Redox-driven control of magnetism and structure of polycrystalline PrBaCo$_2$O$_{5+\delta}$

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Abstract

Controlling oxygen contents ($0.25 \leq \delta \leq 0.83$) and its associated structural and magnetic properties in polycrystalline PrBaCo$_2$O$_{5+\delta}$ are presented. To control oxygen contents, heat treatments were performed using tube furnace in controlled gas environment. Through temperature dependent reductive annealing, oxygen vacancies are formed in PBCO, and changes of associated properties such as lattice expansion and stabilization of antiferromagnetism are observed. When we performed oxidative annealing, oxygens are intercalated into PBCO. This results in stabilization of ferromagnetism. At last, we checked reversibility through consecutive redox reactions. The structural and magnetic phase transitions occur nearly reversibly. Thus, we could control oxygen contents and associated structural and magnetic properties reversibly through conventional gas reaction.

1. Introduction

Cobalt oxides are known to have various properties because cobalt ions can be in various states (valence states and spin states). These various states of cobalt ions are sensitive to the surrounding environment which affects valence states and crystal field interaction of the 3$d$ energy level. The interaction is the same order of magnitude of the Hund’s rule[1]. There are some methods to change the environment around Co ions, such as applying pressure, magnetic fields, and ion intercalation[2–4]. R$^{3+}$Ba$_2$Co$_{2+\delta}$O$_6$ ($R$ = rare earth ions) is A-site ordered double perovskite (AA’BO) which has a structure consisting of alternate stack of A-site cations layers (AO and A’O) with B-site cation layer (CoO$_2$) in order (…AO-BO$_2$-A’O-BO$_2$-AO….) along c-axis (figure 1(a)). This double perovskite is a well-known for facile oxygen ion exchanges. Interestingly, it is known that oxygen vacancies are formed easily in a R$^{3+}$Ba$_2$Co$_{2+\delta}$O$_6$[5]. It makes Co ions in various environments such as octahedra (CoO$_6$) and square pyramids (CoO$_5$), which lead to various valence states and spin states. Thus, depending on oxygen contents, R$^{3+}$Ba$_2$Co$_{2+\delta}$O$_6$ has diverse physical properties such as metal-insulator-transition, spin-state-transition, giant magnetoresistance, superior oxygen exchange behavior, and magnetism[5–12]. In this regard, PrBaCo$_2$O$_{5+\delta}$ (PBCO) is a relevant example, since it has been known that its magnetic ground state is affected by its oxygen contents in bulk magnetometry[13–18]. In some cases, detailed information on its magnetism was studied using magnetic neutron diffraction from selected oxygen stoichiometry where $\delta$ is higher than 0.5 [19–21]. However, reported results are rather inconsistent with each other probably due to processing conditions[13, 17, 18, 21, 22]. It is required to study the relationship between magnetism and oxygen stoichiometry in controlled environment.

In this work, we control oxygen contents of PBCO at relatively low temperature by simple thermal annealing. We observed transitions of structure and magnetism depending on the oxygen content. Then, from successive ex-situ thermal annealing, we checked reversibility between magnetic phases induced by different oxygen contents.
2. Experimental

Polycrystalline samples were prepared by solid state reaction in air. Stoichiometric amounts of Pr$_6$O$_{11}$ (Alfa Aesar, 99.99% in purity), Co$_3$O$_4$ (Alfa Aesar, 99% in purity), and BaCO$_3$ (Alfa Aesar, 99.95% in purity) were carefully weighed and thoroughly ground. The powders were calcined at 1000 °C for 10 h. The powders were pressed into pellets with 20 MPa for 1 min. The pressed pellets were sintered at 1100 °C for 10 h. For controlling oxygen contents of as-synthesized PBCOs, additional heat treatments were performed in an environment-controlled tube furnace. For forming oxygen vacancies, as-synthesized PBCOs were annealed at the annealing temperatures ($T_{as}$), where $T_{as}$ were set in between 100 °C and 400 °C for 12 h in the flow of 3% H$_2$ and 97% Ar gas. The flow rate was fixed to 20 standard square cubic centimeter per minute (sccm). In each case, oxygen contents of PBCOs were determined by iodometric titration. This is a general method which used to determine oxidizing agent concentration in a solution. The principal of this method is reduction of high valent cobalt sample in acidic solution by a reductant. First, the sample was mixed with KI solution. In this step, important to prevent oxidation by removing the air using nitrogen or argon gas for several minutes. Furthermore, acidic solution (HCl) was used to dissolve the sample. As a result, Co$_{2+}$ was formed due to reduction of trivalent and tetravalent cobalt. Moreover, iodine also formed from this reaction and this liberated iodine was titrated with Na$_2$S$_2$O$_3$ solution. Starch was used as indicator and added before the end-point of titration. The reaction condition was maintained under inert atmosphere. For checking possible oxygen intercalation, as-synthesized samples were annealed at 300 °C for 12 h in O$_2$ gas flow with the same flow rate. For confirming reversibility of oxygen contents, successive annealing experiments were performed: i.e. thermal annealing of an as-synthesized sample at 300 °C for 12 h in the forming gas and then for 12 h in O$_2$. X-ray powder diffraction (Malvern PANalytical Xpert Powder) was used to
check potential structural changes from various annealing experiments. Rietveld refinements were taken place on all the diffraction patterns with Fullprof software package[24]. SQUID magnetometry (Quantum Design MPMS-7) was used to characterize magnetic properties. Field-cooled temperature dependent magnetization was measured under 100 Oe field in the range of 15 K to 300 K (400 K for a selected sample). Field dependent magnetization measurements were done at 20 K up to 7 T of applied field.

3. Results and discussions

Before thermal annealing, we characterized as-synthesized samples which were prepared by solid state reaction. For characterizing crystal structure, x-ray diffraction pattern was obtained at room temperature and Rietveld refinement was performed. Refinement result and experimental data are matched well (figure 1(b)). For refinement, two variables were fixed. The first is the oxygen contents. To avoid possible misled result by the low sensitivity of x-ray diffraction for light element, oxygen in this case, we fixed oxygen occupancy of the oxygen with the value which was obtained by iodometric titration. The second is the space group. It is reported that PBCO can have 112-type ($a_p$, $a_p$, $2d_p$) lattice constant in cubic perovskite structure) double perovskites structure in P4/mmm tetragonal symmetry or 122-type in Pmnrn orthorhombic symmetry depending on oxygen contents[5, 13–15]. Thus, space group of each sample was selected by the oxygen contents. Thus, it was confirmed that as-synthesized PBCO is in 112-type tetragonal unit cell with lattice parameters ($a = 3.9065$ Å and $c = 7.6330$ Å) without any secondary phase. Reductive thermal annealing was performed for as-synthesized PBCO samples at several annealing temperatures for forming oxygen vacancies in PBCO (figure 2(a)). From the results of iodometric titration, we could see that the oxygen content is decreased as $T_a$ is increased (figure 2(b)). When annealed below $T_a = 150$ °C, the value of oxygen content changed from as-synthesized PBCO slightly. However, when $T_a = 200$ and 300 °C, the oxygen contents changed abruptly. Thus, it seems PBCO barely react with forming gas up to 150 °C. After iodometric titration, x-ray diffraction patterns were taken, and Rietveld refinements were performed in same manner as case of as-synthesized sample (figure 2(c)). For PBCO with $\delta = 0.71$ and 0.74, the XRD pattern is similar to that of synthesized PBCO. Lattice constants changed slightly with the same symmetry. We denote this phase as $T_1$. For PBCO with $\delta = 0.55$, lattice constants are abruptly changed. (200) diffraction, which was a single peak when annealed below 150 °C, split into (200) and (040) diffraction peaks. It indicates structural phase transition from tetragonal symmetry to orthorhombic symmetry. We denote this phase as $O$, that doubling unit cell along $b$-axis occurred[14, 25]. Also, another transition from orthorhombic structure to tetragonal (P4/mmm) structure with different lattice constants at the higher temperature leads us to define another tetragonal phase called as $T_2$ in case of PBCO with $\delta = 0.25$. Thus, tetragonal ($T_2$, $\delta \sim 0.25$)—orthorhombic ($O$, $\delta \sim 0.55$)—tetragonal ($T_1$, $0.71 \leq \delta$) phase transition occurs during reductive thermal annealing. Note that, when annealed at 400 °C, XRD pattern indicates PBCO is decomposed (data not shown). Lattice constants of each sample at room temperature are shown in table S1 (available online at stacks.iop.org/MRX/8/015502/mmedia). The unit-cell volume increases with decrease of oxygen contents.

To establish relationship between oxygen vacancy and magnetism in PBCO, filed-cooled temperature dependent magnetization under 100 Oe of applied field and field dependent magnetization at 20 K were measured. From the temperature dependent magnetization measurement, we could estimate the Curie temperature ($T_C$) of as-synthesized PBCO is about 165 K (figure 3(a)). When we annealed the PBCO up to 150 °C, we observed only a slight decrease of the Curie temperature. It showed typical paramagnetic to ferromagnetic transition with different $T_C$. Similar $T_C$ of PBCO annealed up to 150 °C can be considered PBCO barely react up to 150 °C. The result is consistent with those of XRD and iodometric titration. In addition to this fact, we observed slight decrease of magnetization at low temperature, which implies the formation of another magnetic phase from the PBCOs annealed up to 150 °C. Decreasing magnetization below $T_{N_a}$ would be explained by phase separation scenario which PBCO is consisted of antiferromagnetic matrix with embedded ferromagnetic clusters, where $\delta \sim 0.74$[20]. This phase separation scenario is also proposed in other $R$Ba$_2$Co$_2$O$_{4+\delta}$ materials [12, 26]. When the temperature becomes lower than $T_{N_a}$, contribution of antiferromagnetic matrix leads to a decrease in magnetization. For analysis, we defined it as $T_{N_a}$ which is the temperature that magnetization starts to decrease. It is clearly seen that $T_{N_a}$ increases by higher temperature annealing: 60 K for as-synthesized PBCO, 70 K for PBCO annealed at $T_a = 100$ °C, and 75 K for PBCO annealed at $T_a = 150$ °C. Interestingly, when the annealing temperature is above 200 °C where the oxygen contents changed a lot, we can see dramatic change in magnetism. The cusp found in $M$ versus $T$ curves of PBCO annealed at 200 °C is from paramagnetic to ferrimagnetic transition at about 235 K. However, below the temperature, antiferromagnetism is kicked into the system. Thus, the magnetization below 180 K is nearly 0. And eventually, when annealed at 300 °C, magnetization is nearly 0 and no transition was observed in the range of our measurement. We performed additional $M$ versus $T$ experiments up to 400 K. We could not see the sudden transition. It means
antiferromagnetism is stabilized in PBCO. Thus, antiferromagnetism in PBCO becomes dominant as decreasing oxygen content. To see ground state of PBCOs, $M$ versus $H$ curves were taken at 20 K (figure 3(b)). When annealed below 150 °C, clear magnetic hysteresis is observed. The coercivity for as-synthesized PBCO is about 350 Oe. When annealed at 200 °C, it showed the reduced canted magnetic moments and no hysteresis. This indicates stabilization of antiferromagnetic ground state. When annealed 300 °C, we could observe clear antiferromagnetic behavior. The remnant magnetization is systematically decreased upon increase of annealing temperature. Note that, since all the samples are not fully saturated even in the highest fields, we used remnant magnetization. PBCO is not fully saturated up to even 14 T [14]. This can be explained by coexistence and competing of ferromagnetic and antiferromagnetic interactions due to comparable ground-state energy at low temperature in PBCO [27].

After we checked formation of oxygen vacancies in PBCO by simple reductive annealing, we performed oxidative thermal annealing in O$_2$ flow to intercalate oxygen. After the sample was annealed at 300 °C in O$_2$, x-ray diffraction pattern and iodometric titration were taken to check oxygen content in PBCO. The refinement showed the oxidized PBCO still keep tetragonal symmetry (figure 4(a)). However, its tetragonality ($c/a = 1.957$) is greatly increased compared to the case of reduced PBCO. In this oxygen-rich PBCO ($\delta = 0.83$) from
iodometric titration, lattice constant \(a\) is decreased and \(c\) is increased. In addition, unit-cell volume is greatly reduced \((V = 58.139 \text{ Å}^3)\), which is commonly found in perovskite oxides upon oxidation\([28, 29]\). \(M\) versus \(T\) curve shows that the magnetic transition temperature is 180 K, which increased by 15 K from the case of as-synthesized PBCO (figure 4(b)). It is consistent with that \(T_c\) is increased as increasing oxygen contents in EuBaCo\(_2\)O\(_{5+\delta}\) and other double perovskite oxides\([30, 31]\). Ferromagnetic behavior was observed without antiferromagnetic phase. \(M\) versus \(H\) curve show increase of remnant magnetization and the magnetic moment at the highest magnetic field is found to be about 1.5 \(\mu_B/\text{Co}\), and like other cases saturation is not reached (figure 4(c)). It seems ferromagnetism in PBCO becomes dominant as increasing oxygen content. This systematic relation between magnetism and oxygen contents may be explained by change of interaction depending on valence states of Co ions\([16, 18, 32]\). Double exchange between Co\(^{3+}/\text{Co}^{4+}\) shows ferromagnetic behavior. And super-exchange between Co\(^{3+}/\text{Co}^{3+}\) shows antiferromagnetic behavior. Therefore, in low temperature, due to ratio of Co\(^{3+}\) is relatively higher in oxygen-rich PBCO, ferromagnetic behavior and electric conductivity are enhanced in oxidized PBCO\([21]\). On the other hand, antiferromagnetic behavior is enhanced in reduced PBCO due to ratio of Co\(^{4+}\) is decreased in oxygen-deficient PBCO.

We confirmed that higher temperature heat treatment in the forming gas induces oxygen vacancies, while heat treatment in \(O_2\) intercalate oxygens in the PBCO. In addition, we established relation between oxygen contents and associated properties. After establishing relation among oxygen contents, structure, and magnetism upon gas reaction, we performed consecutive annealing at 300 °C to see reversibility in this relation. Heat treatment in oxygen was performed after annealing in forming gas. X-ray diffraction pattern was obtained, and secondary phase was not observed. It was confirmed that the x-ray diffraction patterns and the oxygen contents of consecutively annealed case and directly annealed case were very similar (\(\delta = 0.81\) and \(\delta = 0.83\), respectively). Therefore, refinements showed there were no significant differences of lattice constants. Also, magnetization data shows there was no significant difference of magnetism between consecutively and directly

![Figure 3](image3.png)

*Figure 3.* (a) Temperature dependent magnetization measurements were performed with 100 Oe. Magnetization is decreased as oxygen contents are decreased and eventually antiferromagnetism is stabilized. (b) Field dependent magnetization measurements at 20 K. Remnant magnetization is decreased as oxygen contents are decreased.

![Figure 4](image4.png)

*Figure 4.* (a) XRD patterns of directly annealed (up) and consecutively annealed (down) PBCO at 300 °C. Lattice constants are nearly same in both cases. (b) Temperature dependent magnetization and (c) field dependent magnetization are seen. The XRD and SQUID results are nearly same in both consecutively and directly annealed cases.
annealed cases. As a result, it was confirmed that controlling oxygen contents and physical properties of PBCO through heat treatment is nearly reversible.

4. Conclusions

In this work, we studied A-site double perovskite PrBaCo₂O₅₊ₓ₋ₓ, which can freely take and release oxygens in low temperature. The change of oxygen contents in the PBCO lead to transform the materials magnetically and structurally. The materials can be from antiferromagnetic tetragonal phase to ferromagnetic tetragonal phase. In between two phases, the material can be in antiferromagnetic/ferrimagnetic orthorhombic phase. The results suggest the materials’ magnetism can be easily and nearly reversibly tuned by conventional gas reaction at low temperature.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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