Hyperfine Interact
DOI 10.1007/s10751-011-0486-2

Mössbauer study on Y-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$

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Abstract Mössbauer study on a Y-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$ has been conducted by using a single crystal specimen. The spins are in the *c*-plane down to 60 K. For $18h_{VI}$ site Fe, the quadrupole shifts and the outermost line width change around 195 K, where the transition from ferrimagnetic to proper screw spin structure takes place. Below 50 K, the spin reorientation transition to a longitudinal conical structure was also recognized. At 16 K, the spins incline about 15° from the *c*-plane.

Keywords Y-type hexaferrite · $Ba_2Mg_2Fe_{12}O_{22}$ · Magnetic transition · ^{57}Fe Mössbauer spectroscopy · Quadrupole shift

1 Introduction

A Y-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$ has a hexagonal structure ($R\bar{3}m$) with the lattice constants of $a = 5.880$Å and $c = 43.515$Å at room temperature. The Fe^{3+} ions and Mg^{2+} ions equally occupy six crystallographic sites: two tetrahedral sites ($6c_{IV}$ and $6c^*_{IV}$) and four octahedral sites ($3a_{VI}$, $3b_{VI}$, $6c_{VI}$, and $18h_{VI}$) [1, 2]. The material is a ferrimagnet with the Curie temperature of 553K. The Fe^{3+} spins are in the *c*-plane, i.e. along [1 $\bar{1}$ 0] direction. Below 195K, the spins form a proper screw structure with the propagation vector along the *c*-axis. The turn angle of the helix is about 70° at 9 K [2]. It was found recently that a spin reorientation transition to a

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Published online: 08 December 2011

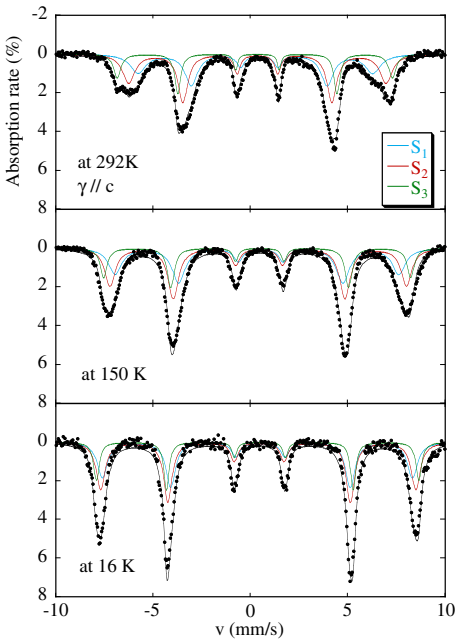

Fig. 1 Mössbauer Spectrum of single crystal $Ba_2Mg_2Fe_{12}O_{22}$ at 292, 150, and 16 K

longitudinal conical structure takes place below 50 K [3]. The spins incline about 10–20° from the *c*-plane. The magnetoelectric behavior, or multiferroic behavior, was also found, and thus the interests on this material have been revived. The Mössbauer spectroscopic studies on this material, however, have not been conducted so much [4, 5]. This is presumably because of its complex spectrum originated from the six crystallographic Fe sites. Moreover, in the ferrimagnetic region, Fe ions on $18h_{VI}$ site (site symmetry *.m*) decompose into three types, since there are three different electric field gradient (EFG) axes with respect to the spin direction $[1\,\bar{1}\,0]$. Here in this paper, we report the detailed Mössbauer spectrum of $Ba_2Mg_2Fe_{12}O_{22}$ by using a single crystal specimen.

2 Experiments

The single crystal of $Ba_2Mg_2Fe_{12}O_{22}$ was prepared by the flux method [1, 2]. The *c*-plane platelet with about 6 mm × 4 mm × 40 μm size was used as absorber. The ^{57}Fe Mössbauer spectroscopy was conducted in conventional transmission geometry by using ^{57}Co-in-Rh (25 mCi) as the γ ray source. The incident γ ray direction was parallel to the *c*-axis. Doppler velocity scale was calibrated with respect to Fe-metal. Lorentzian line shapes were assumed for the spectrum analysis.

3 Results and discussions

The paramagnetic spectrum at 583 K apparently consists of an asymmetric broad doublet. At this point we cannot analyze as a superposition of the sex doublets, but

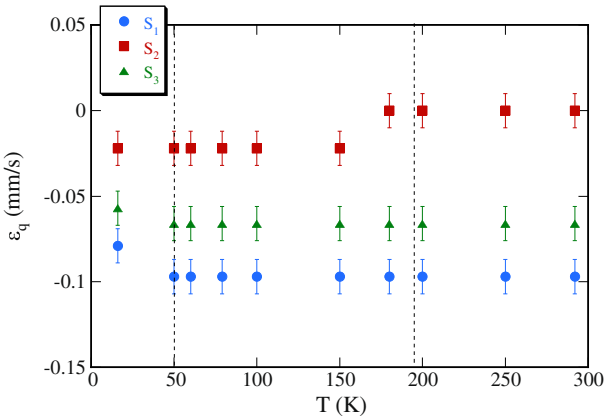

Fig. 2 Temperature dependence of the quadrupole shift (ε_q) for the three subspectra

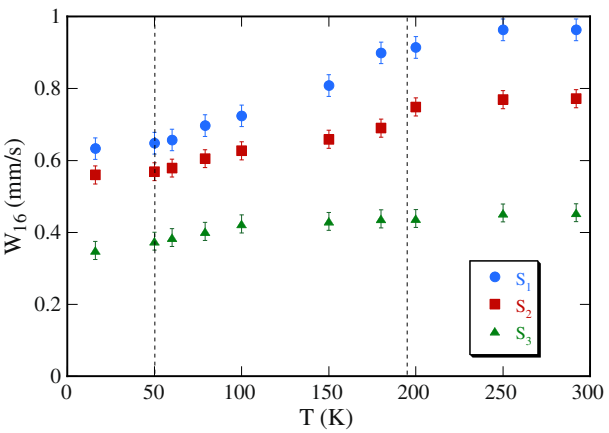

Fig. 3 Temperature dependence of the outermost line width (W_{16}) for the three subspectra

we tentatively obtain the average quadrupole splitting (QS) of about 0.43 mm/s. In Fig. 1, the magnetically ordered spectrum at 292, 150, and 16 K are shown. Considering the strength of magnetic interaction (or magnitude of hyperfine field) [2, 4, 5] and the site symmetry, we classified the six types of Fe^{3+} into three groups: from the inner one, termed S_1 ($6c_{IV}$, $6c_{VI}$, $3b_{VI}$), S_2 ($18h_{VI}$), and S_3 ($6c^*_{IV}$, $3a_{VI}$) for convenience. The intensity ratio should be S_1:S_2:S_3 = 1.67:2:1. The absorption line intensity ratios are 3:4:1:1:4:3 above 60 K, which indicates that the spins are in the c-plane. The isomer shifts (IS) are 0.36, 0.36, and 0.29 mm/s for S_1, S_2, and S_3, respectively, indicating that all Fe ions are in 3+ state. The hyperfine fields (H_{hf}) are 374.5, 410.5, and 439.1 kOe, respectively. The quadrupole shifts (ε_q) are −0.10, 0.00, and −0.07 mm/s, respectively. For S_1 and S_3, where all the constituent sites have three-fold axial symmetry, the principal axis of EFG (z-axis) is in the c-direction and thus approximately $-4\varepsilon_q = e^2qQ/2 = QS$. The observed ε_q values for S_1 and S_3 seem to be in accordance with this relation. On the other hand for S_2, it is not valid, because the constituent $18h_{VI}$ site does not have any axial symmetry. In the ferrimagnetic region, S_2 is actually composed of three subspectra having different ε_q's, which apparently results in $\varepsilon_q = 0.00$ in the analysis. At 16 K, IS 's are 0.44,

0.42, and 0.43 mm/s for S_1, S_2, and S_3, respectively, and H_{hf}'s are 494.8, 503.0, and 514.5 kOe, respectively. The intensities of 2–5 lines decrease below 50 K. The line intensity ratio is about 3:3.5:1:1:3.5:3 at 16 K, which indicates that the spins are no longer in the *c*-plane but incline about 15° from the *c*-plane. This corresponds well to the longitudinal conical spin structure below 50K.

In Fig. 2, the temperature dependences of ε_q are shown. That of S_2 changes from 0.00 to −0.022 mm/s below 195K. At the same time the outermost line width W_{16} (FWHM) of S_2 becomes sharper as shown in Fig. 3. These features can be explained by calculating ε_q of $18h_{VI}$ by using the crystal structure parameters [1]. The three *z*-axes (calculated) are directed about ±10° from the *c*-plane. Above 195K, the angles between the *z*-axes and $[1\,\bar{1}\,0]$ give three ε_q^{cal} of 0.189, −0.026, and −0.082mm/s. The average of the three is 0.027mm/s. Since the moment rotates in the *c*-plane below 195K, the angular factors are averaged, which gives unique ε_q^{cal} of −0.012mm/s. Although the values are slightly different from the analyzed ones, its changing nature through 195K is consistent. On the other hand for S_1 and S_3, no changes in ε_q occur around 195K, since the spins are still in the *c*-plane. Below 50K, the magnitudes of ε_q for these two decrease, which correspond to the longitudinal conical spin structure. From the angular factor, we can estimate that the spins of S_1 and S_3 incline about 14° and 12°, respectively, from the *c*-plane. The values are in good agreement with that estimated by the 2–5 line intensity.

References

1. Momozawa, N., Yamaguchi, Y., Mita, M.: J. Phys. Soc. Jpn. **55**, 1350 (1986)
2. Momozawa, N., Nagano, Y., Utsumi, S., Abe, M., Yamaguchi, Y.: J. Phys. Soc. Jpn. **70**, 2724 (2001)
3. Ishiwata, S., Taguchi, Y., Murakawa, H., Onose, Y., Tokura, Y.: Science **319**, 1643 (2008)
4. Albanese, G., Carbucicchio, M., Deriu, A., Asti, G., Rinaldi, S.: Appl. Phys. **7**, 227 (1975)
5. Deriu, A., Licci, F., Rinaldi, S., Besagni, T.: J. Magn. Magn. Mater. **22**, 257 (1981)