Structure and magnetic properties of Co-Zn substituted hexagonal ferrites

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Abstract. In this study to understand the substitutional effect of Co-Zn on structural and magnetic properties of the $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ M-type hexagonal ferrites with concentration ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were synthesized by the ceramic method. The results of x-ray diffraction show polycrystalline with single phase. Scanning electron microscopy micrographs shows the hexagonal ferrites that are composed of small particles with large porosity, roughly of spherical shapes. The substitution of Fe^{3+} ion by Co^{2+} and Zn^{2+} has changed magnetic properties of hexagonal ferrites.

1 Introduction

The hexagonal ferrites as permanent magnets have been used for thousands of years [1] and play an important role in daily-life applications [2–6]. The development of magnetic materials with material derived from mineral minerals has been first described in 1925 and continues in 1938 the hexagonal crystal with the composition $\text{PbFe}_{7.5}\text{Mn}_{3.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$ [7]. A few years ago Philips Laboratories had developed ferrites ($\text{BaFe}_{12}\text{O}_{19}$) that is known by many names, including barium hexaferrite, barium ferrite, hexagonal ferrite, ferroxdure, Mferrite and BaM had a high electrical resistivity of $108 \Omega\text{cm}$ and the high magnetic uniaxial anisotropy along the c-axis. The compound hexagonal ferrite, $\text{BaFe}_{12}\text{O}_{19}$ with a melting point of 1390°C , a coercivity of $160\text{--}255 \text{ kA/m}$, magnetically hard, the maximum density is 5.295 g/cm^3 [8–12]. The effect of dopants on hexagonal ferrite has been largely done by researchers in order to enhance the properties of the magnet. Amitava Moitra et.al investigated aluminum-substituted M-type barium hexaferrite [13]. M-type hexagonal ferrites with $\text{BaCo}_x\text{Fe}_{12-x}\text{O}_{19}$ ($x = 2.0, 3.0$) composition had prepared by C. C. Chauhan et.al [14]. Al^{3+} and Cr^{3+} co-substituted barium hexaferrite $\text{BaCr}_x\text{Al}_x\text{Fe}_{12-2x}\text{O}_{19}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) nanoparticles had showed all the magnetic parameters saturation magnetization (M_s), remanence magnetization (M_r) and coercivity (H_c) decreases with increase of Al^{3+} and Cr^{3+} content x [15]. The substitution of Co^{2+} and Ti^{4+} ions in barium ferrite mainly lead to the replacement Fe^{3+} ions distributed in octahedral positions $12k$ and $4f_2$ and had decreased of the coercivity for $x = 0$ is clearly observed for the value 391 kA/m and drops down to 35 kA/m for $x = 1.2$ [16]. $\text{BaFe}_{10}\text{Al}_2\text{O}_{19}$ /poly (o-toluidine) (BFA/POT) composite [17], Co_2Z barium ferrite composite with the added

graphite powder [18], Fe^{3+} ion in barium hexaferrite were replaced by magnetic (Mn, Co, Ni and Cu), non-magnetic (Zn) and dielectric ions (Ti) [19] were prepared for microwave absorbing properties. This paper is to report a detailed microstructural and magnetic study of the $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ M-type hexagonal ferrites with concentration $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ using x-ray diffraction (XRD) and scanning electron microscope (SEM) for analyzing its structures, and permagraph techniques for magnetic properties.

2 Experimental procedure

Hexagonal ferrite, $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ M-type hexagonal ferrites ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were synthesized from stoichiometric mixtures of Fe_2O_3 , BaCO_3 , Co_3O_4 , ZnO and by the ceramic method. Samples were sintered at 1100°C for 3 h. The samples were characterized using Phillips x-ray diffraction (XRD) $\text{Co-K}\alpha$ with 40 kV and 30 mA and scanning electron microscopy FE-SEM FEI Inspect F50 for analyzing structures, hysteresis loops recorded by Permagraph techniques from magnet physik Dr. Steingroever GmbH with maximum external field of 1 tesla for magnetic properties.

3 Results and discussion

The hexagonal ferrites were characterized using x-ray diffraction (XRD) Phillips $\text{Co-K}\alpha$ with 2θ interval $30 - 60^\circ$ for analyzing the structure. Figure 1 shows XRD patterns of the $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ powder, with various compositions of x ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$). According to the reference pattern of international crystal diffraction data (ICDD) number #98-015-7056, the

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crystal structure of samples $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ are polycrystalline with single phase.

Fig.1. XRD pattern of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ hexagonal ferrites ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$).

Fig. 2. The lattice parameter of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ hexagonal ferrites ($x = 0.0; 0.2; 0.4; 0.6; 0.8; 1.0$).

This indicates that Co and Zn ions have been successfully substituted the Fe ions. As seen from the Fig. 1, we observed ten crystal orientations such as (008), (017), (114), (023), (025). In the crystal orientations (017) and (114), clearly observed that the peaks of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ decrease by Co-Zn incorporation. This should be attributed to the change of lattice parameter values from the standard of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ which refer to ICDD no. 98-015-7056. The changes in the lattice parameter can be caused Co-Zn substituted ions. Lattice parameter of all samples are shown in table 1.

Table 1. The lattice parameter and average crystallite size of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ hexagonal ferrites ($x = 0.0; 0.2; 0.4; 0.6; 0.8; 1.0$).

Composition $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$	Lattice parameter		
	A (Å)	b (Å)	c (Å)
$\text{BaFe}_{12}\text{O}_{19}$	5.896	5.896	23.322
$\text{BaFe}_{11.6}\text{Co}_{0.2}\text{Zn}_{0.2}\text{O}_{19}$	5.313	5.313	23.319
$\text{BaFe}_{11.2}\text{Co}_{0.4}\text{Zn}_{0.4}\text{O}_{19}$	5.535	5.535	23.494
$\text{BaFe}_{10.8}\text{Co}_{0.6}\text{Zn}_{0.6}\text{O}_{19}$	5.014	5.014	23.393
$\text{BaFe}_{10.4}\text{Co}_{0.8}\text{Zn}_{0.8}\text{O}_{19}$	5.659	5.659	23.492
$\text{BaFe}_{10}\text{CoZnO}_{19}$	5.597	5.597	23.399

Fig. 3. The SEM micrographs of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ hexagonal ferrites (a) $x = 0.2$ and (b) $x = 0.4$

Figure 3 shows the SEM micrographs of the hexagonal ferrites $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ ($x = 0.0; 0.2; 0.4; 0.6$) powders. The barium hexaferrite are composed of small particles with large porosity, roughly of spherical shapes, less than $2 \mu\text{m}$ after milling for 1 hour by using high energy ball mill. While the lattice parameters changes (table 1), according to the SEM micrographs (Fig.3) show no particle size change significantly that caused by substitution of Fe^{3+} ion by Co^{2+} and Zn^{2+} .

Figure 4 shows hysteresis loops in the second quadrant and the magnetic energy density $(\text{BH})_{\text{max}}$ of hexagonal ferrites that obtained from measurement using Permagraph techniques from magnet physik Dr. Steingroever GmbH with maximum external field of 1 tesla. The substitution of Fe^{3+} ion by Co^{2+} and Zn^{2+} has changed magnetic properties of hexagonal ferrites such as remanent magnetization (M_r), coercive force (H_c), the saturation magnetization (M_s) and magnetic energy density $(\text{BH})_{\text{max}}$. From tables two can observe M_s , M_r , H_c and $(\text{BH})_{\text{max}}$ values vary from 0.23 to 0.32 T, 0.153 to 0.184 T, 40.67 to 229.89 kA/m and 1.36 to 16.47 kJ/m³, respectively. M_s value increases insignificantly, while H_c and $(\text{BH})_{\text{max}}$ values decreases with increasing substitution of Co and Zn in Fe. On the other hand, M_r value increases with $x=0$ to $x=0.4$ and decreases with $x=0.6$ to $x=1.0$. This is because the limit of the substitution of Fe^{3+} ion by Co^{2+} and Zn^{2+} of hexagonal ferrites.

Table 2. Magnetic values of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ hexagonal ferrites ($x = 0.0; 0.2; 0.4; 0.6; 0.8; 1.0$).

Composition $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$	M_r (T)	H_c (kA/m)	M_s (T)	BH_{maks} (kJ/m ³)
$\text{BaFe}_{12}\text{O}_{19}$	0.153	229.89	0.23	16.47
$\text{BaFe}_{11.6}\text{Co}_{0.2}\text{Zn}_{0.2}\text{O}_{19}$	0.182	108.38	0.28	5.00
$\text{BaFe}_{11.2}\text{Co}_{0.4}\text{Zn}_{0.4}\text{O}_{19}$	0.184	129.97	0.27	7.04
$\text{BaFe}_{10.8}\text{Co}_{0.6}\text{Zn}_{0.6}\text{O}_{19}$	0.170	58.96	0.29	3.08
$\text{BaFe}_{10.4}\text{Co}_{0.8}\text{Zn}_{0.8}\text{O}_{19}$	0.169	66.20	0.30	2.39
$\text{BaFe}_{10}\text{CoZnO}_{19}$	0.155	40.67	0.32	1.36

Fig. 4. Room temperature hysteresis loops of $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ hexagonal ferrites ($x = 0.0; 0.2; 0.4; 0.6; 0.8; 1.0$)

4 Conclusions

Hexagonal ferrites $\text{BaFe}_{12-2x}\text{Co}_x\text{Zn}_x\text{O}_{19}$ with $x = 0.0; 0.2; 0.4; 0.6; 0.8; 1.0$ were prepared the ceramic method successfully. According to the diffraction pattern of all samples are polycrystalline with single phase. SEM micrographs shows the hexagonal ferrites that are composed of small particles with large porosity, roughly of spherical shapes and less than $2 \mu\text{m}$. The substitution of Fe^{3+} ion by Co^{2+} and Zn^{2+} has changed magnetic properties of hexagonal ferrites. M_s value increases, while H_c and $(BH)_{\text{max}}$ values decreases. On the other hand, M_r value increases with $x=0$ to $x=0.4$ and decreases with $x=0.6$ to $x=1.0$.

The authors thank Kementerian Riset, Teknologi dan Pendidikan Tinggi Republik Indonesia under grant PUPT 2018 for the financial support

References

1. K.-H. Müller, G. Krabbes, J. Fink, S. Gruß, A. Kirchner, G. Fuchs, and L. Schultz, "New permanent magnets," *J. Magn. Magn. Mater.*, vol. **226–230**, pp. 1370–1376, (2001).
2. S. W. Eun, W. H. Choi, H. K. Jang, J. H. Shin, J. B. Kim, and C. G. Kim, "Effect of delamination on the electromagnetic wave absorbing performance of radar absorbing structures," *Compos. Sci. Technol.*, vol. **116**, pp. 18–25, (2015).
3. R. H. Kadam, S. T. Alone, G. K. Bichile, and K. M. Jadhav, "Measurement of atomic number and mass attenuation coefficient in magnesium ferrite," *Pramana - J. Phys.*, vol. **68**, no. 5, pp. 869–874, (2007).
4. Erfan Handoko, et al, "Measurement of Complex Permittivity and Permeability of Hexagonal Ferrite Composite Material Using a Waveguide in Microwave Band," 2016 International Conference on Radar, Antenna, Microwave, Electronics, and Telecommunications Measurement pp. 28–30, (2016).
<https://doi.org/10.1109/ICRAMET.2016.7849576>
5. Erfan Handoko et al (2018) *Mater. Res. Express* in press <https://doi.org/10.1088/2053-1591/aac4d7>.
6. K. Khan and S. Rehman, "Microwave absorbance properties of zirconium-manganese substituted cobalt nanoferrite as electromagnetic (EM) wave absorbers," *Mater. Res. Bull.*, vol. **50**, pp. 454–461, (2014).
7. R. C. Pullar, "Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics," *Prog. Mater. Sci.*, vol. **57**, no. 7, pp. 1191–1334, (2012).
8. P. E. Garcia-Casillas, A. M. Beesley, D. Bueno, J. A. Matutes-Aquino, and C. A. Martinez, "Remanence properties of barium hexaferrite," *J. Alloys Compd.*, vol. **369**, no. 1–2, pp. 185–189, (2004).
9. G. Tan and X. Chen, "Structure and multiferroic properties of barium hexaferrite ceramics," *J. Magn. Magn. Mater.*, vol. **327**, pp. 87–90, (2013).
10. M. J. Molaei, A. Ataie, S. Raygan, M. R. Rahimpour, S. J. Picken, F. D. Tichelaar, E. Legarra, and F.

- Plazaola, "Magnetic property enhancement and characterization of nano-structured barium ferrite by mechano-thermal treatment," *Mater. Charact.*, vol. **63**, pp. 83–89, (2012).
11. U. Topal, H. Ozkan, and H. Sozeri, "Synthesis and characterization of nanocrystalline BaFe₁₂O₁₉ obtained at 850 C by using ammonium nitrate melt," *J. Magn. Magn. Mater.*, vol. **284**, pp. 416–422, (2004).
 12. X. Shi, Y. Pu, and D. Liu, "Preparation of magnetic barium ferrite powders by microwave hydrothermal method," *J. Ceram. Process. Res.*, vol. **13**, no. SPL. ISS.2, pp. 414–417, (2012).
 13. A. Moitra, S. Kim, S. G. Kim, S. C. Erwin, Y. K. Hong, and J. Park, "Defect formation energy and magnetic properties of aluminum-substituted M-type barium hexaferrite," *Comput. Condens. Matter*, vol. **1**, no. 1, pp. 45–50, (2014).
 14. C. C. Chauhan, R. B. Jotania, and K. R. Jotania, "Structural Properties of Cobalt Substituted Barium Hexaferrite Nanoparticles Prepared By a Thermal Treatment Method," vol. **4**, no. 3, pp. 363–369, (2013).
 15. R. C. Alange, P. P. Khirade, S. D. Birajdar, A. V. Humbe, and K. M. Jadhav, "Structural, magnetic and dielectrical properties of Al-Cr Co-substituted M-type barium hexaferrite nanoparticles," *J. Mol. Struct.*, vol. **1106**, pp. 460–467, (2016).
 16. J. Zhou, H. Ma, M. Zhong, G. Xu, Z. Yue, and Z. He, "Influence of Co-Zr substitution on coercivity in Ba ferrites," *J. Magn. Magn. Mater.*, vol. **305**, no. 2, pp. 467–469, (2006).
 17. K. Chen, L. Li, G. Tong, R. Qiao, B. Hao, and X. Liang, "Fabrication and absorbing property of microwave absorbers based on BaAl₂Fe₁₀O₁₉ and poly(o-toluidine)," *Synth. Met.*, vol. **161**, no. 21–22, pp. 2192–2198, (2011).
 18. T. Wang, C. Pan, Y. Wang, G. Tan, H. Wang, R. Li, and F. Li, "Improvement of absorption performance for Co₂Z barium ferrite composite by increasing the reflected electromagnetic wave from air-absorber interface," *J. Magn. Magn. Mater.*, vol. **354**, pp. 12–16, (2014).
 19. H. Sözeri, Z. Mehmedi, H. Kavas, and A. Baykal, "Magnetic and microwave properties of BaFe₁₂O₁₉ substituted with magnetic, non-magnetic and dielectric ions," *Ceram. Int.*, vol. **41**, no. 8, pp. 9602–9609, (2015).