Experimental report

30/08/2021

Proposal:	**5-31-2743**		**Council:**	10/2019

Title: Magnetic structure transitions on novel layered cobalt oxides

Research area: Materials

This proposal is a new proposal

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Samples: CaCo6O11
SrCo6O11
BaCo6O11

Instrument	Requested days	Allocated days	From	To
D2B	3	3	18/09/2020	21/09/2020
D20	3	0		

Abstract:

Intriguing mangetoelectronic properties were reported for the magnetoplumbite-related layered cobalt oxide SrCo6O11. The magnetism of SrCo6O11 is illustrated as an Ising-like anisotropy of Co(3) site in trigonal bipyramidal coordination along the c axis and a field-induced stepwise transition from 1/3-plateau ferrimagnet to 3/3-plateau ferromagnet. Recently, we successfully synthesized novel layered oxides of CaCo6O11 and BaCo6O11 and observed various magnetic phases differing from that of SrCo6O11. CaCo6O11 displays an antiferroparamagnet with 0/3-plateau, whereas BaCo6O11 exhibited simple ferromagnetism. Another type of field-induced phase transition from antiferroparamagnet to ferrimagnet was also observed for CaCo6O11. These intriguing behavior were obvserved macroscopically, but the detail magnetic structures were not determined yet. In this study, we aim to elucidate the magnetic structures of these oxides and further investigate the field-induced magnetic structure transition from 0/3 to 1/3 plateau for CaCo6O11.

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Introduction

The magnetoplumbite-derived oxide $SrCo_6O_{11}$ consists of three crystallographic Co sites: Co(1) at 6*g* site in edge-sharing octahedra layers, Co(2) at 4*e* site in face-sharing octahedra of pillars, and Co(3) at 2*d* site in trigonal bipyramids (Figure 1a). This oxide exhibits fascinating magnetoelectronic properties;[1–3] the magnetism of Co(3) is illustrated as a Ising-like anisotropy along *c* axis, whereas Co(1) and Co(2) ions mainly contribute to the metallic transport.[2,4] $SrCo_6O_{11}$ exhibits a field-induced stepwise transition from $^1/_3M_s$-ferrimagnet to $^3/_3M_s$-ferromagnet, where the M_s represents the saturation magnetization (Figure 1b). This feature also drives the spin-valve effect resulting in a giant magnetoresistance in atomic scale.[2] The resonant soft X-ray scattering spectra demonstrated the existence of multiple metastable phases with different periodicities as the devil's staircase.[3] Although the detailed properties for $SrCo_6O_{11}$ were elucidated, the overall relationship between structure and magnetism for the ACo_6O_{11} system has not been unveiled because of the absence of related compounds other than $SrCo_6O_{11}$.

We recently succeeded in the high-pressure synthesis of new compounds, $CaCo_6O_{11}$ and $BaCo_6O_{11}$. $CaCo_6O_{11}$ exhibited a field-induced magnetic phase transition from the probable antiferroparamagnet (AFP) with $^0/_3$-plateau to ferrimagnet (FerriM) with $^1/_3$-plateau, whereas $BaCo_6O_{11}$ displayed a simple ferromagnet (FM) with $^3/_3$-plateau (Figure 1b). The various magnetic phases induced by *A*-site substitution and magnetic field are illustrated in an intriguing phase diagram for the ACo_6O_{11} system (Figure 1c). A previous study demonstrates that the antiferromagnetic superexchange interactions for the next-nearest layers Co(3) sites are predominant based on the axial next-nearest neighboring Ising model, whereas conduction electrons mediate ferromagnetic interactions between the nearest layers.[3] It can be interpreted as a new-type of field-induced magnetic transition for $CaCo_6O_{11}$ from antiferroparamagnet with ↑↕↓ alignment[6] to ferrimagnetic $^1/_3$-plateau with ↑↑↓ alignment, where ↕ represents the paramagnetic or disordered state attributed to the magnetic frustrations. Since the above magnetic models were not well examined by NPD except for $SrCo_6O_{11}$, we conducted NPD measurements on $CaCo_6O_{11}$ and $BaCo_6O_{11}$.

Experiments

The polycrystalline samples of $BaCo_6O_{11}$ and $CaCo_6O_{11}$ (each ~1 g) were synthesized under high pressures up to 8 GPa and high temperature of ~1000 °C by using a Walker-type high-pressure apparatus. The samples were ground in a mortar, washed several times with deionized water, and compressed into pellets of ~8 mm in diameter and ~4 mm in thickness. The powder neutron diffraction experiment was conducted at D2B beamline of ILL. The sample was cooled down to 2 K by using a cryomagnet and a refrigerator. The NPD patterns in zero magnetic field were collected at 2 and 50 K. The wavelength was 1.598 Å.

Results

$BaCo_6O_{11}$: Figure 2a shows NPD data of $BaCo_6O_{11}$ at 2 and 30 K in zero field. A low-intensity magnetic reflection at 2θ = ~20° was observed at 2 K, which is more clearly confirmed in the difference between 2 and 30 K. This is consistent with the magnetization measurement that a magnetic transition occurs at ~12 K, whereas the appearance of 101 reflection was not explained by a simple ferromagnetic structure that was proposed by magnetization study. The present result proposes that the initial magnetic structure model with a simple parallel alignment of localized spins at Co(3) sites should be revised. Since the quality of the present data was not enough to determine the detailed magnetic structure, further study is needed.

$CaCo_6O_{11}$: Figure 2a shows NPD data of $BaCo_6O_{11}$ at 2 and 50 K in zero field. No clear magnetic reflection was observed in the data at 2 K, which is inconsistent with the antiferromagnetic model proposed using by magnetization data. Application of external magnetic field up to 5 T hardly changed the NPD patterns. The probable reason why we did not observe magnetic reflection in any conditions is that the magnetic intensities were too low to detect in the low-intensity data. Thus, we plan to conduct another NPD experiments with more suitable conditions.

References

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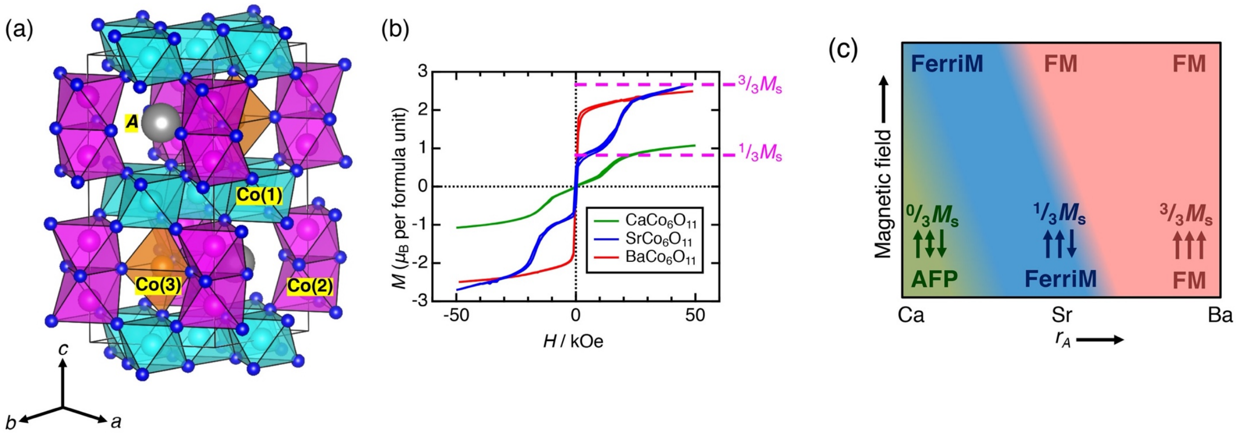

Figure 1. (a) Crystal structure of ACo_6O_{11} (A = Ca, Sr, Ba). (b) Isothermal magnetization curves at 1.8 K for polycrystalline ACo_6O_{11} (A = Ca, Sr, Ba). (c) Magnetic phase diagram of ACo_6O_{11} (A = Ca, Sr, Ba).

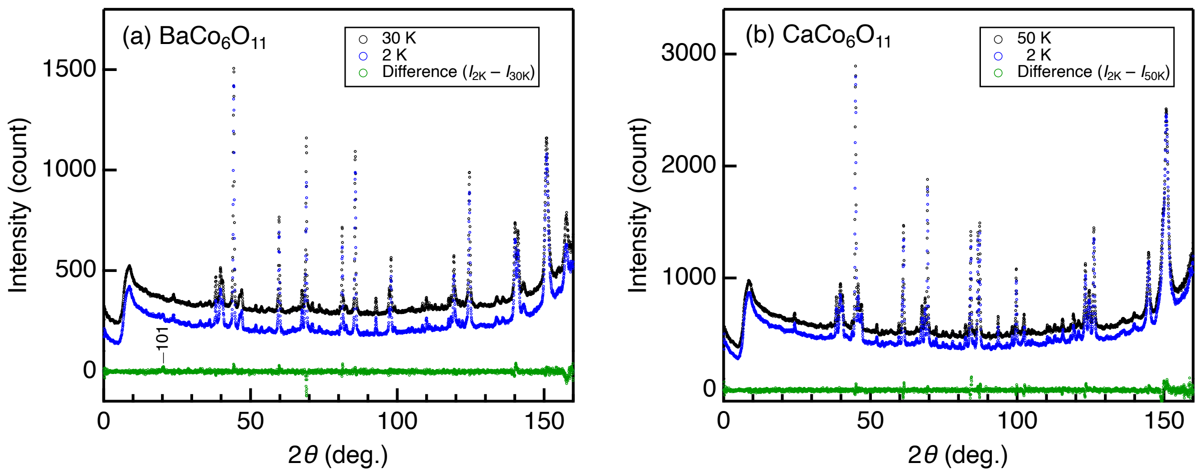

Figure 2. (a) NPD patterns of $BaCo_6O_{11}$ collected at 30 K (black) and 2 K (blue) in zero field using D2B diffractometer, and their difference (green). (b) NPD patterns of $CaCo_6O_{11}$ collected at 50 K (black) and 2 K (blue) in zero field using D2B diffractometer, and their difference (green).