

SYNTHESIS AND CHARACTERIZATION OF BARIUM-HEXAFERRITE NANOPARTICLES FOR MICROWAVE ABSORPTION

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ABSTRACT

Prior to its use for microwave absorption, a hard ferrite was synthesized and characterized. A mixture of iron oxide (Fe_2O_3) and barium carbonate (BaCO_3) was milled using the mechanical alloying technique and sintered at a temperature of 900°C for 10 hours to form barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$). X-ray diffractometry (XRD), vibrating sample magnetometry (VSM) and scanning transmission electron microscopy (STEM) were used to investigate the crystalline phase formation, the material's magnetic hysteresis-loop properties and particle size respectively. From the XRD results it is shown that at 900°C the full phase of barium hexaferrite was formed. The VSM result shows that at a temperature as low as 900°C , the saturation magnetization can achieve a value as high as 53.5 emu/g and the sample possesses a coercivity as high as 1071.9 Oe. The STEM result shows that the particle size is 300-400 nm. The high magnetization and coercivity values are good for large microwave absorption losses. Barium hexaferrite were mixed with magnetite to form composite. A suitable absorber giving high losses was formed to contain 15 wt% magnetite.

Keywords: mechanical alloying; barium hexaferrite; X-ray phase analysis; VSM; STEM.

INTRODUCTION

Although absorbing materials are a useful part of modern-day defense systems, very little published knowledge exists on the fabrication of such materials especially microwave absorbing materials. The present research attempts to fabricate absorbing material compositions suitable for absorption at high frequency. Absorption of EM waves occurs in magnetic materials due to the magnetic losses[1]. Ferrites were chosen as the best materials for microwave absorption because they exhibit high magnetic losses in the vicinity of their ferromagnetic resonance. An interesting choice is barium hexaferrite. Barium hexaferrites ($\text{BaFe}_{12}\text{O}_{19}$) with a magnetoplumbite structure are well

known as hard magnetic materials which are based on iron oxides. Hexagonal ferrites are referred to as hard because the direction of magnetization cannot be changed easily to another axis[2]. Moreover, it has a fairly large magnetocrystalline anisotropy, a high Curie temperature, a large saturation magnetization, a high coercive force, good chemical stability and corrosion resistivity[3]. In fact, hexaferrites materials can be used across the whole GHz region[4]. The presence of large barium ions and the slightly modified crystal structure causes the barium hexaferrite to have high-valued magnetic properties unlike spinel and garnets[5]. Furthermore, extrinsic properties such as fine particle size that contribute to high values of magnetic coercivity are strongly related to microstructure. In fact, the high coercivity values are associated with the nanometer grain size. Thus, high coercivity (H_c) materials have nanoscale crystallites. This indicates that barium hexaferrite is a potentially good microwave absorber since highly H_c means high hysteresis absorption loss if the saturation magnetization is also high. In the development of suitable absorbers, there are two elements which are important i.e. composition and processing. An absorbers material can be produced either as ceramics or as composites[1]. Therefore, Ba-hexaferrite were used to mix with magnetite for further investigation.

METHOD

This research work can be divided into two stages. Barium hexaferrite ($BaFe_{12}O_{19}$) was prepared via the mechanical alloying method for the first stage. The starting raw materials of Barium Carbonate ($BaCO_3$) 99.80% and Iron Oxide (Fe_2O_3) 99.5% from Alfa Aesar were used without further purification. They were weighed according to targeted proportions and mixed using normal ball milling for homogeneity. It was further milled using a SPEX8000D mill in a hardened steel vial together with 10 grinding balls having a diameter of 12 mm each to obtain nanometer particle size. The milling time and Ball to Powder weight Ratio (BPR) which was 5 hours and 10:1 respectively were used for the preparation of ferrite nanoparticles used in this research. The powder was then sintered at $900^{\circ}C$ for 10 hours. Then a brown barium ferrite powder was obtained. For the second stage, magnetite powder without further purification was also weighed according to a targeted proportion with different percentages to be mixed with barium hexaferrite for making composites. It was mixed using mortar and pestle for homogeneity. The crystalline phase formation of barium hexaferrite, magnetite and composites powder was further investigated with X-ray diffraction (XRD) spectra using an X-Pert PANalytical diffractometer (PW3050/60) using $CuK\alpha$ radiation in the range 20° to 80° , the magnetization vs magnetic field (M-H) plot of barium hexaferrite was obtained using a vibrating sample magnetometer (VSM) and the average particle size was obtained from the scanning transmission electron microscope (STEM). The permeability of the composite materials was obtained by measuring the impedance using an Agilent 4291B from 10 MHz to 1 GHz.

RESULTS AND DISCUSSIONS

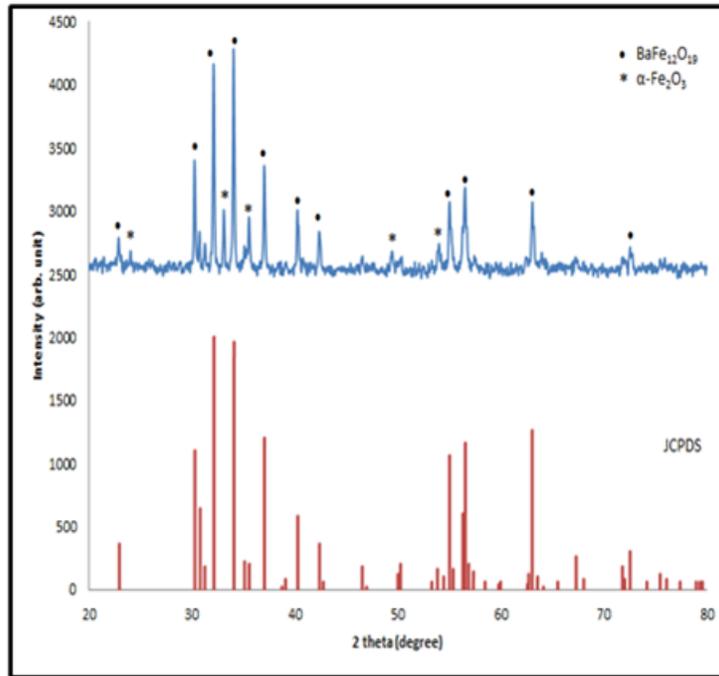


Figure 1 shows an X-ray diffraction pattern of $\text{BaFe}_{12}\text{O}_{19}$ after being sintered at 900°C for 10 hours

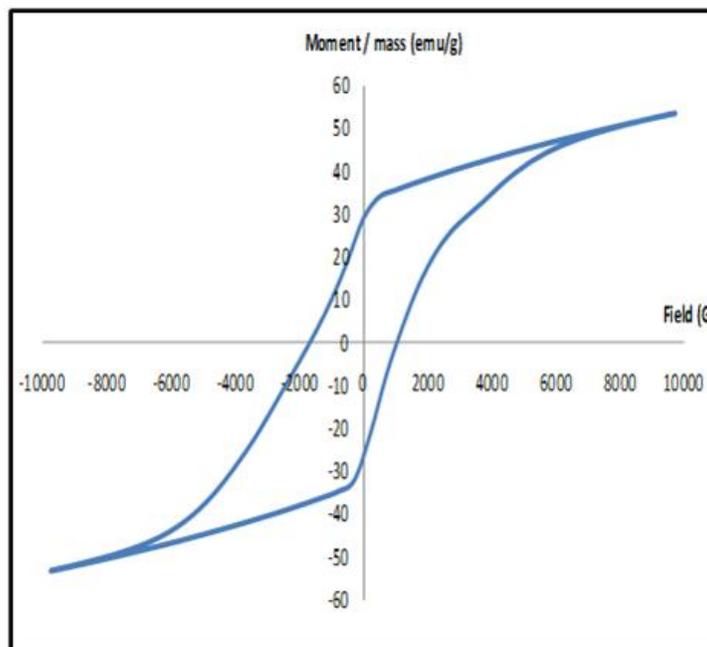
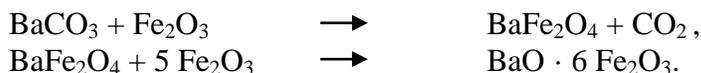


Figure 2: M-H hysteresis curve measured using a VSM

Figure 1 shows an X-ray diffraction pattern of BaFe₁₂O₁₉ after being sintered at 900°C for 10 hours. It was well indexed with the hexagonal BaFe₁₂O₁₉ standard data of JCPDS (39-1433). The patterns show that the formation of the hexaferrite phase of BaFe₁₂O₁₉ has occurred by two main steps of formation mechanism of barium hexaferrite which takes place in solid state reaction [6, 7] as shown below:



A diffusion process is important in these reactions and it will affect the particle size. At lower temperatures with smaller particle size, it will lead to the formation of barium hexaferrite. By milling the powders via high energy ball milling, it can decrease the synthesis temperature of barium ferrite [8]. It is because during the powder being milled at room temperature, the intermediate BaFe₂O₄ was formed which is the most important factor to decrease the sintering temperature of barium ferrite. If BaCO₃ and Fe₂O₃ are not milled, it tends to form BaFe₂O₄ at temperature of above 400 °C. The BaFe₁₂O₁₉ phase starts formed at temperature of 800°C [9, 10]. At temperatures below 900°C, hematite and barium oxide will form barium monoxide which will then, at 900°C, diffuse into hematite to form barium hexaferrite. By sintering sample at 900°C, the fraction of BaFe₁₂O₁₉ will be raised up whereas, the amount of hematite still remains [9]. That is the reason to the figure whereby we could see the hematite phase still occurring at position 24.072°, 33.1196°, 35.5472°, 49.4041° and 53.9119°. When the precursors are heated to 900°C directly, α-Fe₂O₃ forms a stable phase and does not react with Ba²⁺. Therefore, there exists a small amount of residue in the sample [11].

The studies of magnetic properties were focused on the M-H hysteresis curve measured using a VSM. As shown in Figure 2, the synthesized barium hexaferrite possesses high coercivity and high saturation magnetization. It shows hard magnetic properties with a coercivity as high as 1071.9 Oe and a saturation magnetization of 53.5 emu/g. In the absence of an applied field, materials that can retain permanent magnetization are known as hard magnets [12]. The hysteresis internal areas shows that it is good as an electromagnetic wave absorber. It was reported that the coercivities of the milled powder is better than that of the unmilled powders [8]. It was reported that the variation of the particles size does not affect the saturation magnetization. As-milled samples and sample sintered at 600°C have low saturation magnetization (≤10 emu/g) and low coercivity due to the presence of antiferromagnetic hematite and paramagnetic wustite phase [10]. High coercivity was obtained due to the formation of the hexaferrite phase. High coercivity values are associated with the nanosize whereby it is in nanometer scale, the new absorption mechanism would appear and nanosized ferrite will absorb more microwave energy [13]. Magnetic properties strongly depend on the grain size and nanoscale crystallites materials have high coercivity [6] which was obtained by mechanical alloying [14]. High value of coercivity is related to particles which have significantly smaller than the single-domain particle size which is about (~1.0 μm) [15]. When the size of barium ferrite particles was reduced, the number of particles with single domain increases [13]. It also can perform well when the particles are in single

domain ($\sim 1.0 \mu\text{m}$) which will exhibit high saturation magnetization with large coercivity, chemically homogeneous, narrow size distribution and can disperse well[16]. Thus, the ferromagnetic resonance will absorb more energy. In fact, when the surface spins of ferrites nanoparticles are disordered there will be an exchange coupling between the surface and the core which gives rise to a variety of spins distributions within a single domain [13]. Thus, surface spin can result in high hysteresis loss and microwave absorption will improve[13].

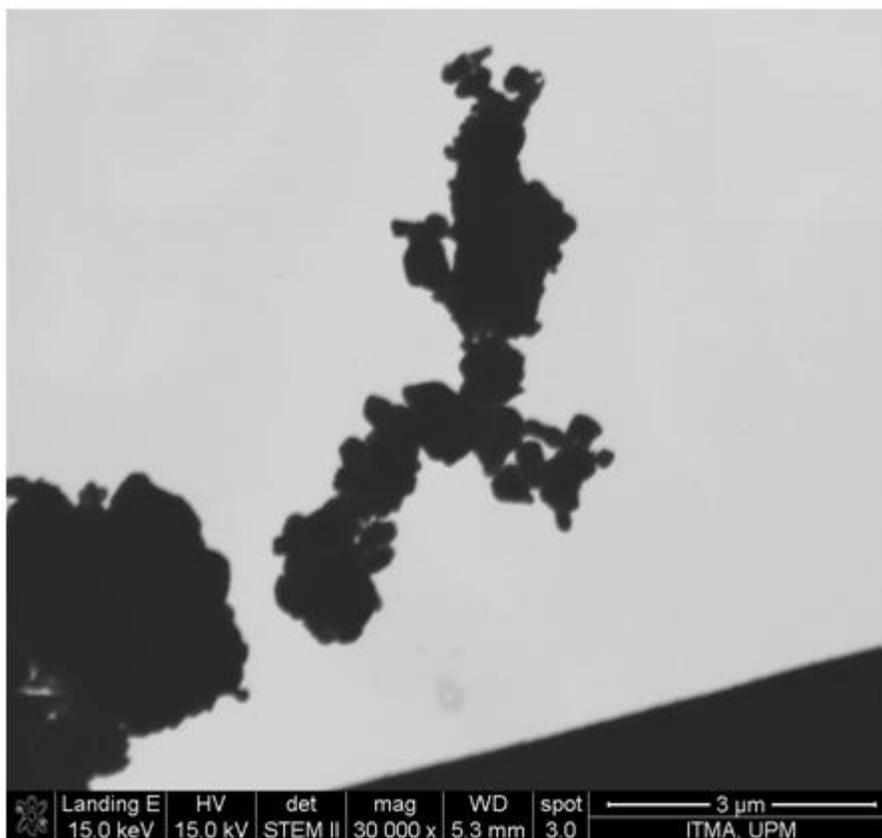


Figure 3: STEM results of Barium hexaferrite powder sintered at 900°C

Figure 3 shows STEM results of barium hexaferrite powder sintered at 900°C and figure 4 shows the average particle size was 300-400 nm which was obtained by STEM measurement. By using Scherrer equation, the crystallite size was calculated from the most intense peak (104) and the result is 53.48 nm for sample $\text{BaFe}_{12}\text{O}_{19}$ after sintering. From the STEM result and the graph of particle size distribution, the average particle sizes of $\text{BaFe}_{12}\text{O}_{19}$ is in the range of 300-400 nm. Therefore, it will exhibit formation of single domains as reported previously that the critical diameter of barium hexaferrite is 460nm[17]. By increasing the temperature, it will lead to the formation of large grains with more than single-domain limit of $\sim 1\mu\text{m}$ [9]. From the pattern and particle size estimation, it is expected that the powders sintered at 900°C should have good magnetic properties [9]. With the reduction of the size of barium ferrite particles, the number of

particles with single domains increases. However, if the size is below the critical diameter, magnetic particles cannot support more than one domain. It is because when surface spins of ferrite nanoparticles are disordered, and the exchange coupling between the surface and core gives rise to a variety of spin distribution within a single domain particles. In addition, the expected ferromagnetic resonance behavior will absorb more energy whereas the surface spin can result in high hysteresis loss. Thus, the microwave absorption is expected to be improved and this will be further discussed.

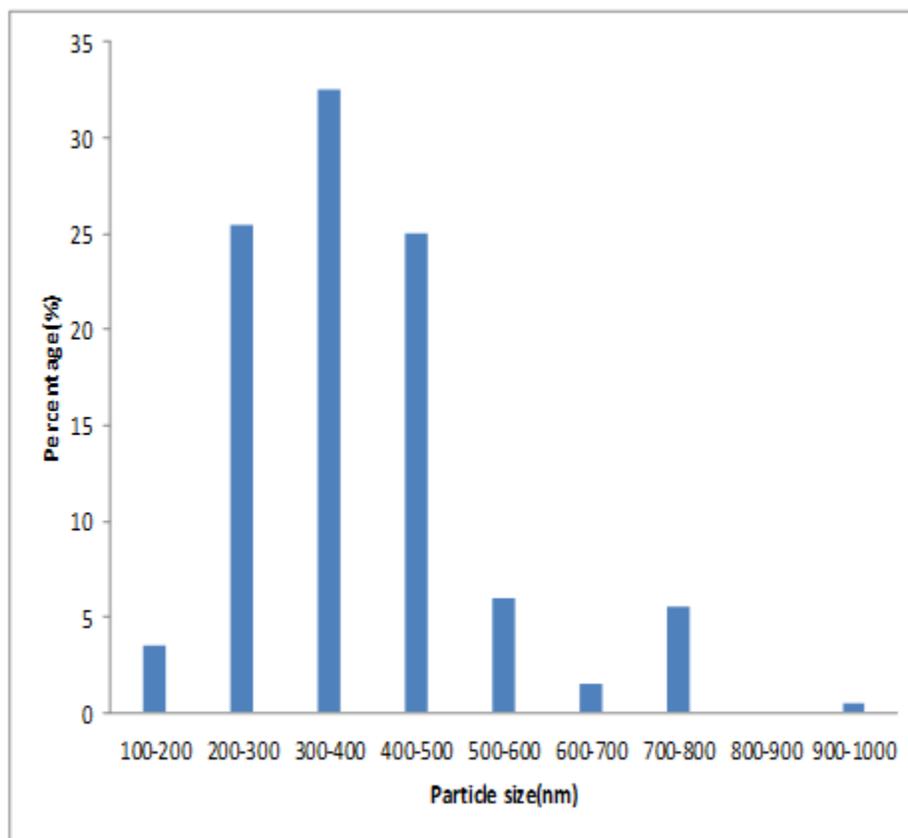


Figure 4: Particle size histogram

Magnetic composites are interesting for microwave applications. By simply varying the volume fractions of the constituent phases, the electromagnetic properties of the composites can be effectively tuned[1]. Therefore, different weight percentages of Fe_3O_4 were mixed with $\text{BaFe}_{12}\text{O}_{19}$ to obtain composite powder. Figure 5 shows X-ray diffraction of the single phase magnetite, barium hexaferrite sintered at 900°C and composite powder with different weight percentages of Fe_3O_4 . From the results, it can be observed clearly that there are two sets of phases which are $\text{BaFe}_{12}\text{O}_{19}$ and Fe_3O_4 obtained for the composite sample. Moreover, there were 9 peaks which represent the $\text{BaFe}_{12}\text{O}_{19}$ phase were observed at angle 30.417° , 32.283° , 34.243° , 37.136° , 40.402° , 42.455° , 55.240° , 56.733° and 63.172° . On the other hand, there are two Fe_3O_4 peaks at angle 35.456° and 62.985° . It is clear that the composite samples vary with the weight

percentage of Fe_3O_4 . Although there are only 2 peaks representing Fe_3O_4 , it can be observed that the increment weight percentage of Fe_3O_4 affects the overall composition of the composite. It is because the weight percentage increases, all the peaks of the dominant phase which is $\text{BaFe}_{12}\text{O}_{19}$ starts to decrease, whereas the Fe_3O_4 phase starts to increase with the weight percentage.

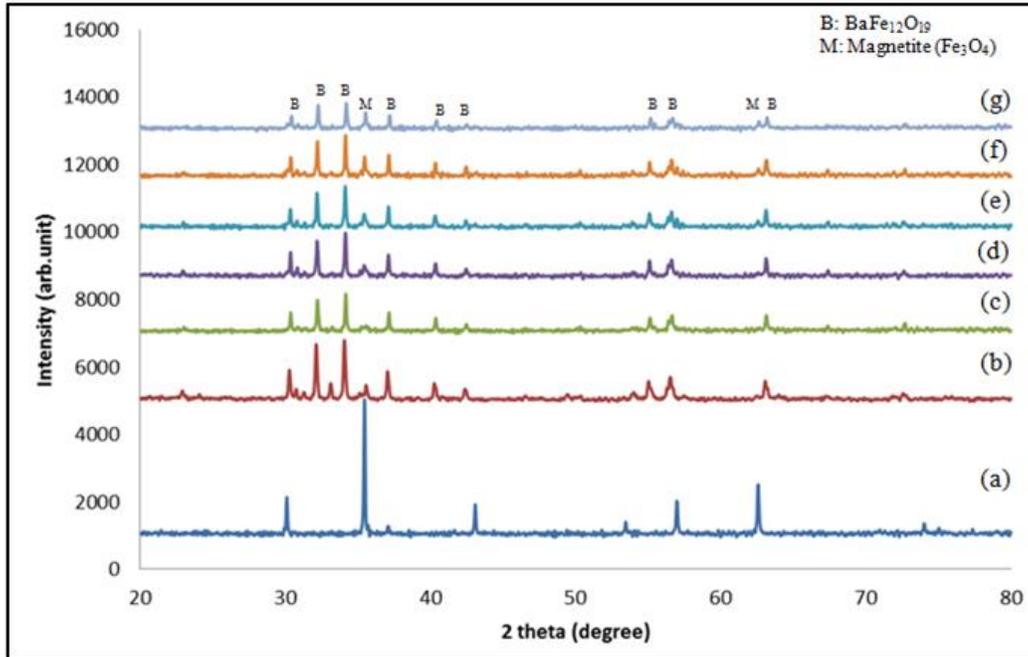


Figure 5: XRD results of a) pure Fe_3O_4 , b) pure $\text{BaFe}_{12}\text{O}_{19}$ and for composite ($\text{BaFe}_{12}\text{O}_{19} + x \text{Fe}_3\text{O}_4$), c) $x=3\text{wt}\%$, d) $x=6\text{wt}\%$, e) $x=9\text{wt}\%$, f) $x=12\text{wt}\%$, g) $x=15\text{wt}\%$

The material absorption capability which may be frequency dependent, depends on the extrinsic material properties which are permittivity and permeability[18]. However, ferrite phases have approximately similar permittivity values[1], therefore, the analysis was focused on the permeability parts which give larger differences between phases. Figure 7 shows real and imaginary permeability spectra of the composites with different weight percentages of Fe_3O_4 in frequency range of 10MHz to 1GHz. From figure 6(a), the permeability part show a trend of the composite material; so also the imaginary part in figure 6(b) which is also well known as loss factor. For all the samples, the permeability and loss factor show fairly constant values with frequency. However, they rise slightly around 500 MHz. This phenomenon is attributed to both permeability and loss factor value which are approaching to the resonance frequency in the GHz range. Moreover, it can be observed that the amount of weight percentage was directly proportional with the permeability value whereby as the weight percentage is increased, the real permeability value also increased. The same trend goes for the loss factor part. When the weight percentage of magnetite is high, the loss factor is also high, thus, magnetite can be considered as the main composite material as $\text{BaFe}_{12}\text{O}_{19}$ just gives localized magnetic field within certain region of Fe_3O_4 . Furthermore, in the region

between 10 to 400MHz, it indicates domain wall contribution is dominant, whereas the rises show the spin contribution is dominant whereby resonance will occur.

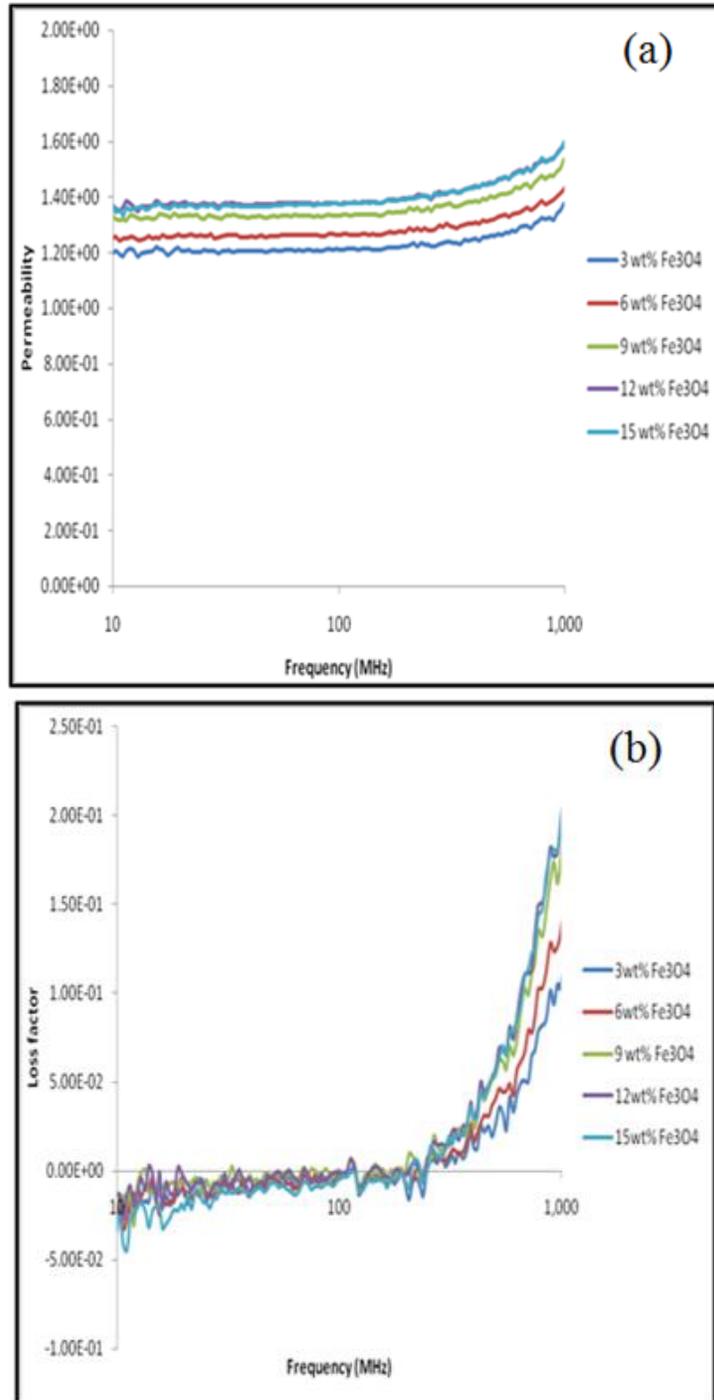


Figure 6: a) real permeability part and b) imaginary part versus frequency.

CONCLUSION

In conclusion, a good crystalline barium hexaferrite phase has been synthesized and the properties of the material needed for a good microwave absorption i.e. high magnetization and large coercivity have been obtained. The high magnetization is due to the high degree of crystallinity and the high coercivity depends on the nanometer grain size besides magnetocrystalline anisotropy. Magnetite plays a role as an absorber medium while barium hexaferrite act as bias field that act upon magnetite. The best composition of the composite is $\text{BaFe}_{12}\text{O}_{19}+15\text{wt}\%\text{Fe}_3\text{O}_4$. It has the potential of being used as an electromagnetic wave absorber.

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