$_3$. The crystal structure of La$_{0.5}$Ba$_{0.5}$CoO$_3$ slightly changes from cubic (Pm$_3m$) to tetragonal (P4/mmm) below about 140 K, agreeing with the previous work. 13) Below 140 K, the a is shorter than the c, which originates from the elongation of CoO$_6$ octahedra along the apical oxygen direction, as shown in Fig. 3(b).

Figure 4 shows the magnetic susceptibilities (M/H) measured under 0.1 T for (a) LaBaCo$_2$O$_6$ and (b) La$_3$Ba$_2$Co$_3$O$_{10}$. LaBaCo$_2$O$_6$ shows a paramagnetic behavior, obeying a Curie–Weiss law with effective moment $P_{\text{eff}} = 2.81(2) \mu_B$ and Weiss constant $\theta_0 = 208.0(7)$ K between 280 K and 400 K. The value of $P_{\text{eff}} = 2.81(2) \mu_B$ indicates a mixed spin state of IS and LS states for Co$^{3+}$(Co$^{3+}$/Co$^{4+}$). A ferromagnetic interaction represented as a positive Weiss constant $\theta_0 = 208.0(7)$ K could be due to the double exchange (DE) interaction generated by $e_g$-electrons in IS state. Actually at $T_c = 175$ K, LaBaCo$_2$O$_6$ exhibits a ferromagnetic transition, accompanying with a sharp increase of M/H but without any structural change. Succes-

<table>
<thead>
<tr>
<th>Distance</th>
<th>Angle</th>
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<tr>
<td>Co–O</td>
<td>1.9414 Å</td>
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Table I. Refined structural parameters and selected bond distances and angles of (a) LaBaCo$_2$O$_6$ and (b) La$_3$Ba$_2$Co$_3$O$_{10}$.}

(a) LaBaCo$_2$O$_6$

<table>
<thead>
<tr>
<th>Space group: P4/mmm</th>
<th>La</th>
<th>1a</th>
<th>$R_w = 0.50(8)$ Å²</th>
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<tr>
<td>$a = 3.89984(7)$ Å</td>
<td>Ba</td>
<td>1b</td>
<td>$R_w = 0.50(8)$ Å²</td>
</tr>
<tr>
<td>$c = 7.7145(2)$ Å</td>
<td>Co</td>
<td>2h</td>
<td>$z = 0.248(1)$</td>
</tr>
<tr>
<td>$V = 117.329(4)$ Å³</td>
<td>O1</td>
<td>1c</td>
<td>$R_w = 1.14(9)$ Å²</td>
</tr>
<tr>
<td>$R_{\text{exp}} = 7.58%$</td>
<td>O2</td>
<td>2i</td>
<td>$z = 0.2356(3)$</td>
</tr>
<tr>
<td>$R_1 = 1.46%$</td>
<td>O3</td>
<td>1d</td>
<td>$R_w = 0.84(6)$ Å²</td>
</tr>
<tr>
<td>$R_2 = 2.76%$</td>
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(b) La$_3$Ba$_2$Co$_3$O$_{10}$

<table>
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<tr>
<th>Space group: Pm$_3m$</th>
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<th>$R_w = 0.67(8)$ Å²</th>
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<tr>
<td>$a = 3.88813(4)$ Å</td>
<td>Co</td>
<td>1b</td>
<td>$R_w = 0.46(8)$ Å²</td>
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<tr>
<td>$V = 58.779(1)$ Å³</td>
<td>O</td>
<td>3c</td>
<td>$R_w = 1.30(9)$ Å²</td>
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<td>$R_{\text{exp}} = 7.76%$</td>
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<tr>
<td>$R_1 = 6.25%$</td>
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</tr>
<tr>
<td>$R_2 = 3.42%$</td>
<td></td>
<td></td>
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<tr>
<td>$R_3 = 3.52%$</td>
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Fig. 3. The temperature dependence of lattice parameters, bond distances and bond angle for (a) LaBaCo$_2$O$_6$ and (b) La$_3$Ba$_2$Co$_3$O$_{10}$. The inset in (b) shows the peak width of selected reflection from powder neutron diffraction data, as a function of temperature.
Fig. 4. The temperature dependence of magnetic susceptibilities for (a) \( \text{LaBaCo}_2\text{O}_6 \) and (b) \( \text{La}_2\text{Ba}_2\text{Co}_3\) under 0.1 T on zero-field cooled (ZFC) and field cooled (FC) processes. The inverse magnetic susceptibility vs temperature plots are shown in (c) with the spin configurations of low spin (LS) and intermediate spin (IS) states for Co\(^{2+}\) and Co\(^{4+}\), where the solid and dotted lines represent the Curie–Weiss fittings for \( \text{LaBaCo}_2\text{O}_6 \) and \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3\text{O}_3 \), respectively.

Excessively it shows a magnetic transition around 140 K below which a significant difference of \( M/H–T \) curves is observed between zero field cooled (ZFC) and field cooled (FC) processes. A similar cluster glass behavior was reported in \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) \( (0.18 \leq x \leq 0.50) \) by Itoh et al.\(^{17,18} \) Such cluster glass behavior could occur as a result of the competition between randomly distributed ferromagnetic and antiferromagnetic interactions. This magnetic transition corresponds to the structural change around 140 K. On the other hand, \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3\) also shows similar behaviors; a paramagnetic behavior with \( \theta_{\text{eff}} = 2.95(1) \mu_B \) and Weiss constant \( \theta_{\text{gb}} = 221.6(5) \) K, a ferromagnetic transition at \( T_C = 190 \) K and a cluster glass transition around 140 K. Below 140 K, the neutron diffraction study reveals that both compounds show only ferromagnetic peaks and no antiferromagnetic ones. It is worth to note that \( T_C \) of \( \text{LaBaCo}_2\text{O}_6 \) is 15 K lower than that of \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3\text{O}_3 \). This is different from the case of perovskite manganites in which the suppression of structural disorder is great advantage to the hopping of \( e_g \)-electrons generated by DE interaction,\(^{8,19} \) resulting in the increase of \( T_C \). Figure 5 shows the magnetization curves of (a) \( \text{LaBaCo}_2\text{O}_6 \) and (b) \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3\) at 5, 130 and 300 K.

Figure 6 shows the temperature variations of electrical resistivity measured at 0 and 9 T and magnetoresistance (MR) effect at 9 T for (a) \( \text{LaBaCo}_2\text{O}_6 \) and (b) \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3\) at 5, 130 and 300 K. The MR (%) is given by MR (%) = \( (\rho(0) – \rho(H))/\rho(0) \times 100\% \) where \( \rho(H) \) is electrical resistivity at 9 T and \( \rho(0) \) at zero magnetic field. The resistivity \( (\rho_{\alpha}) \) of \( \text{LaBaCo}_2\text{O}_6 \) exhibits a metallic behavior between 125 and 400 K, and it gradually changes to semiconductive one below 125 K. The magnetic field dependence of resistivity is not observed at low temperature but slightly observed around \( T_C \), as shown in Fig. 6(a). The resistivity \( (\rho_{\beta}) \) of \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3\) also shows a metallic behavior down to 140 K, and then it increases with decreasing temperature below 140 K. The \( \rho_{\beta} \) runs up to a tenfold value of \( \rho_{\alpha} \) at 2 K and moreover a large MR effect is observed below 100 K.

The metallic behaviors of both \( \text{LaBaCo}_2\text{O}_6 \) and \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3 \) can be described as the hopping of \( e_g \)-electrons generated by DE interaction, which is evident from positive Weiss constants in the paramagnetic states and ferromagnetic transitions. The values of \( P_{\text{eff}} \) in the paramagnetic states and magnetization in the magnetically ordered states indicate mixed spin states of LS and IS on Co\(^{3+}\) and Co\(^{2+}\) in both \( \text{LaBaCo}_2\text{O}_6 \) and \( \text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_3\text{O}_3 \), where the expected electron configurations are LS \( (t_{2g}^5, S = 0) \) and IS \( (t_{2g}^1, t_{2g}^1, S = 1) \) for Co\(^{3+}\) and LS \( (t_{2g}^3, S = 1/2) \) and IS \( (t_{2g}^1, t_{2g}^1, S = 1) \) for Co\(^{2+}\).
S = 3/2) for Co⁴⁺. We have not exactly determined the electron configurations of each ion. However, it is thought that the IS and LS states are dominant in Co⁴⁺ and Co⁵⁺ ions respectively, because the DE interaction functions in such states much more effectively. This is consistent with the magnitude of saturation moment. The smaller $P_{\text{eff}}$ and saturation moment in LaBaCoO₆ tell us a little larger ratio of LS state or a smaller amount of $e_g$-electron in it. LaBaCoO₆ has a smaller unit cell volume than La₀.₃Ba₀.₇CoO₃, and the increasing $\Delta C$ increases LS population and decreases $e_g$-electrons. This might be a cause of the lowering of $T_C$ by 15 K in LaBaCoO₆, in contrast to the case of LaBaMn₂O₆ ($T_C$ = 330 K) and La₀.₃Ba₀.₇MnO₃ ($T_C$ = 280 K). The number of $e_g$-electron is equal in LaBaMn₂O₆ and La₀.₃Ba₀.₇MnO₃, therefore, the absence of structural disorder in LaBaMn₂O₆ enhances ferromagnetic transition.

Such mixed spin states of LS and IS could be related to magnetic glassy states at low temperatures. Both LaBaCoO₆ and La₀.₃Ba₀.₇CoO₃ transform to magnetic glassy states below about 140 K. The magnetic transitions are accompanied by the structural changes. Fauth et al. proposed that the structural distortion from cubic to tetragonal in La₀.₃Ba₀.₇CoO₃ is due to the partial $d_{3z²−r²}$-type orbital ordering. This is supported by the present results of structural refinement, namely the elongation of CoO₆ octahedra along the apical oxygen direction is consistent to the $d_{3z²−r²}$-type orbital ordering. The $d_{3z²−r²}$-type orbital ordering results in the change of magnetic interaction into an antiferromagnetic one from the ferromagnetic one generated by DE interaction. The $e_g$-electrons in IS state of Co³⁺⁺ (Co⁵⁺/Co⁴⁺) is responsible for the $d_{3z²−r²}$-type orbital ordering. In a mixed state of LS and IS, the $d_{3z²−r²}$-type orbital ordering partially occurs and consequently the competition between randomly distributed ferromagnetic and antiferromagnetic interactions leads to magnetic glassy state. The sharp increase of resistivity at low temperature is also consistent with the partial $d_{3z²−r²}$ orbital ordering, namely the reduced electron hopping path from three- to one-dimension by such orbital ordering results in increase of the resistivity.

A similar scenario can be considered for LaBaCo₂O₆. However, the manners of structural change and resistivity at low temperature in LaBaCo₂O₆ are somewhat different from those in La₀.₃Ba₀.₇CoO₃; the noncentrosymmetric distortion of apically compressed CoO₆ octahedra becomes close to a centrosymmetric one below 140 K and the increase of resistivity at low temperature is a little. The A-site ordered LaBaCo₂O₆ has the apically compressed and noncentrosymmetric CoO₆ octahedra, which is caused by the structural characteristic that the CoO₂ layer is sandwiched by the two types of rock-salt layer, LaO and BaO, with different lattice sizes. We know that the similar apically compressed octahedra are favorable for the layer-type $d_{3z²−r²}$-type orbital ordering and the peculiar (noncentrosymmetric) distortion of MnO₆ octahedra is relaxed by the $d_{3z²−r²}$-type orbital ordering in RBaMn₂O₆.¹⁶ For example, a similar structural transition with a higher to lower distortion on cooling has been observed in RBaMn₂O₆ ($R$ = Tb, Dy, Ho and Y)⁷,¹⁵ From these considerations, we propose that LaBaCo₂O₆ exhibits the partial $d_{3z²−r²}$ orbital ordering below 140 K, contrary to the $d_{3z²−r²}$ orbital ordering in La₀.₃Ba₀.₇CoO₃. The $d_{3z²−r²}$ orbital ordering associated with A-type antiferromagnetic metal well explains magnetic glassy state and a little increase of resistivity at low temperature in LaBaCo₂O₆; the random distribution of the ferromagnetic and the antiferromagnetic interactions and the reduction of electron hopping paths from three- to two-dimension by the partial $d_{3z²−r²}$ orbital ordering. The increase of magnetization under high magnetic fields in the cluster glass states of both LaBaCo₂O₆ and La₀.₃Ba₀.₇CoO₃ suggests the conversion of the partial orbital ordered states to ferromagnetic metal state by magnetic fields. Much more remarkable MR effect in La₀.₃Ba₀.₇CoO₃ might be related to more insulative $d_{3z²−r²}$-type orbital ordering. In order to clarify the partial $d_{3z²−r²}$ and $d_{3z²−r²}$ orbital orderings, however, further experiments should be needed and are now in progress.

4. Summary

To summarize, we have successfully synthesized a new A-site ordered perovskite cobaltite, LaBaCo₂O₆ and investigated its structural and physical properties. The obtained results are compared to those of the ordinary A-site disordered La₀.₃Ba₀.₇CoO₃. Both LaBaCo₂O₆ and La₀.₃Ba₀.₇CoO₃ show metallic behaviors generated by DE interaction and ferromagnetic transitions at $T_C$ = 175 K (LaBaCo₂O₆) and $T_C$ = 190 K (La₀.₃Ba₀.₇CoO₃). The obtained magnetic properties reveal mixed spin states of LS and IS of Co³⁺⁺ (Co⁵⁺/Co⁴⁺) in both compounds. The ratio of LS state estimated from $P_{\text{eff}}$ and saturated magnetization is higher in LaBaCo₂O₆ than in La₀.₃Ba₀.₇CoO₃. The lowering of $T_C$ by 15 K in LaBaCo₂O₆ is due to a lower ratio of IS state with $e_g$-electrons responsible for ferromagnetic metal generated by DE interaction. Below about $T_C$ = 140 K, both compounds exhibit structural change and magnetic glassy (cluster glass) behaviors. The refined structural data and electromagnetic properties suggest a
partial $d_{3z^2-r^2}$ orbital ordering for LaBaCo$_2$O$_6$ below $T_c = 140$ K, in contrast to a partial $d_{z^2-r^2}$ orbital ordering for La$_{0.5}$Ba$_{0.5}$CoO$_3$. The $d_{3z^2-r^2}$ orbital ordering in LaBaCo$_2$O$_6$ has a close relation to the structural characteristic that the CoO$_2$ layer is sandwiched by the two types of rock-salt layer, LaO and BaO, with different lattice sizes. The peculiar (noncentrosymmetric) distortion of CoO$_6$ octahedra is well relaxed by the $d_{3z^2-r^2}$ orbital ordering.

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