Magnetotransport Property for the Magnetoplumbite-Derived Oxide BaCo$_6$O$_{11}$

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We studied magnetotransport property for the layered cobalt oxide BaCo$_6$O$_{11}$, which was recently reported as a novel compound with isostructure of magnetoplumbite-derived oxide of SrCo$_6$O$_{11}$. A polycrystalline sample of BaCo$_6$O$_{11}$ exhibits metallic behavior in the electrical resistivity below the ferromagnetic transition temperature of 11.5 K. A tunneling-type magnetoresistance up to $\pm 20\%$ was observed at 11.5 K and 90 kOe. These observations propose a half-metallic electronic state for BaCo$_6$O$_{11}$. [doi:10.2320/matertrans.MT-MN2019033]

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1. Introduction

Layered cobalt oxides have been extensively investigated because of their various structures and electronic properties like thermoelectricity for Na$_x$CoO$_2$, Ca$_3$Co$_4$O$_9$, and Bi$_2$Sr$_2$Co$_2$O$_y$, in addition to superconductivity for hydrate Na$_x$CoO$_2$$\cdot$1.3H$_2$O.$^{1-4}$ Their complex correlations between the lattice and electronic states provide a rich variety of intriguing properties.

SrCo$_6$O$_{11}$, which is synthesized by high-pressure synthesis method,$^5$ crystallizes in magnetoplumbite-derived structure (see the crystal structure in Fig. 1(a)). This oxide contains three crystallographic Co sites, two of which are coordinated by six oxide ions in Kagomé layers [Co(1) at 6g site] and interlayer pillars [Co(2) at 4e site] contributing electric conductivity, the other of which forms triangular bipyramid [Co(3) at 2d site] with localized spins responsible for the magnetism.$^6$ The single crystal of SrCo$_6$O$_{11}$ exhibits a stepwise magnetoresistance at low temperatures of several K,$^7,8$ being interpreted as an atomic scale spin-valve effect derived from its structural feature. Furthermore, owing to its multiple magnetic interactions, SrCo$_6$O$_{11}$ also demonstrates a 1/3 plateau with a ferrimagnetic structure ($\uparrow\uparrow\downarrow$) for isothermal magnetization curve at several K, followed by ferromagnetic transition with 3/3 plateau ($\uparrow\uparrow\uparrow$) at a high magnetic field.$^7$ The magnetic property is predominated by competitive magnetic interactions between Co spins: ferromagnetic RKKY interactions between the nearest interlayer Co(3) sites and the antiferromagnetic superexchange interactions between the second-nearest interlayer Co(3)-sites. The 1/3 plateau state is considered to be achieved among these competitive magnetic interactions, based on the theoretical framework of the ANNNI model.$^9$

We have recently reported the synthesis of polycrystalline samples of Ca- and Ba-analogues, CaCo$_6$O$_{11}$ and BaCo$_6$O$_{11}$.$^{10}$ CaCo$_6$O$_{11}$ exhibited antiferromagnetic-like behavior at low temperature, whereas BaCo$_6$O$_{11}$ was a soft ferromagnet. CaCo$_6$O$_{11}$ also displayed a magnetic transition from antiferro(para)magnetic-like 0/3-plateau to ferromagnetic-like 1/3-plateau under a higher magnetic field of above 10 kOe, which did not saturate as ferromagnet in the field up to 100 kOe, unlike SrCo$_6$O$_{11}$. The Sr substitution by smaller/larger Ca/Ba ions alters the magnitude of superexchange interactions, leading to antiferromagnetic/ferromagnetic properties for (Ca/Ba)Co$_6$O$_{11}$.

In this study, we succeeded in synthesizing an almost pure polycrystal of BaCo$_6$O$_{11}$ and performed electrical resistivity measurement to investigate magnetotransport property for BaCo$_6$O$_{11}$. Metallic behavior below the ferromagnetic transition temperature of 11.5 K was observed. Tunneling-type negative magnetoresistance up to $\pm 20\%$ was attributed to the suppression of grain-boundary resistance. These observations propose a half-metallic picture for BaCo$_6$O$_{11}$ as well as SrCo$_6$O$_{11}$. 

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2. Experimental Procedure

The composition of the raw material was adjusted to reduce the amount of the BaCo$_{12}$O$_{19}$ impurity included in our previous study. In our previous study, the atomic ratio of elements in the raw material was set to stoichiometric (Ba:Co = 1:6), but the BaCo$_{6}$O$_{11}$ sample obtained through calcination in air and high-pressure and high-temperature treatment contained substantial amount of BaCo$_{12}$O$_{19}$ phase (17 mass%). Since the amount of Ba in the final product was less than the starting composition, we estimated that part of Ba element was lost during the calcination in the air. The amount of lost Ba was estimated by the Rietveld analysis, and the mixing ratio of the raw materials was adjusted to Ba:Co = 1:5.43. We placed the mixture in a furnace and fired it at 1173 K for 12 hours in the air to obtain the precursor. An oxidizing agent KClO$_4$ was added to the precursor BaCo$_{6}$O$_{y}$ (y was estimated to be ~9) at a molar ratio of BaCo$_{6}$O$_{y}$:KClO$_4$ = 1:1. The mixture was charged into a platinum capsule, and the capsule was put into an octahedral shaped pressure-transmitting medium made of magnesium-cobalt oxides. The pressure was compressed to 8 GPa using a Walker-type high-pressure apparatus. The sample was heated at 1373 K in 15 min, retained at this temperature for 30 min, and cooled down to room temperature. The applied pressure was maintained during the heat treatment and then slowly released. The obtained polycrystalline sample was washed several times with distilled water. The pellet for electrical resistance measurement was prepared by treating the obtained BaCo$_{6}$O$_{11}$ powder separately with KCl under the same pressure and temperature conditions as initially synthesized.

The synchrotron X-ray powder diffraction (SXRD) pattern at room temperature was collected at the BL02B2 beamline of SPring-8 equipped with a Debye-Scherrer camera. The sample was charged in a Lindemann glass capillary tube with an inner diameter of 0.2 mm. The wavelength was determined to be 0.50012 Å using a CeO$_2$ standard. A Rietveld refinement program RIETAN-FP was adopted for the Rietveld analysis. The crystal structure was drawn using the VESTA-3 software. We adopted a superconducting quantum interference device (SQUID, MPMS3, Quantum Design Inc.) for magnetic measurements. Magnetic susceptibility was measured between 1.8 and 300 K under an external magnetic field of 90 kOe. Isothermal magnetization curves were collected at 5 K in external magnetic fields up to 50 kOe. Electric resistivity was measured by DC four-probe method using Quantum Design Physical Properties Measurements system (PPMS). Electric contacts were made with silver wires and silver paste. Electrical resistance was measured in a temperature range between 1.9 K and 300 K in zero-field and external field of 90 kOe perpendicular to the current. Magnetoresistance was measured in a temperature range from 10 K to 25 K in a magnetic field between -50 kOe and 50 kOe.

3. Results and Discussions

Figure 1(b) shows the SXRD pattern of BaCo$_{6}$O$_{11}$ prepared from the off-stoichiometric composition (Ba:Co = 1:5.43), together with the data in the previous report. In this study, we observed that the BaCo$_{6}$O$_{11}$ phase crystallized as the primary phase as well as the previous study and also that the amount of the BaCo$_{12}$O$_{19}$ impurity was decreased significantly by adjusting the Ba:Co ratio. A trace of BaCo$_{12}$O$_{19}$ was still observed but its quantity was reduced from ~17 mass% to ~0.5 mass%, which was estimated from the intensity of the main diffraction peak for BaCo$_{12}$O$_{19}$ around 2θ = 11.38°. Figure 2 shows the SXRD patterns of BaCo$_{6}$O$_{11}$ and the Rietveld refinement result. The primary phase was indexed as the isostructure of SrCo$_{6}$O$_{11}$, which belongs to the hexagonal space group of $P6_3/mmc$ (space group no. 194). The atomic fractional coordinates obtained from the final refinement were as follows: Co(2) (0, 0, 0.14683(4)), O(1) (0.1725(2), -0.1725(2), 0.07762(13)), O(2) (0.1453(3), -0.1453(3), 3/4), and O(3) (2/3, 1/3, 0.4217(2)). The refined structure parameters were almost the same as those in the previous study. Metal-oxygen bond lengths calculated from the refined structure parameters (Table 1) were also close to those in the previous study.

Figure 3(a) displays the temperature dependence of the magnetic susceptibility for BaCo$_{6}$O$_{11}$. A ferromagnetic transition was observed at 11.5 K, confirming that the property of the sample in this study is basically the same as the previous one. Figure 3(b) illustrates the temperature dependence of the electrical resistivity measured in zero-field and 90 kOe. In the zero-field resistivity, the temperature dependence was very small in the whole temperature range measured (see the inset of Fig. 3(b)), although a slight semiconductor-like feature was observed probably because of the contribution of the grain-boundary resistance. A sudden drop in resistivity was observed simultaneously with the magnetic transition at 11.5 K. This behavior is similar to resistivity for the single-crystalline SrCo$_{6}$O$_{11}$ sample, indicating similar electronic states for these compounds. The resistivity in the magnetic field of 90 kOe was substantially suppressed below 60 K, leading to the maximum value of negative magnetoresistance of ~20% at the magnetic transition temperature (Fig. 3(c)). The negative magnetoresistance is a tunneling-type one derived from the suppression of the grain-boundary resistance, which is widely observed in polycrystalline half-metallic ferrimagnets.
Therefore, we estimated that the ground state of BaCo₆O₁₁ is half-metallic as well as SrCo₆O₁₁. Figure 4(a) shows the isothermal magnetization curves for BaCo₆O₁₁. BaCo₆O₁₁ displayed soft ferromagnetism, as in the previous paper. Figure 4(b) exhibits the magnetic field dependence of the magnetoresistance for BaCo₆O₁₁. A slight negative magnetoresistance was observed at 25 K, followed by the gradual increase in the magnitude of the magnetoresistance leading to 16% at 10 K and 50 kOe. We did not observe the stepwise change like SrCo₆O₁₁.

Based on the above-demonstrated electrical resistivity and magnetoresistance data, we propose that the magnetotransport property for BaCo₆O₁₁ is interpreted in the half-metallic framework as well as SrCo₆O₁₁. The absence of stepwise change in resistivity in the magnetic field for BaCo₆O₁₁ is consistent with the sample ferromagnetic property for this compound, unlike the field induced 1/3- to 3/3-plateau magnetic transition for SrCo₆O₁₁. Considering the fact that the local crystal structures around the Co(1) and Co(2) sites involved in electrical conduction are almost same in SrCo₆O₁₁ and BaCo₆O₁₁, the magnetic structure consisting of localized spins at Co(3) is altered within the half-metallic framework.

4. Conclusion

We have synthesized a nearly single-phase polycrystalline sample of BaCo₆O₁₁. The magnetotransport property of BaCo₆O₁₁ is similar to that of SrCo₆O₁₁, both of which are interpreted as the half-metallic picture. BaCo₆O₁₁ exhibits a tunneling-type negative magnetoresistance derived from the suppression of grain-boundary resistance. We plan to synthesize single crystals of AC₀₆O₁₁ (A = Ca, Sr, Ba) family.
and further study of magnetotransport property will be performed on single-crystal samples.

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REFERENCES