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Magnetic and microwave absorption properties of Mn⁴⁺ doped barium-natural ferrites prepared by the modified solid-state reaction method

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Abstract. Microwave wide-spread results in electromagnetic interference, environmental pollution, and hazards for health, thus microwave absorber is immediately needed. Mn⁴⁺ doped barium natural ferrites were synthesized using the modified solid-state reaction method, which is a combination of the sol-gel method and the solid-state reaction. Commercial Ba(NO₃)₂, MnO₂ and natural Fe₃O₄ were used as raw materials. Structural, magnetic properties and microwave absorption of the barium ferrites were characterized using XRD, VSM, and VNA, respectively. The results reveal that phase of BaFe_{2.37}Mn_{0.63}O₁₉ dominates the diffraction peaks with the average size of crystallite 23.74 nm after adding Mn⁴⁺ ions in the barium ferrites. *M_s* value of the barium ferrite decreases with increasing concentrations of Mn⁴⁺ due to the surface effect of the nanoparticle. The MBF3 exhibited excellent performance that absorbs all given microwave frequencies with *R_L* below -10 dB and bandwidth of 4 GHz compared to the other samples.

1. Introduction

Nowadays, the use of technology application increase, starting from portable telephone equipment, handphone, Local Area Network (LAN), Intelligent Transport System (ITS) [1] GPS, television signal. It is also followed by the rise of the microwave which spreads in environments. Microwave (MW) is a wave that has a high-frequency level of 0.3 GHz – 300 GHz. The rise of microwave spreading causes Electromagnetic Interference (EMI), hazards for human health, environment adulteration [2,3,4,5]. Accordingly, it is necessary for the existence of microwave absorbing materials. There is a requirement that should be fulfilled by microwave absorber materials, namely magnetism characteristic of soft magnetic, the size of crystal in 30 nm [6] and the homogeneity of the material. The microwave absorbing materials can be used as the veneering of RADAR (Radio Detection and Ranging) Machine [7].

Iron sand is one of the natural resources which contain magnetic materials such as magnetite (Fe₃O₄) [8], hematite (α -Fe₂O₃) and maghemite (γ -Fe₂O₃) that can be used as raw materials to make a barium hexaferrite (BaFe₁₂O₁₉). The notable advantages of barium hexaferrite such as cost-effectiveness, high coercivity field (*H_c*), strong remanent (*M_r*) and saturation magnetisation (*M_s*) make them attractive for such usage [9]. Development of this magnetic material is needed in various application fields. Substituting diamagnetic cations into barium ferrite is one of effort to improve their magnetic properties [10–13]. Application of BaFe₁₂O₁₉ material become attention today is as the absorbent material of



microwave (RAM). Mn^{4+} doped barium – natural hexaferrite was synthesised to reach absorbent material characteristic of the microwave. Mn^{4+} ions have ionic radius almost same with ferrite and paramagnetic characteristics [14]. On previous research, barium hexaferrite with doping Mn^{4+} ions to become $\text{Ba}_{(1-x)}\text{Mn}_x\text{Fe}_{12}\text{O}_{19}$ was prepared using the solid-state reaction method at various temperature sintering to obtain the porosity and density of the materials. The optimum condition can be achieved at the temperature of 1100 °C [15]. Therefore, the influence of Mn^{4+} on structure, magnetic properties, and microwave absorption ability of the barium hexaferrite prepared using the modified solid-state reaction method, will be analysed in X-Band. The method was an annexation between solid-state reaction and sol-gel methods. It is necessary for repairing the solid-state reaction method in getting the homogeneity and nanometer size of particles [16]. The size influenced the surface area and magnetism characteristics of the materials, whereas the homogeneity of such material was very influential toward the distribution of atom.

2. Experimental

Fe_3O_4 , $\text{Ba}(\text{NO}_3)_2$ with the purity 99%, MnO_2 , HNO_3 , $\text{C}_2\text{H}_2\text{O}_4$, polyethylene glycol, ethanol were used as raw materials. $\text{Ba}_{(1-x)}\text{Mn}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0; 0.1; 0.2$ in mol) were synthesized using the modified solid-state reaction method. After knowing the composition of the material, then sol-gel synthesis was done initially by mixing liquid precursor. The precursor was stirred using a magnetic stirrer and adding polyethylene glycol (PEG) until formed a sol. PEG has a function for controlling the size. After forming the sol, ethanol was added to make the solubility of sol [17]. One hour later, it will form a gel while stirring evenly. The concentrated gel will be obtained and then heated at a temperature of 150 °C. The liquid precursor in ferrite nitrate was yellowish-brown. Thus, it was added barium nitrate and manganese nitrate. The existence of Fe^{3+} ion led to brown colour, whereas yellow came from ion Fe^{2+} . Brown liquid colour revealed the domination of Fe^{3+} ions from Fe^{2+} ions.

The concentrated gel was calcinated at a temperature of 350 °C for an hour to obtain a material powder. Afterwards, the powder was compacted and sintered. This process is part of the solid-state reaction method. This process aimed to direct spin and condensed material so that the reaction between load on solids or pellets which usually called pre-diffusion inter one atom with others atom. Compression was done by using mechanic press tools with pressure per area of 1 ton formed coin pellets with the diameter around of 1.33 cm and thickness around 0.42 cm. Finally, the pellets were sintered at a temperature of 1100 °C for 5 hours [15].

The X-ray Diffractometer (XRD–PHILIPS PW1710) with Cu–K α radiation ($\lambda=1.541874$ Å) was used to determine microstructure and phase of the as-synthesized ferrite pellets, respectively. Magnetic properties of the ferrites were measured using the vibrating sample magnetometer (Oxford VSM 1.2 H). The microwave (MW) absorption properties of the ferrites were recorded using a vector network analyzer (VNA–Advantest R3770) in the frequency range of 8–12 GHz [18]. The MW absorption was measured using the Transmission/Reflection Line (TRL) method with Reflection Loss (R_L) as the following equation:

$$R_L = 20 \text{ Log} \sqrt{S_{11}^2 + jS_{11}^2} \quad (1)$$

Where S_{11} real is bounding wave, and S_{11} imaginer is an absorbent wave in the material.

3. Results and discussion

Figure 1 shows the XRD patterns of Mn^{4+} doped barium ferrites. The phase of $\text{BaFe}_{12}\text{O}_{19}$ with hexagonal crystal system dominates the diffraction peaks of MBF1. Meanwhile, the phase of BaFe_2O_4 with orthorhombic crystal system appears as the minor phase, which is an intermediate phase and anti-magnetic materials. These results are appropriate with the previous results [19]. Adding Mn^{4+} ions in

the structure of the barium ferrite (MBF2) yields two phases of $\text{BaFe}_{2.37}\text{Mn}_{9.63}\text{O}_{19}$ and BaFe_2O_4 . The XRD pattern is dominated by peaks of $\text{BaFe}_{2.37}\text{Mn}_{9.63}\text{O}_{19}$ with orthorhombic crystal system, and BaFe_2O_4 as the minor phase. The interaction between Mn^{4+} with $\text{BaFe}_{12}\text{O}_{19}$ generates the existence of $\text{BaFe}_{2.37}\text{Mn}_{9.63}\text{O}_{19}$. Also, the inter atoms distribution of MBF2 is more uniform compared to MBF1. The MBF3 has similar phases with MBF2. The observed peaks of the pattern are attributed to $\text{BaFe}_{2.37}\text{Mn}_{9.63}\text{O}_{19}$ and BaFe_2O_4 . BaFe_2O_4 shows the high intensity at the position of $2\theta = 33.47^\circ$. The dominant phase of MBF3 is similar to the dominant phase of MBF2, but the minor phase of MBF3 is slighter than MBF2. The minor phase of BaFe_2O_4 decreases with increasing Mn^{4+} . Besides, the MBF3 has the smallest size of the crystal, i.e. ~ 23.740 nm.

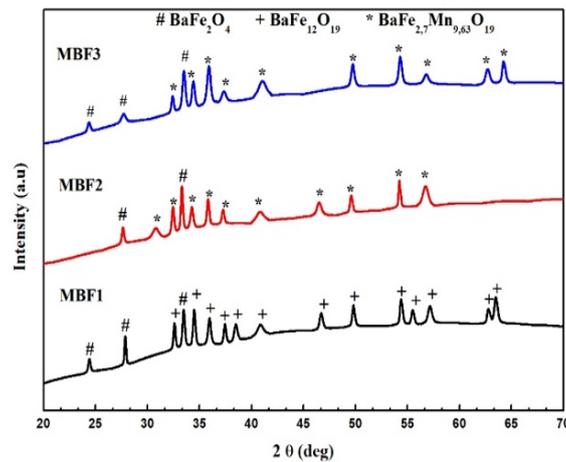


Figure 1. XRD patterns of Mn^{4+} doped barium ferrites after the sintering process

Figure 2. shows the effect of Mn^{4+} on the crystallite size of the samples after the sintering process. The crystallite size of the sintered samples decreases with the increasing concentration of Mn^{4+} from 32.960 to 23.740 nm; this size is categorized as superparamagnetic. Crystallite size determines the surface area of samples and the magnitude of microwaves absorption. The small crystal size will enlarge the surface area of the material so that the interaction between the microwaves and magnetic spins is increasing. However, there is a specific limitation in reaching efficient absorption characteristics. The soft magnetic material has a high absorption level of microwaves if the material has super-paramagnetic characteristics [14].

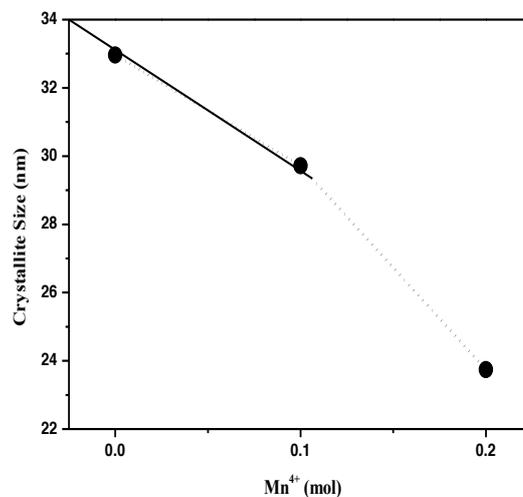


Figure 2. Effect of Mn^{4+} ions on crystallite size of the sintered barium ferrites

Figure 3 describes a magnetic hysteresis loop of the barium ferrites. It can be observed that all barium ferrites have characteristic as soft magnetic behaviour, which is proved by slender curves [20]. Incorporation of Mn^{4+} ions in the structure of the barium ferrites yields increasing their coercivity field and significant decreasing saturation magnetization. Mn^{4+} reduces the unpaired spin magnetic moment so that the energy (coming from the external magnetic field) needed to direct the spin is smaller, which is marked by a decrease in the value of saturation magnetization from 15.40 to 10.27 emu/g lead to decreasing susceptibility (X_m) and permeability (μ_r). The relationship between the magnetization, susceptibility, and permeability are given by Eq. 2 and Eq. 3.

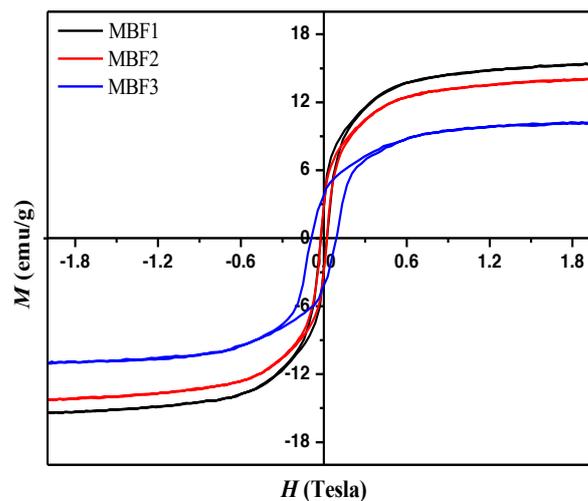


Figure 3. Magnetic hysteresis loop of the Mn^{4+} doped barium ferrites

$$M = X_m H \quad (2)$$

$$X_m = \mu_r + 1 \quad (3)$$

Table 1. Magnetic properties of the Mn^{4+} doped barium ferrites

Sample	X_m (emu.T/g)	μ_r (emu.T/g)	M_s (emu/g)
MBF1	9.503×10^{-6}	1.00001	15.40
MBF2	8.684×10^{-6}	1.000009	14.09
MBF3	6.299×10^{-6}	1.000006	10.27

The measurement principle of microwave absorption is to measure reflection loss (R_L) due to an interaction between materials with microwave given. The microwave absorption in the material is based on the material compactness, and the amount of material (thickness) [7]. Most solid materials have a possibility that extra energy will be more considerable because the gap between grains in the material is closer or dense.

Figure 4 depicts the microwave frequency-dependent reflection loss for the Mn^{4+} doped barium ferrites. It can be observed that the MBF3 absorbs all given microwave frequencies with R_L below -10 dB and bandwidth of 4 GHz. The best absorption with $R_L \sim -18$ dB is found at the frequency of 10.5 GHz. The

most profound spare energy and the widest absorption of bandwidth indicate the optimum absorber. The decreasing saturation magnetization plays an essential role in a natural frequency change of the barium ferrite lead to reducing its reflection loss. Selection of proper microwave absorbers in the X-band is essential to avoid electromagnetic interference (EMI) which can damage electronic devices and cause signal degradation [21].

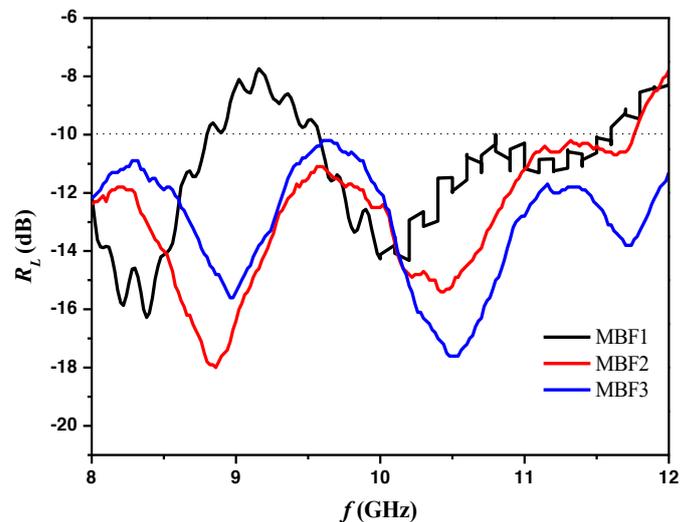


Figure 4. Microwave frequency-dependent reflection loss for the Mn^{4+} doped barium ferrites

4. Conclusion

A new magnetic materials with compositions of $\text{Ba}_{(1-x)}\text{Mn}_{(x)}\text{Fe}_{12}\text{O}_{19}$ ($x = 0; 0.1; 0.2$ mol) were synthesized using the modified solid-state method at the sintering temperature of 1100°C . Incorporation of Mn^{4+} ions in the barium ferrites yielded a change of its phase. $\text{BaFe}_{2.37}\text{Mn}_{9.3}\text{O}_{19}$ phases with orthorhombic crystal system and the smallest crystal size, i.e., 23.740 nm, dominated diffraction peaks of the barium ferrites. The saturation magnetization, susceptibility, and permeability, as well as reflection loss of the barium ferrite, decreased with increasing concentrations of Mn^{4+} ions. MBF3 exhibited excellent performance in microwave absorption ability due to the presence of $\text{BaFe}_{2.37}\text{Mn}_{9.63}\text{O}_{19}$ phase and surface effect of the nanoparticle.

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