ISSN (Print) 1226-1750
ISSN (Online) 2233-6656
Journal of Magnetics 23(4), 644-647 (2018) https://doi.org/10.4283/JMAG.2018.23.4.644

Mössbauer Studies of $BaCoZnFe_{16}O_{27}$ W-type Hexaferrite

Jeonghun Kim, Jung Tae Lim, Hyunkyu Kim, and Chul Sung Kim*

Department of Physics, Kookmin University, Seoul 02707, Republic of Korea

(Received 9 July 2018, Received in final form 22 October 2018, Accepted 24 October 2018)

A polycrystalline $BaCoZnFe_{16}O_{27}$ sample was prepared by the solid-state reaction method and wet ball-milling. The refined X-ray diffraction patterns revealed that the prepared sample was hexagonal with the space group $P6_3/mm$. To determine the spin transition temperature (T_S), the temperature dependence of the zero-field-cooled magnetization curves were measured under applied fields of 100 to 1000 Oe at various temperatures ranging from 4.2 to 295 K. T_S is the temperature at which the spin changes from the planar to the conical direction at the 135 K. From the hysteresis curves at various temperatures ranging from 4.2 to 295 K, the coercivity showed a change in slope at T_S. Mössbauer spectra were obtained at various temperatures ranging from 4.2 to 295 K, and the magnetic hyperfine field and electric quadrupole splitting of the sample showed abrupt changes around T_S.

Keywords : W-type hexaferrite, Mössbauer spectroscopy, spin transition

1. Introduction

W-type hexaferrite with a unit formula of $BaMe_2Fe_{16}O_{27}$, where Me is divalent cations such as Ni, Mn, Co, Zn, and Cu, has a similar, but not identical, crystal structure to $BaFe_{12}O_{19}$ (M-type). W-type hexaferrite consists of spinel units (S-block) and hexagonal filled layers containing Ba atom (R-block), and its unit cell is composed of SSRS*S*R* [1-3]. In particular, W-type hexaferrites ($BaCo_2Fe_{16}O_{27}$, Co_2W) show high saturation magnetization and microwave absorption characteristics, because they have a large magnetic anisotropy. In addition, W-type hexaferrite has been studied for its magnetoelectric (ME) effect according to various complex spin states. The ME effect can affect permittivity, permeability, and ferromagnetic resonance, and it can be affected by magnetic anisotropy and a spin structure induced from hyperfine interaction according to site occupancy of metal ions [4]. Furthermore, it can be applied as an antenna and a microwave absorber because of the high ferromagnetic resonance frequency and the moderate permeability. For W-type hexaferrites containing Co^{2+} on divalent ionic sites, a spin transition phenomenon has been reported because the Co^{2+} ion at the octahedral site makes a strong planar contribution to the anisotropy [5, 6].

In this study, Co ions were substituted with nonmagnetic Zn ions. By substituting the Zn ion that prefer to occupy the tetrahedral site, the saturation magnetization could be increased [7]. $BaCoZnFe_{16}O_{27}$ was synthesized using the solid-state method, and its crystalline structure was investigated by X-ray diffraction (XRD) measurements. Furthermore, the $BaCoZnFe_{16}O_{27}$ sample was investigated using a vibrating sample magnetometer (VSM), Mössbauer spectrometer and network analyzer (NA) to characterize its static and dynamic magnetic properties.

2. Experimental Details

The $BaCoZnFe_{16}O_{27}$ W-type hexaferrite was synthesized by the solid-state reaction method. The starting materials were Fe_2O_3, $BaCo_3$, ZnO, and Co_3O_4. These materials were placed in a ball-mill jar with distilled water and zirconia balls, and ball-milled for 24 h with a dispersant (Sannopco 5468CF) at 0.3 wt.%. The mixture was dried and ground after the ball-milling process. The obtained powder was calcinated at 1000 °C for 3 h and sintered at 1275 °C for 3 h in air, where the heating rate was 4 °C/min.

©The Korean Magnetics Society. All rights reserved.
*Corresponding author: Tel: +82-2-910-5121
Fax: +82-2-910-4728, e-mail: cskim@kookmin.ac.kr

This paper was presented at the IcAUMS2018, Jeju, Korea, June 3-7, 2018.

The XRD measurements were performed with Cu $K\alpha$ radiation and analyzed by the Rietveld refinement method using the FULLPROF program. VSM was used to measure the magnetic properties. The magnetic hysteresis curves were measured by changing the temperature at the maximum applied field of 15 kOe, and the temperature dependence of the zero-field-cooled (ZFC) magnetization curves was measured by changing the magnetic field. The Mössbauer spectra were measured using a constant accelerated ^{57}Co source in a Rh matrix and a Mössbauer spectrometer. The microwave properties of the BaCoZn-$Fe_{16}O_{27}$ sample were characterized by an NA.

3. Results and Discussion

As shown in Fig. 1, the formation of a W-type hexaferrite $BaCoZnFe_{16}O_{27}$ structure was confirmed by XRD, and the XRD patterns were refined using the Rietveld refinement method. The red points are the experimental data, and the black line represents the calculated data. Below the black line, the bar and blue line are the Bragg position and error, respectively. The crystalline structure was confirmed to be hexagonal with space group $P6_3/mmc$ at room temperature. The lattice constants were a_0 = 5.907 and c_0 = 32.96 Å.

The ZFC curves at various temperatures ranging from 4.2 to 295 K are shown in Fig. 2. Measurements were made at various magnetic fields between 100 and 1000 Oe, and it was confirmed that the spin transition temperature (T_S) is 135 K under all applied magnetic fields. These results show that, even under a high magnetic field, T_S does not change. At an applied field of 1000 Oe, the magnetization decreases from T_S to 295 K, because the magnetization of $BaCoZnFe_{16}O_{27}$ W-type hexaferrite depends on the temperature [2, 8]. This is consistent with the H_{hf} shown in Fig. 6(a) analyzed in the Mössbauer spectra.

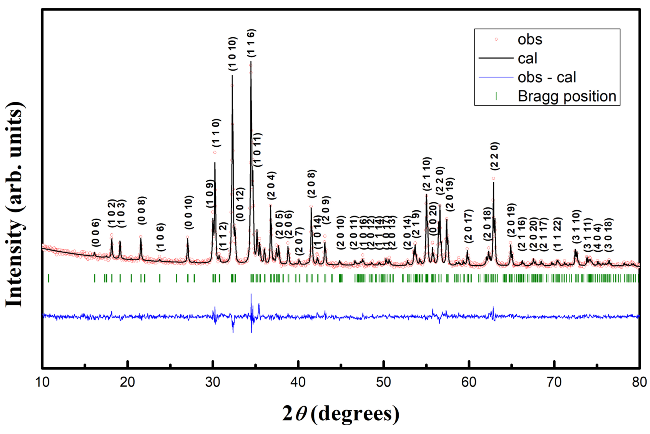

Fig. 1. (Color online) XRD patterns of $BaCoZnFe_{16}O_{27}$ at 295 K and analysis based on the Rietveld refinement method.

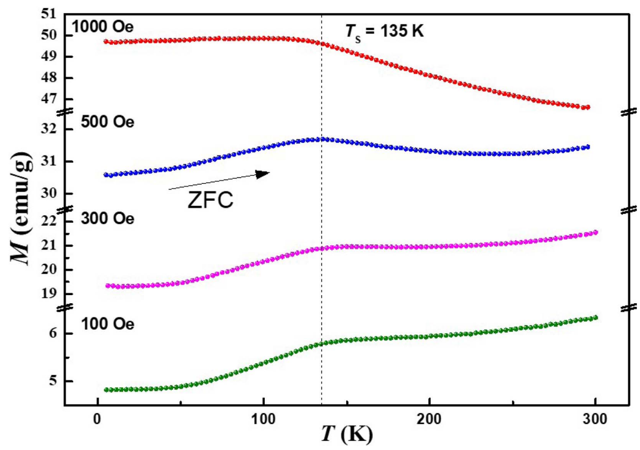

Fig. 2. (Color online) ZFC curves under applied fields of 100 to 1000 Oe for $BaCoZnFe_{16}O_{27}$.

Figure 3 shows the magnetic hysteresis curves at various temperatures in the range of 4.2 and 295 K. the curves were used to obtain a graph of the coercivity (H_C) dependence of the temperature, as shown in Fig. 4. The saturation magnetization (M_S) decreased with increasing temperature. The H_C graph shows a change in the slope at T_S. This is caused by the change in the spin structure from planar to conical.

The microscopic magnetic properties were obtained by Mössbauer spectroscopy. Fig. 5 shows the analysis of the Mössbauer spectra at various temperatures between 4.2 and 295 K. The W-type hexaferrite had seven crystallographic sites ($4f_{VI}$, $6g$, $4f$, $4e$, $4f_{IV}$, $12k$, and $2d$) with five magnetic sites ($4f_{VI}$, $6g + 4f$, $4e + 4f_{IV}$, $12k$, and $2d$), and all the spectra were analyzed by least-square fitting,

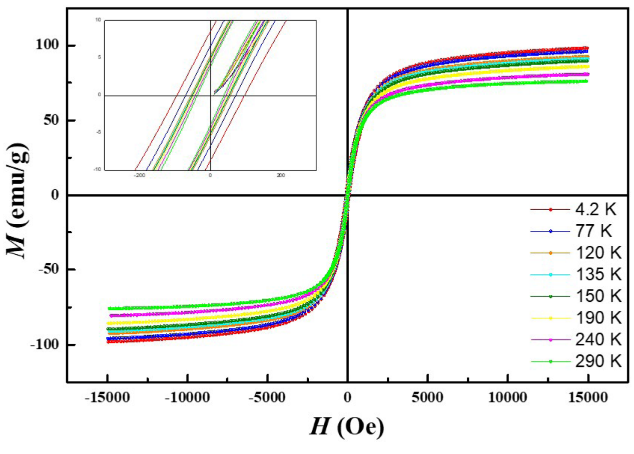

Fig. 3. (Color online) Magnetic hysteresis curves of BaCoZn-$Fe_{16}O_{27}$ obtained at as much as 15 kOe at various temperatures.

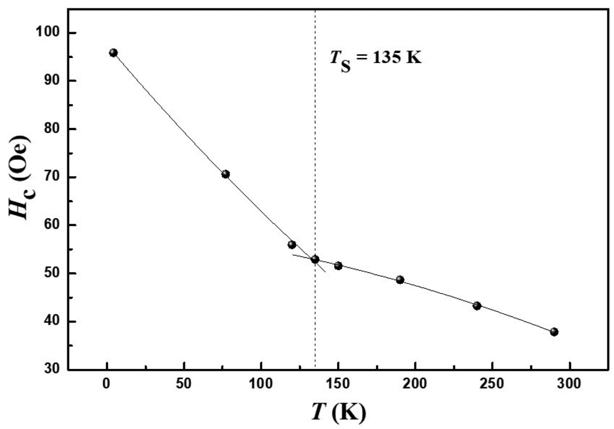

Fig. 4. (Color online) Temperature dependent coercivity of $BaCoZnFe_{16}O_{27}$.

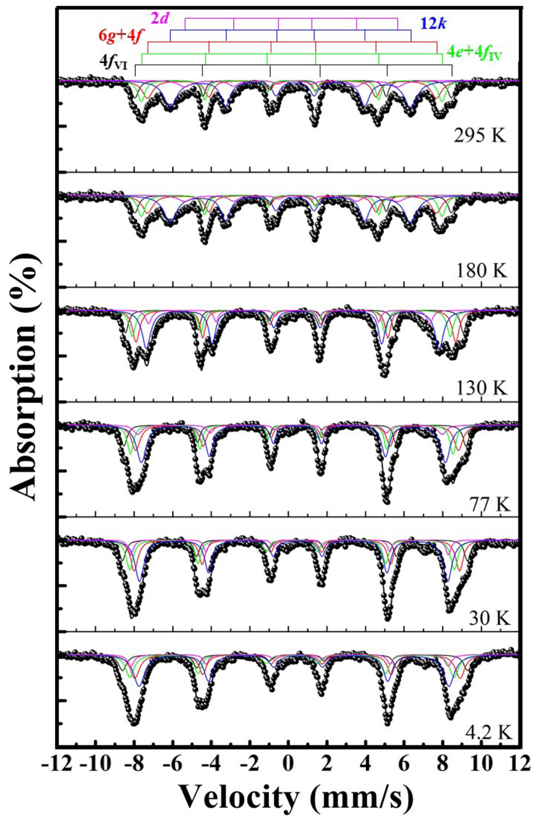

Fig. 5. (Color online) Mössbauer spectra of $BaCoZnFe_{16}O_{27}$ at various temperatures.

revealing five distinguishable sites corresponding to $4f_{VI}$, $6g + 4f$, $4e + 4f_{IV}$, $12k$, and $2d$ [9, 10]. The $4f_{VI}$ site had the largest H_{hf}, and the $12k$ and $2d$ sites decreased rapidly with increasing temperature. Changes were observed in the slopes of the magnetic hyperfine field (H_{hf}) and quadrupole splitting (ΔE_Q) at 135 K, as shown in Fig. 6. This behavior is consistent with the T_S value confirmed in the ZFC data. The value of H_{hf} decreased with increasing

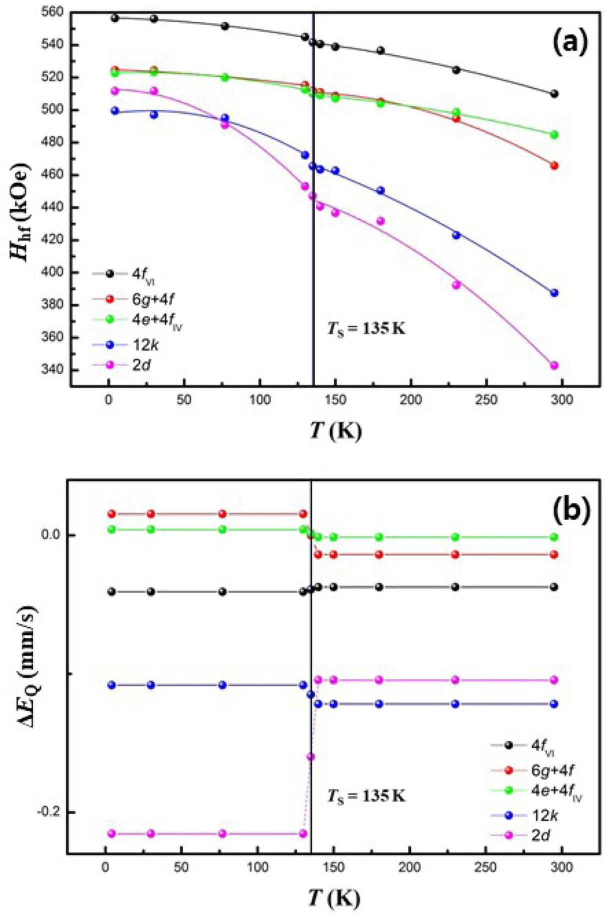

Fig. 6. (Color online) Temperature dependence of (a) magnetic hyperfine field and (b) quadrupole splitting for $BaCoZnFe_{16}O_{27}$.

temperature because of a reduction in the super exchange interaction [11]. This coincides with a decrease in M_S. The obtained value of the isomer shift (δ) confirmed that the Fe ion state was determined to be Fe^{3+} [12].

Figure 7 shows the permittivity (ε') and permeability (μ') spectra between 50 MHz and 4 GHz. The ε' was almost constant at 8 and the dielectric loss (tan δ_ε) was less than 0.05 for all measured frequency ranges. The μ' remained almost constant initially ($\mu' = 5.17$) and then decreased at 400 MHz. Further, the magnetic loss (tan δ_μ) increased gradually with increasing frequency. These results show that the maximum ε', μ', and tan δ_μ are higher than those of the reported La^{3+} doped CoZn–W hexaferrite [13].

4. Conclusions

The W-type hexaferrite $BaCoZnFe_{16}O_{27}$ was investigated using XRD measurements, VSM, and Mössbauer spectroscopy. The crystal structure was determined to be

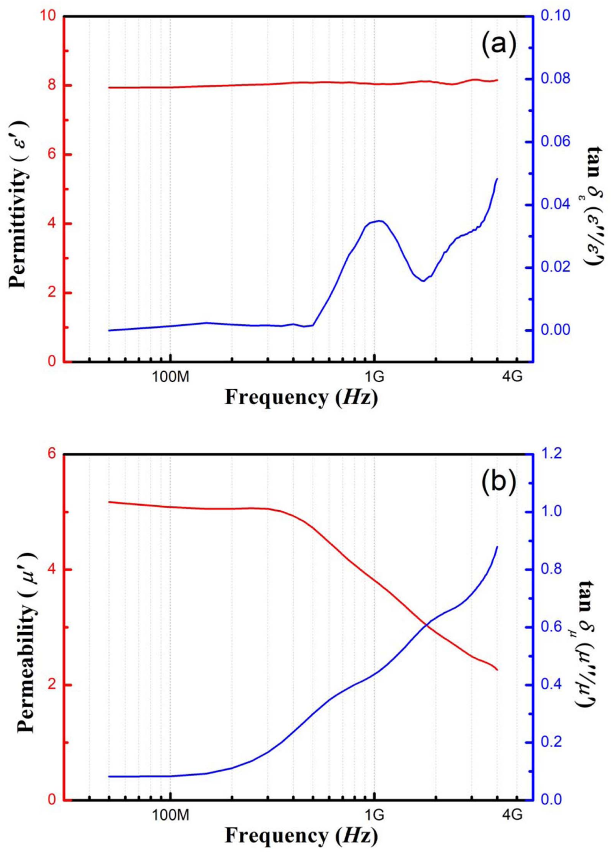

Fig. 7. (Color online) Frequency dependence of the (a) permittivity, dielectric loss, (b) permeability, and magnetic loss for $BaCoZnFe_{16}O_{27}$.

hexagonal with the space group $P6_3/mmc$. The ZFC curves were measured at magnetic fields in the range of 100 and 1000 Oe, and the T_S did not change. The hysteresis-curve-dependent temperature shows that the value of the saturation magnetization decreased with increasing temperature, and the value changed trend of the coercivity change at T_S. Furthermore, it was confirmed that the H_{hf} and ΔE_Q values obtained from the Mössbauer spectra yield a Ts that is consistent with the results of VSM. From the results obtained using the NA, the material could be a possible candidate for a microwave absorbing material because of the high tan δ_μ.

Acknowledgements

This work was supported by the 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).

References

[1] A. Hooda, S. Sanghi, A. Agarwal, and R. Dahiya, J. Magn. Magn. Mater. **349**, 121 (2014).
[2] H. Kim, B. U. Ko, I. Shim, B. W. Lee, and C. S. Kim, IEEE Trans. Magn. **51**, 2002603 (2015).
[3] R. C. Pullar, Prog. Mater. Sci. **57**, 1191 (2012).
[4] S. H. Chun, Y. S. Chai, B. G. Jeon, H. J. Kim, Y. S. Oh, I. Kim, H. Kim, B. J. Jeon, S. Y. Hamm, J. Y. Park, S. H. Lee, J. H. Chung, J. H. Park, and K. H. Kim, Phys. Rev. Lett. **108**, 177201 (2012).
[5] A. Collomb, D. Samaras, S. Hadjivasiliou, C. Achilleos, J. Tsoukalas, J. Pannetier, and J. Rodriguez, J. Appl. Phys. **64**, 5983 (1988).
[6] X. Z. Zhou, I. Horio, A. H. Morrish, Z. W. Li, and K. Hanawa, IEEE Trans. Magn. **27**, 4651 (1991).
[7] Y. Q. Song, Y. Fang, L. Y. Wang, W. P. Zhou, Q. Q. Cao, D. H. Wanga, and Y. W. Du, J. Appl. Phys. **115**, 093905 (2014).
[8] Z. W. Li, G. Q. Lin, N. L. Di, Z. H. Cheng, and C. K. Ong, Phys. Rev. B. **72**, 104420 (2005).
[9] J. T. Lim, I. Shim, E. J. Hahn, and C. S. Kim, AIP Adv. **7**, 056108 (2017).
[10] M. J. Iqbal, R. A. Khan, S. Mizukami, and T. Miyazaki, Ceram. Int. **38**. 4097 (2012).
[11] J. T. Lim, J. C. Sur, I. B. Sim, and C. S. Kim, J. Korean Phys. Soc. **70**, 81 (2017).
[12] J. T. Lim, S. J. Kim, J. C. Sur, and C. S. Kim, Sci. Adv. Mater. **10**, 686 (2018).
[13] L. W. Deng, L. Ding, K. S. Zhou, S. X. Huang, Z. W. Hu, and B. C. Yang, J. Magn. Magn. Mater. **323**, 1895 (2011).