LTCC processed CoTi substituted M-type barium ferrite composite with BBSZ glass powder additives for microwave device applications

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Hexagonal magnetoplumbite ferrites typically have sintering temperatures above 1100°C in order to stabilize a single phase compound, which is much higher than the melting point of silver leading to device fabrication challenges. Application of low temperature co-fired ceramics (LTCC) technologies may prove effective in decreasing the sintering temperature of hexagonal ferrites. Ferrite powders combined with glass frit powder is an effective pathway to lowering the sintering temperature. Here, hexagonal M-type barium ferrite (i.e., $\text{Ba(CoTi)}_{1.5}\text{Fe}_9\text{O}_{19}$) ceramics, combined with BBSZ glass powder as a sintering aid were synthesized. Co and Ti ions where used to substitute for Fe cations in order to modify the magnetic anisotropy field. The density, microstructure, magnetic properties and complex permeability are reported. The BBSZ glass addition was shown to improve the densification and magnetic properties of the barium ferrite. The densification of the BaM ferrite $\text{Ba(CoTi)}_{1.5}\text{Fe}_9\text{O}_{19}$ was further enhanced by the glass aid at low firing temperatures of below 900°C because of the formation of a liquid phase. Complex permeability of ferrites sintered at 900°C was also influenced by the BBSZ addition and the resonance frequency was shown to decrease with increased amounts of the glass modifier. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4945041]

I. INTRODUCTION

Due to the rapid development of advanced wireless communication technologies such as mobile communication handsets and satellite communication platforms, massive amounts of miniaturized microwave components have been required. To meet these needs, low temperature co-fired ceramics (LTCC) technology, which has been used to fabricate multilayer devices in the past, has been investigated to reduce the size of microwave ferrite components.

Silver has been extensively used as the internal electrodes in multilayer devices due to its high conductivity. However, the melting point of silver is 961°C, which poses an upper limit on the firing temperature of ferrites. Therefore, it is necessary to develop ferrite ceramics with sintering temperature around 900°C.¹

M-type barium ferrites (BaM) have been broadly applied as a permanent magnetic, magnetic recording media, microwave absorbing material and in microwave devices on account to its high saturation magnetization, tunable coercivity, high magnetocrystalline anisotropy field and excellent chemical stability.² To be compatible with this wide range of applications, researchers have

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explored the substitution of various trivalent cations for the \( Fe^{3+} \) ion in, for example, BaM ferrites. The \( Fe^{3+} \) ions can be replaced by an assortment of trivalent cations such as \( Sc^{3+} \), \( In^{3+} \), \( Ga^{3+} \) etc.,\(^{3-5}\) or divalent-tetravalent cation pairs such as Co-Ti, Zn-Ti, Co-Sn, Co-Zr, Ni-Ti, Co-Ir\(^{6-11}\) and so on. However, because of the sintering temperature of BaM ferrites is higher than 1100°C, which is much higher than the melting point of silver, it is important to reduce the sintering temperature of BaM ferrites.

The use of a low melting point glass or oxide has been shown effective in many cases in lowering the sintering temperature of the host ceramic.\(^{12}\) Here, we employ \( Bi_2O_3 - B_2O_3 - SiO_2 - ZnO \) (BBSZ) glass powder to lower the BaM ferrites effective sintering temperature because of its low melting point\(^{13}\) and excellent microwave dielectric properties.\(^{14}\) The effect of this sintering aid on sintering temperature, microstructure, densification, magnetic properties and microwave properties have been investigated.

II. EXPERIMENT

The BaM ferrite, i.e., \( Ba(\text{CoTi})_{1.5} Fe_9 O_{19} \), was prepared by solid-state reaction method. The raw materials \( BaCO_3 \), \( Fe_2 O_3 \), \( CoO \), and \( TiO_2 \) of analytical purity were mixed in the proper nominal ratios and then calcined at 1000 °C for 6 hours. The BBSZ was synthesized by combination of \( H_3 BO_3 \), \( Bi_2 O_3 \), \( SiO_2 \), \( TiO_2 \), which were mixed for 6 hours according to the mole ratio 70%, 25%, 10% and 35% and then dried. The precursor mixture was introduced to a corundum crucible and sintered at 1000°C for 2 hours, then quenched in deionized water to form glass. The glass was powdered and then mixed with the precursor of BaM ferrite at different weigh percentages of 1% to 5% for 4 hours. The powders were then dried and mixed with 15% PVA for granulation. The resulting powders were dry-pressed at 100MPa into pellets and toroidal samples and then sintered at various temperatures: 900°C, 920°C, 940°C, and 980°C, for 6 hours.

The bulk densities of sintered samples were measured by the Archimedes method. The phase purity and microstructure were investigated by room temperature X-Ray diffraction (XRD) using a Cu K\( \alpha \) radiation source and scanning electron microscope (SEM), respectively. Magnetic hysteresis loops were measured by vibrating sample magnetometry (VSM) with an applied field from -10kOe to 10kOe. The complex permeability spectra were measured using an impedance analyzer.

III. RESULTS AND DISCUSSION

XRD patterns of the \( Ba(\text{CoTi})_{1.5} Fe_9 O_{19} \) sintered with different amounts of BBSZ additive and sintered at 900°C are shown in Fig. 1. It is observed that the peak positions can be attributed to

![XRD patterns of \( Ba(\text{CoTi})_{1.5} Fe_9 O_{19} \) ferrite samples with different amounts of BBSZ additive sintered at 900°C for 6 h.](image-url)
TABLE I. Lattice constants, coercivity and sintering density of the \( Ba(CoTi)_{1.5}Fe_9O_{19} \) ferrites with different contents of BBSZ sintered at 900°C.

| BBSZ contend | \( a(Å) \) | \( c(Å) \) | \( c/a \) | Density (g/cm\(^3\)) | \( H_c \) (Oe) |
|--------------|-------------|-------------|----------|-----------------------|----------------|
| 1%           | 5.89065     | 23.26154    | 3.94889  | 4.395                 | 245.449        |
| 2%           | 5.89326     | 23.26975    | 3.94854  | 4.572                 | 212.98         |
| 3%           | 5.89047     | 23.23245    | 3.94438  | 4.659                 | 207.474        |
| 4%           | 5.89207     | 23.2476     | 3.94557  | 4.815                 | 189.264        |
| 5%           | 5.8934      | 23.27389    | 3.94914  | 4.822                 | 171.371        |

nearly pure barium ferrite phase, which can be seen from a comparison to the PDF file #43-0002. \( α-Fe_2O_3 \) appeared due to the utilization of steel ball in ball-milling. Besides that, no obvious second phase was detected in the XRD patterns, which means that there is no reaction between BBSZ and \( Ba(CoTi)_{1.5}Fe_9O_{19} \). The peaks of the doped BaM ferrite appear at the same position as denoted by the PDF file #43-0002, but with slightly different intensities. In the substituted ferrite samples, the \( Co^{2+} \) and \( Ti^{4+} \) cations seem to have been incorporated into the hexagonal structure to form a single hexagonal phase. Table I presented the lattice constant of the samples in Fig. 1. The lattice constants \( a \) and \( c \) of the samples can be calculated from the formula:\(^{15}\)

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + 2hk + k^2}{a^2} \right) c_l^2
\]

Where \( d \) is the interplanar distance and \( h, k \) and \( l \) are Miller indices. A pure M-type barium ferrite \( (BaFe_{12}O_{19}) \) consists of a hexagonal structure with lattice parameters \( a=5.892 \) Å and \( c=23.183 \) Å in the space group P6\( \bar{3} \)mmc. (JCPDS File # 43-0002). However, as shown from the table, the lattice constants \( a \) have slightly lower values while the parameters \( c \) have slightly higher values with the addition of BBSZ content. Besides that, the \( c/a \) value remains unchanged at 3.94 Å suggesting a conservation of unit cell volume: These values are a little higher than the pure BaM. These alterations can be attributed to the glass addition. The density of samples, as presented in Table I, can be seen to increase with the addition as the BBSZ content which also enhances the grain size of the sintered material.\(^6\)

Figure 2(a) shows SEM images of \( Ba(CoTi)_{1.5}Fe_9O_{19} \) ferrites with different BBSZ contents after sintering at 900°C. When added BBSZ contend is 1%, the BaM ferrites have a relatively dense surface microstructure with typical platelet morphology, with few intergranular pores. The morphology become different while the glass addition increased to 2%, a bimodal granular structure can be visualized, and the particles stack more compactness than the morphology was showed in BBSZ 1%. In BBSZ 3%, the microstructure morphology is still looked closely. Besides that, the particles is seemed be covered by translucent material though it is not obviously. Moreover, this situation is accelerating while the BBSZ adding concentration increase to 4% and 5%. Reference 17 exhibit the densification mechanism of the BBSZ glass on LMT ceramics, which could be cited to explain the densification mechanism and phenomenon occured in Fig. 2(a). Due to BBSZ glass would melt and form liquid phase in sintering procedure,\(^{18}\) the liquid glass would spread and diffuse into the lowest energy configuration e.g. pores and small grains. However, the results of the liquid BBSZ diffusion appeared nonuniformity in BBSZ 4% and become increasingly in BBSZ 5%. It could be attributed by two reasons: first, time and intensity of second ball-milling with BBSZ was not enough; second, nonuniformity of grain growth made the liquid glass prefer to diffuse into small grains positions. From the density showed in table I and morphology showed in Fig. 2(a), it could be concluded that added BBSZ enhanced densification and density of ferrite.

SEM images of BaM ferrites with 4% BBSZ glass added and sintered at different temperature are shown in Fig. 2(b). As seen from the images, the grain size of ferrites increase significantly with sintering temperature. From the images, pores between the large grains are observed at 920°C, 940°C and 980°C sintering conditions. Densification of ferrites and the uniformity of grain size are clearly enhanced when sintering temperature increases beyond 900°C. According to the results in Fig. 1, no obvious secondary phase occured in the XRD patterns, it is reasonable to infer that when
FIG. 2. (a) SEM images of $\text{Ba(CoTi)}_{1.5}\text{Fe}_9\text{O}_{19}$ added with different contents of BBSZ sintered at 900°C for 6h (b) SEM of $\text{Ba(CoTi)}_{1.5}\text{Fe}_9\text{O}_{19}$ added with 4% BBSZ sintered at different temperature.

With the sintering temperature increasing to the softening point (~430°C), BBSZ begins to melt and forms liquid phase to exist at grain boundary and wet the surface of ferrite particles. Existence of liquid phase provides an environment that turns the solid-state reaction sintering into liquid phase sintering procedure. In liquid phase sintering, the mechanisms of grain growth and densification can be...
FIG. 3. VSM image of Ba(CoTi)$_{1.5}$Fe$_9$O$_{19}$ added with different contends of BBSZ sintered at 900°C for 6h.

divided into three types, which depends on the concentration of liquid phase (BBSZ): (1) diffusion of the constituent atoms in the ferrite lattice: zero or an insufficient amount of liquid phase present at grain boundaries; (2) solution-reprecipitation process: a thin layer of BBSZ-rich liquid phase to surround/wet all grains; (3) diffusion of atoms through the BBSZ-rich liquid layer—excessive amount of BBSZ.  

Figure 3 shows the hysteresis loops of the Ba(CoTi)$_{1.5}$Fe$_9$O$_{19}$ ferrites sintered at 900°C with an inset enlarging the area of remanence. To illustrate the variations between samples, Fig. 4 exhibits the variation of saturation magnetization and coercivity of samples in Fig. 3. It can be seen that the variation of saturation magnetization can be divided into two regions: (1) with the BBSZ additive content ranges from 1% to 3% the $M_s$ increases from 1% to 2% due to the increase of crystallization and then it decreases while the addition of non-magnetic BBSZ reaches to 3%; (2) $M_s$ increases and get a maximum with the content reaches 4%, because crystallization and densification of ferrite attained to maximum, then decreases sharply while the content reaches 5%, because excessive adding of non-magnetic glass weakened the contribution of magnetization in ferrite. Besides that, the coercivity of samples decreases linearly together with increasing glass content. Therefore, it is reasonable to deduce that the non-magnetic BBSZ glass powders have filled the space between grains through the liquid phase sintering procedure and as a result reduces the number of effective pinning centers related to grain boundary density and magnetic anisotropy fields.

FIG. 4. Variation of saturation magnetization and coercivity with increasing BBSZ content.
FIG. 5. (a) Real part of the complex permeability spectra of BaM ferrites with additives of BBSZ and sintered at 900°C (b) Imaginary part of the complex permeability spectra of BaM ferrites with additives of BBSZ and sintered at 900°C.

Figures 5(a) and 5(b) show the real ($\mu'$) and imaginary ($\mu''$) parts of permeability spectra in the frequency range of 1 GHz to 3 GHz. Figure 5(a) exhibits the variation of the real part of permeability. The $\mu'$ remains near 1 until a sharp resonance is encountered with a center frequency near 2.7 GHz corresponding to domain wall resonance. The imaginary ($\mu''$) part of permeability increases with frequency reaching a maximum in loss corresponding to the resonance in $\mu'$. The resonance frequency ($f_r$) decreases clearly with increasing BBSZ content from 1% to 4% until the content reaches 5%. The resonance frequency ($f_r$) of BaM is in connection with the magnetic anisotropy field ($H_a$) by the expression: $2\pi f_r = \gamma H_a$, where $\gamma$ is the absolute gyromagnetic ratio. From Fig. 5, we can see that the coercivity, which relates to the anisotropy field of ferrite, decreases near linearly with increasing glass content. This can explain the resonance frequency decrease with additions of BBSZ from 1% to 4%. However, the permeability of polycrystalline ferrites also could be attributed to double interaction of spin rotation and domain wall motion. Domain wall motion influences by grain size, and can be strengthened with the increase in grain size. Based on this, we can conclude that the increase of resonance frequency at 5% in Fig. 5 results from the increasing of grain size due to the excessive use of frit.

IV. CONCLUSIONS

M-type barium ferrites ($Ba(\text{CoTi})_{1.5}Fe_9O_{19}$) were synthesized through the traditional solid state method and then mixed with BBSZ glass powder to promote high density at comparatively
low sintering temperatures. We synthesised \( \text{Ba(CoTi)}_{1.5}\text{Fe}_9\text{O}_{19} \) ferrite with BBSZ glass powder at 900°C. Densification and grain growth was enhanced with added BBSZ concentration increasing due to the liquid sintering mechanism. Saturation magnetization of \( \text{Ba(CoTi)}_{1.5}\text{Fe}_9\text{O}_{19} \) ferrite sintered at 900°C risen to maximum at 4% added BBSZ concentration because of densification enhanced. Moreover, BBSZ additive decreased anisotropy energy of ferrite, which lead to decrease coercivity (from 1% to 5% ) and resonant frequency (from 1% to 4% ). However, excessive BBSZ weakened the contribution of magnetization of ferrite and as a result, \( M_s \) decreased while added BBSZ concentration at 5%. Besides that, increase of resonant frequency at 5% results from the increasing of grain size also due to the excessive use of glass.

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