Spin orientation in (Ti-Mn) Ba ferrite estimated from resonant X-ray magnetic scattering

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Abstract. Synchrotron radiation has been utilized for producing the intensity difference in resonant X-ray magnetic scattering (RXMS) of ferrimagnetic BaTiMnFe₁₀O₁₉ at the BL-6C beamline of the Photon Factory. The energy of incident X rays was selected as \( E = 7.1245 \) keV within the threshold region of Fe \( K \) absorption edge from the observation of X-ray magnetic circular dichroism (XMCD). An asymmetrical ratio between RXMS intensities in left- and right-handed circular polarizations makes it possible to determine the magnetic crystal structure. The residual functions of \( \sum (\Delta R_{\text{obs}} - \Delta R_{\text{calc}})^2 \) related to the ratio were used to evaluate magnetic moments for individual Fe sites in the least-squares calculations, refined as multiplicity parameters of atomic scattering factor. The canting angles of the spin of Fe atoms have been derived for BaTiMnFe₁₀O₁₉, which are 90°, 0° and 31° for octahedral 2\( a \), 4\( f_2 \) and 12\( k \) sites, respectively.

1. Introduction
Resonant X-ray magnetic scattering (RXMS) has attracted much interest as a useful tool to determine the magnetic structure even for a tiny single crystal. It is interpreted that RXMS has a merit to increase the Bragg intensity with the resonant enhancement between charge and magnetic scattering [1]. In the site-specific study, RXMS has great advantage to determine the magnetic occupancy for the multi-component system more than two kinds of targeted atoms. M-type BaTiMnFe₁₀O₁₉ is ferrimagnetic oxide with dielectric and magnetic properties to be useful for magnetic recording, microwave application and so on [2]. A hexagonal-ferrite structure contains five independent Fe sites, which are tetrahedral 4\( f_1 \), bipyramidal 2\( h \), and octahedral 2\( a, 4f_2 \) and 12\( k \) sites. BaFe₁₀O₁₉ has the strong uniaxial anisotropy in magnetization along \( c \) axis, while the substitution of two Fe\(^{3+} \) by Ti\(^{4+} \)Mn\(^{2+} \) results in a weakening of the magnetic interactions. Therefore, the detailed justification requires to determine a ferrimagnetic structure with the canting of magnetic moments by the RXMS study. In the use of neutron diffraction technique, various approaches have been reported on comparison between magnetic anisotropy and magnetic structure for substituted Ba ferrites [3-6].

In this study, the spin orientation for Fe sites of BaTiMnFe₁₀O₁₉ is determined by X-ray magnetic circular dichroism (XMCD) and RXMS methods with the help of site-occupancy refinements. We aim at the complete analysis of magnetic crystal structure with a sufficient number of Bragg reflections.

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2. Experimental

2.1. Synchrotron experiments
RXMS and XMCD experiments were performed at BL-6C of Photon Factory. The phase retarder of a diamond (001) was set near the 111 Bragg condition in the asymmetrical Laue case and produced circularly polarized X-rays. Incident X-rays switched between right-handed (helicity: +1) and left-handed (helicity: -1) polarizations were used for RXMS and XMCD experiments. A Rigaku AFC5 four-circle diffractometer was used in the horizontal geometry of scattering plane with circular polarization. Site-occupancy experiments were performed by using a vertical-type four-circle diffractometer at BL-10A. Conventional intensity measurements were made using a Rigaku AFC7 four-circle diffractometer with a graphite (002) monochromator for Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å).

$\text{BaTiMnFe}_{10}\text{O}_{19}$ has M-type hexaferrite structure with the space group $P6_3/mmc$ (no. 194) and cell dimensions of $a = 5.9010(3)$ and $c = 23.209(2)$ Å. A crystal of $0.20 \times 0.15 \times 0.05$ mm$^3$ was mounted on short glass fiber on a rare-earth magnet in a magnetic field of 0.14 T on a goniometer head. Intensity measurements of RXMS were made by an $\omega-2\theta$ scan technique at a wavelength of $\lambda = 1.7402$ Å ($E = 7.1245$ keV) of the Fe $K\alpha$ edge. The measurements for Bragg reflections were repeatedly scanned at a scan speed of 0.5 °/min in a width of 1.0° in $\omega$. In total, 263 reflections were measured up to $\sin \theta/\lambda = 0.4$ within a range of $0 \leq h_1, h_2 \leq 5$ and $0 \leq l \leq 20$. Standard reflections were used for the correction. Lorentz and polarization and absorption effects were corrected before crystal-structure analyses.

2.2. Magnetic satellite reflections of Tb
A preliminary diffraction experiment for Tb has been made around the 002 reflection in order to observe the magnetic satellite reflections and support the RXMS system. The photon energy of $E = 7.5180$ keV, which corresponds to the $2p$ to $5d$ transition, was tuned to be 2.9 eV higher than an inflection point of Tb metal at $L_{III}$ edge. Terbium has a hexagonal close-packed structure with space group $P6_3/mmc$ (no. 194) and cell dimensions of $a = 3.6010(3)$ and $c = 5.6936(2)$ Å [7]. A paramagnetic phase transforms to an antiferromagnetic phase at $T_N = 230$ K and to a ferromagnetic one at $T_C = 215$ K. The 002±$\tau$ magnetic satellite reflections of Tb was observed at a temperature of $T = 220$ K (Fig. 1), having the RXMS intensity from Tb in the spiral phase [8].

Figure 1. The 002±$\tau$ magnetic satellite reflections of Tb.

2.3. XMCD of $\text{BaTi}_x\text{Mn}_x\text{Fe}_{12-2x}\text{O}_{19}$
XMCD reflects the spin and orbital polarization of the unoccupied states of an atom, which is given by an absorption difference between opposite circular polarizations with spin parallel direction. Namely, the spin-dependent absorption can be defined as $\Delta \mu/\mu$ with the thickness-free normalization, where $\Delta \mu$ and $\mu$ are spin-dependent and total absorption coefficients.

The absorption measurements were made in beam size of 1 × 1 mm$^2$ at the Fe $K\alpha$ edge with two
ionization chambers filled with N$_2$ (monitor) and 85% N$_2$ + 15% Ar gas. The external magnetic field was 0.4 T through a pair of rare-earth magnets in the Faraday configuration. A thickness of samples was adjusted for the suitable absorption. A negative peak of XMCD signal at the threshold region ($E = 7.1245$ keV) was used in this study, which is due to Fe$^{3+}$ origin in octahedral sites (Fig. 2).

3. Results and discussion
The spin orientation can be estimated on an asymmetrical ratio described in Eq.(1):

$$AR = \frac{Y_+ - Y_-}{Y_+ + Y_-} = \frac{-4 \cos 2\theta (1 - \cos 2\theta)}{1 + \cos^2 2\theta} \times \frac{(F_0' + F_0)F'' - F'F'' - F''F_0'}{|F^2|_{\text{charge}}},$$  \hspace{1cm} (1)

where $Y_+$ and $Y_-$ are the scattering intensities for left- and right-handed circular polarizations and $F_0', F_0'', F', F'', F''', F'''_0$ and $F''''_0$ are structure factors on the Thomson, magnetic, real and imaginary parts of anomalous and resonant magnetic scattering, respectively. A resonant magnetic scattering factor previously reported was used in this study, which is $f''' = 0.23$ at $E = 7.1282$ keV [9]. The observed and calculated ratios $\Delta R_{\text{obs}}$ and $\Delta R_{\text{calc}}$ were obtained from intensity difference of RXMS measurements and from crystal-structure calculations with resonant magnetic scattering factors, respectively. Finally, the residual functions of $\Sigma (\Delta R_{\text{obs}} - \Delta R_{\text{calc}})^2$ were used to evaluate magnetic moments for individual sites, refined as a multiplicity parameter for atomic scattering factor in the least-squares calculations. The multiplicity for each Fe site can be related to an inclination or canting of magnetic moment of Fe.

Since the canting depends on the site-preference of Ti and Mn, the site occupancy of BaTiMnFe$_{10}$O$_{19}$ was first determined for five Fe sites by the combination studies of conventional X-ray diffraction (Mo K$_\alpha$ radiation) and anomalous scattering at the Fe K edge ($\lambda = 1.7485$ Å). The percentage of Ti$^{4+}$Mn in the total of individual Fe sites are 0, 0, 42, 0 and 19% for 2$a$, 2$b$, 4$f_1$, 4$f_2$ and 12$k$ sites, respectively, suggesting that Ti and Mn prefers either 4$f_1$ or 12$k$ sites [10].

Based on Eq.(1), the degree of the spin canting of BaTiMnFe$_{10}$O$_{19}$ was determined by using the RXMS intensities measured at $E = 7.1245$ keV, which is the energy at the threshold of the absorption edge and interpreted as Fe$^{3+}$ origin in six-coordinated Fe octahedron [11]. There is a minimum in each plot of site-multiplicity and residual function for octahedral 2$a$, 4$f_2$ and 12$k$ sites (Fig. 3), which are considered to be observable with the X-ray energy so far examined. The sharp opening of a parabola on 4$f_2$ or 12$k$ sites gives the good convergence in the calculations. The values of site-multiplicity determined for 2$a$, 4$f_2$ and 12$k$ sites are 0.0, 1.0 and 0.86, resulting canting angles of 90°, 0° and 31°, respectively, where up and down spins correspond to 0° and 180°, respectively.

The magnetic structure obtained in this study has been compared with M-type BaFe$_{12}$O$_{19}$ and BaTiCoFe$_{10}$O$_{19}$. The former is known with a Gorter model [12], where spin orientations of 0°, 0°, 180°, 180° and 0° for 2$a$, 2$b$, 4$f_1$, 4$f_2$ and 12$k$ Fe sites, confirmed by the neutron diffraction study [3].

![Figure 2. XMCD spectra of BaTiMnFe$_{12-2x}$O$_{19}$ at Fe K edge.](image-url)
The spin orientations for BaTiCoFe$_{10}$O$_{19}$ were reported on the neutron [5] and XRMS studies [13], where spin orientations for 2$a$, 4$f_2$ and 12$k$ sites are 60°, 135° and 75° from neutron work and 118°, 180° and 65° from RXMS study, respectively. The magnitudes of canting angles are different especially in 4$f_2$ site, where the spin orientation of BaTiMnFe$_{10}$O$_{19}$ is opposite to the others. Two adjacent 4$f_2$ sites share the O-O edge and form double octahedra. Ti and Mn atoms of BaTiMnFe$_{10}$O$_{19}$ do not occupy the 4$f_2$ site, while Ti and Co of BaTiCoFe$_{10}$O$_{19}$ prefer the site. The magnetic structure is surely affected by the substitution of the transition-metal ions, because the scheme of site occupancy is totally different among the three compounds. Since the analysis of M-type Ba ferrite is expected to be complex due to mixed contribution of five Fe sites, the structural modifications with the opening angle of magnetic helices would help to identify the source of the magnetic anisotropy change.

4. Conclusion
The magnetic helices of Fe atoms have been derived to minimize the residuals $\sum(\Delta R_{\text{obs}} - \Delta R_{\text{calc}})^2$. The canting angles of BaTiMnFe$_{10}$O$_{19}$ are 90°, 0° and 31° for 2$a$, 4$f_2$ and 12$k$ sites, respectively.

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