Magnetic Compton scattering studies of magneto-dielectric $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$

R. Shinoda,¹ M. Itou,² Y. Sakurai,² H. Yamamoto,³ N. Hirao,³ Y. Baba,³ A. Iwase,¹ and T. Matsui^{4,a)}

¹Department of Materials Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

²Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Sayo, Hyogo 679-5198, Japan

³Japan Atomic Energy Agency (JAEA-Tokai), Tokai, Ibaraki 319-1195, Japan

⁴Research Organization for the 21st century, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

(Presented 16 January 2013; received 4 November 2012; accepted 11 January 2013; published online 9 April 2013)

We revealed that the $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$ ceramic samples exhibited ferromagnetic-dielectric behavior below the magnetic transition temperature of about 35 K. The origin of their magnetic ordering was expected to super-exchange coupling of $\text{Co}^{4+}(d^5)\text{-O}^{2-}\text{-Mn}^{4+}(d^3)$ with bonding angle of 180° and/or $\text{Mn}^{4+}(d^3)\text{-O}^{2-}\text{-Mn}^{4+}(d^3)$ with bonding angle of 90° . The magnetic spin momentum estimated by the magnetic Compton profiles (MCP) of the samples had similar temperature dependence as that determined by the temperature dependence of magnetic moment by superconducting quantum interference device, which meant that the observed magnetic moments could be ascribed to the spin moment. The shapes of the MCPs of the samples were completely same regardless of the temperature measured. This result indicates that there are no changes of the momentum space distribution of spin density between ferromagnetic and paramagnetic states. So, this magnetic transition is simply caused by a thermal fluctuation of the spin. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4799476>]

I. INTRODUCTION

Magneto-dielectric materials that may be applied to various functional devices, such as spintronics devices and novel sensors, have recently attracted increasing interests due to their unique physical phenomena.¹⁻³ In such materials, the magnetic natures can be known through the Kanamori-Goodenough rule for super-exchange coupling, which implies that the exchange interaction between $3d^n$ transition metal ions (n : number of d -electron) separated by an oxygen ion can be ferromagnetic in several cases; such as $3d^5\text{-O}^{2-}\text{-}3d^3$ with bonding angle of 180° as well as $3d^3\text{-O}^{2-}\text{-}3d^3$ with bonding angle of 90° . Hence, it is quite interesting to synthesize $\text{A}(\text{B}_{1-x}\text{B}'_x)\text{O}_3$ (B and B': $3d$ magnetic ions) perovskite oxides from the viewpoint of magnetic ordering, because two $3d$ magnetic ions may have different electron configurations, that is, the different d -electron numbers.⁴⁻⁶

Based on this idea, we have ever investigated the structural, magnetic, and dielectric properties of Mn doped BaCoO_3 .⁶ In particular, $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$ (BCMO) sintered ceramics was found to exhibit unique physical properties. The BCMO ceramics are ferromagnetic below about 35 K and paramagnetic above that temperature. Moreover, the BCMO ceramics show abrupt increase in resistivity below 35 K. Thus, the BCMO ceramics behave as a ferromagnetic insulator at lower temperature below 35 K, and as a paramagnetic semiconductor above that temperature. However, the details of the magnetic transition occurred at that temperature range has been still uncertain. Thereby, if we can survey the behaviors of the spin-polarized electron of this material at

around the transition temperature, they may be quite important information to know the origin of such magnetic transition. It should be noted, here, that magnetic Compton scattering is a unique probe for spin-polarized electron moment distribution ferromagnetic materials, and its cross section is proportional only to spin component of magnetization.⁷⁻¹¹

In the present studies, we have tried to evaluate the magnetic Compton profiles (MCPs) of the BCMO ceramic samples using the magnetic Compton scattering technique, in order to clarify their ferromagnetic origin. The valence state of the B-site ions was also checked by a soft X-ray photoelectron spectroscopy (XPS).

II. EXPERIMENTAL PROCEDURE

The BFMO ceramic samples were prepared from the desired amount of BaCO_3 , Co_3O_4 , and Mn_3O_4 . The mixture was calcined at 1273 K and was broken up by ball milling method for 6 h. Then the BFMO samples were grounded again and were pressed in a die with 10 mm in diameter. Finally, the compacts were sintered at 1273 K for 48 h to obtain the BFMO ceramic samples. The stoichiometry of the samples was confirmed by an electron probe micro-analyzer. Structural characterization of the samples was investigated by X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation. Magnetic Compton scattering experiments were carried out at the beam line BL08W of the synchrotron radiation facility SPring-8. The samples were set on the cold head of the refrigerator in the vacuum chamber attached for the BL08W. The MCPs were measured at 8 K, 20 K, 30 K, 40 K, and 50 K using circularly polarized 182 keV X-rays. Scattered X-rays were detected by a ten-element Ge detector at a scattering angle of 178.5° . We have also carried out the temperature dependence

^{a)}Author to whom correspondence should be addressed. Electronic mail: t-matsui@21c.osakafu-u.ac.jp. FAX: +81-72-254-9912.

FIG. 1. X-ray diffraction scan for the $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$ sintered sample and the calculated peak intensities for the $\text{Ba}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ phases with 2H, 10H, and 12H crystal structure.

of magnetization measurements using a superconducting quantum interference device (SQUID) magnetometer. To evaluate the valence state of the Mn ions, XPS analysis using synchrotron soft-x-ray radiation was performed at KEK BL27A in High Energy Accelerator Research Organization.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD scan for the $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$ sample as well as the calculated diffraction intensities for the perovskite related 2H, 10H, and 12H type hexagonal crystal structure having the long range ordered B-O_6 octahedrons.^{12,13} The scan for the sample reveals that the sample is mainly consisted of the mixture of the phases with the 10H and 12H hexagonal crystal structures, which is consistent with our previous works.^{5,6}

The magnetization loops measured by SQUID at 8, 20, 30, 40, 50, and 300 K applying a magnetic field ranging from -50 to 50 kOe are shown in Fig. 2. The temperature dependence of the magnetic moment of the samples applying magnetic field of 50 Oe is also shown in Fig. 3(a). As can be seen in the figure, some kind of magnetic transition can be observed around 30 K. According to the inverse susceptibility ($1/\chi$) versus temperature plot that is shown in Fig. 3(b), the plots form a straight line above 50 K suggesting that the

FIG. 2. Magnetic hysteresis curves at 8, 20, 30, 40, 50, 300 K for $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$ sintered sample.

FIG. 3. (a) Temperature dependence of the magnetization for the $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$ sintered sample at 50 Oe. (b) $1/\chi$ versus T plots for the $\text{Ba}(\text{Co}_{0.85}\text{Mn}_{0.15})\text{O}_{3-\delta}$ sintered sample.

Curie-Weiss law dominates. In addition, the magnetization loop measured at 300 K is found to show apparently paramagnetic behavior. Whereas below 30 K, the remanent magnetization as well as the coercive force are observed suggesting that the sample has ferromagnetic spin ordering, although the paramagnetic portion still exist in these temperature regions. The values of the remanent magnetization and the coercive force at 8 K are $0.42 \mu_B/\text{f.u.}$ and 6.4 kOe , respectively. Consequently, some kind of ferromagnetic-paramagnetic transition occurred at around 30–50 K. We also accurately determine the magnetic transition temperature to be 32 K by Arrott plot of the magnetization data below 50 K. Here, it should be noted that the drastic change in the resistivity occurs at almost same temperature, which is clearly described in Ref. 6.

To investigate the ferromagnetic origin of the BCMO samples, we performed the XPS analysis using synchrotron soft-X-ray radiation of $h\nu = 3100 \text{ eV}$ to investigate the valence state of the B site transition metal ions. Figure 4 shows the $\text{Mn}2p$ core level spectra of the samples. Comparing the observed value of the peak shift with the reliable database, the Mn ions are speculated to exist as tetravalent state in the present samples. Unfortunately, the peak shift of the Co ions

FIG. 4. $\text{Mn}2p$ core level XPS spectra using synchrotron soft-x-ray radiation of $h\nu = 3100 \text{ eV}$.

could not be measured due to the overlapping of the Co2*p* and Ba3*d* core level spectra.

In the present BCMO samples, the ferromagnetic ordering could be observed at low temperature region. Since at that temperature region the sample is fairly good insulator, the possible ferromagnetic origin of the BCMO samples should be super-exchange interaction. Hereafter, the possible ferromagnetic origin of the present BCMO samples is considered to be ferromagnetic super-exchange coupling of Co⁴⁺(*d*⁵)-O²⁻-Mn⁴⁺(*d*³) with bonding angle of 180° and/or Mn⁴⁺(*d*³)-O²⁻-Mn⁴⁺(*d*³) with bonding angle of 90°.

Next, we discuss about the momentum space distribution of spin density around the magnetic transition temperature. Figure 5(a) shows the temperature dependent of the MCPs of the BCMO samples measured at the maximum magnetic field of 25 kOe of the system. As can be seen in the figure, the MCP signals of the samples become smaller with increasing in the temperature, suggesting that the spin magnetic moment of the samples should significantly decrease. In addition, it is also known that the shapes of the MCPs indicate the spin-polarized electron momentum density distribution. Figure 5(b) shows the temperature dependence of the shapes of the MCPs normalized by the spin moment. Each MCP is found to be almost identical shape, regardless of the measured temperature. This result suggests that no change of the momentum space distribution of spin density between ferromagnetic state and paramagnetic state. In other words, this magnetic transition is revealed as that it is simply dominated by the thermal fluctuation, not by other physical reason such as spin state transition.

Here, the absolute values of spin magnetic moment at each temperature can be obtained by the integrating for the MCPs along *p_z*. The result of which is shown in Fig. 6. The magnetization values of the samples measured by SQUID are also inset in the figure. In contrast that the results of SQUID measurements reflect the magnetic moment from both spin and orbital contributions, the magnetic moments estimated from the MCPs correspond to the spin magnetic moment of the samples. As is clearly indicated in the figure, the curve from the MCPs is almost corresponding to that for the SQUID

FIG. 5. (a) The magnetic Compton profiles for the temperature of 8, 20, 30, 40, and 50 K. (b) Comparison of the shape of magnetic Compton profile for the Ba(Co_{0.85}Mn_{0.15})O_{3-δ} sintered sample respective temperature.

FIG. 6. The temperature dependence of the values of spin magnetic moment measured by MCP and the magnetization data measured by SQUID at 25 kOe.

measurement. This simply indicates that the spin magnetic moment mainly contributes to the ferromagnetism of the present BCMO sintered samples, not by the orbital magnetic moment.

IV. SUMMARY

The ferromagnetic to paramagnetic transition in the BCMO ceramic samples occurred at 32 K, and the saturation magnetization, residual magnetization, and coercive force at 8 K were determined to be about 0.42 $\mu_B/f.u.$ and 6.4 kOe, respectively. And the origin of the magnetic ordering of BCMO is expected to be super-exchange coupling of Co⁴⁺(*d*⁵)-O²⁻-Mn⁴⁺(*d*³) with bonding angle of 180° and/or Mn⁴⁺(*d*³)-O²⁻-Mn⁴⁺(*d*³) with bonding angle of 90°. The spin magnetic moment estimated by the MCPs mainly contributes to the ferromagnetism of the present BCMO sintered samples. Each MCP is found to have almost identical shape, regardless of the measured temperature. So, this magnetic transition is simply caused by thermal spin fluctuation.

ACKNOWLEDGMENTS

The MCP experiments were performed under the approval of SPring-8 proposal 2012A1175. The soft-x-ray XPS measurements were performed under the approval of KEK-PF proposal 2009G037 and 2011G638. Financial support from Grants-in-Aid for Scientific Research (C) #09016741 from Japan Society for the Promotion of Science is gratefully acknowledged.

¹C. Nan *et al.*, *J. Appl. Phys.* **103**, 031101 (2008).

²M. Fiebig *et al.*, *Nature (London)* **419**, 818 (2002).

³T. Kimura *et al.*, *Nature (London)* **426**, 55 (2003).

⁴K. Katsube *et al.*, *J. Appl. Phys.* **105**, 07D904 (2009).

⁵T. Inoue *et al.*, *Trans. Mat. Res. Soc. Jpn.* **31**(1), 193–196 (2006).

⁶T. Inoue *et al.*, *IEEE Trans. Magn.* **41**(10), 3496–3498 (2005).

⁷A. Koizumi *et al.*, *Phys. Rev. Lett.* **86**(24), 5589–5592 (2001).

⁸A. Koizumi *et al.*, *Phys. Rev. B* **69**, 060401(R) (2004).

⁹S. Mizusaki *et al.*, *Phys. Rev. B* **74**, 052401 (2006).

¹⁰B. L. Ahuja *et al.*, *Appl. Phys. Lett.* **99**, 062512 (2011).

¹¹S. Kosugi *et al.*, *J. Appl. Phys.* **109**, 07B737 (2011).

¹²V. A. Cherepanov *et al.*, *J. Solid State Chem.* **153**, 205–211 (2000).

¹³J. M. Gonzalez-Calbet *et al.*, *J. Solid State Chem.* **111**, 202–207 (1994).