

Pressure effects on the charge-ordering transition of BaYCo₂O_{5,0}Y. Moritomo,^{1,2} M. Hanawa,^{1,2} Sheng Xu,³ H. Ishikawa,¹ Y. Ohishi,⁴ K. Kato,⁴ T. Honma,⁵ P. Karen,⁶ M. Karppinen,⁵ and H. Yamauchi⁵¹*Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan*²*PRESTO, JST*³*Department of Crystalline Materials Science, Nagoya University, Nagoya 464-8603, Japan*⁴*JASRI/SPring-8, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan*⁵*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*⁶*Department of Chemistry, University of Oslo, Blindern N-0315, Oslo, Norway*

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Pressure effects on the charge-ordering (CO) transition have been investigated for an oxygen-deficient double-perovskite cobalt oxide, BaYCo₂O_{5,0}, through resistivity measurements using a piston-cylinder-type clamp cell. The charge-ordering temperature T_{CO} rises (+19 K/GPa) as pressure increases, making a sharp contrast with the pressure suppression of T_{CO} seen for the isostructural BaSmFe₂O_{5,0}. We have further determined the atomic coordinates under elevated pressures, and ascribed this unexpected behavior of BaYCo₂O_{5,0} to the pressure enhancement of the orthorhombic distortion s ($\equiv a - b$).

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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 BaRCo₂O₅ type ($R = Y, Ho, Dy, \text{ and } Tb$), attract considerable scientific interest.^{2,3,8} BaYCo₂O₅ has an orthorhombic crystal structure ($Pmmm$; $Z=2$), containing corner-shared CoO₅ square pyramids as principal building units, and is isostructural with BaSmFe₂O₅ that shows a ‘‘Verwey-type’’ transition¹ at $T_{CO} = 230$ K. BaYCo₂O₅ 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_{CO} (≈ 220 K), chain-type CO along the b axis takes place, accompanied by a kink in resistivity.² Here, we emphasize that the CO and SO patterns of BaYCo₂O₅ are the same as those of BaSmFe₂O₅. Having similar T_{CO} , the two compounds make a good couple for comparison. Akahoshi and Ueda⁴ insisted that BaYCo₂O₅ separates into orthorhombic and tetragonal phases below T_{CO} , and that there is no anomaly in resistivity at T_{CO} though there is a clear anomaly in differential scanning calorimetry (DSC) curve. They as-

cribed 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_{CO} and on the crystal structure for BaYCo₂O₅. We have found that T_{CO} of BaYCo₂O₅ rises (+19 K/GPa) as pressure increases, making a sharp contrast to the pressure suppression of T_{CO} in BaSmFe₂O₅.⁹ This unexpected behavior is ascribed to the pressure enhancement of the orthorhombic distortion s ($\equiv a - b$) in BaYCo₂O₅. Actually, T_{CO} under physical and chemical pressures scales well to s for both BaYCo₂O₅ and BaSmFe₂O₅.

II. EXPERIMENT

Polycrystalline sample of BaYCo₂O_{5+ δ} with $\delta \approx 0$ was obtained through a two-step synthesis route. The direct solid-state synthesis in air starting from a stoichiometric mixture of BaCO₃, Y₂O₃, and Co₃O₄ readily results in single-phase BaYCo₂O_{5+ δ} with $\delta > 0$. Here, calcination was carried out at 1000 °C for 10 h and sintering of a pelletized sample at 1100 °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 N₂ gas (in a thermobalance) at 800 °C for 12 h. For this sample δ 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 BaSmFe₂O_{5,0} sample was described elsewhere.^{9,10}

The resistivity (ρ) 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 ($\sim 0.5 \times 1 \times 2$ mm³) 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

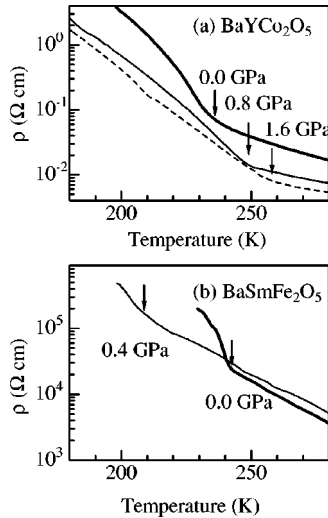


FIG. 1. Physical pressure effects on resistivity ρ of (a) $\text{BaYCo}_2\text{O}_{5.0}$ and (b) $\text{BaSmFe}_2\text{O}_{5.0}$. The pressure values quoted are those measured at room temperature. Downward arrows indicate the charge-ordering temperatures T_{CO} .

those measured at room temperature. (The applied pressure relaxes at a rate of $-7\%/100$ K.) Pressure-induced changes in the ρ - 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 2θ range of 5° – 30° . Precipitation method¹¹ was adopted to obtain fine and homogeneous powders: the waiting time was 120 min (30 min) for $\text{BaYCo}_2\text{O}_{5.0}$ ($\text{BaSmFe}_2\text{O}_{5.0}$). 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 ρ is shown for $\text{BaYCo}_2\text{O}_{5.0}$ under various pressures. The ρ - T curve at ambient pressure ($P=0.0$ GPa; thick curve) shows a steep rise at 234 K for $\text{BaYCo}_2\text{O}_{5.0}$, 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 $\text{BaSmFe}_2\text{O}_{5.0}$ also shows the charge-

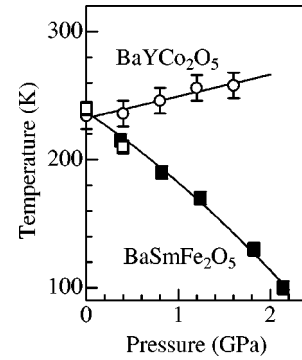


FIG. 2. Pressure dependence of the charge-ordering temperature T_{CO} . Open circles and squares represent data determined in this study for $\text{BaYCo}_2\text{O}_{5.0}$ and $\text{BaSmFe}_2\text{O}_{5.0}$, respectively. Closed squares are data points for $\text{BaSmFe}_2\text{O}_{5.0}$ from Ref. 9. The straight line for $\text{BaYCo}_2\text{O}_{5.0}$ is least-squares-fitted. The curved line for $\text{BaSmFe}_2\text{O}_{5.0}$ is a guide for the eye.

ordering transition at $T_{\text{CO}}=240$ K, as indicated by arrows in Fig. 1(b). In contrast to $\text{BaYCo}_2\text{O}_{5.0}$, T_{CO} of $\text{BaSmFe}_2\text{O}_{5.0}$ steeply decreases to ≈ 205 K at $P=0.4$ GPa. [Unfortunately, we cannot determine T_{CO} above $P>0.4$ GPa because ρ becomes too high ($>10^5$ Ω 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 $\text{BaYCo}_2\text{O}_{5.0}$ in the $Pm\bar{3}m$ 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 line¹⁴ equipped with a large Debye-Scherrer camera.¹⁵ As temperature decreases below T_{CO} , the orthorhombic distortion s ($\equiv a-b$) increases. Here, we em-

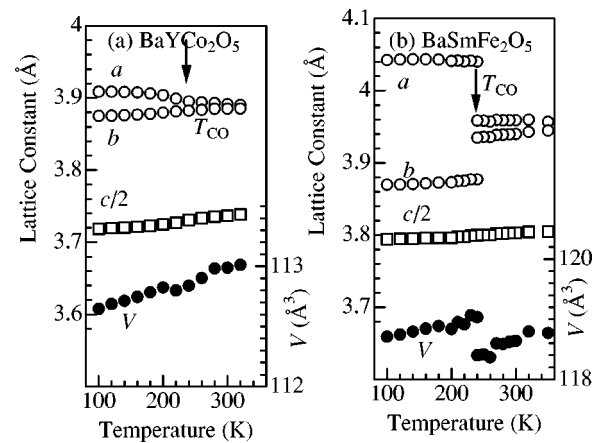


FIG. 3. Temperature dependence of lattice constants a , b , and c and unit cell volume (V , closed circles) of (a) $\text{BaYCo}_2\text{O}_{5.0}$ and (b) $\text{BaSmFe}_2\text{O}_{5.0}$. The data of the latter compound are from Ref. 9. Downward arrows show the charge-ordering temperature T_{CO} . $Pm\bar{3}m$ ($Z=2$) description was adopted also below T_{CO} for convenience.

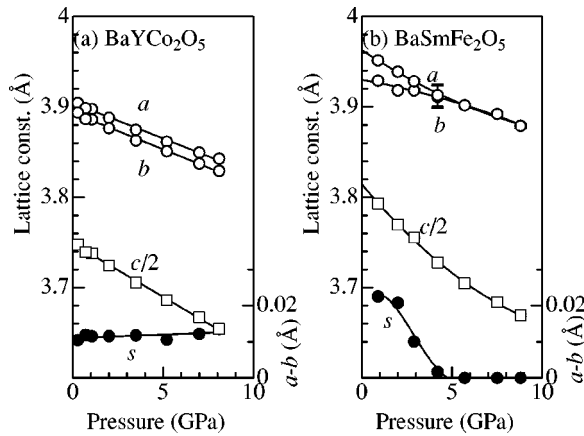


FIG. 4. Pressure dependence of lattice constants a , b and c and orthorhombic distortion s ($\equiv a - b$; closed circles) of (a) BaYCo₂O_{5,0} and (b) BaSmFe₂O_{5,0} at 300 K.

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 BaYCo₂O_{5,0}. Note that the magnitude of the increase in V upon cooling through T_{CO} agrees well with that previously reported for BaYCo₂O_{5,0}.²

Figure 3(b) shows temperature variation of a , b , c , and V for isostructural BaSmFe₂O_{5,0}. Similarly to the case of BaYCo₂O_{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 BaSmFe₂O_{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 ($\equiv a - b$) for BaYCo₂O_{5,0} at 300 K. In line with the pseudotetragonal ($a \approx b \gg c/2$) structure, the pressure effect is found to be anisotropic. The pressure coefficient of c [$\equiv -1/c(dc/dP) = 0.31\%/GPa$] 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 s for BaSmFe₂O_{5,0} at 300 K. The data of BaSmFe₂O_{5,0} above $P > 5$ GPa were analyzed with the tetragonal model ($a = b$). The magnitude of s for BaSmFe₂O_{5,0} steeply decreases with pressure and disappears above $P = 4$ GPa, making sharp contrast with the behavior seen for BaYCo₂O_{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 BaYCo₂O_{5,0} against s . The filled circles represent the data for isostructural phases BaHoCo₂O₅ and BaTbCo₂O₅.⁸ 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

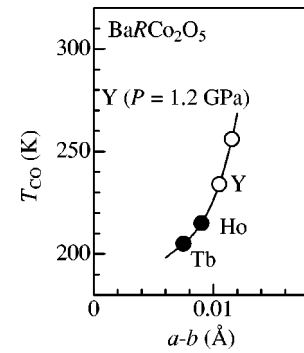


FIG. 5. Interrelation between T_{CO} and orthorhombic distortion s ($\equiv a - b$) for BaYCo₂O₅. Filled circles represent BaHoCo₂O₅ (Ref. 8) and BaTbCo₂O₅ (Ref. 8). The curve is a guide for the eye. The error bars for the horizontal axis are within the symbol size.

the stability of the CO state in BaRCO₂O₅. Here, we note that a similar scaling relation between s and T_{CO} is observed also in BaRFe₂O_{5,0}.⁹ This common feature suggests that the correlation originates in the chain-type CO along the b axis, for which the orthorhombic distortion is indispensable.^{16,17} 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 BaYCo₂O_{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) BaYCo₂O_{5,0} and (b) BaSmFe₂O_{5,0} at 300 K. For the Rietveld structural refinement, the oxygen z coordinates at the $2s$ and $2r$ Wyckoff sites ($Pmmm$) were assumed to be the same (z_O) and the overall isotropic atomic displacement parameter Q was adopted. In BaYCo₂O_{5,0}, the reliability factor R_1 ($\equiv \sum_K |I_{K,calc} - I_K| / \sum_K I_{K,calc}$) was small enough (1.80% to 2.51%). R_1 of BaSmFe₂O_{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

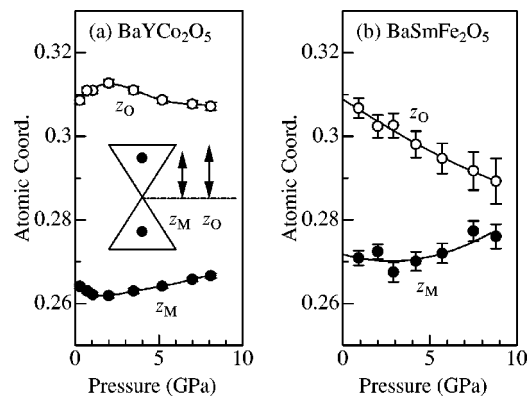


FIG. 6. Pressure dependence of atomic coordinate of (a) BaYCo₂O_{5,0} and (b) BaSmFe₂O_{5,0} at 300 K. The origin of the z coordinate is at the level of apical oxygens, as shown in the inset. Solid curves are guides to the eye.

the lower-pressure region of $\text{BaYCo}_2\text{O}_{5.0}$, 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 $\text{BaSmFe}_2\text{O}_{5.0}$. This is because the SmO bond distance ($d_{\text{SmO}}=2.45 \text{ \AA}$ at 0.9 GPa) of $\text{BaSmFe}_2\text{O}_{5.0}$ is already comparable with the sum of the ionic radii [$=2.46 \text{ \AA}$ (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: $d_{\text{SmO}}=2.46 \text{ \AA}$ (2.47 \AA) at 2.9 GPa (5.7 GPa).

IV. SUMMARY

In summary, we have investigated pressure effects on the charge-ordering transition in $\text{BaYCo}_2\text{O}_{5.0}$. Surprisingly, the charge-ordering temperature T_{CO} rises (+19 K/GPa) as pressure increases, making a sharp contrast with the pressure

suppression of T_{CO} in the isostructural $\text{BaSmFe}_2\text{O}_{5.0}$. This unexpected behavior of $\text{BaYCo}_2\text{O}_{5.0}$ is ascribed to the pressure enhancement of the orthorhombic distortion s . We have further found that T_{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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