



Mössbauer and magnetic properties of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$

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Received: 9 July 2021 / Revised: 22 July 2021 / Accepted: 2 August 2021 / Published online: 25 August 2021
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Abstract

We have studied the crystal structure and magnetic properties of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ using X-ray diffraction (XRD), a vibrating sample magnetometer (VSM) and a Mössbauer spectrometer. We analyzed the XRD patterns to apply FullProf Rietveld refinement. From the XRD analysis, we found the crystal structure of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ is hexagonal(R-3m). The temperature-dependent magnetic properties of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ were measured by a VSM. The hysteresis loops were measured at several temperatures. From the zero-field-cooled–field-cooled (ZFC–FC) experiment, the spin re-orientation temperature (T_s) of this sample was 209 K. In the results of the Mössbauer spectrometer experiment from 4.2 to 295 K, the magnetic hyperfine fields (H_{hf}) decreased with respect to increase in temperature. The isomer shift values were between 0.1 and 0.4 mm/s, and represented the ion states of the sample, which were the balanced Fe^{3+} state at all temperatures. H_{hf} and quadrupole splitting values showed abrupt change at 209 K, we deduced that this is occurred because of spin re-orientation.

Keywords Hexaferrite · Mössbauer spectroscopy · Magnetic properties

1 Introduction

Hexaferrite is a multiferroic material that is classified into M, U, W, Y, X and Z according to the chemical formula. Among them, the Y-type hexaferrite has the chemical structure of $(\text{Ba}, \text{Sr})_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ (Me = a bivalent transition metal) [1, 2]. The Y-type hexaferrite has attracted considerable attention owing to its great magnetic properties. Recently, studies on the reavlation of its magnetoelectric (ME) effect at room temperature are being done actively. In previous work, a study result on the ME effect expressed at room temperature were presented. [3, 4]. Some of Y-type hexaferrite ($\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$, $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Ni}_2(\text{Fe}_{0.97}\text{Al}_{0.03})_{12}\text{O}_{22}$) samples were reported to exhibit the ME effect at room temperature [5, 6]. These reports have led to research on substitution and doping for many elements, especially for transition metal. It is expected that the substitution and doping lead to various property changes. In the case of $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, the nonlinear ME effect was reported at microwave frequencies [7].

Additionally, a study on Mg doped $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ reported that the Mg doped Y-type hexaferrite has a helical spin structure at low temperature [14].

In this study, we synthesized the $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ by a solid state reaction method. We then evaluated the magnetic properties of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ using the VSM and Mössbauer spectrometer. The purpose of this study was to observe the change of the magnetic properties by doping Mg ions to $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$.

2 Experiments and discussion

$\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ was synthesized by solid-state reaction method. High-purity powders of BaCO_3 (99.98%), CoO (99.99%), MgO (99.999%), Fe_2O_3 (99%) were used as the starting materials of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$. This sample was finely ground in agate mortar for 1 h to create a mixture. And then this mixture was calcinated at 1000 °C. After grinding this sample again for 1 h, it was palletized into a cylindrical shape. The palletized sample was sintered at 1100 °C for 10 h in air. To remove BaFe_2O_4 , frequently generated secondary phase of barium hexaferrite, we carried out final sintering at 1150 °C for 10 h in air. The crystal structure was measured by XRD with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The XRD results were analyzed by Rietveld refinement with

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FullProf. The magnetic properties of the sample were measured by VSM. We measured the M – H hysteresis loop at several temperatures as well as M – T curves (ZFC–FC) from 4.2 to 295 K. To obtain the Mössbauer spectra using Mössbauer spectroscopies with a moving ^{57}Co source, we performed Mössbauer experiments from 4.2 to 295 K.

By analyzing the XRD data, we found that the crystal structure of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ was hexagonal and it belonged to the $R\text{-}3\text{m}$ group as shown in Fig. 1. The lattice constants were obtained $a_0 = 5.864 \text{ \AA}$ and $c_0 = 43.531 \text{ \AA}$. This is smaller than $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$ but the ratio between c_0 and a_0 (c_0/a_0) is remained 7.423 [8]. These decreases were caused by the ionic radius of Mg^{2+} (0.72 \AA) being smaller than that of Co^{2+} (0.745 \AA).

We measured the M – H hysteresis loops at several temperatures as shown in Fig. 2. The coercivity (H_c) of the sample decreased with respect to increasing the temperature. This is because the magnetic planar anisotropy was decreased [13]. We measured the temperature dependence of magnetization (ZFC–FC) by VSM. This was measured under external magnetic field (100 Oe) from 4.2 to 295 K. Figure 3 shows the result of the ZFC–FC measurement. The ZFC curve (red curve) rose to 209 K with respect to the temperature and had the biggest magnetization at 209 K. After 209 K, it slowly decreases up to 295 K owing to the spin re-orientation. Under 209 K, the spin structure is helical, and becomes a collinear ferrimagnetic after 209 K [9]. Referring to the T_s of $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$ of 215 K [10] and $\text{Ba}_2\text{Co}_{1.5}\text{Mg}_{0.5}\text{Fe}_{12}\text{O}_{22}$ at 203 K [11, 12], we decided that the T_s of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ is 209 K. From these results, it can be observed that T_s decreases as the doped Mg increases. The reason of this decrease was predicted that Mg ions substitution at Co ions induced the decrease of the magnetic anisotropy [15]. In general, as the magnetic anisotropy decreases, the energy is required to change the spin structure. This is because the tendency

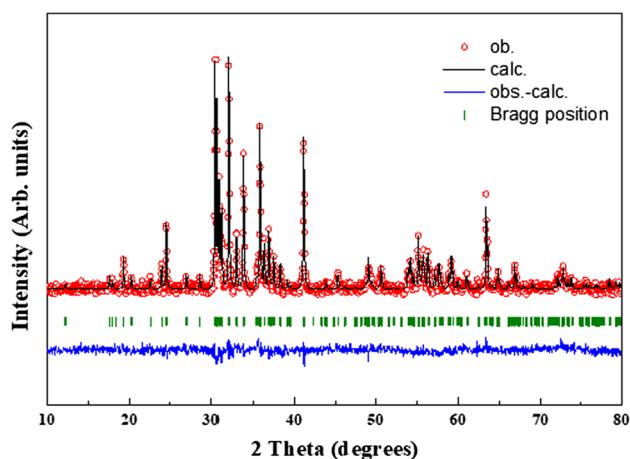


Fig. 1 XRD patterns of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$

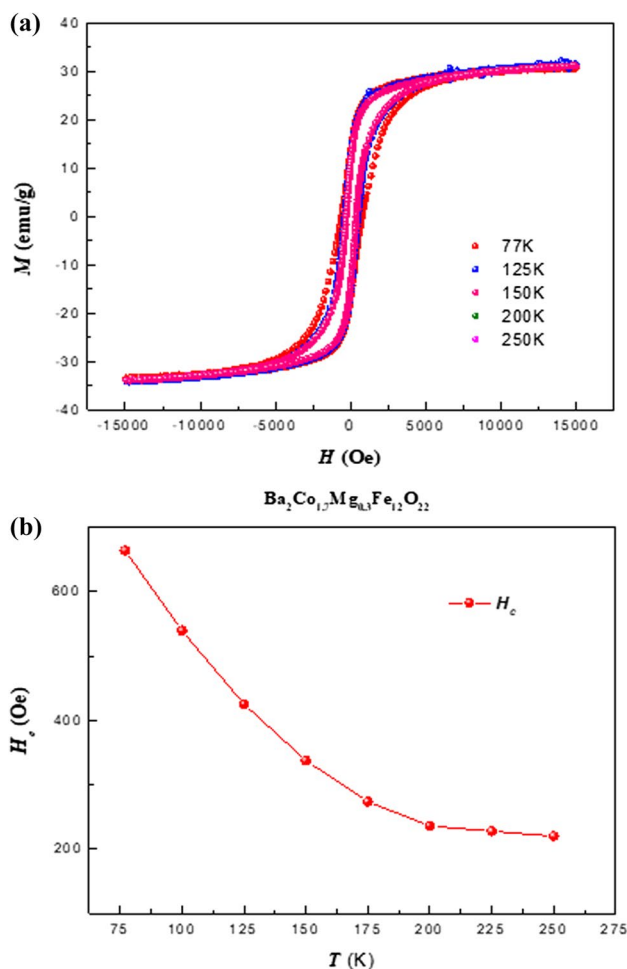


Fig. 2 **a** Temperature dependence hysteresis loops and **b** H_c – T graph for $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$

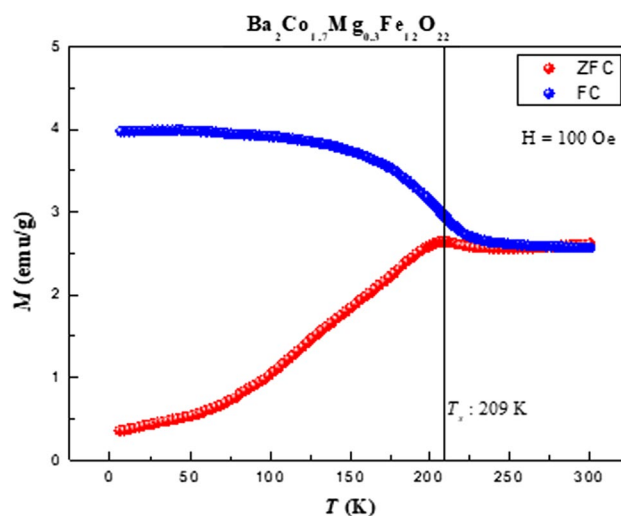
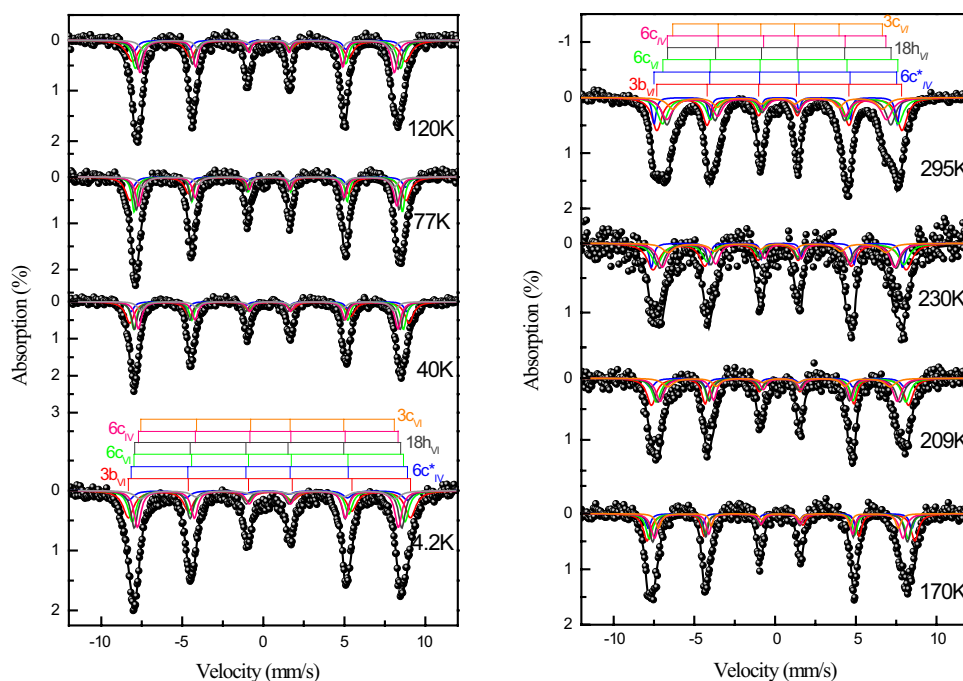


Fig. 3 Zero-field-cooled – field-cooled (ZFC–FC) curve $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$

Fig. 4 Mössbauer spectra of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ from 4.2 to 295 K



of the spin to align in one direction decreases. Therefore, spin re-orientation occurs at a lower temperature.

Figure 4 shows the Mössbauer spectra from 4.2 to 295 K. We fitted these spectra using the least squares method with six Lorentzian sextets of Fe sites ($3b_{VI}$, $6c_{IV}^*$, $6c_{VI}$, $18h_{VI}$, $6c_{IV}$, and $3a_{VI}$). The parameters of Mössbauer are listed in Table 1. Figure 5 shows that H_{hf} sites decreased with respect to increase in temperature because the super exchange interaction of the linkage of the $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ was getting weak [12]. For all the 209 K, the H_{hf} curves exhibited a change in the slopes; this is because the spin re-orientation occurred at 209 K. For all temperature values and Fe sites, the isomer shift (δ) values were maintained between 0.1 and 0.4 mm/s. We confirmed that the ion states of Fe were in the balanced Fe^{3+} state. We represent the quadrupole splitting values for 4.2–295 K in Fig. 6. Below 209 K temperature, although the temperature was changed, the quadrupole splitting values were stable. However, abrupt changes occurred through the 209 K. The quadrupole splitting is a value that changes with the gradient of the magnetic field; this abrupt change can be explained by the change in the structure of the magnetic hyperfine field. In general, the Y-type hexaferrite under the T_s has the helical spin structure. After T_s , the structure changes to a collinear ferrimagnetic spin structure. The

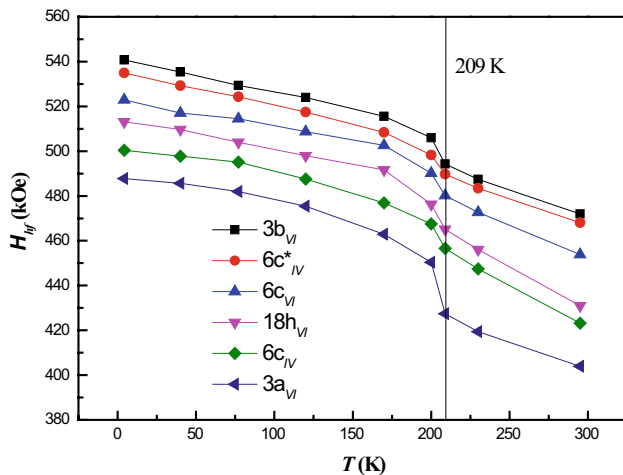
helical and collinear ferrimagnetic spin structure created different magnetic structure. Therefore, through the spin re-orientation temperature, the quadrupole splitting graph showed abrupt changes and we confirmed that the T_s is 209 K.

3 Conclusion

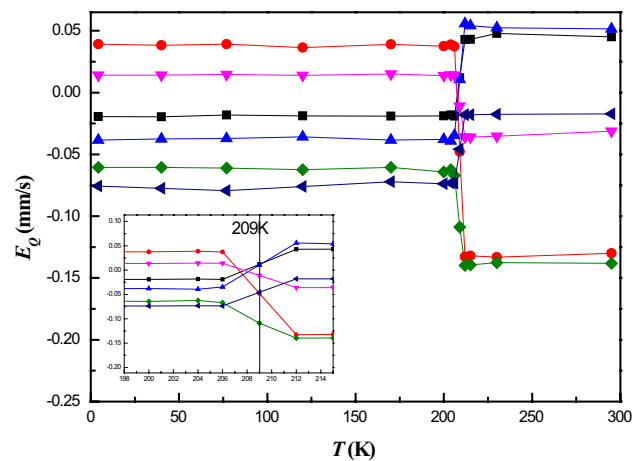
In conclusion, we studied $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ using a XRD, a VSM and a Mössbauer spectrometer. We defined the crystal structure of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ as hexagonal through the XRD analysis. By measuring the zero-field-cooled and field-cooled from 4.2 to 295 K, we determined that the T_s is 209 K. The spin structure changed from helical magnetic to collinear ferrimagnetic at T_s . Using the Mössbauer spectrometer, we evaluated the temperature dependence of the magnetic hyperfine field, the isomer shift and the electric quadrupole splitting. The magnetic hyperfine fields decreased as the temperature increased because the super exchange interactions between Fe^{3+} and O^{2-} ions weakened. The isomer shift values were maintained between 0.1 and 0.4 mm/s, and the Fe ions in $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ existed in the balanced Fe^{3+} state. The electric quadrupole splitting

Table 1 Mössbauer parameters of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ from 4.2 to 295 K

T (K)		Site					
		$3b_{VI}$	$6c_{IV}^*$	$6c_{VI}$	$18h_{VI}$	$6c_{IV}$	$3a_{VI}$
4.2	H_{hf} (kOe)	541	535	523	513	500	488
	δ (mm/s)	0.39	0.24	0.36	0.28	0.34	0.33
	ΔE_Q (mm/s)	-0.019	0.039	-0.037	0.015	-0.061	-0.079
	Area (%)	23.31	7.58	20.0	20.28	20.86	7.97
77	H_{hf} (kOe)	529	524	515	504	495	482
	δ (mm/s)	0.31	0.32	0.35	0.26	0.34	0.40
	ΔE_Q (mm/s)	-0.018	0.039	-0.037	0.015	-0.061	-0.079
	Area (%)	24.19	7.98	18.99	19.61	20.07	9.16
120	H_{hf} (kOe)	523	517	509	498	488	475
	δ (mm/s)	0.37	0.30	0.33	0.28	0.30	0.31
	ΔE_Q (mm/s)	-0.019	0.039	-0.038	0.015	-0.061	-0.072
	Area (%)	23.41	7.57	19.5	20.8	19.86	8.85
209	H_{hf} (kOe)	494	490	480	465	457	427
	δ (mm/s)	0.29	0.22	0.36	0.25	0.33	0.29
	ΔE_Q (mm/s)	0.012	-0.048	0.011	-0.011	-0.011	-0.046
	Area (%)	24.2	7.43	19.65	20.39	19.22	9.11
230	H_{hf} (kOe)	487	483	472	456	447	419
	δ (mm/s)	0.23	0.25	0.30	0.22	0.35	0.14
	ΔE_Q (mm/s)	0.048	-0.133	0.052	-0.031	-0.14	-0.017
	Area (%)	25.82	8.58	18.81	19.39	18.62	8.78
295	H_{hf} (kOe)	473	469	453	430	423	403
	δ (mm/s)	0.22	0.13	0.27	0.25	0.25	0.17
	ΔE_Q	0.045	-0.130	0.052	-0.031	-0.138	-0.017
	Area (%)	24.65	8.03	19.68	19.48	48.75	9.41

**Fig. 5** Magnetic hyperfine field (H_{hf}) of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ from 4.2 to 295 K

values exhibited abrupt changes at 209 K; we deduced that this was caused by spin re-orientation.

**Fig. 6** Electric quadrupole splitting (ΔE_Q) of $\text{Ba}_2\text{Co}_{1.7}\text{Mg}_{0.3}\text{Fe}_{12}\text{O}_{22}$ from 4.2 to 295 K

Acknowledgements This work was supported by Mid-Career Researcher Program, through the National Research Foundation of Korea (NRF), with a grant funded by the Ministry of Education, Science and Technology (MEST) (NRF-2017R1A2B2012241).

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