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$BiFeO_3$ tailored low loss M-type hexaferrite composites having equivalent permeability and permittivity for very high frequency applications

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ABSTRACT

Co–Ti substituted M-type hexaferrite composites, consisting of $Ba(CoTi)_{1.2}Fe_{9.6}O_{19}$ with various amounts of Bi_2O_3 (0–8 wt%), were successfully synthesized by conventional ceramic processes. The effects of Bi_2O_3 upon the composite microstructure, magnetic properties, and magnetic and dielectric properties sintered at low temperatures were systematically investigated. The present studies aim to develop magneto-dielectric materials possessing equivalent values of permeability and permittivity, as well as low magnetic and dielectric losses, which allow for miniaturizing efficient antennas at the very high frequency band (VHF, 30–300 MHz). The present experiments show that addition of $BiFeO_3$, observed in the polycrystalline hexaferrite composites, acts to reduce loss factors (i.e., $\tan\delta_\mu/\mu' = 0.014$, $\tan\delta_\varepsilon/\varepsilon' = 0.00071$) while concomitantly retaining high and equivalent values of permeability and permittivity (i.e., $\mu' \sim 12$ and $\varepsilon' \sim 12$ at 300 MHz).

1. Introduction

In recent decades, the rise of mobile systems and devices for personal data communications and multimedia digital broadcasting services, the communication technologies, materials, and devices operating at very high frequency (VHF) (i.e., 30–300 MHz) have attracted much attention. Among those applications, radio frequency (rf) antenna are assuredly one of the most important components in VHF systems. However, the length of antenna is usually required to be a quarter of the electromagnetic wave in vacuum, e.g., ~40 cm for VHF applications [1]. This is obviously too large to be used for mobile devices or in compact systems. Some solutions to reducing the size of antennas are proposed. (a) The design of miniature antenna structures may result in poor figures of merit (FOM). (b) Use of high dielectric constant materials leads to the drawbacks [2–4]. The electromagnetic field is confined to an area with high permittivity, yielding poor efficiency and narrow bandwidth of the antenna). In addition, due to low characteristic impedance, it is difficult for the high dielectric constant material to impedance match the antenna. Finally, (c) these issues could be overcome by using the magneto-dielectric materials having high and equivalent values of permeability and permittivity. A transmission wavelength inside an antenna base can be calculated in terms of the formula $\lambda = c/f\sqrt{\varepsilon_r\mu_r} \approx c/f\sqrt{\varepsilon'\mu'}$ (λ is the transmission wavelength, c is the velocity of light, f is the transmission frequency, ε_r is the relative permittivity, μ_r is the relative permeability, ε' is the real permittivity and μ' is the real permeability.), where the dielectric loss and magnetic loss are assumed to be very small. It is no doubt that increasing permeability is superior to increasing permittivity to reduce the size of the antenna [5]. Additionally, the impedance of antenna is calculated in terms of the following formula, $Z = \sqrt{\mu_0\mu_r/\varepsilon_0\varepsilon_r} \approx \sqrt{\mu_0\mu'/\varepsilon_0\varepsilon'} = \eta_0$ (where Z is the impedance of the antenna, μ_0 is the permeability of free space, ε_0 is the permittivity of free space and η_0 is the impedance of free space). It is clear that the impedance of the materials used for antenna is the same as free space for the case in which magnetic permeability (μ') and permittivity (ε') are equivalent [6–8]. Furthermore, it is clearly important for the design of high efficiency antennas when both dielectric and magnetic loss of the magnetic materials are low, i.e. low loss tangent values. However, it is extremely challenging to achieve the desired materials having relatively high permeability, low permittivity and equivalent μ' and ε' at certain frequency

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bands. This is a primary goal of the rf magnetics community and communication industry.

Generally, ferrite materials not only have low permittivity and high magnetic permeability, but also possess high electrical resistivity. There is no doubt that ferrites are ideal materials for use in miniature high frequency antennas. In the ferrite family, either spinel or hexagonal ferrites are often used for the design of antennas, depending upon the operating frequency of antennas. Spinel ferrites have high permeability, but the cutoff frequency is low (~300 MHz) due to Snoek's limit [9]. Accordingly, the operating frequency of spinel ferrites is usually below 100 MHz, whereas hexagonal ferrites, with high magneto-crystalline anisotropy and cutoff frequencies >1 GHz, can operate at a high frequency (VHF). Hexagonal ferrites show permeability much lower than that of spinel ferrites at low frequencies, but they are irreplaceable at high frequencies (>100 MHz).

Eventually, ferrite antenna materials have been widely investigated in order to gain low losses and equivalent values of permeability and permittivity [10,11]. Either spinel or hexagonal ferrites may be effective candidates as antenna substrate materials depending upon the selection of operating frequencies. Therefore, the Co_2Z hexagonal ferrite has been investigated for many years due to its easy *c*-plane and high permeability that are available for microwave devices [12–15]. Previous studies on Co_2Z ferrites demonstrated equivalent values of μ' and ε' (i.e., ~13), however magnetic loss tangents were >0.05 and >0.1 at a frequency beyond 100 MHz and 250 MHz, respectively [5]. Additionally, high sintering temperatures (>1200 °C) and complex phase transformation are often inevitable during optimal sintering processes for the Co_2Z ferrites, which indeed makes the formation of a single phase structure more difficult than other hexaferrites. Nevertheless, Su et al., have recently demonstrated in *Z*- and *Y*-phase mixed hexaferrites give rise to low magnetic and dielectric losses over a frequency range of $0.3 < f < 1$ GHz [16].

Among the hexaferrites, M-type hexagonal ferrite (BaM: $BaFe_{12}O_{19}$) is relatively simple in structure and fabrication processes. Therefore, here we propose three strategies to realize low temperature sintering, high permeability and low losses of the BaM ferrite: (1) an additive, such as Bi_2O_3, is employed to lower sintering temperatures and modify morphology of polycrystalline ferrites, while retaining the desired crystallographic structure and parameters; (2) low magnetic loss may be achieved by an extra phase e.g. $BiFeO_3$ having high electrical resistivity and weak magnetism; and, (3) the uniaxial (*c*-axis) magnetic anisotropy can be reduced and even transformed to the easy basal plane (*c*-plane) by the substitution of Fe in BaM ferrite with cations Sc^{3+}, ($Co^{2+} + Ti^{4+}$), etc. [17,26]. It is anticipated that such substitutions enable the enhancement of permeability due to the reduction in magnetic anisotropy energy. In present work, we investigate the microstructure, magnetic properties, and high frequency magnetic spectra of (CoTi)-doped BaM ferrite. Combined with a secondary phase of Bi_2O_3, the (CoTi)-doped BaM ferrites, are revealed to have low magnetic and dielectric losses, as well as high permeability at 10–300 MHz. Interestingly, equivalent values of permeability and permittivity were measured in the ferrite composites indicating characteristic impedance identical to that of free space.

2. Experimental procedure

$Ba(CoTi)_{1.2}Fe_{9.6}O_{19}$ M-type hexaferrites with various amounts of the secondary Bi_2O_3 phase (0–8 wt%) were prepared by solid-state reaction. Starting materials, reagent grade Fe_2O_3, $BaCO_3$, CoO, and TiO_2, were mixed for 1 h in a planetary ball-mill. The mixture was then calcined at 1100 °C for 2 h and ground with the Bi_2O_3 additive for an additional 2 h. The resultant powders were dry-pressed to form toroidal and disk-shaped samples, and finally sintered at 925 °C for 3 h in air.

The crystallographic structure and morphology of the samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. Room temperature magnetic measurements were carried out using a vibrating sample magnetometer (VSM) with applied fields up to 15 kOe. The DC electrical resistivity of the obtained disk-shaped samples was measured with Ag electrodes via the two-probe technique. The complex permeability and permittivity were measured using an Agilent E4991A RF Impedance/Materials Analyzer from 1 MHz to 1 GHz with 16454A and 16453A test fixtures.

3. Results and discussion

3.1. Structural characteristics

The XRD patterns of $Ba(CoTi)_{1.2}Fe_{9.6}O_{19} + Bi_2O_3$ (x = 0–8 wt%) hexaferrite composites are illustrated in Fig. 1. It is found that the $Ba(CoTi)_{1.2}Fe_{9.6}O_{19}$ ferrites show a single phase structure until the Bi_2O_3 content exceeds 5 wt%. It is assumed that when small amounts of Bi_2O_3 are introduced, Bi^{3+} ions enter the lattice of the hexagonal phase. A second phase of $BiFeO_3$ was verified as the doping of Bi_2O_3 was increase beyond 5 wt%. It is well known that $BiFeO_3$ is a multiferroic material, presenting both ferroelectric and weak ferromagnetic response at room temperature [18]. It is predictable that the highly electrically resistive phase may reduce the magnetic loss of the ferrites. This assumption will be revealed and discussed in later sections.

3.2. Morphology of samples

Fig. 2(a) presents the morphology of $Ba(CoTi)_{1.2}Fe_{9.6}O_{19}$ ferrites with different Bi_2O_3 contents. It is noticed that the average grain size increases from 0.54 to 1.94 μm due to the Bi_2O_3-assisted sintering for low doping levels of Bi_2O_3. However, crystal growth may be inhibited with excessive Bi_2O_3, (i.e., great than 5 wt%), leading to a reduction of the average grain size to ~1.47 μm, as depicted in Fig. 2(b). We show that the introduction of bismuth oxide is able to lower sintering temperatures due to the low melting temperature (820 °C) of Bi_2O_3. Liquid-phase assisted solid phase sintering is more likely to give rise to large grains and high density in polycrystalline ferrites. It is therefore somewhat surprising that a high concentration of (⩾5 wt%) of Bi_2O_3 does not result in a visible increase in the grain size. Actually, a liquid phase layer not only accelerates the mass transfer but also generates a wetting meniscus at grain boundaries, providing an additional capillary pressure drive force during the high temperature sintering process [19]. It is speculated that the grain growth is restricted because of the thick liquid phase layer generated by excessive Bi_2O_3 (⩾5 wt%).

3.3. Static magnetic properties

Fig. 3(a) shows magnetic hysteresis loops of $Ba(CoTi)_{1.2}Fe_{9.6}O_{19}$ ferrites with various Bi_2O_3 contents. The values of magnetization

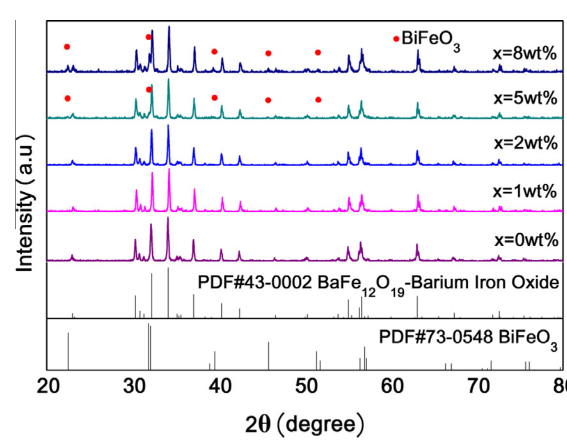

Fig. 1. XRD patterns of the samples sintered at 925 °C with different Bi_2O_3 contents (x wt%).