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Electrical properties of low-temperature-fired ferrite–dielectric composites

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Abstract

The effects of the $BaO\cdot(Nd_{0.8}Bi_{0.2})_2O_3\cdot 4TiO_2$ (BNBT) to NiCuZn ferrite ratio and addition of Bi_2O_3–B_2O_3–SiO_2–ZnO (BBSZ) glass on the sintering behavior, microstructure evolution, dielectric and magnetic properties of BNBT–NiCuZn ferrite composites were investigated in developing low-temperature-fired composites for high frequency electromagnetic interference (EMI) devices. The results indicate that these composites can be densified at 900 °C and exhibit superior dielectric and magnetic properties with the addition of BBSZ glass. The dielectric system used in the ferrite–dielectric composites reported in the previous studies mostly belong to the ferroelectricity group, which are not suitable for use in the high frequency range (>800 MHz) due to the selfresonance frequency limit. In this study, the dielectric constant remains nearly a constant over a wide range of frequencies (100 MHz to 1 GHz) and the magnetic resonance frequencies are larger than 100 MHz for the BNBT + BBSZ glass–NiCuZn ferrite composites. Therefore, the BNBT + BBSZ glass–NiCuZn ferrite composites can be a good candidate material for high frequency EMI device applications.

Keywords: C. Dielectric property; C. Magnetic property; Ferrite–dielectric composites; NiCuZn ferrite; $BaO\cdot(Nd_{0.8}Bi_{0.2})_2O_3\cdot 4TiO_2$

1. Introduction

With the growing appetite for handheld electronic devices, these devices will undergo further miniaturization, reduction in weight and portability. Through the integration of inductors, capacitors and resistors into one monolithic chip component, the integrated component will offer better performance and save more space on the printed circuit board during assembling. Therefore, the passive components will become a compact integrated passive component.

In today's market, communication equipment is diversifying and acquiring ultrahigh levels of performance, such as multi-band phones. These trends increase the complexity of issues related to noise suppression because of the wide noise frequency band (800 MHz to 2 GHz) [1]. Recently, multilayer chip LC filters with high attenuation and wide bandwidth have been developed as a promising electromagnetic interference (EMI) device [2]. They are made with a cofired multilayer structure of ferrite, dielectric and internal conductors. One of the most important processes in manufacturing defect-free multilayer chip LC devices involves capacitor and inductor material cofiring. Mismatched densification kinetics, chemical reaction and thermal expansion mismatch between the layers could generate undesirable defects such as delamination, cracks and camber in the final products [3–6]. To solve the densification and thermal expansion mismatch problems, a composite ceramic material prepared by mixing dielectric and magnetic materials can be used to fabricate an EMI filter. Therefore, ferrite–dielectric composites have attracted much attention. Several ferrite–dielectric composites, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3 + Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_2O_4$ [7], $BaTiO_3 + Ni_{0.5}Zn_{0.5}Fe_2O_4$ [8], garnet ferrite + $Pb(Zr_{0.52}Ti_{0.48})O_3$ [9], $Ba_3Co_2Fe_{24}O_{41}$ + $ZnTiO_3$ [10], $Bi_2(Zn_{1/3}Nb_{2/3})O_7 + (Ni_{0.3}Cu_{0.1}Zn_{0.6}O)$–$(Fe_2O_3)_{0.8}$ [11] and $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3 + (Ni_{0.3}Cu_{0.1}Zn_{0.6}O)$–$(Fe_2O_3)_{0.8}$ [12], have been successfully produced. However, these systems have many drawbacks, such as (1) chemical reactions between the two constituents easily occur during sintering at high temperatures which results in the deterioration of the respective properties. (2) The densification temperatures of the composites are often greater than 950 °C, which limits the use of high-electrical-conductivity Ag or Cu metals as internal metallization. (3) The dielectric systems

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belong to the ferroelectricity group, which are not suitable for use in the high frequency range (800 MHz to 2 GHz) due to the selfresonance frequency limit.

Tungsten-bronze type like $BaO–Nd_2O_3–TiO_2$ (BNT) ceramics are widely used in microwave devices due to their high dielectric constants and low losses [13–15]. The substitution of Bi for Nd (BNBT ceramics) can decrease the resonant frequency temperature coefficient and increase the BNT based ceramic dielectric constant [16,17]. In our previous study, we observed that BNBT can be successfully densified at 900 °C with the addition of $Bi_2O_3–B_2O_3–SiO_2–ZnO$ glass and produce superior dielectric properties ($\varepsilon_r = 84$, $Q \times f = 2999$) [18]. In this study, a low-temperature-fired (950 °C) ferrite–dielectric composite was developed. $BaO\cdot(Nd_{0.8}Bi_{0.2})_2O_3\cdot 4TiO_2$ (BNBT) and $(Ni_{0.28}Cu_{0.12}Zn_{0.6}O)–(Fe_2O_3)_{0.99}$ (NiCuZn ferrite) were chosen as the dielectric and magnetic materials, respectively. The effects of the BNBT to NiCuZn ferrite ratio and addition of $Bi_2O_3–B_2O_3–SiO_2–ZnO$ (BBSZ) glass on the sintering behavior, microstructure evolution, dielectric and magnetic properties of the composites were investigated.

2. Experimental procedure

The $BaO\cdot(Nd_{0.8}Bi_{0.2})_2O_3\cdot 4TiO_2$ ceramic (BNBT) was prepared from reagent-grade $BaCO_3$, Nd_2O_3, Bi_2O_3, and TiO_2, which were mixed and then calcined at 1200 °C for 2 h. NiCuZn ferrite with a composition of $(Ni_{0.28}Cu_{0.12}Zn_{0.6}O)–(Fe_2O_3)_{0.99}$ were prepared from reagent-grade NiO, CuO, ZnO and Fe_2O_3, mixed and then calcined at 740 °C for 2 h. For the BBSZ glasses, high purity Bi_2O_3, ZnO, H_3BO_3, and SiO_2 powders were weighed according to the 25% Bi_2O_3–30% H_3BO_3–10% SiO_2–35% ZnO (in mole%) composition. The powders were mixed, dried, and melted at 1000 °C for 30 min. The melt was then quenched in water to form glass. The glass was powdered homogeneously and then mixed with BNBT powder at 20–25 wt% proportion to obtain the BNBT + BBSZ glass powder. The BNBT + glass powders with different amounts of NiCuZn ferrite powders (Table 1) and the samples with the weight ratio of BNBT to NiCuZn ferrite = 20:80 added with various content of BBSZ glass (Table 2) were milled for 24 h in acetone using YTZ balls. The powders were dried in an oven and then mixed with PVA for granulation. The powders were dry-pressed at 180 MPa into pellets and toroidal bodies. These specimens were then debindered at 500 °C and sintered at 900 °C for 2 h.

Table 1
Chemical compositions of the samples with various BNBT + BBSZ glass powder to NiCuZn ferrite ratio.

Samples	BNBT:BBSZ (wt%)	BNBT + BBSZ:NiCuZn ferrite (wt%)
B8N2	80:20	80:20
B6N4	80:20	60:40
B4N6	80:20	40:60
25B4N6	75:25	40:60
B2N8	80:20	20:80

Table 2
Chemical compositions of the samples with the weight ratio of BNBT to NiCuZn ferrite = 20:80 added with various content of BBSZ glass.

Samples	BNBT:NiCuZn ferrite (wt%)	BNBT + NiCuZn ferrite:BBSZ (wt%)
B2N8	80:20	96:4
5B2N8	80:20	95:5
10B2N8	80:20	90:10
20B2N8	80:20	80:20

Thermal shrinkage was measured using a dilatometer (Netzsch DIL 420C). The densities of the sintered samples were determined using the Archimedean method. The true densities were measured using a pycnometer (Micromeritics, AccuPyc 1340) for the BBSZ glass of 6.58 gm/cm^3, the BNBT powder of 6.0 gm/cm^3, and NiCuZn ferrite of 5.2 gm/cm^3 to calculate the theoretical densities of the sintered samples using the mixture rule. The crystalline phase identification was carried out using X-ray diffractometry (Siemens, D5000) with Cu-K_α radiation. The microstructure was observed using scanning electron microscopy (Hitachi S4100). Dielectric and magnetic properties (relative dielectric constant (K) and initial permeability (μ_i)) were measured using an LCR meter (YHP 4291A, YHP Co., Ltd.).

3. Results

The relative densities of the samples sintered at 900 °C as a function of the BNBT + BBSZ glass powder to NiCuZn ferrite ratio are shown in Fig. 1. The samples B2N8 and B4N6 did not result in comparable densification (below 90%). This is in good agreement with the finding observed by Hsu et al. [12] who reported that the densification of PNZT–NiCuZn ferrite composites decreased with the presence of 10–20 vol% ferrites. This can be explained by the lower onset shrinkage temperature and higher densification rate of BNBT than NiCuZn ferrite as shown in Fig. 2, which resulted in the formation of large densified BNBT aggregates before the densification onset of

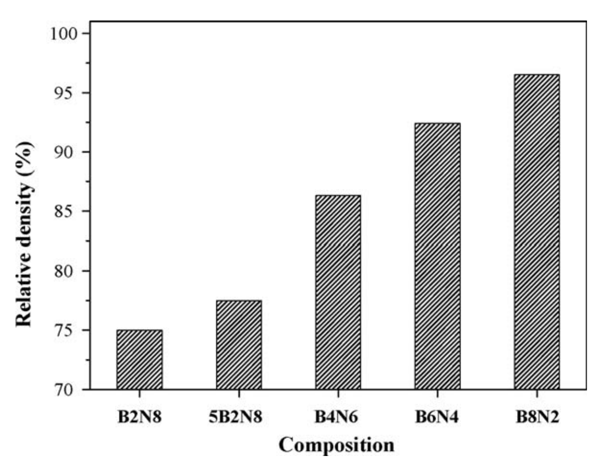

Fig. 1. Relative densities of the samples sintered at 900 °C as a function of the BNBT + BBSZ glass powder to NiCuZn ferrite ratio.

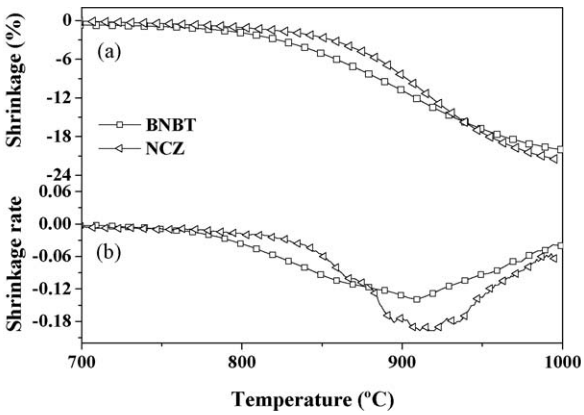

Fig. 2. Dilatometric analyses results of BBNT ceramic and NiCuZn ferrite.

NiCuZn ferrite. The densified BNBT aggregates may act as a densification constraint to inhibit the densification of NiCuZn ferrite during sintering. Note that the relative densities increased significantly with the addition of higher BBNT content. For the samples B6N4 and B8N2, the densities reached about 92% and 96% at 900 °C, respectively. The variation of the relative densities of the samples with the BNBT to NiCuZn ferrite = 20:80 ratio with the amount of BBSZ glass addition is shown in Fig. 3. The relative density increased with increasing BBSZ glass. Note that the relative density increased from 75% to 95% as the BBSZ glass content increased from 4 wt% (B2N8) to 20 wt% (20B2N8). This result indicates that BBSZ glass can effectively promote the densification of the ferrite–dielectric composites.

Fig. 4 shows the XRD patterns of samples with various BNBT + BBSZ glass powder to NiCuZn ferrite ratio sintered at 900 °C. No phases other than BNBT and NiCuZn ferrite are found.

Fig. 5 shows the microstructures of samples with various BNBT + BBSZ glass powder to NiCuZn ferrite ratio sintered at 900 °C. In the case of the sample B2N8, a porous microstructure with little densification is observed. For the samples B8N2 and B6N4, more dense and uniform microstructures are observed, which are consistent with the relative densities results observed in Fig. 3. Note that with increasing amounts of BBSZ glass for the samples with the BNBT to NiCuZn ferrite = 20:80 ratio, the number of pores decreased and the amount of acicular grains increased.

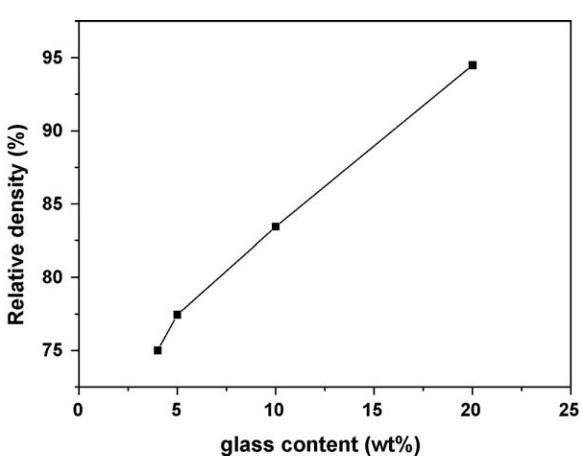

Fig. 3. Variation of the relative densities of the samples with the BNBT to NiCuZn ferrite = 20:80 ratio with the amount of BBSZ glass addition.

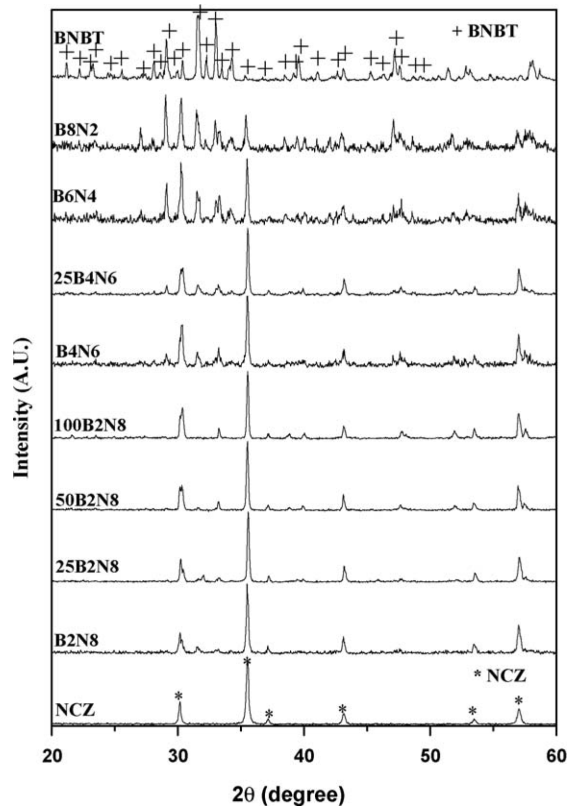

Fig. 4. XRD patterns of the samples with various BNBT + BBSZ glass powder to NiCuZn ferrite ratio sintered at 900 °C.

The effects of the BNBT + BBSZ glass powder to NiCuZn ferrite ratio sintered at 900 °C on the dielectric constant and initial permeability are shown in Figs. 6 and 7, respectively. As expected, the dielectric constant of the composites increased with increasing BNBT + BBSZ glass content and a larger initial permeability is observed with increasing NiCuZn ferrite content. The dielectric constant and initial permeability of the sample 25B4N6 are larger than sample B4N6 due to the increase in the relative density as shown in Fig. 1. The effects of the addition of BBSZ glass on the dielectric constant and initial permeability for the samples with the ratio of BNBT to NiCuZn ferrite = 20:80 are shown in Figs. 8 and 9, respectively. The dielectric constant and initial permeability of the sample increased with increasing BBSZ glass content due to the increase in the relative density. Note that the dielectric constant remains nearly a constant for all samples over a wide range of frequencies (100 MHz to 1 GHz) and the magnetic resonance frequencies for all samples are larger than 100 MHz. Therefore, the BNBT + BBSZ glass–NiCuZn ferrite composites can be a good candidate material for high frequency EMI device applications.

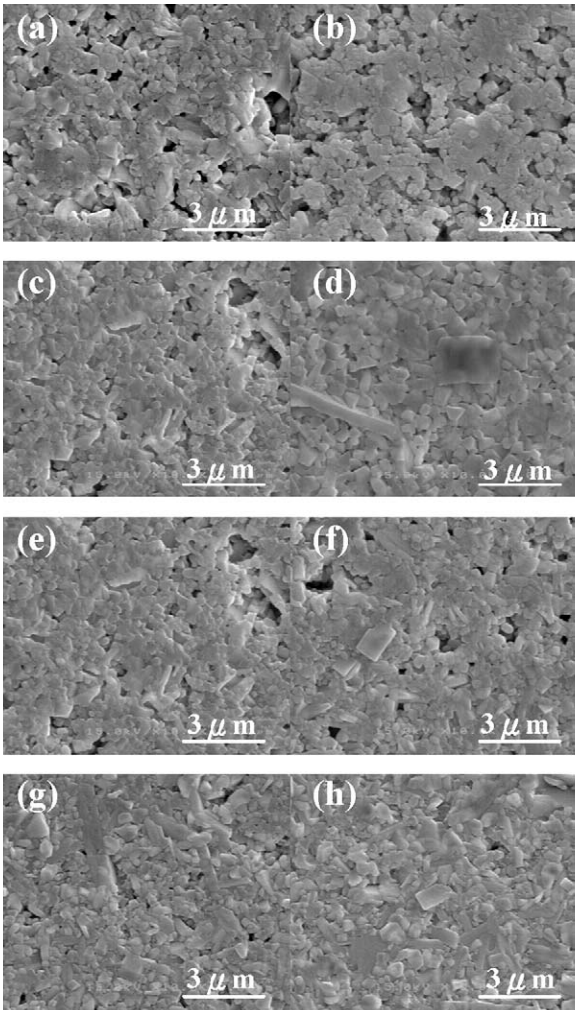

Fig. 5. Microstructures of samples with various BNBT + BBSZ glass powder to NiCuZn ferrite ratio sintered at 900 °C (a) B2N8, (b) 5B2N8, (c) 10B2N8, (d) 20B2N8, (e) B4N6, (f) 25B4N6, (g) B6N4 and (h) B8N2.

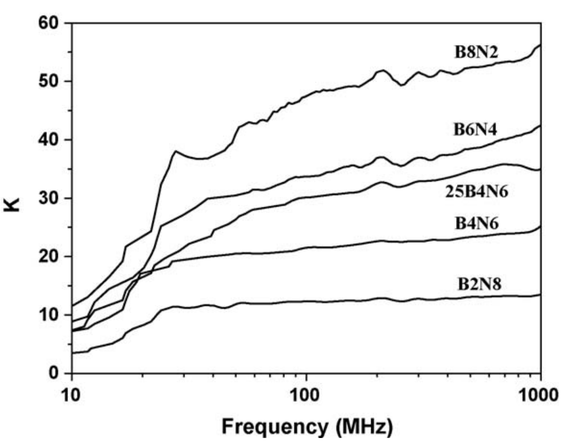

Fig. 6. Effects of the BNBT + BBSZ glass powder to NiCuZn ferrite ratio sintered at 900 °C on the dielectric constant.

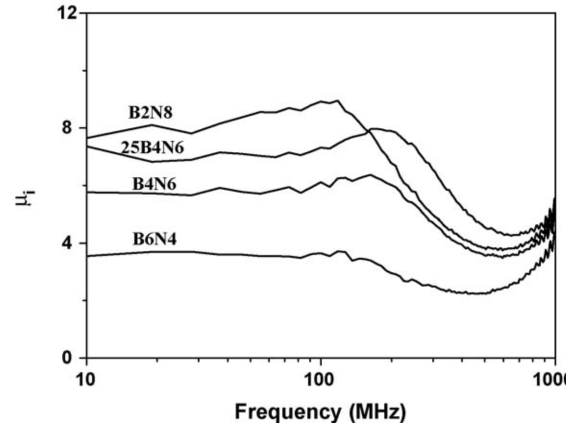

Fig. 7. Effects of the BNBT + BBSZ glass powder to NiCuZn ferrite ratio sintered at 900 °C on the initial permeability.

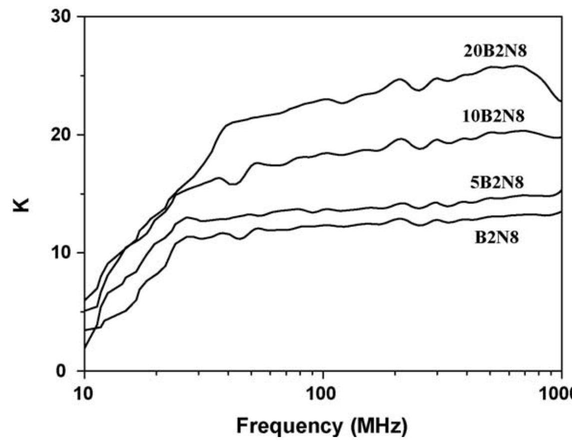

Fig. 8. Effects of the addition of BBSZ glass on the dielectric constant for the samples with the BNBT to NiCuZn ferrite = 20:80 ratio.

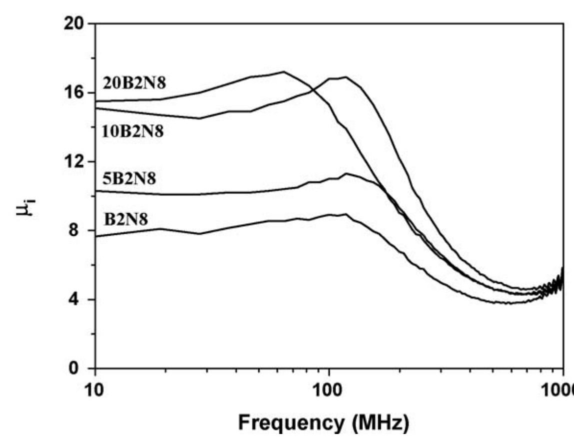

Fig. 9. Effects of the addition of BBSZ glass on the initial permeability for samples with the BNBT to NiCuZn ferrite = 20:80 ratio.

4. Conclusions

A low-temperature-fired (900 °C) BNBT–NiCuZn ferrite composite was developed. BBSZ glass can be used as a sintering aid to reduce the densification temperature of BNBT–NiCuZn ferrite composite below 900 °C. The composites exhibit nearly no chemical reaction between the dielectric and magnetic materials during sintering and superior dielectric and magnetic properties over a wide frequency range. The dielectric and magnetic properties of the composites can be fine tuned by changing the BNBT + BBSZ glass powder to NiCuZn ferrite ratio. The ferrite–dielectric composites reported in the previous studies are mostly not suitable for use in the high frequency range due to the selfresonance frequency limit. In this study, the dielectric constant remains nearly a constant over a wide range of frequencies (100MHz to 1 GHz) and the magnetic resonance frequencies are larger than 100 MHz for the BNBT + BBSZ glass–NiCuZn ferrite composites. Therefore, the BNBT + BBSZ glass–NiCuZn ferrite composites can be a good candidate material for high frequency EMI device applications.

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