Influence of Ti addition on the microwave absorbing behavior of Ba$_{0.6}$Sr$_{0.4}$Fe$_{12-x}$Ti$_x$O$_{19}$ system at X-band frequencies

Y.E. Gunanto$^1$, L. Cahyadi$^2$ and W. A. Adi$^3$

$^1$Department of Biology Education, Faculty of Education, University of Pelita Harapan, Karawaci, Tangerang 15811, Indonesia
$^2$Faculty of Science and Technology, University of Pelita Harapan, Karawaci, Tangerang 15811, Indonesia
$^3$Centre for Science and Technology of Advanced Materials – National Nuclear Energy Agency, Kawasan Puspiptek Serpong, Tangerang Selatan, Banten, Indonesia

Corresponding author : yohanes.gunanto@uph.edu

Abstract. The synthesis and characterization of Ba$_{0.6}$Sr$_{0.4}$Fe$_{12-x}$Ti$_x$O$_{19}$ system ($x = 0, 1, 2, 3$) have successfully performed by mechanical milling through solid state method. Stoichiometric quantities of BaCO$_3$, SrCO$_3$, Fe$_2$O$_3$, and TiO$_2$ were mixed. The mixture were first milled for 48 h and sintered at 1000 °C for 5 hrs. The refinement of x-ray diffraction shows that a single phase material with a hexagonal structure and lattice parameters appears to increase with increasing Ti doping. The mechanical milling resulted in powders of all samples with mean size of 90 nm. Results of hysteresis curve shows that the samples are ferromagnetic and have low coercivity after Ti doping. Results of VNA evaluation show that the sample after Ti doping has absorption peaks with high reflection loss values at frequency ~ 11 GHz. We concluded that this study has been successfully known effect of Ti addition on the microwave absorbing behavior of Ba$_{0.6}$Sr$_{0.4}$Fe$_{12-x}$Ti$_x$O$_{19}$ system at X-band frequencies.

1. Introduction
Electromagnetic wave absorber material is a material that can weaken the electromagnetic wave energy. Externally, this absorber can reduce the reflection or transmission of a particular object and can be used internally to reduce oscillations caused by the cavity resonance. One of the applications in various electronic devices which are working in the high frequency-range is as signal booster or amplifier, but often have a problem caused by the emission of high frequency noise such as electromagnetic wave interference (EMI). To eliminate the EMI requires a magnetic material which is able to resonate at a specific frequency that is expected to absorb undesirable electromagnetic radiation.

The prerequisites are essential since electromagnetic wave absorber material is a material of high permeability and permittivity. Presently, absorber materials are being developed through the modification of ferrite-based magnetic materials because they have a relatively high permeability [1-4]. Through the structural modification, the material is expected to be utilized as a superior material for electromagnetic wave absorber applications [5-7]. The structural modification is implemented primarily to enhance the permittivity of the material. The magnetic properties of this material are influenced by the presence of Ti atoms. Due to the presence of coupling Ti$^{4+}$ is greatly contributing to
the magnetic properties of this material. In the present study, the authors have carried out a modification of the hexagonal barium strontium hexaferrite system by titanium substitution of the iron atoms. Therefore the objectives of this study is to understand the changes in the parameters’ values of the crystal structure of this material and the influence of Ti addition on the microwave absorbing behavior.

2. Materials and Methods
The synthesis of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ system ($x = 0, 1, 2, 3$) material was performed by using the solid reaction method. This magnetic material is prepared by oxide materials, namely $\text{BaCO}_3$, $\text{SrCO}_3$, $\text{Fe}_2\text{O}_3$, and $\text{TiO}_2$. The four starting materials are mixed by using a Spex 8000 high-energy milling (HEM) apparatus for 10 hours at room temperature. The finely mixed powder was compacted at 5000 psi into pellets and sintered in the THERMOLYNE electric chamber furnace at 1000°C in the air at atmospheric pressure for 10 hours. The qualitative and quantitative phase analysis were carried out using the PW1710 Philips diffractometer equipment (XRD). The Rietveld analysis was performed by employing GSAS special application code [8,9]. The surface morphology and elemental identification of the sample were analyzed by using the JEOL scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively.

3. Results and Discussion
The identification results of XRD pattern on the samples show that the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ system ($x = 0, 1, 2, 3$) has a diffraction intensity pattern that is similar to one another as shown in figure 1.

![Figure 1: Phase identification of x-ray diffraction pattern of the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ ($x = 0, 1, 2, 3$) samples](image)

The diffraction pattern of the product samples shown in Fig. 1 is that of the same single phase for all samples. Therefore, it was necessary for the analysis of phase content in the samples using the GSAS software as shown in figure 2 for the Ti content of $x = 0, 1, 2, 3$. The parameters of crystal structure referred to COD-1008841 for the phases of $\text{BaO.6Fe}_2\text{O}_3$. 
The refinement results have produced very good quality of fitting with the R-factor and the $\chi^2$ (chi-squared) values being very small [9]. The refinement results of the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ ($x = 0, 1, 2, 3$) crystalline structural parameters are shown in table 1.

| $x$  | Space group   | $a = b$  | $c$  | $a = \beta = 90^\circ$ | $V = 700.9(2)\text{ Å}^3$ and $\rho = 5.110\text{ gr.cm}^{-3}$ | $x = 1$ | Space group   | $a = b$  | $c$  | $a = \beta = 90^\circ$ | $V = 695.1(1)\text{ Å}^3$ and $\rho = 5.124\text{ gr.cm}^{-3}$ | $\chi^2 = 1.187$ | Factor R | $wR_p = 6.68$ |
|------|----------------|-----------|------|-----------------------|------------------------------------------------|------|----------------|-----------|------|-----------------------|------------------------------------------------|------|---------|
| 0    | P 63/m m c (194), system: hexagonal | 5.902(8) Å | 23.23(4) Å | $\gamma = 120^\circ$, $V = 700.9(2)\text{ Å}^3$ and $\rho = 5.110\text{ gr.cm}^{-3}$ | Factor R | $wR_p = 6.57$ | $\chi^2 = 1.240$ | Factor R | $wR_p = 6.42$ | $\chi^2 = 1.180$ |
| 1    | P 63/m m c (194), system: hexagonal | 5.86(1) Å | 23.34(5) Å | $\gamma = 120^\circ$, $V = 695.1(1)\text{ Å}^3$ and $\rho = 5.124\text{ gr.cm}^{-3}$ | | | | | | |
| 2    | P 63/m m c (194), system: hexagonal | 5.902(8) Å | 23.23(4) Å | $\gamma = 120^\circ$, $V = 700.9(2)\text{ Å}^3$ and $\rho = 5.110\text{ gr.cm}^{-3}$ | | | | | | |
| 3    | P 63/m m c (194), system: hexagonal | 5.86(1) Å | 23.34(5) Å | $\gamma = 120^\circ$, $V = 695.1(1)\text{ Å}^3$ and $\rho = 5.124\text{ gr.cm}^{-3}$ | | | | | | |

The refinement results provide the experimental evidence that titanium substitution into iron atoms was able to reach the value of $x = 3$ and that with the doping concentration of up to $x \leq 0.3$, the product formed is still of a single phase.

In figure 3 are shown the microstructures of the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ ($x = 0, 1, 2, 3$) sample. The surface morphology results of observations by scanning electron microscope on the samples show that the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ system ($x = 0, 1, 2, 3$) samples has been obtained and that the substitution increases both the density and the inter-grain connectivity in the microstructure of sintered samples.
The microstructure analyses show that the particles’ shape was polygonal with the varied particle sizes distributed homogeneously on the surface of the samples.

Characterization of the magnetic properties of the Ba$_{0.6}$Sr$_{0.4}$Fe$_{12-x}$Ti$_x$O$_{19}$ system (x = 0, 1, 2, 3) magnetic particles has been performed using a vibrating sample magnetometer (VSM) that produced hysteresis curves of magnetic particles as shown in figure 4.

![Surface morphology photos](image)

**Figure 3.** Surface morphology photo of the Ba$_{0.6}$Sr$_{0.4}$Fe$_{12-x}$Ti$_x$O$_{19}$ system (x = 0, 1, 2, 3)

The hysteresis curves of synthesized Ba$_{0.6}$Sr$_{0.4}$Fe$_{12-x}$Ti$_x$O$_{19}$ system are shown in Figure 4 in which respective profiles for x of 0, 1, 2, and 3 are also compared. The hysteresis loop as shown in Figure 4 is characterized with intrinsic saturation $M_s$, remanence field $M_r$ and coercivity $H_c$. The intrinsic saturation, $M_s$ is the state when the material is not able to absorb more magnetic field, so increasing magnetization force will not change the magnetic flux density significantly. Meanwhile, the remanence field $M_r$, is the residual magnetization in a medium once the external magnetic field is removed and coercivity (also called coercive force) is a force required to demagnetize the material so the residual induction becomes zero after magnetizing up to the saturation point. In reference to Figure 6 it seems that $H_c$ is constant however the remanence magnetization decreases along with increasing doping concentration of Ti [10]. Thus, the doping concentration value of x = 1 is the optimal composition for which the magnetic properties was still able to maintain their strength, because after x exceeds the value of 0.1, the remanence magnetization would decrease significantly. A doping concentration of x = 1 is required for further confirmation about the presence of Ti in the sample. Therefore an elemental content analysis of the sample is needed to find out whether the substitution of Ti has been successful in the composition.

![Hysteresis curves](image)

**Figure 4.** The hysteresis curves of Ba$_{0.6}$Sr$_{0.4}$Fe$_{12-x}$Ti$_x$O$_{19}$ system (x = 0, 1, 2, 3)
Figure 5 shows the elemental analysis result of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ (x = 1) samples using the energy dispersive spectroscopy (EDS) method.

The elements content of the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ system (x = 1) is shown in table 2.

| No. | Element          | Mass Fraction (wt%) |
|-----|------------------|---------------------|
| 1.  | Barium (Ba)      | 13.23 ± 0.43        |
| 2.  | Strontium (Sr)   | 2.82 ± 0.32         |
| 3.  | Iron (Fe)        | 44.69 ± 0.39        |
| 4.  | Titanium (Ti)    | 6.47 ± 0.18         |
| 5.  | Oxygen (O)       | 28.48 ± 0.15        |
| 6.  | Carbon (C)       | 4.31 ± 0.10         |

Based on the Table 2 it could be shown that the sample has a Ti content of around 6.47 wt%. It means that substitution of Ti has been successfully achieved in the composition. Additional supporting data is provided by micrograph results from the transmission electron microscope (TEM) observation as shown in figure 6.

In Figure 6 it seemsthat the particles with adopting concentration of x = 1 are nanoparticles with a good homogeneity, uniformity, and having an aggregate particle shape. The range of the particle size is around 50-100 nm.

The microwave absorbing properties of synthesized $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_{12-x}\text{Ti}_x\text{O}_{19}$ system (x = 0, 1, 2, 3) are shown in figure 7 in which respective profiles for x of 0, 1, 2, and 3 are also compared.
Figure 7. The reflection loss (RL) curve of Ba_{0.6}Sr_{0.4}Fe_{12-x}Ti_xO_{19} system (x = 0, 1, 2, 3)

Figure 7 shows the relation between the reflection loss (RL) of Ba_{0.6}Sr_{0.4}Fe_{12-x}Ti_xO_{19} system (x = 0, 1, 2, 3) particles and the microwave frequency X-band in the range of 8-14 GHz when the thickness of the sample is 1.5 mm. There are at least two absorption peaks observed which have a high RL within the frequency range for all samples. Based on the phase composition shown in figure 7, it is evident that the Ba_{0.6}Sr_{0.4}Fe_{12-x}Ti_xO_{19} system (x = 0, 1, 2, 3) has a low RL value, which then increases for the Ti doping concentration x = 1 and decreases again for x = 2 and 3. However, this case shows that the best absorber turns out to be the Ti substituted Ba-Srhexaferrite sample with the Ti doping concentration of x = 0, 1, 2, and 3 which occurred at nearly the same thickness and at practically identical frequencies, there are differences. This can be explained by the effect of electromagnetic properties on the attenuation characteristic in each sample. It was found that substitution with Ti effectively increased the attenuation constant in the entire range of frequencies used here, compared with non-substitution Ti doping concentration x = 0, and the optimum value of microwave absorption was found on the phase composition of Ti doping concentration x = 1. This indicates that Ba_{0.6}Sr_{0.4}Fe_{12-x}Ti_xO_{19} (x = 1) has certain microwave absorption properties in the frequency range of 8 – 14 GHz, absorption peak values of -25 dB at 10.7 GHz and -20.0 dB at 13.8 GHz.

4. Conclusion

Synthesis of Ba_{0.6}Sr_{0.4}Fe_{12-x}Ti_xO_{19} system (x = 0, 1, 2, 3) was successfully performed by solid state reaction through a mechanical milling method. It was found that the best phase composition which was a high performance absorber was Ba_{0.6}Sr_{0.4}Fe_{11}TiO_{19}. The refinement results of X-ray diffraction patterns showed that the Ba_{0.6}Sr_{0.4}Fe_{11}TiO_{19} was a single phase, which has a hexagonal structure (P 63/m m c), a = 5.9587(3) Å, b = 5.9587(3) Å and c = 23.406(1) Å, α=β= 90° and γ = 120°, V = 719.7(1) Å³ and ρ = 5.568 gr.cm⁻³. The mechanical milling resulted in Ba_{0.6}Sr_{0.4}Fe_{11}TiO_{19} powders with a mean particle size of ~850 nm. The TEM micrograph image revealed that the particles’ morphology is an aggregate of fine grains. The magnetic properties of the particle Ba_{0.6}Sr_{0.4}Fe_{11}TiO_{19} shows a low coercivity and a high remanent magnetization. The Ba_{0.6}Sr_{0.4}Fe_{11}TiO_{19} has microwave absorption properties in the frequency range of 8 – 14 GHz, with absorbing peak values of -8 dB at 8.5 GHz and -10.0 dB at 12.5 GHz.
Acknowledgments
This work was supported by the Dikti Competitive Grants 2015 No. DIPA : SP DIPA-023.04.2.189705/2015, The Development of Magnetic Materials Based Composite Systems \((\text{Ba}_{1-y}\text{Sr}_y)\text{O.6Fe}_{2(1-x)}(\text{Mn,Ti})_x\text{O}_3\) for Interference Absorption of Electromagnetic Waves on Cell Phones., Y.E. Gunanto.

References

[1] Kumar A, Agarwala V and Singh D 2013 Effect of Particle Size of \(\text{BaFe}_12\text{O}_{19}\) on The Microwave Absorption Characteristics in X-Band Progres In Electromagnetics Research M \textbf{29} 223-236.

[2] Tudorache F, Popa P D, Brinza F and Tascu S 2012 Structural Investigations and Magnetic Properties of \(\text{BaFe}_12\text{O}_{19}\) Crystals Acta Physica Polonica A \textbf{121} 95-97.

[3] Kanapitsas A, Tsonos C, Psarras G C and Kripotou S 2016 Barium ferrite/epoxy resin nanocomposite system : Fabrication, dielectric, magnetic and hydration studies eXPRESS Polymer Letters \textbf{10} \textbf{3} 227-236.

[4] Gunanto Y E, Cahyadi L and Adi W A 2016 Composition and Phase Analysis of Nanocrystalline \(\text{Ba}_x\text{Sr}_1-x\text{Fe}_{12}\text{O}_{19}\) \((x = 1.0; 0.6; \text{and} 0.4)\) by Using General Structure Analysis System AIP Conference Proceedings \textbf{1725} 020023.

[5] Gunanto Y E, Jobiliong E and Adi W A 2016 Microwave Absorbing Properties of \(\text{Ba}_x\text{Sr}_0.4\text{Fe}_{12-x}\text{Mn}_x\text{O}_{19}\) \((x = 0 – 3)\) Materials in X-Band Frequencies J. Math. Fund. Sci. \textbf{48} \textbf{1} 55-65.

[6] Qin X, Cheng Y, Zhou K, Huang S and Hui X 2013 Microwave Absorbing Properties of W-Type Hexaferrite \(\text{Ba}(\text{MnZn})_x\text{Co}_{2(1-x)}\text{Fe}_{16}\text{O}_{27}\) J. Materials Science and Chemical Engineering \textbf{1} 8-13.

[7] Adi W A and Manaf A 2012 Structural and Absorption Characteristics of Mn-Ti Substituted Ba-Sr Hexaferrite Synthesized by Mechanical Alloying Route J. Basic. Appl. Sci. Res. \textbf{2} \textbf{8} 7826-7834.

[8] Toby B H 2001 EXPGUI a graphical user interface for GSAS Journal of Applied Crystallography \textbf{34} 210.

[9] Idris M S, Osman R AM 2013 Structure Refinement Strategy of Li-Based Complex Oxides Using GSAS-EXPGUI Software Package Advanced Materials Research \textbf{795} 479-482.

[10] Al-Saie A M, Al-Shater A, Arekat S, Jaffar A, Bououdina M 2013 Effect of annealing on the structure and magnetic properties of mechanically milled TiO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} mixture Ceramics International \textbf{39} \textbf{4} 3803-3808.