Pressure effects on the charge-ordering transition of $\text{BaYCo}_2\text{O}_5$$_0$

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Pressure effects on the charge-ordering (CO) transition have been investigated for an oxygen-deficient double-perovskite cobalt oxide, $\text{BaYCo}_2\text{O}_5$$_0$, through resistivity measurements using a piston-cylinder-type clamp cell. The charge-ordering temperature $T_{\text{CO}}$ rises (+19 K/GPa) as pressure increases, making a sharp contrast with the pressure suppression of $T_{\text{CO}}$ seen for the isostructural $\text{BaSmFe}_2\text{O}_5$. We have further determined the atomic coordinates under elevated pressures, and ascribed this unexpected behavior of $\text{BaYCo}_2\text{O}_5$$_0$ to the pressure enhancement of the orthorhombic distortion $s (=a-b)$. 

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I. INTRODUCTION

In perovskite-like $3d$ transition-metal oxides, the barely mobile $d$ electrons together with the on-site Coulomb repulsion ($U$) cause a variety of charge-ordering (CO) and orbital-ordering (OO) transitions.1-4 These CO and OO transitions are amenable to the structural modification via application of hydrostatic pressure (physical pressure) and/or isovalent chemical substitution (chemical pressure),5 because the charge and orbital degree of freedoms couple with the shape of the oxygen polyhedron surrounding the transition metal. In this sense, structural studies are effective for deeper understanding of CO and OO phenomena. Synchrotron x-ray powder diffraction together with the diamond anvil cell (DAC) technique enables us to determine oxygen positions even under high pressures.6,7 Then, we can determine the structural modification under physical pressures, and clarify the physical pressure effects on the CO and OO phenomena.

Among the CO compounds, the double-perovskite oxides of the $\text{BaRCO}_2\text{O}_5$$_0$ type ($R=Y$, Ho, Dy, and Tb), attract considerable scientific interest.2,3,8 $\text{BaYCo}_2\text{O}_5$ has an orthorhombic crystal structure ($Pmmm; Z=2$), containing corner-shared $\text{CoO}_3$ square pyramids as principal building units, and is isostructural with $\text{BaSmFe}_2\text{O}_5$ that shows a “Verwey-type” transition1 at $T_{\text{CO}}=230$ K. $\text{BaYCo}_2\text{O}_5$ undergoes an antiferromagnetic transition at 330 K; the spin ordering (SO) is of the checker-board type ($G$ type) within the bipyramidal layer. With further decrease of temperature below $T_{\text{CO}}$ ($\approx220$ K), chain-type CO along the $b$ axis takes place, accompanied by a kink in resistivity.2 Here, we emphasized that the CO and SO patterns of $\text{BaYCo}_2\text{O}_5$ are the same as those of $\text{BaSmFe}_2\text{O}_5$. Having similar $T_{\text{CO}}$, the two compounds make a good couple for comparison. Akahoshi and Ueda4 insisted that $\text{BaYCo}_2\text{O}_5$ separates into orthorhombic and tetragonal phases below $T_{\text{CO}}$, and that there is no anomaly in resistivity at $T_{\text{CO}}$ though there is a clear anomaly in differential scanning calorimetry (DSC) curve. They ascribed the discrepancy of the data between Ref. 2 and Ref. 4 to the different oxygen stoichiometry.

In this paper, we report the physical pressure effects on $T_{\text{CO}}$ and on the crystal structure for $\text{BaYCo}_2\text{O}_5$. We have found that $T_{\text{CO}}$ of $\text{BaYCo}_2\text{O}_5$ rises (+19 K/GPa) as pressure increases, making a sharp contrast to the pressure suppression of $T_{\text{CO}}$ in $\text{BaSmFe}_2\text{O}_5$.8 This unexpected behavior is ascribed to the pressure enhancement of the orthorhombic distortion $s (=a-b)$ in $\text{BaYCo}_2\text{O}_5$. Actually, $T_{\text{CO}}$ under physical and chemical pressures scales well to $s$ for both $\text{BaYCo}_2\text{O}_5$ and $\text{BaSmFe}_2\text{O}_5$.

II. EXPERIMENT

Polycrystalline sample of $\text{BaYCo}_2\text{O}_5.\delta$ with $\delta=0$ was obtained through a two-step synthesis route. The direct solid-state synthesis in air starting from a stoichiometric mixture of $\text{BaCO}_3$, $\text{Y}_2\text{O}_3$, and $\text{Co}_3\text{O}_4$ readily results in single-phase $\text{BaYCO}_2\text{O}_5.\delta$ with $\delta >0$. Here, calcination was carried out at 1000 $\deg C$ for 10 h and sintering of a pelletized sample at 1100 $\deg C$ for 24 h. For the thus-obtained air-synthesized sample, iodometric titration yielded the amount of excess oxygen at $\delta=0.32(1)$. The excess oxygen was then completely removed by annealing in flowing $\text{N}_2$ gas (in a thermobalance) at 800 $\deg C$ for 12 h. For this sample $\delta$ was determined to be 0.005(3). Differential scanning calorimetry runs showed for the sample a clear peak in both heating and cooling curves around 231–233 K, the precise temperature depending on the heating/cooling rate. Synthesis procedure of the $\text{BaSmFe}_2\text{O}_5.\delta$ sample was described elsewhere.9,10

The resistivity ($\rho$) was measured under pressures up to $P=1.6$ GPa by a standard four-probe method with the use of a clamp-type piston cylinder cell.5 A small piece of the polycrystalline sample ($\sim 0.5 \times 1 \times 2 \mm$) was placed in a sample room, which was filled with Silicone oil as a pressure-transmitting medium. The sample temperature was monitored with a copper-constantan thermocouple attached near the bottom of the sample space. The pressure values are...
The applied pressure relaxes at a rate of $27\%/100$ K.

Pressure-induced changes in the $\rho$-$T$ curves were reproducible in the repeated pressure cycles.

High-pressure x-ray powder-diffraction measurements were performed at SPring-8, BL10XU beamline equipped with the DAC in the $2\theta$ range of $5^\circ$–$30^\circ$. Precipitation method was adopted to obtain fine and homogeneous powders: the waiting time was $120$ min–$30$ min for BaYCo$_2$O$_{5.0}$ (BaSmFe$_2$O$_{5.0}$). The sample powder was sealed in the DAC gasket hole, $0.05$ mm in thickness and $0.15$ mm in diameter, filled with an ethanol/methanol mixture as a pressure-transmitting medium. The x-ray beam size was $0.10$ mm in diameter. The wavelength of the incident x ray was $0.495\,59$ Å, and the exposure time was $8$ min. The Debye-Scherrer rings gave homogeneous intensity distributions, which is a necessary condition for successful Rietveld refinement. The magnitude of the applied pressure was monitored by the wavelength shift of the luminescence line $R_1$ (Ref. 12) from a small piece of ruby placed in the gasket hole.

III. RESULTS AND DISCUSSION

A. Pressure effects on the charge-ordering temperature

In Fig. 1(a) temperature dependence of $\rho$ is shown for BaYCo$_2$O$_{5.0}$ under various pressures. The $\rho$-$T$ curve at ambient pressure ($P=0.0$ GPa; thick curve) shows a steep rise at $234$ K for BaYCo$_2$O$_{5.0}$, due to the carrier localization effect in the charge-ordered phase. The charge-ordering temperature $T_{CO}$ ($=234$ K) at ambient pressure is close to the transition temperature ($=231$–233 K) observed in the DSC measurement. $T_{CO}$ gradually rises as pressure increases. These $T_{CO}$ values are plotted as open circles in Fig. 2 against the applied pressure. The initial pressure derivative of the charge-ordering temperature ($dT_{CO}/dP$) is $+19$ K/GPa. The isostructural BaSmFe$_2$O$_{5.0}$ also shows the charge-ordering transition at $T_{CO}=240$ K, as indicated by arrows in Fig. 1(b). In contrast to BaYCo$_2$O$_{5.0}$, $T_{CO}$ of BaSmFe$_2$O$_{5.0}$ steeply decreases to $\approx205$ K at $P=0.4$ GPa. [Unfortunately, we cannot determine $T_{CO}$ above $P>0.4$ GPa because $\rho$ becomes too high ($>10^5$ $\Omega$ cm) to measure.] These $T_{CO}$ values are plotted as open squares in Fig. 2 against the applied pressure.

B. Temperature effects on crystal structure

Figure 3(a) shows temperature variation of the lattice constants $a$, $b$ and $c$ and unit cell volume ($V$, closed circles) for BaYCo$_2$O$_{5.0}$ in the $Pmmm$ description. The lattice constants were refined by the Rietveld analysis [RIETAN2000 (Ref. 13)] on the x-ray powder diffraction data obtained at SPring-8, BL02B2 beam line$^{14}$ equipped with a large Debye-Scherrer camera.$^{15}$ As temperature decreases below $T_{CO}$, the orthorhombic distortion $s$ ($=a-b$) increases. Here, we em-
phasize that the unit cell volume $V$ shows a slight increase at $T_{CO}$, which rules out the simple volume effects as the origin for the pressure enhancement of $T_{CO}$ in BaYCo$_2$O$_5.0$. Note that the magnitude of the increase in $V$ upon cooling through $T_{CO}$ agrees well with that previously reported for BaYCo$_2$O$_5.0$. 

Figure 3(b) shows temperature variation of $a$, $b$, $c$, and $V$ for isostructural BaSmFe$_2$O$_5.0$. Similarly to the case of BaYCo$_2$O$_5.0$, both the $s$ and $V$ values increase as temperature decreases below $T_{CO}$. For $V$ the increase is as large as 0.7% upon cooling through $T_{CO}$. This fact dictates that physical pressure will suppress $T_{CO}$ of BaSmFe$_2$O$_5.0$ by decreasing the stability of the low-temperature phase that has larger volume.

C. Pressure effects on structure

Figure 4(a) shows pressure effects on the lattice constants $a$, $b$, and $c$ determined from Rietveld refinements and on the orthorhombic distortion $s (=a-b)$ for BaYCo$_2$O$_5.0$ at 300 K. In line with the pseudotetragonal ($a=a=b=c/2$) structure, the pressure effect is found to be anisotropic. The pressure coefficient of $c$ $[=-1/c(dcdP)=-0.31\%/GPa]$ is larger than those of the other two lattice constants, $a$ ($0.21\%/GPa$) and $b$ ($0.20\%/GPa$). We point out that the $s$ value slightly increases with pressure. Figure 4(b) shows pressure effects on $a$, $b$, $c$, and $V$ for BaSmFe$_2$O$_5.0$ at 300 K. The data of BaSmFe$_2$O$_5.0$ above $P>5$ GPa were analyzed with the tetragonal model ($a=b$). The magnitude of $s$ for BaSmFe$_2$O$_5.0$ steeply decreases with pressure and disappears above $P=4$ GPa, making sharp contrast with the behavior seen for BaYCo$_2$O$_5.0$.

Here, we point out that the pressure effect on $s$ correlates with that on $T_{CO}$ (compare Fig. 2 and Fig. 4). We plotted in Fig. 5 $T_{CO}$ (open circles) of the compressed BaYCo$_2$O$_5.0$ against $s$. The filled circles represent the data for isostructural phases BaHoCo$_2$O$_5$ and BaTbCo$_2$O$_5$. By using the quantity $s$ as a scaling parameter, both the physical and the chemical pressure data are found to form a single unified curve. This suggests that the orthorhombic distortion $s$ is significance for the stability of the CO state in BaRCO$_2$O$_5$. Here, we note that a similar scaling relation between $s$ and $T_{CO}$ is observed also in BaRFee$_2$O$_5.0$. This common feature suggests that the correlation originates in the chain-type CO along the $b$ axis, for which the orthorhombic distortion is indispensable. Fulfillment of this correlation between $s$ and $T_{CO}$ may take priority over the volume change effect, and we see that despite a slight volume increase upon the CO transition in BaYCo$_2$O$_5.0$, the applied pressure increases $T_{CO}$.

D. Pressure effects on atomic coordinates

Finally, let us investigate deformation of the $MO_5$ square-pyramidal shape under physical pressure. Figure 6 shows pressure effects on the atomic coordinates of (a) BaYCo$_2$O$_5.0$ and (b) BaSmFe$_2$O$_5.0$ at 300 K. For the Rietveld structural refinement, the oxygen $z$ coordinates at the $2s$ and $2r$ Wyckoff sites ($Pmmn$) were assumed to be the same ($z_{O}$) and the overall isotropic atomic displacement parameter $Q$ was adopted. In BaYCo$_2$O$_5.0$, the reliability factor $R_1 (\equiv \Sigma_k [|I_K_{calc}-I_{k,l}|/\Sigma_k I_{k,l}]$ was small enough ($1.80\%$ to $2.51\%$). $R_1$ of BaSmFe$_2$O$_5.0$, however, is rather large ($1.76\%$ to $4.72\%$) due to the slight broadening of the diffraction profiles, especially in the high-pressure region. Except for the stability of the CO state in BaRCO$_2$O$_5$, the origin of the $z$ coordinate is at the level of apical oxygens, as shown in the inset. Solid curves are guides to the eye.
the lower-pressure region of BaYCo$_2$O$_5.0$, physical pressure decreases the $z$ coordinate of the base oxygen atom of the square pyramid [$z_O$; see Fig. 6(a)], and hence compresses the pyramid along the $c$ axis. The analogous compression is much enhanced for BaSmFe$_2$O$_{5.0}$. This is because the SmO bond distance ($d_{\text{SmO}} = 2.45 \text{ Å}$ at 0.9 GPa) of BaSmFe$_2$O$_{5.0}$ is already comparable with the sum of the ionic radii $[= 2.46 \text{ Å} \ (\text{Ref. 18})]$ of O$^{2-}$ and Sm$^{3+}$, and hence the reduction of $c$ pushes down the oxygen coordinate toward the oxygen apex. Actually, the SmO bond distance is nearly unchanged even under pressures: $d_{\text{SmO}} = 2.46 \text{ Å} (2.47 \text{ Å})$ at 2.9 GPa (5.7 GPa).

**IV. SUMMARY**

In summary, we have investigated pressure effects on the charge-ordering transition in BaYCo$_2$O$_5.0$. Surprisingly, the charge-ordering temperature $T_{\text{CO}}$ rises (+19 K/GPa) as pressure increases, making a sharp contrast with the pressure suppression of $T_{\text{CO}}$ in the isostructural BaSmFe$_2$O$_{5.0}$. This unexpected behavior of BaYCo$_2$O$_5.0$ is ascribed to the pressure enhancement of the orthorhombic distortion $s$. We have further found that $T_{\text{CO}}$ scales to $s$ under both physical and chemical pressures. Thus, high-pressure structural approach was demonstrated to be a powerful tool to understand the charge-ordering phenomena in transition metal oxides.

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15. The x-ray diffraction patterns of our BaYCo$_2$O$_5.0$ powders can be reproduced by single phase model with $Pnmm$ structure at least down to 100 K. The reliable factor $R_1 = (\Sigma_i w_i (y_i - \gamma_i) \Sigma_i w_i y_i^2)^{1/2}$ is 4.0–4.4% below 150 K.