Microstructures, Magnetic Properties and Microwave Absorption Characteristics of Ti^{2+}-Mn^{4+}Substituted Barium Hexaferrite

Struktur Mikro, Sifat Kemagnetan dan Karakteristik Penyerapan Gelombang Mikro dari Barium Hexaferrite Tersubstitusi Ti^{2+}-Mn^{4+}

Maykel Manawan[a, *], Azwar Manaf[a], Bambang Soegijono[a],
and Asep Yudi Hercuadi[b]

[a]Materials Science Study , Postgraduate Program of Faculty of Mathematics and Natural Sciences
University of Indonesia, Depok 16424, Indonesia
[b]Research Center for Electronics and Telecommunication, Indonesian Institute of Sciences (LIPI)
Komplek LIPI Gd 20, jl. Sangkuriang 21/54D, Bandung 40135, Indonesia

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Abstract

The effect of Ti^2-Mn^{4+} substitution on microwave absorption has been studied for $BaFe_{12-2x}Ti_xMn_xO_{19}$ ferrite, where x varies from 0.2, 0.4, 0.6, and 0.8. Ti^2-Mn^{4+} ions were obtained from TiO and MnO_2 precursors which were mechanically alloyed together with $BaCO_3$ and Fe_2O_3 precursors. X-ray diffraction (XRD) patterns for sintered samples confirmed that the materials are consisted with single phase BHF structure. Unit cell volume and crystallite size was found increase with increasing x. Crystallite size for all samples below 70 nm, but the grain morphology shown that the grains is in range of 200-400 nm, which concluded that each grain are polycrystalline. The saturation magnetization is increases up to x = 0.4 and decrease for higher x values, while the coercivity remains decreases monotonically. These results were interpreted in terms of the site preferential occupation of Ti_2^+ and Mn_4^+ at low level substitution. These substitution revealed of enhanced reflection loss (RL) up to 25 dB for x = 0.6. It is suggested that the synthesized can be employed as effective microwave absorbers in various devices.

***Keywords:** BHF, Substitution, microstructure, LAS, reflection loss.*

Abstrak

Pengaruh Ti^{2+}-Mn^{4+} substitusi pada penyerapan gelombang mikro telah dipelajari untuk $BaFe_{12-2x}Ti_xMn_xO_{19}$ ferit , di mana *x* bervariasi dari 0,2; 0,4; 0,6; dan 0,8. Ti^{2+}-Mn^{4+} ion diperoleh dari TiO dan MnO_2 prekursor yang mekanis paduan bersama $BaCO_3$ dan Fe_2O_3 prekursor. Difraksi sinar-X (XRD) pola sampel disinter menegaskan bahwa bahan bahan yang terdiri dengan struktur fase tunggal BHF. Volume sel satuan kristal dan ukuran ditemukan peningkatan dengan meningkatnya *x*. Ukuran kristal untuk semua sampel di bawah 70 nm, tetapi morfologi butir menunjukkan bahwa kristal adalah di kisaran 200-400 nm, yang menyimpulkan bahwa setiap butir adalah polikristalin. Saturasi magnetisasi adalah meningkat hingga *x* = 0,4 dan penurunan untuk nilai-nilai *x* yg tinggi, sedangkan koersivitas tetap menurun secara monoton. Hasil ini ditafsirkan dalam hal pendudukan preferensial situs dari Ti^{2+} dan Mn^{4+} pada substitusi tingkat rendah. Substitusi ini berpengaruh kehilangan refleksi (RL) hingga 25 dB untuk *x* = 0.6. Disarankan bahwa sintesis dapat digunakan sebagai peredam gelombang mikro yang efektif di berbagai perangkat.

Kata kunci: BHF, Substitusi, struktur mikro, LAS, kehilangan refleksi.

I. INTRODUCTION

Recently, the number of communication devices thatutilize gigahertz range microwave radiation has increased. However, electromagnetic interference (EMI) has become serious. One promising technique to prevent EMI is the use of microwave absorption materials [1]. Spinel-type ferrites and metallic magnetic materials have been used as conventional microwave absorption materials. However, spinel-type ferrites is a soft magnetic with planar an isotropy which is show a Snoek’s limit [2], where the magnetic loss decreases drastically at several gigahertz. Metallic magnetic materials [3], [4] show high permeability, but they have to be insulated to prevent an eddy current. In the other hand, BHF has a high saturation magnetization, high Curie temperature, high resistance and chemically stable lead to low-cost and easy application. Unfortunately, its strong uniaxial an isotropy leads to low permeability and too high resonant frequency f_0 = 42.5 GHz [5].

In order to satisfy the utilization requirements of this compound, many studies have focused on tailoring hexaferrites with modified magnetic properties by substituting Fe^{3+} ions with divalent, trivalent and tetravalent cations or cations combinations [5]. For this purpose, several methods have been used to prepare the

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* Corresponding Author.
Email: maykel.t01@ui.ac.id

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particles including sol–gel [6], mechano-combusition [7], ammonium nitrate melt [8], citrate–nitrate gel combustion [9], co-precipitation [10] and mechanical alloying [11]. The last method has been recently adopted due to its simplicity in operation and handy experimental equipment [12].

Most of ionic substitutions were reported to decrease in magnetic saturation as well as the coercivity e.g. La^{3+}[13], Mn^{3+} [14], Co^{2+}-Ti^{4+} [15], Co^{2+}-Zr^{4+} [16], Ti^{4+}-Mn^{4+} [17] – [19] and many other combinations. Referring to Bsoul, Mahmood and Lehlooh work on Ti^{2+}-Ru^{4+} [20] and Liu et. al. on Co^{2+}-Mn^{2+}-$2Sn^{4+}$ [21] which shows an increase in magnetic saturation, we use Ti^{2+}-Mn^{4+} contrary from Ti^{4+}-Mn^{2+} to demonstrate the site preferential mechanism. The static and high-frequency magnetic properties have been measured. The predicted absorption and reflection loss demonstrates that $BaFe_{(12-2x)}Ti_xMn_xO_{19}$ may be a good candidate for electromagnetic materials with low reflectivity at microwave frequency.

II. EXPERIMENTAL

Samples of $BaFe_{12-2x}Ti_xMnxO_{19}$ with x = 0, 0.2, 0.4, 0.6, and 0.8 were prepared via mechanical alloying and solid state reaction technique. Stoichiometric quantities of $BaCO_3$, Fe_2O_3, TiO, and MnO_2 were milled in planetary ball mill for 20 hours. The milled powders were pelletized and sintered at 1100 ^oC for 2 hours. As sintered samples were re-milled and washed with dilute HCl.

The X-Ray Diffraction (XRD) of re-milled samples was performed using Philips PW3710 diffracto meter with Co-Kα radiation. The bulk densities were measured using FH-MD density meter. The grain morphology was characterized using FEI-F50 Scanning Electron Microscope (SEM). The M-H loops were measured in applied fields of 0-2000 kA/m at room temperature using Permagraph-L magnetometer. The microwave measurement was conducted on ADVANTEST R3770 Vector Network Analyzer. Further a computer program implementing Rietveld refinement used to determine microstructure from a diffraction patterns. Image processing software (ImageJ 1.47v) used to determine the average grain sizes from SEM photograph.

Saturation magnetization M_s and anisotropy field H_a were deduced from numerical analysis of the magnetization curves based on the law of approach saturation [22]:

$$M(H) \approx M_s\left(1 - \frac{A}{H} - \frac{B}{H^2} \dots\right) + \chi_d H \qquad (1)$$

where $M(H)$ is the specific magnetization at magnetic field strength H, χ_d is the high field susceptibility, A/H term is related to existence of inhomogeneities and theoritally should vanish at high fields and B/H^2 term is related to magnetocrystalline. A more rigorous approach gives [23]:

$$M(H) \approx M_s\left(1 - \beta\left(\frac{K}{M_s H}\right)^2\right) \qquad (2)$$

where K is the anisotropy constant which assumes from $K_1 \gg K_2$, β is the isotropic uniaxial constant (4/15 for hexagonal). In order to apply the approach to saturation law, M is plotted versus $1/H^2$. The region to validate the LAS is determined by the tangent to reduce magnetization M/M_s as the function of reduced field H/H_a.

Microwave absorption properties were evaluated by reflection loss (RL), which derived from the following formula:

$$RL = 20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right| \qquad (3)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\frac{2\pi}{c}\sqrt{\mu_r\varepsilon_r}fd\right] \qquad (4)$$

Where μ_r and ε_r are the complex relative permeability and permittivity, respectively, of the composite medium and c is the velocity of light in free space. The situation with RL less than -20 dB (‘‘matching situation’’) was considered were the sample shows adequate microwave absorption.

III. RESULT AND DISCUSSION

A. Phase Analysis and Morphology

XRD patterns of sintered samples in Figure 1 shows a typical structure of BHF with space group of P63/mmc. All peaks of substituted BHF appear in the same position as the un-substituted BHF, which concluded to a successful synthesized of single phase BHF.

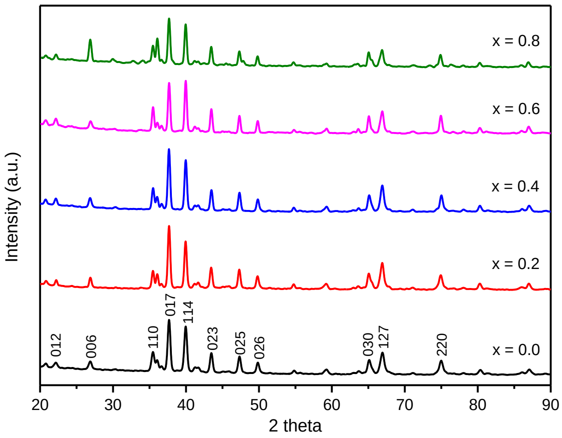

Figure 1. XRD Pattern of $BaFe_{12-2x}Ti_xMn_xO_{19}$.

Table 1 shows the quantitative analysis of XRD patterns. Lattice parameter c was found to increase with substitution, while lattice parameter a almost unchanged. It follows the fact that all hexagonal ferrites exhibit constant lattice parameter a and vary lattice parameter c [24]. The variation in lattice parameters with x indicates that substitutions occurred on crystallographic sites. The increase in lattice parameter with increasing Ti^{2+} and Mn^{4+} ions may be understood on the basic of ionic radii. The ionic radii for Fe^{3+}, Ti^{2+} and Mn^{4+} ions in octahedral coordination is 0.64, 0.86 and 0.53 Å respectively [25]. Since ions with larger radii tend to occupy octahedral sites and smaller radii tend to occupy tetrahedral and or bipyramidal sites, we conclude that Ti^{2+} ion occupy $4f_2$ and 2a sites, while Mn^{4+} ion occupy $4f_1$ and 2b sites. This hypothesis is consistent with previous studies on Co-Mn-2Ti, Mn-Sn, and Ti-Ru substituted BHF [26], [21], [20].

TABLE I
LATTICE CONSTANT *a* AND *c*, CELL VOLUME, X-RAY DENSITY, BULK DENSITY, POROSITY, CRYSTALLITE SIZE AND GRAIN SIZE OF $BaFe_{12-2x}Ti_xMn_xO_{19}$.

x	0	0.2	0.4	0.6	0.8
a (Å)	5.885	5.893	5.885	5.892	5.897
c (Å)	23.171	23.193	23.195	23.199	23.213
Volume ($Å^3$)	695.01	697.45	695.75	697.58	699.13
T.D (g/cm^3)	5.31	5.29	5.30	5.29	4.63
B.D (g/cm^3)	4.73	4.65	4.72	4.69	4.16
Porosity (%)	11.02	12.10	10.94	11.34	10.15
Crystallite Size (nm)	36.18	51.54	47.08	60.83	42.31
Grain Size (nm)	285.56	298.12	294.48	291.67	374.86

Figure 2 shows SEM images of $BaFe_{12-2x}Ti_xMn_xO_{19}$ (x = 0.0 and 0.8) samples. It clearly be seen that the microstructure is affected by substitution. With the aid of Image J software, the average grain size is observed to be increase with increasing x. It also appears that densification decrease with increasing x, it is confirmed with XRD refinement result.

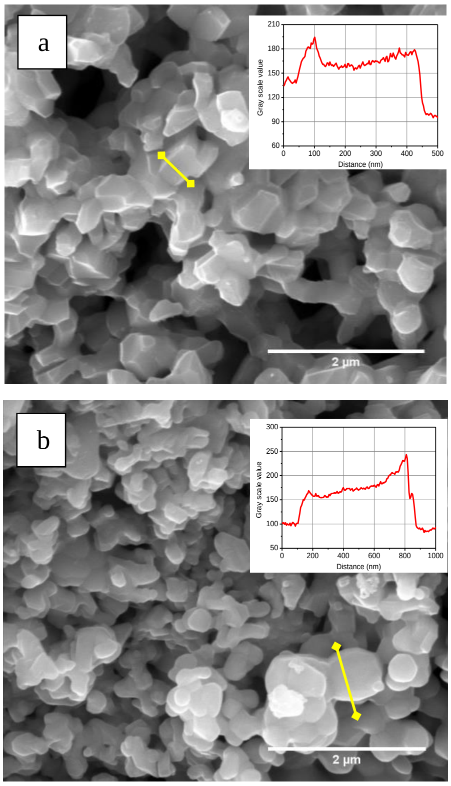

Figure 2. SEM Micrograph of $BaFe_{12-2x}Ti_xMnxO_{19}$:
(a) x = 0.0 and (b) x = 0.8

B. Magnetic Properties

The effect of Ti^{2+}-Mn^{4+} content on magnetic properties for all examined samples are shown in Figure 3. The results show that the undoped BHF sample possesses the largest intrinsic coercivity (H_c = 282.5 kA/m) which is the characteristic of a hard magnetic material due to strong uniaxial anisotropy along the *c*-axis. H_c decreases as substitution increases, attributed to the change of the easy axis magnetization from *c*-axis to *c*-plane.The low coercivity in x = 0.8 indicates that the domain wall motion is the dominant and the sample become a soft magnetic.

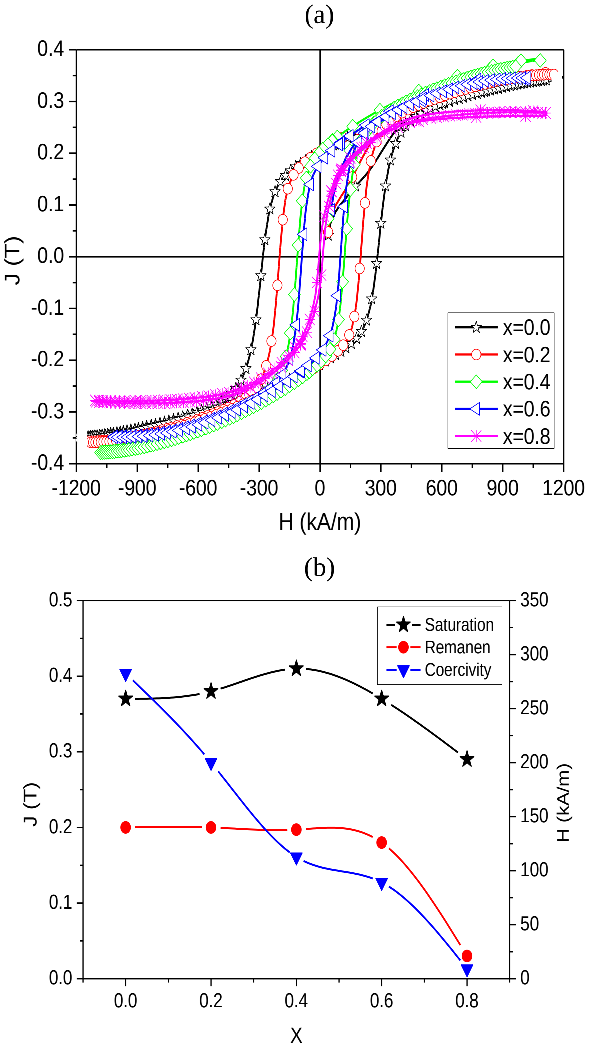

Figure 3. Magnetic Properties of $BaFe_{12-2x}Ti_xMn_xO_{19}$: (a) *M-H* Loops, (b) M_s, M_r and H_{ci} vs. Composition (x).

In M-type hexagonal ferrite, Fe^{3+} ions occupied seven octahedral sites 12k and 2a, and trigonal site 2b, with spin-up direction, two octahedral sites $4f_1$ and two tetrahedral sites $4f_2$ with spin-down direction. At low substitution, the mechanism of replacement Fe^{3+} ion at particular site is guided by ionic radii and electro negativity of the candidates. Sharp decrease in coercivity value isdirectly related to the anisotropy that is primarily related to the intrinsic effect associated with the replacement of Fe^{3+} ions at both $4f_2$ and 2b sites. These two sites contribute to the large an isotropy field [27]. Another factor responsible for the decrease in coercivity is the extrinsic effect caused by the increase in grain size with the substitution, as depicted in the SEM morphology.

Table 2 represents the variation of magnetic properties with substitution. Saturation magnetization and anisotropy is derived from the lawof approach saturation. The saturation magnetization initially increases from x = 0.0 to x = 0.4 (10.8%). It is due to replacement of Fe^{3+} ions (5 μB) at $4f_1$ and $4f_2$ sites by Ti^{2+} (2 μB) and Mn^{4+} (3 μB) ions causing magnetization reduction in spin down states. However, Ms decreases with further substitution (x> 0.4) is associated with the replacementof Fe^{3+} ions at 2a and 2b spin-up sites by Ti^{2+} and Mn^{4+}. These results are consistent and well agree with those reported by Bsoul et al. [20] who have observed 11% increase in M_s upon substituting Fe^{3+} ion by Ti^{2+}-Ru^{4+} for x = 0.2. The ferromagnetic resonance (FMR) shift from high frequency to low frequency which is can be a good candidate for microwave absorber material. Tilt angle pronouncedly confirmed that easy magnetization is change from c-axis to c-plane as x increase.

TABLE II
SATURATION AND REMANENCE MAGNETIZATION, COERCIVITY, ANISOTROPY FIELD, ANISOTROPY CONSTANT, FERROMAGNETIC RESONANCE (FMR) FREQUENCY AND TILT ANGLE OF $BaFe_{12-2x}Ti_xMn_xO_{19}$.

x	M_S (T)	M_r (T)	H_c (kA/m)	H_a (kA/m)	K (x105 J/m^2)	FMR (GHz)
0.0	0.37	0.20	282.54	777.15	2.67	27.34
0.2	0.38	0.20	200.13	569.26	2.04	20.03
0.4	0.41	0.20	112.72	548.19	2.12	19.29
0.6	0.37	0.18	89.11	531.41	1.85	18.70
0.8	0.29	0.03	9.18	425.08	1.16	14.96

C. Microwave Absorption Characteristic

Figure 4 shows the variation of reflection loss verses frequency for all $BaFe_{12-2x}Ti_xMn_xO_{19}$ samples. There is no loss peaks are observed in undoped BHF because it high ferromagnetic resonance frequency and it show very low microwave absorption. The reflection loss is significant indoped samples. It shows the reflection loss peaks is increase with increasing x, has maximum value at x = 0.6 (25 dB) and reduce at x = 0.8 (15 dB). The loss peak consistently shifted from high to low frequency, it shows a same trend as the FMR. The FMR phenomenon cannot be characterized due to measurement equipment limitation (8-12.4 GHz).

The observed magnetic spectra are in agreement with the mechanism of natural magnetic resonance involving domain-wall displacement and domain rotation. These motion lag behind the applied magnetic field cause magnetic loss in the material correlated with the area inside the magnetic loops [28]. This is the reason why x = 0.8 lower in reflection loss as compare to others.

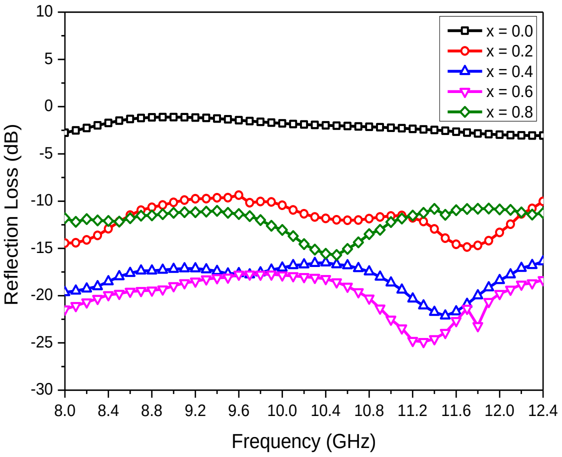

Figure 4. Reflection Loss of $BaFe_{12-2x}Ti_xMn_xO_{19}$.

CONCLUSIONS

This study has demonstrated that the substitution of Ti^{2+} and Mn^{4+} ions makes considerable change in extrinsic properties in terms of grain size, porosity and intergranular network. The substitution pronouncedly decreases coercivity for whole range of substitution, while increasing magnetization until x = 0.4 and decrease at high substitution. This phenomenon can be understood by the preferential occupation mechanism of Ti^{2+}-Mn^{4+} ions when replacing Fe^{3+} ions at certain level of substitution.

Ti^{2+}-Mn^{4+} substituted BHF can be utilized as good microwave absorber for high frequency above 1 GHz, and the operating frequency can be controlled by substitution ratio of Ti^{2+} and Mn^{4+}.

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REFERENCES

[1] Y. Naito and K. Suitake, “Application of ferrite to electromagnetic wave absorber and its characteristics”, *IEEE Trans. Microwave Theory and Tech.*, vol. 19, p. 65-72, 1971.

[2] J. L. Snoek, “Dispersion and absorption in magnetic ferrites at frequencies above one Mc/s”, *Physica*, vol. 14, p. 207, 1948.

[3] S. Yoshida, M. Sato, and Y. S. E. Sugiwara, “Permeability and electromagnetic-interference characteristics of Fe-Si-Al alloy flakes polymer composite”, *Journal of Applied Physics*, vol. 85, p. 4636, 1999.

[4] M. Matsumoto and Y. Miyata, “Thin electromagnetic wave absorber for quasi-microwave band containing aligned thin magnetic metal paticles“, *IEEE Transactions on Magnetics*, vol. 33, p. 532, 1997.

[5] R. C. Pullar, “Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics”, *Progress in Materials Science*, vol. 57, p. 1191–1334, 2012.

[6] M. Han, Y. Ou, W. Chen, and L. Deng, “Magnetic properties of Ba-M-type hexagonal ferrites prepared by the sol–gel method with and without polyethylene glycol added”, *Journal of Alloys and Compounds*, vol. 474, no. 1-2, p. 185–189, 2009.

[7] Ataie and S. Zojaji, “Synthesis of barium hexaferrite nano-particles via mechano-combustion route“, *Journal of Alloys and Compounds*, vol. 431, no. 1-2, p. 331–336, 2007.

[8] U. Topal, H. Ozkan, and L. Dorosinskii, Finding optimal Fe/Ba ratio to obtain single phase BaFe12O19 prepared by ammonium nitrate melt technique, *Journal of Alloys and Compounds*, vol. 428, pp. 17-21, 2007.

[9] S. Chaudhury, S. Rakshit, S. Parida, Z. Singh, K. S. Mudher, and V. Venugopal, "Studies on structural and thermo-chemical behavior of MFe12O19(s) (M = Sr, Ba and Pb) prepared by citrate–nitrate gel combustion method", *Journal of Alloys and Compounds,* vol. 455, no. 1-2, pp. 25-30, 2008.

[10] K. S. Moghaddam and A. Ataie, "Role of intermediate milling in the processing of nano-size particles of barium hexaferrite via co-precipitation method", *Journal of Alloys and Compounds,* vol. 426, no. 1-2, pp. 415-419, 2006.

[11] Mendoza-Suárez, J. Matutes-Aquino, J. Escalante-García, H. Mancha-Molinar, D. Ríos-Jara, and K. Johal, "Magnetic properties and microstructure of Ba-ferrite powders prepared by ball milling", *Journal of Magnetism and Magnetic Materials,* vol. 223, no. 1, pp. 55-62, 2001.

[12] S. Wang, J. Ding, Y. Shi, and Y. Chen, "High coercivity in mechanically alloyed BaFe10Al2O19", *Journal of Magnetism and Magnetic Materials,* vol. 219, no. 2, pp. 206-212, 2000.

[13] Seifert, J. Topfer, F. Langenhorst, J. M. LeBreton, H. Chiron, and L. Lechevallier, "Synthesis and magnetic properties of La-substituted M-type Sr hexaferrites", *Journal of Magnetism and Magnetic Materials,* vol. 321, pp. 4045-4051, 2009.

[14] K. Lee, J. C. Sur, I.-B. Shim, and C. S. Kim, "The effect of manganese substituted M-type hexagonal Ba-ferrite", *Journal of Magnetics,* vol. 14, no 2, pp. 93-96, 2009.

[15] Teh, N. Saravanan, and D. Jefferson, "A study of magnetoplumbite-type (M-type) cobalt–titanium-substituted barium ferrite, BaCoxTixFe12−2xO19 (x = 1–6)", *Materials Chemistry and Physics,* vol. 105, pp. 253-259, 2007.

[16] Z. W. Lia and L. Chen, "Studies of static and high-frequency magnetic properties for M-type ferrite BaFe(12-2x)CoxZrxO19", *Journal of Applied Physics,* vol. 92, pp. 3902-3907, 2002.

[17] Turilli, F. Licci, and S. Rinaldi, "Mn2+, Ti4+ substituted barium ferrite", *Journal of Magnetism and Magnetic,* vol. 59, no. 1-2, p. 127–131, 1986.

[18] Repi and A. Manaf, "Substitution effect of (Mn, Ti) to the dielectric properties of barium-strontium hexaferrite for absorbing electromagnetic waves", in *ICTAP*, Bandung, 2012.

[19] Priyono and A. Manaf, "Magnetic and absorption characteristics of Mn and Ti subsituted barium hexaferrite for microwave absorber", in *ICICI-BME*, Bandung, 2009.

[20] Bsoul, S. Mahmood, and A.-F. Lehlooh, "Structural and magnetic properties of BaFe12−2xTixRuxO19", *Journal of Alloys and Compounds,* vol. 498, p. 157–161, 2010.

[21] Y. Liu, M. G. B. Drew, and Y. Liu, "Preparation and magnetic properties of barium ferrites substituted with manganese. cobalt and tin", *Journal of Magnetism and Magnetic Materials,* vol. 323, p. 945–953, 2011.

[22] R. Grössinger, "Correlation between the inhomogeneity and the magnetic anisotropy in polycrystalline ferromagnetic materials", *Journal of Magnetism and Magnetic Materials,* vol. 28, no. 1-2, p. 137–142, 1982.

[23] R. W. McCallum, "Determination of saturation magnetization, anisotropy field, mean field interaction, and switching field distribution for nanocrystalline hard magnets," *Journal of Magnetism and Magnetic Materials,* vol. 292, p. 135–142, 2005.

[24] P. Wohlfart, *Handbook of Magnetic Material Vol. 3*, Netherlands: North-Holland, 1982.

[25] R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomie distances in halides and chalcogenides", *Acta Crystalloraphy,* vol. A32, pp. 751-767, 1976.

[26] S. Gairola, V. Vermaa, A. Singh, L. Purohit, and R. Kotnala, "Modified composition of barium ferrite to act as a microwave absorber in X-band frequencies", *Solid State Communications,* vol. 150, pp. 147-151, 2010.

[27] Singh, S. B. Narang, I. Hudiara, Y. Bai, and F. Tabatabaei, "Static magnetic properties of Co and Ru substituted Ba–Sr ferrite", *Materials Research Bulletin,* vol. 43, no. 1, pp. 176-184, 2008.

[28] M. P. Sharrock and L. W. Carlson, "The application of barium ferrite particles in advanced recording media", *IEEE Transactions on Magnetics,* vol. 31, no. 6, pp. 2871-2876, 2002..