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Microstructure and magnetic properties of $BaFe_{12}O_{19}/BaTiO_3$ composite materials prepared by high-energy milling

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Magnetic and dielectric composite powders from BaM-ferrite and $BaTiO_3$ were fabricated by a high-energy milling process and subsequent annealing. It is shown that the $BaTiO_3$ phase dominated after high-energy milling for 40 h with increasing $BaTiO_3$ content up to 20 wt.%. On the other hand, the $BaFe_{12}O_{19}$ phase dominated after annealing the mixed sample at 900°C for 3 h in air. The lattice constant of the c-axis for the high-energy milled sample increased with $BaTiO_3$ content, but the $BaFe_{12}O_{19}$ phase was formed as a stable structure after annealing and little change was seen with $BaTiO_3$ content. From the HR-TEM micrographs, partial mismatch in orientation was observed in 10 nm nanosized microstructures. It is also shown that magnetic hysteresis loops for the mixed powder of $BaFe_{12}O_{19}/BaTiO_3$ were affected by the properties of the $BaFe_{12}O_{19}$ matrix with a rather large spacing in the c-axis direction. A narrowed hysteresis loop was formed after the high-energy milling process because of the mechanical stress-induced magnetic structural deformation and modified domain structure by the high-energy milling process. The stable hard ferrite $BaFe_{12}O_{19}$ structure can be achieved after annealing at 900°C through the rearrangement of atoms. The microwave absorbing property was enhanced from the composite powder of $BaFe_{12}O_{19}/BaTiO_3$ obtained by the mechanical milling. The reflection loss of the $BaFe_{12}O_{19}/BaTiO_3$ composite was over -25 dB at 16.5 GHz and about -15.3 dB for only the barium ferrite ($BaFe_{12}O_{19}$).

Key words: Barium ferrite composite, High-energy milling, Microwave absorber.

Introduction

The high-energy milling process has been the subject of great interest in recent years. The non-equilibrium nature of the milling process creates the opportunity to prepare solids with improved and novel physical or chemical properties.

Hexagonal ferrites have found many applications in a wide variety of permanent magnets, recording media, and as microwave materials due to their good chemical stability and magnetic properties. Recently, Ba- and Sr-ferrites in the form of thin films have been produced [1]. Recently, these hexagonal ferrites have been used as microwave absorbers with low materials constants (complex permeability and permittivity) and low magnetic anisotropy which gives a resonance frequency over 1 GHz for the application as microwave absorbing materials [2]. On the other hand, M-type Ba-ferrite has a strong anisotropic preference in the c-axis for easy magnetization and little change in magnetic moment to external electromagnetic wave which makes it suitable as a microwave absorber. It is known that M-type hexagonal ferrites have a ferrimagnetic resonance frequency (f_r) of 50-60 GHz due to their large crystalline magnetic anisotropy and their microwave properties can be enhanced to cover a lower frequency range of f_r by substituting Fe^{3+} with other metal ions such as Ti^{4+}, Sn^{4+}, Co^{2+}, Zn^{2+} and Mn^{2+}, etc.

Microwaves in the GHz range are increasingly being used in a wide range of mobile communication systems, with the result that electromagnetic interference (EMI) is becoming a serious problem. Recently, mechanically-activated processes for ferrite materials have been widely used with great attention to applications. In particular, high-energy milling provides the greatest modification to atomic arrangements in solids [3].

Spinel type ferrites are used as electromagnetic wave absorbers in the MHz range, for applications such as the suppression of TV ghost images [4]. However, these types of ferrite do not function well in the GHz range, due to a drop in the complex permeability, as given by Snoek's limit. Barium ferrite with a magnetoplumbite structure (BaM-type: $BaFe_{12}O_{19}$) is a well known permanent magnetic material [5, 6]. The complex permeability of barium ferrite increases at the natural resonance frequency, which is calculated from the value of the anisotropy field. It has been reported that the M-type hexaferrite in which Fe^{3+} was substituted by several tetravalent (Ti^{4+}, Sn^{4+} and Zr^{4+}) and divalent Mn^{2+} showed good electromagnetic wave absorption properties [7].

In this study, the composite processing by mech-

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anical alloying of barium ferrite and barium titanate was investigated on the characteristics of magnetic phenomena, microstructure, microwave absorbing properties for magnetic/dielectric nano-composite materials. The microwave absorbing properties were characterized from the materials constants of complex permeability and permittivity and the reflection loss was calculated.

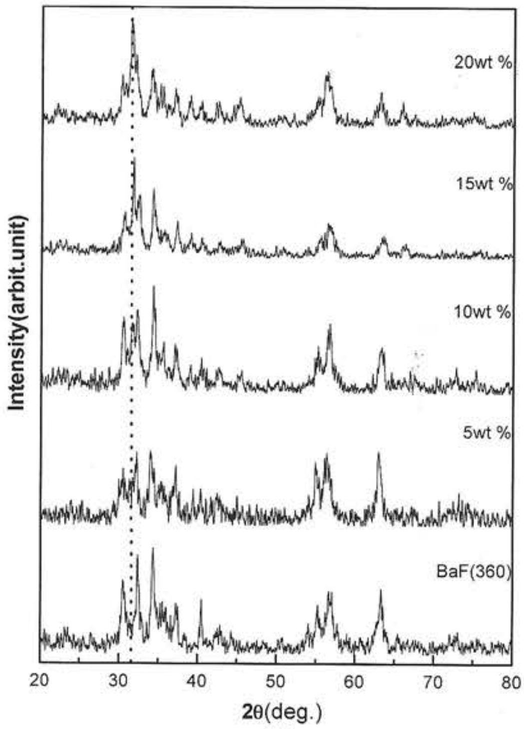
Experimental Procedure

Nano-structured composites of M-type barium ferrite and barium titanate were fabricated by high-energy milling with starting materials supplied by MUE Industry (Korea) and FERRO (US), respectively, in a planetary ball mill (Fritsch, 'pulverisette 5') at room temperature. The high-energy milled powder was annealed at 900°C for 3 h in air. The crystal structure was studied using an X-ray diffractometer with Cu K_{α}. The microstructure and powder morphology were examined using a field-emission scanning electron microscope (FE-SEM: JSM-6700F, JEOL) and a transmission electron microscope (TEM: JEM4010, JEOL).

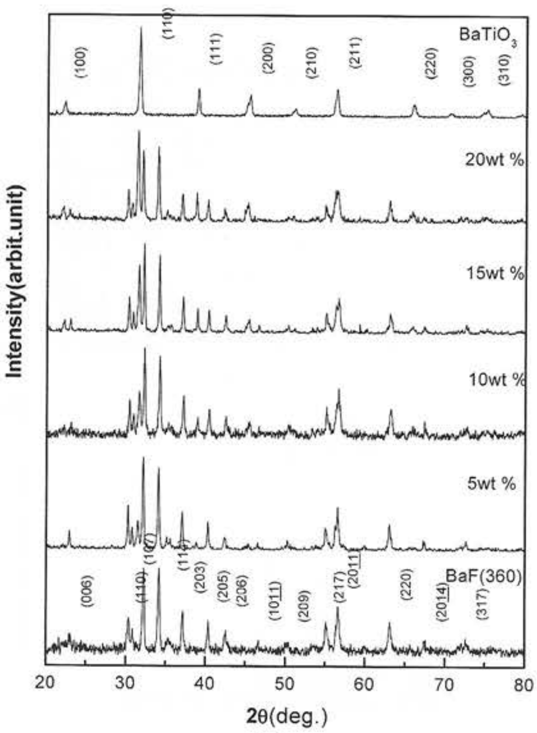
Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 15 kOe. The complex permeability and permittivity of the composites were measured using an HP8720C network analyzer and HP8516A S-parameter test set with a toroidal sample (outer diameter of 7 mm, inner diameter of 3 mm, powder/Si-rubber=4/1 in weight percent).

Results and Discussion

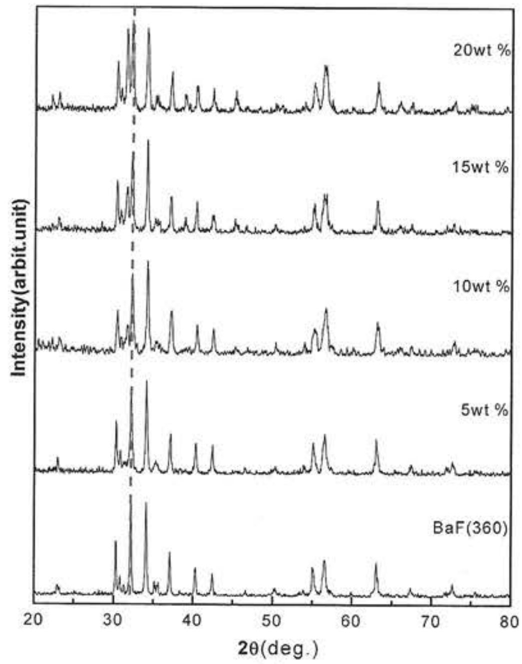
Figure 1 shows XRD patterns illustrates the effect of the high-energy milling process on the change in the dominant phase in the composite materials of barium ferrite (BF) and barium titanate (BT) powder. After mixing the raw materials, XRD patterns showed a



(b)



(a)



(c)

Fig. 1. XRD patterns of composite materials of barium ferrite (BF) and barium titanate (BT) with barium titanate content; (a) as mixed, (b) high-energy milled for 40 h (dotted line for BT phase), (c) annealed at 900°C (dashed line for BF phase), respectively.

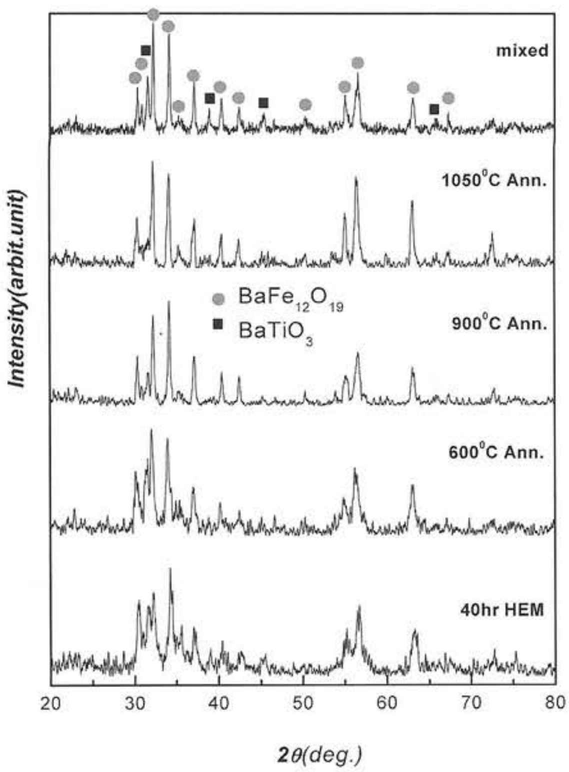
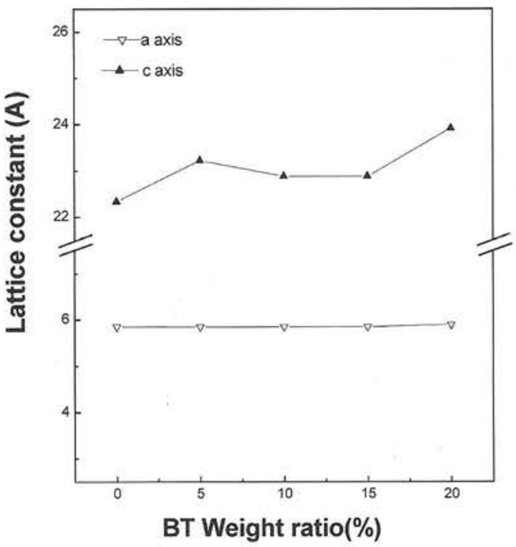


Fig. 2. XRD patterns of BF/BT composites fabricated after high-energy milling and annealing for 40 h at the indicated temperatures.

mixture as prepared from BF and BT as shown in Fig. 1(a). The BF/BT powder mixture was subjected to a subsequent high-energy miling process for 40 h to prepare the composite between the ferromagnetic and dielectric materials as microwave absorbers. It is shown that the BT-dominant phase (dotted line as marked) was produced after high-energy milling and finally the BF-dominant single phase was obtained after annealing at 900°C as presented in Fig. 2. For the sample annealed at 900°C, the peaks from the barium ferrite phase became much more dominant due to diffusion of cations Ti^{4+} and rearrangement into the crystalline structure of barium ferrite.

The mechanical milling effect on the variation of the crystalline lattice constant is also presented in Fig. 3. It is also seen that the lattice constant in the c-axis calculated from the lattice parameters after high-energy milling increased with the amount of BT content due to its crystalline deformation and rearrangement in the c-axis which means that barium titanate was partially formed as a nano-composite in the barium ferrite matrix.



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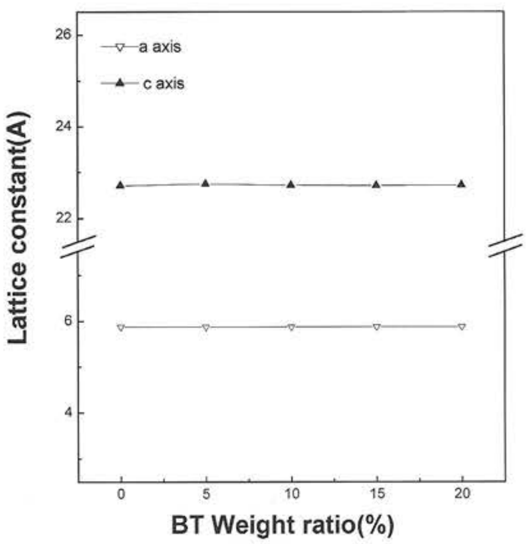
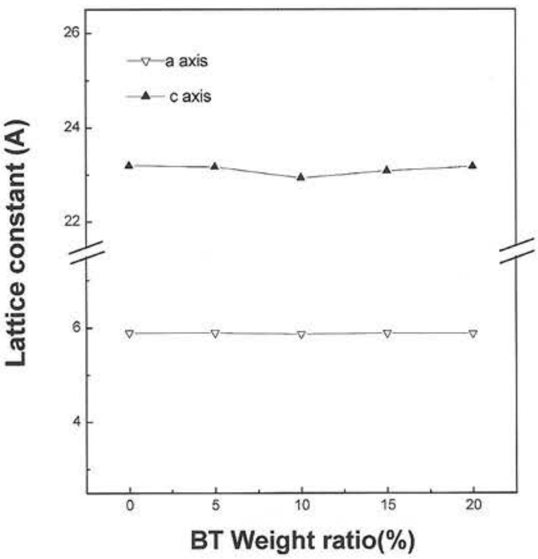


(a)



(c)

Fig. 3. Lattice constants of barium ferrite composite with barium titanate powders as a function of preparation conditions; (a) as mixed, (b) high-energy milling for 40 h, (c) annealed at 900°C.

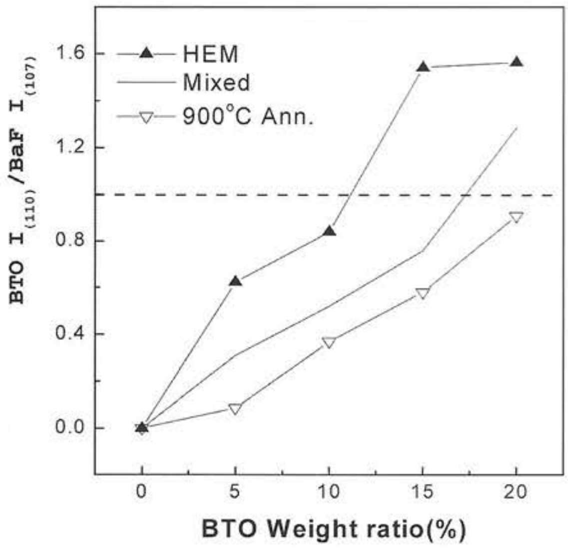


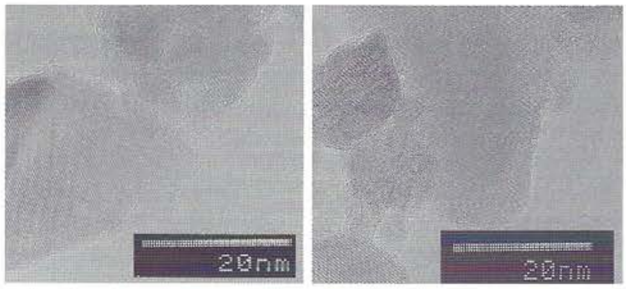
Fig. 4. Variation of XRD intensity for major peaks of BF and BT phase with BT content in weight percent (HEM=high-energy milled).

Figure 4 shows the variation of the XRD major peak intensity ratio of BF/BT composites. As shown in Fig. 3, the intensity of the BT phase increased by the mechanical milling process but decreased after annealing. It is suggested that the Ti^{4+} ions in barium titanate diffused locally in the barium ferrite lattice and resulted in a decrease in the intensity of the BT phase after high-energy milling. It can be seen that the BF/BT composites were formed with BF as the dominant phase when the amount of BT was 10 wt.% as shown in Fig. 4.

Figure 5 shows the microstructures of the powder of barium ferrite, barium titanate and the composite materials. Relatively large particles were present in the raw materials as shown in Fig. 5(a)-(c). On the other hand, it is seen that the particle size was reduced after high-energy milling with an agglomerated morphology in Fig. 5(d) and particle sintering was observed after annealing at 900°C.

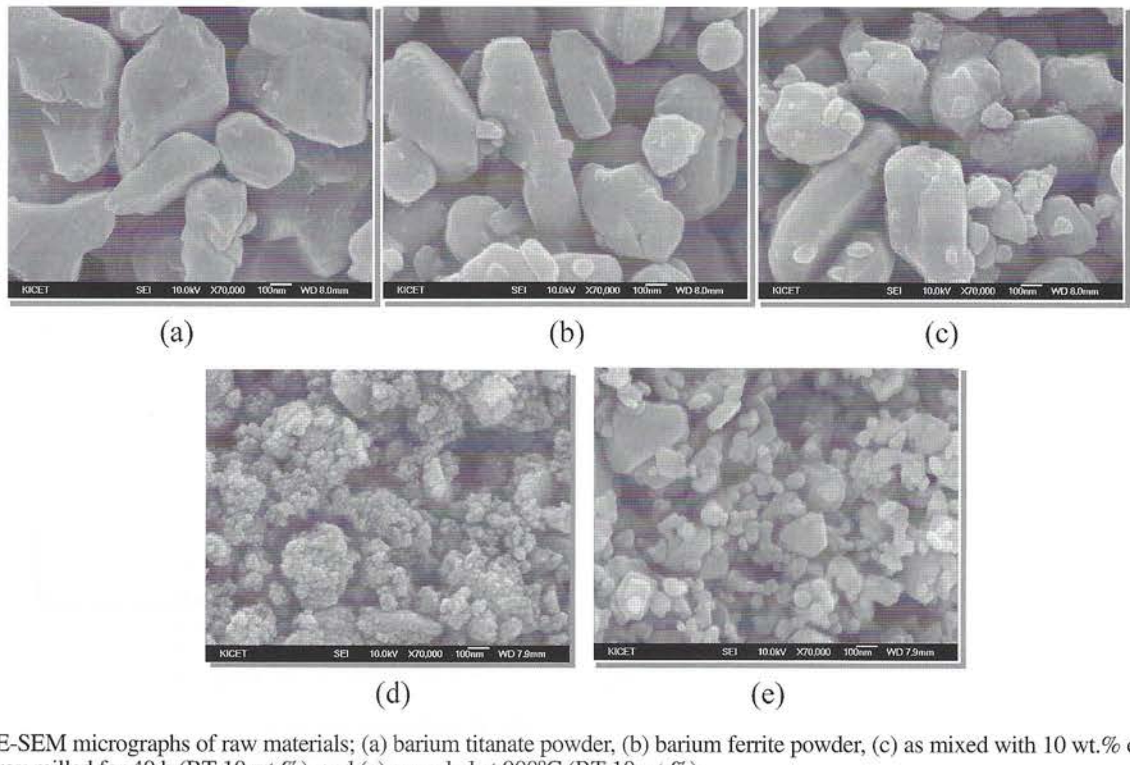
The HRTEM images of high-energy milled BF/BT composite materials are shown in Fig. 6 which reveals a partial mismatch in orientation was formed, indicating the nanocrystallinity of composite materials. The barium ferrite particles are agglomerated and are covered, after high-energy milling, with barium titanate particles as shown in Fig. 5(d), Fig. 6, respectively.

In order to explain the result of the lattice change in



(a) (b)

Fig. 6. High resolution TEM micrographs of BF/BT nanocomposite particles with BT content fabricated by high-energy milling for 40 h; (a) 10 wt.%, (b) 20 wt.%.



(a) (b) (c) (d) (e)

Fig. 5. FE-SEM micrographs of raw materials; (a) barium titanate powder, (b) barium ferrite powder, (c) as mixed with 10 wt.% of BT, (d) high-energy milled for 40 h (BT 10 wt.%), and (e) annealed at 900°C (BT 10 wt.%).

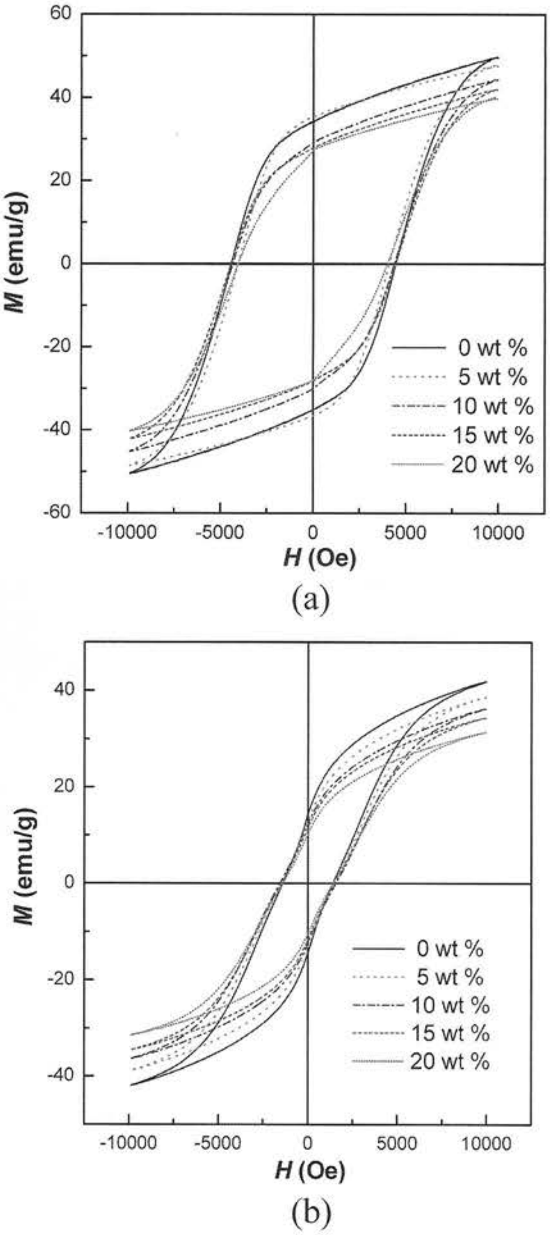


Fig. 7. Magnetic measurements of each BF/BT composite materials as a function of BT content; (a) as mixed, (b) high-energy milled, and (c) annealed at 900°C.

the c-axis shown in Fig. 3, magnetic characterization was performed to elucidate the effect of the dominant phase change from materials processing as shown in Fig. 7. Hysteresis loops of the composite materials with the amount of BT addition revealed that the ferromagnetic hysteresis behavior was affected by mechanical milling resulting in deformation of the BF lattice as shown in Fig. 7(b). Before applying the mechanical energy to prepare the composites as mixed, the ferromagnetic loop of the barium ferrite has been shifted slightly by the non-magnetic constituent. The distribution of saturation magnetization for each material in Fig. 7 shows a small difference but the coercivity exhibited the typical variations for high-energy milling and annealing pro-

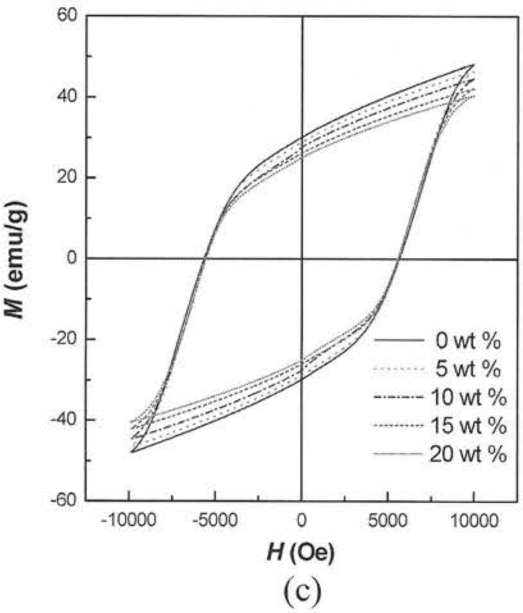


Fig. 7. Continued.

cesses. It is seen that the ferromagnetic behavior has formed after annealing the high-energy milled sample. Nanostructured ferrites prepared by high-energy milling processes are often inherently unstable owing to their small constituent sizes, non-equilibrium cation distributions, disordered spin configurations, and high chemical activity. Annealing of the mechanically milled ferrites recrystallizes the nanostructure and causes its transition from an excited metastable state into the low-energy crystalline state.

Figure 8 shows the enhanced microwave absorbing properties for high-energy milled BF/BT composite material. Compared with other materials as shown in Fig. 8(a) and (c), the high-energy milled nano-composite material exhibited a higher reflection loss at 16.5 GHz which is related to the anisotropy due to the effect of mechanical energy on the magnetic properties of barium

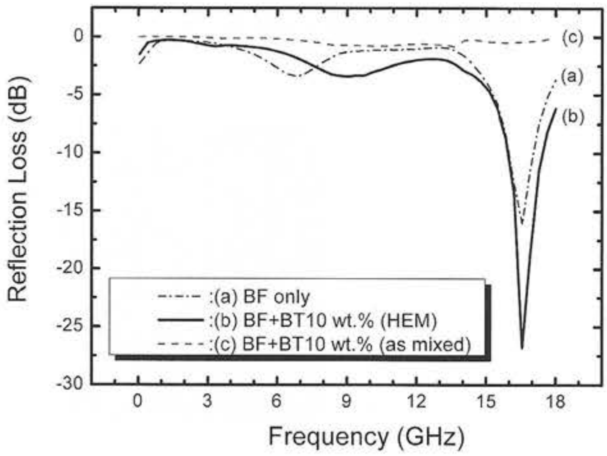


Fig. 8. Reflection loss of BF/BT composites; (a) barium ferrite (BF) powder, (b) BF+BT 10 wt.% fabricated by high-energy milling, and (c) BF+BT 10 wt.% as mixed.

ferrite after high-energy milling. Because the barium ferrite molecule is composed of several different atoms, the atoms on the surface of crystalline grains possess various coordination states. When the particle size of nanocrystalline composite oxides is reduced, the number of atoms with unsaturated coordination is increased, and interface polarization and multiple scattering become important factors of the attenuation [8]. When magnetic/dielectric composites have a nanostructure as shown in Fig. 6, the structure of a crystallite may consist of the multiple magnetic domains rather than a single, and the coercive force of the material increases greatly. It is also supposed that high-energy milled BF/BT nanocomposite materials may lead to relatively large hysteresis attenuation and the absorbing properties can be enhanced greatly as shown in Fig. 8.

Conclusions

Composites made of barium ferrite with a small amount of barium titanate were fabricated by a high-energy milling process in this study. A modified M-type barium ferrite phase was obtained and the magnetic properties were investigated after mechanical milling and annealing. The composites (barium ferrite + barium titanate 10 wt.%) prepared by high-energy milling exhibited good microwave absorption properties, over -25 dB. It can be concluded that using a two-phase microstructure composed of ferromagnetic barium ferrite and dielectric barium titanate with a nanoscale structure, is an effective method of increasing the reflection loss. Using a nanocrystalline composite material as a microwave absorber is therefore quite unique and a promising method to improve and control properties.

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