Effect of Different Weight Fraction on Dielectric Properties of Barium Ferrite-Barium Titanate Composites

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Abstract. Barium ferrite-barium titanate composite systems, (1-x)BaFe$_{12}$O$_{19}$–(x)BaTiO$_3$ with different weight fractions of x = 0.0, 0.1, 0.3 and 0.5 were prepared via the conventional solid state reaction method using nano-sized starting materials. The x-ray diffraction peaks of the composite samples show two phases which can be indexed by the hexagonal barium ferrite and tetragonal barium titanate. Field emission scanning electron microscope (FESEM) image of sample with x = 0.1 shows formation of nano-sized BaTiO$_3$ grains spreading evenly among the micron-sized BaFe$_{12}$O$_{19}$ grains after sintering at 1000 °C. The dielectric properties studies at room temperature of the composites samples show that sample with BaTiO$_3$ weight fraction of x = 0.1 has the highest dielectric constant, ε' and lowest loss tangent, tan δ in the studied frequency range between 1 Hz and 1 MHz. Its highest dielectric constant value is ~ 1.2 × 10$^3$ and its lowest loss tangent is 0.06 at 50 Hz.

1. Introduction
Barium ferrite (BaFe$_{12}$O$_{19}$) is known as a permanent magnetic material which can also be categorize as a ferrimagnetic material that has great properties such as high saturation magnetization, anti-erosion, better chemical stability, great coercivity and low cost material. It has a very wide range of application such as in a high-density recording media and electromagnetic wave absorber [1], [2]. Barium ferrite was also used in microwave communication, microwave dark room and the anti-electromagnetic wave radiation [3]. Barium ferrite has hexagonal structure and can be characterized in magneto-plumbite oxide group and can be classified as hard magnetic materials [4]. Ferrite is one of a ferromagnetic oxide that has both dielectric and magnetic properties when applied with high frequency and is suitable for microwave applications [5]. In barium ferrite compounds the Fe$^{3+}$ ions occupy the sub lattice at different sites that lead to different magnetic properties. Addition of nonmagnetic materials into barium ferrite compound will influence its sub lattice [6] and magnetic properties.

Fine and dense barium titanate (BaTiO$_3$) with nano-sized particles make it an outstanding dielectric material [7]. Barium titanate, is known as a ferroelectric material and has been studied widely because of its potential application such as in multilayer ceramics capacitors (MLCC), positive temperature coefficient of resistance (PCTR) thermistors, piezoelectric sensors, transducers, actuators and ferroelectric random access memories (FRAM) and electro-optic devices [8]. Barium titanate is also an excellent material for field-induced piezoelectric transducer because of its high polarization, high permittivity and high induced strain [9].

Due to the widely usage of barium ferrite and barium titanate respectively, we combined both materials and tried to obtain information whether there are any improvement of the composite system.
properties compared to the parent materials. However in this paper we only focus on the dielectric properties of the composites samples prepared from nano-sized barium ferrite and barium titanate powders.

2. Experimental methods

(1-x)BaFe\(_{12}\)O\(_{19}\) – (x) BaTiO\(_3\) composites have been prepared using the conventional solid state reaction technique. Nano-sized barium ferrite, BaFe\(_{12}\)O\(_{19}\) and barium titanate, BaTiO\(_3\) powders were weighed according to different weight fractions where x = 0.0, 0.1, 0.3 and 0.5. 3 g of the powders mixture was weighed according to the fixed ratios and ground using Fritsch planetary mono mill for 1 hour at a speed of 350 rpm. 1 g of the mixed and ground powder was uni-axially pressed into pellet shape at 290 MPa for 2 minutes. The pellet was then sintered at 1000 °C for 6 hours in air. X-ray diffractometer (XRD) (Bruker D8 Advanced) was used to identify the crystalline structure and phases of the samples with different ratios. The observations were made at angle between 20-80 °. The morphology of the fracture surface of the pellets was observed using field emission scanning electron microscope (SEM) (Gemini Supra Series), which is equipped with energy dispersive X-ray for elemental analysis. Dielectric properties of the samples as a function of frequency were studied at room temperature using High Frequency Response Analyzer (HFRA Solartron 1265) in the frequency range of 1 Hz to 1 MHz. Silver paint was painted on both surfaces of the pellet as electrodes for better electrical contact.

3. Results and discussion

Figure 1 (a) shows the XRD spectrum for all samples. Sample with x = 0.0 shows peaks of a single phase BaFe\(_{12}\)O\(_{19}\) that can be indexed with the standard JCPDS file number 39-1433 with hexagonal structure. The (hkl) of the prominent peaks are shown in the figure. The peaks of tetragonal structured BaTiO\(_3\) (5-0626) emerges when it is added to the BaFe\(_{12}\)O\(_{19}\). Intensity of the BaTiO\(_3\) peaks increase with increasing of its composition in the composites.

Figure 1(b) illustrates the XRD patterns of the samples between 20 of 31.0 ° - 35.0 ° showing the strongest BaFe\(_{12}\)O\(_{19}\) peaks of (1 0 7) and (1 1 4); and BaTiO\(_3\) peak of (1 1 0). The BaTiO\(_3\) peak intensity increases with x but the peak shifted slightly to the right showing a decrement of the lattice spacing due to the increasing BaTiO\(_3\) content. On the other hand the BaFe\(_{12}\)O\(_{19}\) peaks shift slightly to the left when x = 0.1 and shift to right with further x increment. This could be due to the modification of the original crystal structure arrangement when smaller size BaTiO\(_3\) substitutes the larger BaFe\(_{12}\)O\(_{19}\) in the lattice.
Figure 1. (a) XRD patterns for \((1-x)\text{BaFe}_{12}\text{O}_{19} - x\text{BaTiO}_3\) samples with \(x = 0.0, 0.1, 0.3\) and 0.5; (b) in range of 31.0 – 35.0°.
The morphology from the fracture surface of composite sample with \( x = 0.1 \) can be observed in Figure 2. From the SEM micrograph and EDX mapping analysis it is shown that the spherical nano-sized grains (< 50 nm) are \( \text{BaTiO}_3 \) and the micron-sized grains are \( \text{BaFe}_{12}\text{O}_{19} \). The nano-sized \( \text{BaFe}_{12}\text{O}_{19} \) particles change to micron-sized after the sintering process. This is due to the occurrence of diffusion process among the compacted \( \text{BaFe}_{12}\text{O}_{19} \) powders when subjected to a very high temperature. Mallick et al. stated that the grains will combine to form bigger grain because of the thermodynamically driven mass diffusion mechanisms. Bonding of the particles forms larger \( \text{BaFe}_{12}\text{O}_{19} \) with average grain size of 0.2 – 0.3 \( \mu \text{m} \). Ferrite materials can be dense rapidly when subjected to high temperature [10]. The melting point of \( \text{BaFe}_{12}\text{O}_{19} \) is about 1300 °C [11] and the sintering temperature used was 1000 °C while melting point for barium titanate 1620 °C [12].

![SEM micrograph of (1-x)\( \text{BaFe}_{12}\text{O}_{19} \) – x\( \text{BaTiO}_3 \) sample with \( x = 0.1 \)](image)

Figure 2. SEM micrograph of (1-x)\( \text{BaFe}_{12}\text{O}_{19} \) – x\( \text{BaTiO}_3 \) sample with \( x = 0.1 \)

Figure 3 shows the variation of dielectric constant, \( \varepsilon' \) with frequency for all samples at room temperature. The dielectric constant, \( \varepsilon' \) represents the ability of a material to polarize and store electric energy. \( \text{BaFe}_{12}\text{O}_{19} \) shows dielectric behaviour by itself [5]. The dielectric constant of all the (1-x)\( \text{BaFe}_{12}\text{O}_{19} \) – (x)\( \text{BaTiO}_3 \) composites decreases with frequency, which is a common behavior for dielectric materials. The dielectric constant becomes nearly constant at higher frequency with the largest constant range \( (10^4 - 10^6 \text{ Hz}) \) and lower dielectric constant value for sample without \( \text{BaTiO}_3 \) content. The high dielectric constant at lower frequency up to around 100 Hz can be interpreted on the basis of the Maxwell-Wagner interfacial space charge polarization which arises due to the heterogeneity of the sample caused by pores, grain boundaries and layered structures. At low temperature the large well conducting grains that are separated by the thin poorly conducting or insulating intermediate grain boundaries promotes polarization in the samples. Charge carriers may also accumulate at the sample-electrode surface.

Graph of the dielectric constant versus weight fraction, \( x \) for (1-x)\( \text{BaFe}_{12}\text{O}_{19} \) – (x)\( \text{BaTiO}_3 \) at different frequencies is shown in Figure 4. It is found that \( \text{BaTiO}_3 \) addition improves the dielectric
constant of the composite matrix ceramic. At 50 Hz the dielectric constant for $x = 0.0$ is in the power of three and increases two order of magnitude to the power of five for $x = 0.1$. The composite mixture with inhomogeneous microstructure creates dipole because of the changes of valence state of cations and the space charge polarization [13]. Sample with $x = 0.1$ has the highest dielectric constant which is $1.2 \times 10^3$ at 50 Hz at room temperature. The dielectric constant is nearly constant at very high frequencies for samples with BaTiO$_3$. When external field is applied to the sample, the domains of the samples were reoriented and became polarize that will lead to straining in the dielectric of composites [14]. Ferrite is known as a material that can make the values of dielectric constant of some materials decrease because of the exchange interaction. Electrons in ferrite begin to polarize due to electron hopping that can make the displacement of charges that will affect polarization in the direction of external applied field [15]. A study by Lokare et al. (2008) showed that dielectric constant increases when barium titanate ratios increases because of the ferrimagnetic region has surrounded the ferroelectric regions.

**Figure 3.** Frequency dependence of the dielectric constant for $(1-x)$BaFe$_{12}$O$_{19} - x$BaTiO$_3$ samples with different weight fraction ($x = 0.0, 0.1, 0.3$ and $0.5$)
Figure 4. Weight fraction, x dependence of the dielectric constant at different frequencies for \((1-x)\text{BaFe}_{12}\text{O}_{19} - x\text{BaTiO}_3\).

Figure 5 shows the variation of loss tangent, \(\tan \delta\) with frequency for all samples. Loss tangent is the loss of electrical energy in the form of heat due to the oscillation of the charge carriers. For all samples the loss tangent increases with frequency and forms a peak at a very high frequency, except for sample with \(x = 0.1\). The peak represents the relaxation process where the charges cannot keep up with the frequency of the applied ac electric field. The lowest loss tangent value at 50 Hz is for sample \(x = 0.1\) which is 0.06 at room temperature.
Figure 5. Frequency dependence of loss tangent for (1-x)BaFe$_{12}$O$_{19}$–xBaTiO$_3$ samples with difference weight fraction (x = 0.0, 0.1, 0.3, and 0.5)

4. Conclusions
The effect of BaTiO3 addition on the dielectric properties of (1-x)BaFe$_{12}$O$_{19}$ – (x)BaTiO$_3$ composites system with different weight fraction have been studied. XRD results of the sintered composites show the formation of BF and BT phases without other impurity phase. The FESEM micrograph shows nano-sized BT particles are spread among the micron-sized BF. The frequency variation of dielectric constant shows the common dielectric behaviour, which is the dielectric constant decreases when frequency increases. At low frequency the interfacial polarization contributes to the very high dielectric constant. Dielectric constant of the composites increases from the power of three for sample without BaTiO$_3$ at 50 Hz, up to the power of five for sample with x = 0.1. However, higher BaTiO$_3$ fraction (x = 0.3 and 0.5) results in a slight decrement of the dielectric constant. The loss tangent of all samples is very low and increases with frequency. Further study will be done on sample with x = 0.1 due to its potential as a high dielectric constant and low loss material.

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