

Low-temperature fabrication of NiCuZn Ferrite–(Ba_{0.7}Sr_{0.3})TiO₃ composites using granulated powders

Naoto KITAHARA, Hiroaki KAGEYAMA,* Tomoya KAWASAKI,*
Kazutomo ABE,* Hidenobu ITOH** and Junichi TAKAHASHI*[†]

Graduate School of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi, Kanagawa 164–8678, Japan

*Faculty of Engineering, Hokkaido University, Kita-13 Nishi-8, Kita-ku, Sapporo 060–8628, Japan

**Department of Materials Science, Kitami Institute of Technology, Koen-cho 165, Kitami, Hokkaido 090–8507, Japan

NiCuZn ferrite–(Ba_{0.7}Sr_{0.3})TiO₃ (BST) composite ceramics with the BST content of up to 50 vol % were fabricated by sintering compacted powder mixtures at 900°C. The granulation of the BST powder and addition of a Bi₂O₃-based oxide additive effectively assisted the densification of the composite samples. The samples thus fabricated showed required ϵ_r values whereas their μ_r values were considerably reduced, especially for those with lower BST contents. From the detailed examinations on the effect of the Bi₂O₃-based oxide additives and on the process modification to improve the reduced μ_r values, the addition of a Bi₂O₃–ZnO additive with the eutectic composition of as low as 1 wt % was enough to produce a densified 10 vol % BST composite sample with a highest μ_r value. It was also found that the incorporation of ferrite granules calcined at 600°C caused further improvement of μ_r . Thus, a densified 10BST composite sample with $\mu_r = 125$ was fabricated by low-temperature sintering at 900°C.

©2013 The Ceramic Society of Japan. All rights reserved.

Key-words : NiCuZn ferrite, (Ba_{0.7}Sr_{0.3})TiO₃, Composite ceramics, Granulated powder, Bi₂O₃-based additive, Low-temperature sintering

[Received July 31, 2012; Accepted October 23, 2012]

1. Introduction

Composite materials consisting of both the magnetic and dielectric (based on ferroelectric material) components have received a considerable attention in the research and development of electronic devices such as electromagnetic interference (EMI) filters and absorbers, integrated chip inductors and capacitors, and miniaturized antenna^{1)–5)} or in the study on the magneto-electric effect of two-phase multiferroics.^{6)–8)} Typical oxide systems reported for the composites are the combinations of ferrite as magnetic phase and ferroelectrics like Pb(Ti, Zr)O₃, BaTiO₃, (Ba, Sr)TiO₃ or BiFeO₃. In the fabrication of such oxide composites composed of compounds with chemically different natures, sintering of a compacted mixture of each compound at elevated temperatures often results in considerable changes in the magnetic and/or dielectric properties of the host compounds due to chemical reaction or ion substitution occurring during the heat-treatment.^{3),9)} For example, the present authors found that Ni_{0.3}Zn_{0.7}Fe₂O₄–BaTiO₃ composites obtained at 1250°C showed substantially high values of dielectric permittivity in small BaTiO₃ contents.³⁾ This could be explained by the incorporation of a small amount of Ti⁴⁺ into the spinel sublattice, resulting in the electron hopping between Fe²⁺ and Fe³⁺. It was also revealed that the application of a modified processing by surface coating with less reactive ZrO₂ component on granulated BaTiO₃ particles effectively suppressed the cation substitution.¹⁰⁾

An alternating method to avoid or minimize such serious magnetic or dielectric property changes is to fabricate composite materials at a temperature as low as possible. Recently, to co-fire a composite material with a low-melting electrode such as Ag,

which is required for the miniaturization and multi-functionalization of electronic devices based on LTCC (Low Temperature Co-fired Ceramics) technology, studies on the low-temperature firing of magnetic-dielectric composites (hereafter referred to as M–D composites) have been conducted.^{11)–14)} In these studies, composite samples containing NiCuZn ferrite as a magnetic phase were fabricated at 900°C (or lower temperature) with the presence of Bi₂O₃ additive as a sintering aide. The incorporation of the Cu component into NiZn ferrite can decrease the densification temperature of the ferrite while maintaining excellent magnetic properties of high initial permeability and low coercivity.^{15),16)} Thus, NiCuZn ferrite was inevitably used in the low-temperature fabrication of M–D composite materials. For the low-temperature-fired M–D composite samples, their magnetic and/or dielectric properties can be basically adjusted by changing the compositions of the starting NiCuZn ferrite and/or dielectric or the mixing ratio of the corresponding ferrite and dielectric materials. In fact, NiCuZn ferrite-dielectric composites with various properties were successfully fabricated by a conventional fabrication procedure in which preformed powders of a NiCuZn ferrite and dielectric material were mechanically mixed to give mixtures with fixed ratios and then their powder compacts were sintered at around 900°C.^{11)–14)}

As is well known, the magnetic or dielectric property of a ferrite or ferroelectric material can be greatly affected by the resulting microstructure (porosity, grain size and size distribution, or inclusions on grain boundaries) of a sintered sample. For example, ferrite materials showed strong dependences of the initial relative permeability (μ_r) on grain size and porosity.¹⁷⁾ Similar sensitivities to the resulting microstructure of sintered samples were also observed for the relative permittivity (ϵ_r) of ferroelectric materials.¹⁸⁾ This is the case for the low-temperature-fired NiCuZn ferrite-dielectric composites, but there are few

[†] Corresponding author: J. Takahashi; E-mail: tkjun@eng.hokudai.ac.jp

reports on the fabrication and property control of such composites based on a view point of ceramic processing. In the composites, it was commonly observed that an increasing amount of a dielectric component necessarily resulted in a substantial decrease in the sintered density with a simultaneous reduction of μ_r and ϵ_r values, because the dielectric component involved in these composites can be hardly densified without sintering aid at as low temperature as 900°C. Thus, besides the addition of a sintering aid, some modified process should be applied to lower the negative contribution induced by the dielectric component and to produce NiCuZn ferrite-dielectric composites with desired properties. In this study, an attempt to use a granulated and calcined component has been made in the low-temperature fabrication of NiCuZn ferrite-dielectric composites in order to minimize such a negative contribution and to elucidate the effect of the new fabrication process on the resulting magnetic and dielectric properties of the composites. A composite material on which the present authors had focused was NiCuZn ferrite-(Ba_{0.7}Sr_{0.3})TiO₃ composites (NCZ-BST composites) for the application of EM noise filters with specified cut-off frequency characteristics. The cut-off frequency in a noise filter can be adjusted by controlling the capacitance and inductance values of each component in the composite. Therefore, it is important to examine the effect of processing on the magnetic and/or dielectric properties of such composites and to develop a new fabrication method leading to property control.

2. Experimental procedure

2.1 Preparation of (Ba_{0.7}Sr_{0.3})TiO₃ powders

Commercially available powders of BaTiO₃ and SrTiO₃ (Sakai Chemical Industry Co. Ltd., Japan) with their particle sizes of 0.3 μm were mixed in a plastic container using a distilled water containing fixed amounts of a dispersant and a binder for 24 h to prepare a slurry of a mixture with a composition of Ba/Sr = 7/3. After dried, the oxide mixture was calcined at 1200°C for 4 h to form a (Ba_{0.7}Sr_{0.3})TiO₃ powder (BST powder) and then pulverized by wet ball milling for the production of a fine BST powder with an average size of ~0.7 μm. The fine BST powder thus prepared is named as F-BST powder. The granulation of the BST powder was conducted by spray-drying the slurry of the mixed BST powder under the conditions of 160°C, 80°C and 10 ml min⁻¹, for inlet temperature, outlet one and feed rate, respectively. The spray-dried BST powder with a maximum size of ~10 μm was then heated at 1200°C to form a granulated BST powder (G-BST).

2.2 Fabrication and characterization of composite samples

A NiCuZn ferrite powder (Toda Kogyo Co. Japan) from which densified ferrite samples can be obtained by sintering at 900°C without any sintering aid was used as a ferrite source. The composition of the ferrite powder was evaluated by X-ray fluorescence (XRF) analysis to be Ni_{0.25}Cu_{0.18}Zn_{0.42}Fe_{2.14}O_{4.0+δ}. Fixed amounts of the ferrite and F-BST or G-BST powders were weighed to become a BST content of 10–50 vol% and poured into a plastic container with YSZ (yttria stabilized zirconia) balls, to which a required amount of a sintering aid was also added. Sintering aid used in this study was a Bi₂O₃-based oxide or oxide mixture in the system Bi₂O₃-ZnO or Bi₂O₃-CuO, for each of which the corresponding oxide powders were mixed to be a eutectic composition of Bi₂O₃:ZnO = 88:12¹⁹⁾ or Bi₂O₃:CuO = 93:7²⁰⁾ (mol%) and calcined at 700°C. The reason why these compositions were selected was that a liquid phase to be formed

during sintering (at ~750°C or ~770°C for each system) will be able to assist effectively the densification of composite samples at a lower temperature than the Bi₂O₃ additive melting at ~830°C. An additive in the Bi₂O₃-ZnO or Bi₂O₃-CuO system, which was used in this study, is called as the BZ or BC additive, respectively.

After the powders of ferrite, BST and sintering aid were thoroughly mixed in a wet state and dried, the mixtures were formed into disks and toroids by uniaxial and/or cold isostatic pressing. Samples sintered at a fixed temperature (800–900°C) for 4 h were characterized by density measurement (Archimedes method), powder X-ray diffractometry (XRD: Rigaku Co., Rint 2200), microstructure observation with Scanning Electron Microscope (SEM: JEOL Ltd., JSM-6300F), and element analysis with Energy Dispersive X-ray Spectrometer (EDS: JEOL Ltd., JSM-6390LVS). Dielectric permittivity (ϵ_r) and magnetic permeability (μ_r) were measured with an impedance analyzer (Agilent 4285A) and a RF material analyzer (Agilent E4991A), respectively. When the granulation of ferrite powder was required, ferrite granules were prepared by applying the same spray-drying method as that used for the granulated BST powder.

3. Results and discussion

3.1 Fabrication of composite samples using BST granules

In the low-temperature fabrication of composite materials consisting of NiCuZn ferrite and BST components, an increasing content of the BST component that can be hardly sintered at 900°C caused inevitably a substantial lowering of sintered density of the composite, i.e., considerably suppressed magnetic and dielectric properties, if no sintering aid was added. Then we first examined two factors affecting the densification of composite sample containing 50 vol% BST (50BST composite). They were (1) the particle size of the BST component and (2) the amount of the BZ additive. **Figure 1** shows sintered density changes of composites fabricated from different BST powders and a 100% BST sample as a function of the BZ amount after sintering at 900°C. It should be noted that the addition of the BZ additive promoted effectively the densification of composite samples, whereas little densification occurred for the 100BST samples. For 50BST composite samples, an F-BST powder [shown in **Fig. 2(A)**] and a G-BST powder with a maximum size of ~10 μm [Fig. 2(B)] were independently used to fabricate the composites. It can be clearly seen from Fig. 1 that composite

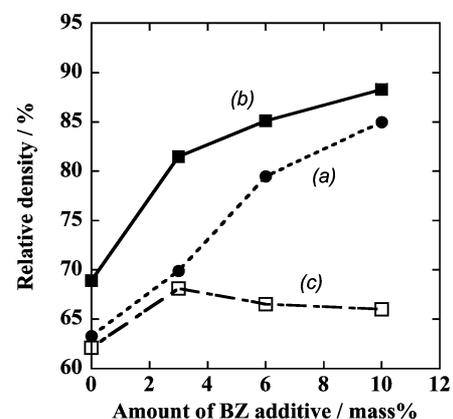


Fig. 1. Relative density changes with amount of BZ additive for 50BST composite samples obtained from (a) F-BST, (b) G-BST and for (c) 100BST sample using F-BST.

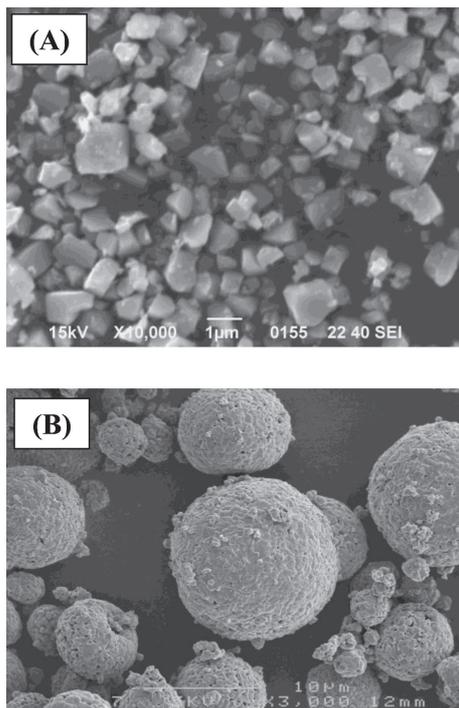


Fig. 2. SEM images of (A) pulverized (F-BST) and (B) granulated (G-BST) BST powders.

samples fabricated from G-BST showed higher values of relative density than those from F-BST at any BZ amount, although density difference between both samples tended to become small with an increasing amount of the BZ additive.

Let us consider the cause(s) of different densification properties based on the mixtures rule and percolation theory in the sintering of composite. In the present composite system, the rule of mixtures assuming that each phase constituting the composite densifies in the same way as it would independently by itself²¹⁾ cannot be adopted because a BST powder, even if it is very fine, can be hardly densified by itself at 900°C. Instead of the rule of mixtures, it is possible to consider BST particles as rigid inclusions and to apply the concept of percolation in which the formation of a continuous network of inclusions plays an important role for sintering.²²⁾ According to this concept, as the volume fraction of inclusions increases a large number of the inclusions form enough inclusion-inclusion contacts to produce a continuous network throughout the sample. If the continuous network of the inclusions is rigid, then the stiffness of the composite structure correspondingly increased, leading to the retardation of the sintering rate. Therefore, for the 50BST composite fabricated from pulverized F-BST particles in this study, a number of rigid F-BST particles present in the composite sample form percolating networks in some regions to suppress the densification of the composite. On the contrary, the reduced number of the G-BST particles (A simple calculation indicated that the number of the G-BST particles required to occupy a fixed volume of 50% BST is smaller by three orders of magnitude than that of the F-BST ones.) inhibit effectively the formation of a continuous network of the G-BST inclusions. This is why much densified composite samples were fabricated when using the granulated BST powder.

Figure 3 reveals the effect of the BZ additive on the densification and ϵ_r of the 20BST and 50BST composites (The density change of the 50BST sample was re-demonstrated here

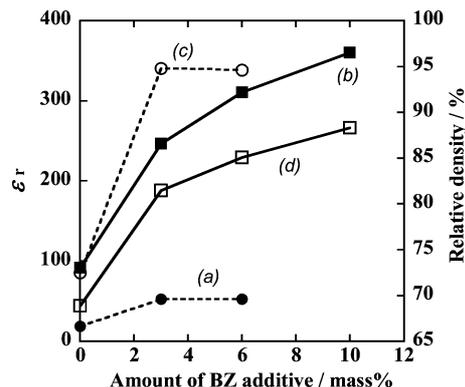


Fig. 3. Changes in ϵ_r and relative density with amount of BZ additive for 20BST and 50BST composite samples; (a) ϵ_r of 20BST, (b) ϵ_r of 50BST, (c) density of 20BST, and (d) density of 50BST.

for clear comparison.). For the 50BST samples, an increase in the BZ amount, which gave rise to an acceleration of the sample densification, caused a simultaneous increase in ϵ_r . On the contrary, 20BST composite samples showed a different behavior. That is, both the density and ϵ_r values reached maxima at 3 wt% BZ, followed by no further increase. These results indicated that the optimum amount of the BZ additive to produce densified composites with maximum ϵ_r values was found to be 3 and 10 wt% for the 20BST and 50BST composites, respectively. Thus, the amount of the BZ additive was adjusted to be 3, 6 and 10 wt% corresponding to an increasing BST content from 10 to 50 vol%.

Powder compacts of composites containing different contents of the G-BST powder and optimum amounts of the BZ additive were sintered at 900°C for 4 h. Its relative density (RD) change is plotted against BST content in Fig. 4(A) where that of composite samples obtained from the F-BST powder with no-additive is also demonstrated. As the BST content increased, the RD values inevitably became lowered, especially for no-additive samples. However, it is obvious that the composite samples to which the optimum amount of the BZ additive was added showed a considerable increase in RD for each sample with different BST contents. The corresponding changes in ϵ_r and μ_r of the sintered composites depicted in Fig. 4(A) can be seen in Fig. 4(B). Compared to ϵ_r values of samples fabricated using the F-BST powder and no additive, those of highly densified composites became very high, which corresponded with those calculated from a useful rule proposed by K. Lichtenecker for mixed phases.²³⁾ These high values are considered to come from the incorporation of the granulated BST powder instead of the fine one. Concerning a μ_r change with BST content in Fig. 4(B), however, the same densified composites showed lower μ_r values than those of calculated ones (a dotted line in the figure which is based on Lichtenecker equation). There have been several papers on densification and magnetic properties of ferrite samples with Bi₂O₃ addition. J. Mürbe et al. reported the effects of Bi₂O₃ addition on the microstructure and μ_r of Ni_{0.20}Cu_{0.20}Zn_{0.62}-Fe_{1.98}O_{3.99} samples sintered at 900°C.²⁴⁾ The grain size of the sintered samples increased for a sample with 0.25 wt% Bi₂O₃ and a homogeneous coarse-grained microstructure was observed for that with >0.5 wt% Bi₂O₃. The corresponding μ_r change was characterized by an increase for small Bi₂O₃ additions and a decrease for >0.5%. Although the authors demonstrated basic concepts of the relation between μ_r and grain size, there was no explanation for the reduced μ_r . In a study conducted by S.-F.

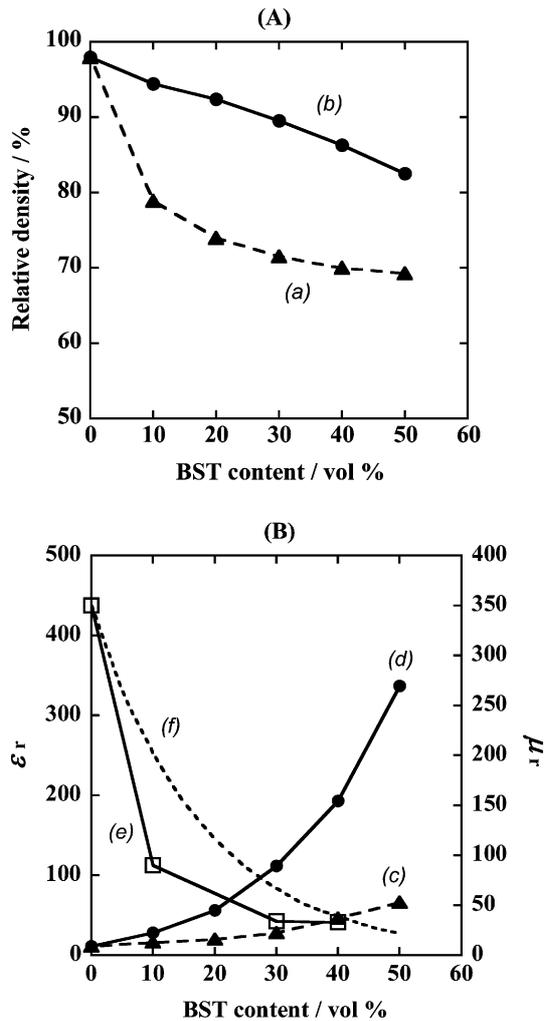


Fig. 4. BST content dependences of (A) relative density for samples fabricated from (a) F-BST and (b) G-BST and (B) ϵ_r changes for samples with (c) no-additive and (d) BZ additive, and μ_r changes for (e) the same sample as (d) and (f) a model sample(calculated).

Wang et al., the addition of 1.5 wt% Bi_2O_3 to a commercial ferrite of $\text{Ni}_{0.38}\text{Cu}_{0.12}\text{Zn}_{0.50}\text{Fe}_2\text{O}_4$ prepared by solid-state reaction benefited the densification and μ_r but deteriorated the quality factor of ferrite samples sintered in a range of 850–1050°C.²⁵⁾ Thus, the effect of Bi_2O_3 addition on the magnetic properties of ferrite could be different from system to system, especially depending on the composition of ferrite, the morphology and size of a starting ferrite powder as well as sintering conditions. Therefore, the examination on the effect of Bi_2O_3 -based additive(s) used in this study on μ_r of sintered ferrite samples is required to elucidate the cause(s) of the considerable reduction of μ_r shown in Fig. 4(B).

3.2 Examination of the effect of Bi_2O_3 -based additives on low-temperature sintering of NiCuZn ferrite

In the previous section, the addition of the BZ additive was found to be necessarily required to fabricate the densified NiCuZn ferrite–BST composite samples at 900°C. However, the additive showed opposing effects on their magnetic and dielectric properties of the sintered composites, i.e., a remarkable decrease in μ_r against a substantial increase in ϵ_r . It was also found that

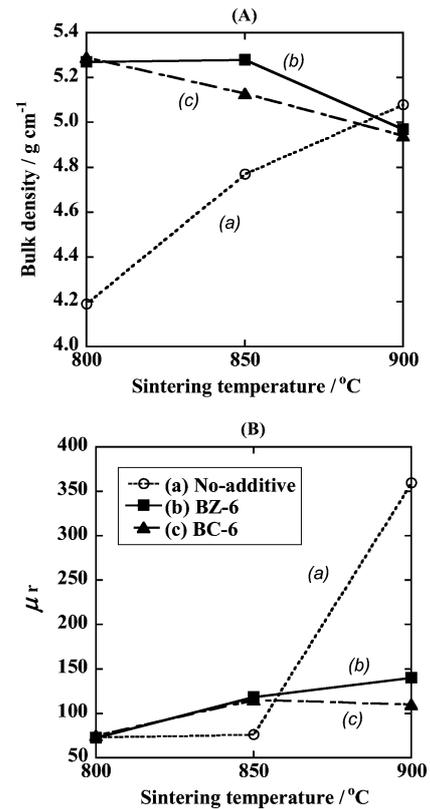


Fig. 5. (A) Bulk density and (B) μ_r changes as a function of sintering temperature for NiCuZn ferrite samples to which (a) no-additive and (b) BZ-6 or (c) BC-6 was added.

the BZ addition resulted in little effect on the densification of the 100BST sample (Fig. 1), suggesting that the BZ additive preferentially reacted with the ferrite component of the composites during sintering. Then, we examined in this section the effects of Bi_2O_3 -based oxide additives on the densification and μ_r change of the NiCuZn ferrite samples sintered at lower temperatures ranging from 800 to 900°C.

Figure 5 shows changes of (A) bulk density and (B) μ_r of NiCuZn ferrite samples with the addition of (a) 6 wt% BZ or (b) 6 wt% BC, the latter of which corresponds to a eutectic composition in the Bi_2O_3 –CuO system and melts at $\sim 770^\circ\text{C}$, and (c) without an additive as a function of sintering temperature. The amount of the additives was selected because the reaction product(s) could be readily detected at such a higher concentration level. Compared to no-additive samples, densification was considerably promoted by the BZ or BC addition at 800 and 850°C while slight increases were observed for μ_r of the sintered samples. At 900°C, it was clear that there was no benefit of using the BZ or BC additive for the promotion of sintered density of ferrite. Besides, a surprisingly drastic change was observed in μ_r of 900°C-sintered samples. A larger μ_r value of the no-additive ferrite sample was remarkably reduced when the BZ or BC additive was used. SEM observation of ferrite samples obtained at 850°C revealed that the grain size of the no-additive ferrite sample [Fig. 6(A)] were very small, whereas the BZ-6-added sample [Fig. 6(C)] consisted of largely grown grains in some portion, indicating that the addition of BZ-6 (or BC-6) accelerated in some degree both the densification and the grain growth of ferrite at 850°C. After sintering at 900°C, however, substantial grain growth occurred for the no-additive ferrite with a simultaneous and remarkable increase in μ_r . The microstructure

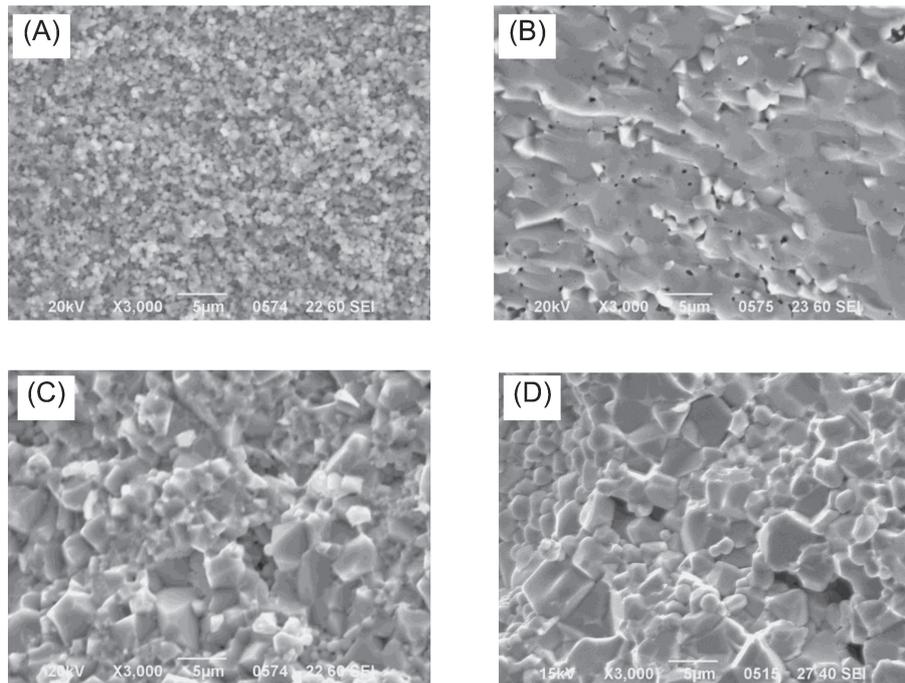


Fig. 6. Fractured surfaces of NiCuZn ferrite samples fabricated under different conditions; (A) sintered at 850°C with no-additive, (B) 900°C with no-additive, (C) 850°C with BZ-6, and (D) 900°C with BZ-6.

of the sample [Fig. 6(B)] indicated the occurrence of transgranular fracture among ferrite grains, which is often observed in coarse-grained ceramics.²⁶⁾ On the contrary, the ferrite sample with the BZ-6 additive showed a different fractured surface [Fig. 6(D)] formed by intergranular fracture which may often occur due to grain boundary phases.²⁶⁾ This result indicated that the fabrication of a ferrite sample consisting of largely grown grains which were bounded tightly was essential and necessarily required to attain a high μ_r value.

In the present composite system including the BZ or BC additive, a liquid phase formed during sintering could give rise to some essential change leading to a considerably reduced μ_r . So, to obtain information on a different possible cause other than grain size effect, the reaction product(s) and compositional change after sintering were examined. XRD patterns of ferrite samples fabricated are shown in Fig. 7. The appearance of much broadened peaks at around $2\theta = 28^\circ$ indicated the formation of some secondary phases during sintering. They could be identified with Bi₂₄Fe₂O₃₉ (marked with ∇ in Fig. 7) and Bi₃₈(Zn, Ni, Cu)O₅₈ (\times) for samples sintered at 800°C, while a somewhat different compound (\blacktriangledown) whose composition was assumed to be Bi_{1.15}Fe_{1.0}(Ni, Cu, Zn)_{0.35}O_{3.58} by EDS analysis was detected for 900°C-sintered samples. This result indicated that a liquid phase originated from the BZ or BC additive reacted with ferrite to form some non-magnetic compounds at grain boundaries, which was confirmed by a compositional image in backscattered electron (BSE) mode shown in Fig. 8. A diffraction peak of the ferrite phase at $2\theta \approx 30^\circ$ in Fig. 7 was found to be more or less shifted to a higher diffraction angle in each sample sintered with the BZ or BC additive, suggesting a change of the composition of the ferrite phase involved. Then, elemental analysis with EDS was carried out for ferrite grains in samples sintered at 900°C. The results are given in Table 1, indicating that the addition of the BZ or BC sintering aid resulted in both a decrease in the Fe content and an increase in the Ni/Zn ratio in each ferrite composition. Concerning the relationship between μ_r and ferrite composition

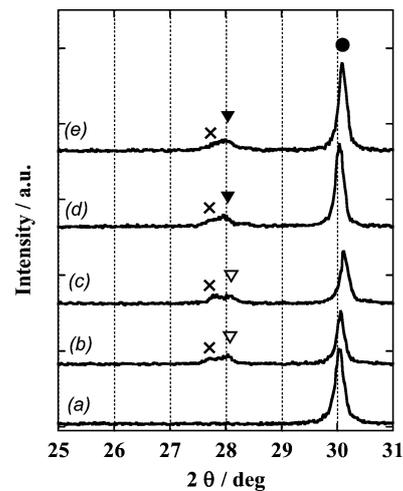


Fig. 7. XRD profiles of NiCuZn ferrite samples fabricated under different conditions; (a) 900°C with no-additive, (b) 800°C with BC-6, (c) 800°C with BZ-6, (d) 900°C with BC-6, and (e) 900°C with BZ-6. Each mark, ●, ×, ▽, \blacktriangledown , indicates ferrite, Bi₃₈(Zn, Ni, Cu)O₅₈, Bi₂₄Fe₂O₃₉, and Bi-Fe-Ni-Cu-Zn-oxide, respectively.

in NiZn and NiCuZn ferrites, it is known that the μ_r value of a ferrite sample decreases with an increasing Ni/Zn ratio,²⁷⁾ whereas it increases with an increasing Fe content.¹⁵⁾ As shown in Table 1, each ferrite sample fabricated using the BZ or BC additive was found to consist of the ferrite phase with a composition of a higher Ni/Zn ratio and a lower Fe content than those of the starting ferrite sample without an additive. Such a compositional change of the ferrite phase strongly affected the resulting μ_r values of the sintered ferrite samples. Therefore, a considerable reduction of μ_r observed for the BZ-6 and BC-6 samples could be explained by the compositional change of the ferrite phase involved and the formation of non-magnetic phases in addition to the inhibited growth of ferrite grains.

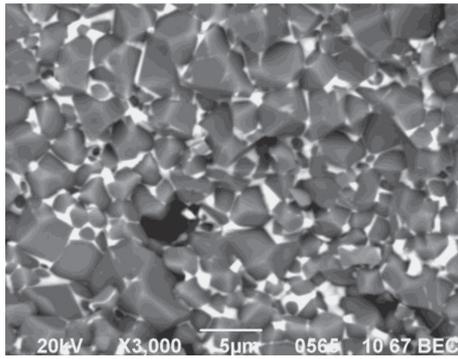


Fig. 8. A BSE image showing the presence of secondary phase(s) located at grain boundaries.

Table 1. Composition of ferrite in a formula; $(\text{Ni}_x\text{Cu}_y\text{Zn}_z)\text{Fe}_w\text{O}_{4+\delta}$

Sample	X	Y	Z	Ni/Zn	W
Starting ferrite	0.25	0.18	0.43	0.58	2.14
BZ-6-added	0.30	0.18	0.45	0.67	2.07
BC-6-added	0.28	0.19	0.44	0.64	2.09

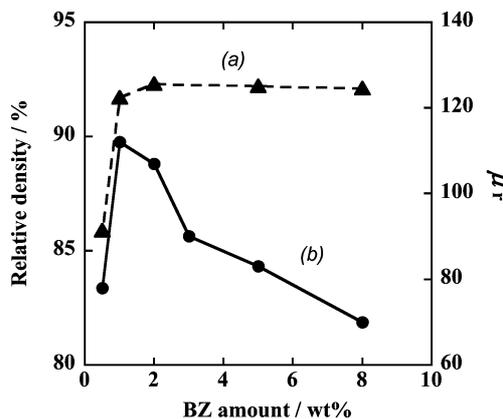


Fig. 9. Changes in (a) relative density and (b) μ_r with amount of BZ additive for 10BST composite samples.

3.3 Modified processing to improve the reduced μ_r of 10BST composite

Although the addition of a larger amount of the BZ or BC additive was found to cause a considerably reduced μ_r for ferrite samples, it was also recognized that densified composite samples, particularly those with higher BST contents, could not be fabricated without the assistance of such additives. In this section, we focused on the composite sample with a lower BST content, i.e., 10BST composite, and tried to find out a better processing to fabricate 10BST composites with improved or controlled μ_r . At first, an optimum amount of the BZ additive, which was selected because little difference was observed between the roles of the BZ and BC additives, was re-examined for the 10BST composite. **Figure 9** illustrates changes in relative density and μ_r with the amount of the BZ additive for the 10BST samples sintered at 900°C. It is clearly seen that the addition of the BZ additive of as low as 1 wt% was enough to obtain a densified sample with a highest μ_r value. It is also surprising that it decreased rapidly with an increase in the BZ amount while no reduction was observed for relative density. **Figure 10** shows SEM images of 10BST composites fabricated with the addition of (A) 1 wt% and (B) 5 wt% BZ (referred to as BZ-1 and BZ-5, respectively),

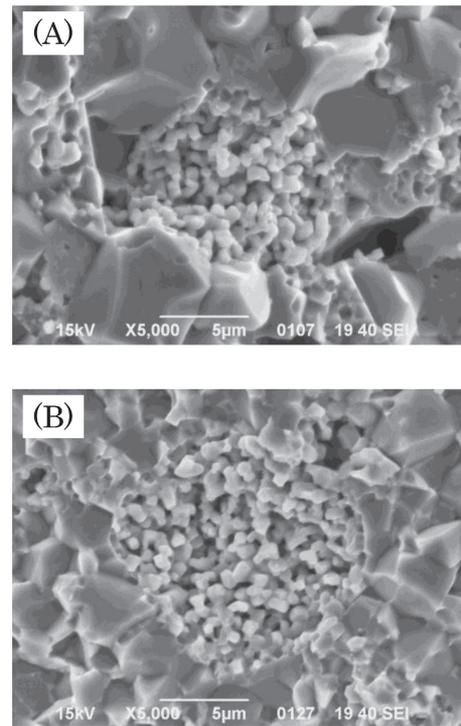


Fig. 10. SEM images of 10BST composite samples with BZ additive of (A) 1 wt% and (B) 5 wt%.

where a porous BST granule is surrounded by ferrite grains in each sample. It can be also demonstrated that the size of the ferrite grains changed correspondingly with the amount of the BZ additive and the BZ-1 composite consisted of larger ferrite grains than the BZ-5 composite. Thus the addition of larger amounts of the BZ additive necessarily resulted in the inhibited growth of ferrite grains, which is one of the major causes leading to the reduction of μ_r .

As a second approach to minimize the reduction of μ_r , we attempted to incorporate granulated ferrite powders, referred to as G-ferrites, as one of the composite components because the G-ferrites were expected to play a role similar to largely grown ferrite grains which could contribute to the improvement of μ_r for the present composite sample. The G-ferrites which were prepared by the same spray-drying method as that employed to obtain the granulated BST powders and successively calcined at 600°C and 800°C for 4 h are hereafter called as G-6 and G-8 ferrite powders, respectively. Powder compacts consisting of a ferrite mixture (a fixed ratio of the G-ferrite and the starting fine ferrite (F-ferrite) powders) and 10 vol% BST granules, to which 1 wt% BZ was added, were then sintered at 900°C for 4 h. Density and μ_r changes of those 10BST composite samples fabricated from several ferrite mixtures with different G-ferrite contents are shown in **Fig. 11** as a function of G-ferrite content, where, for example, a composite sample with a G-ferrite content of 20 vol% was composed of 70 vol% of F-ferrite and 20 vol% of G-ferrite powders, and 10 vol% of BST granules. For a density change of the composite samples fabricated using the G-6 ferrite powder, the relative density decreased with an increase in G-ferrite content. This can be explained by a less sinterable character of the G-8 ferrite powder because of a small difference between calcination (800°C) and sintering (900°C) temperatures. Their μ_r values decreased correspondingly with the decreasing density. On the other hand, composite samples fabricated using the G-6

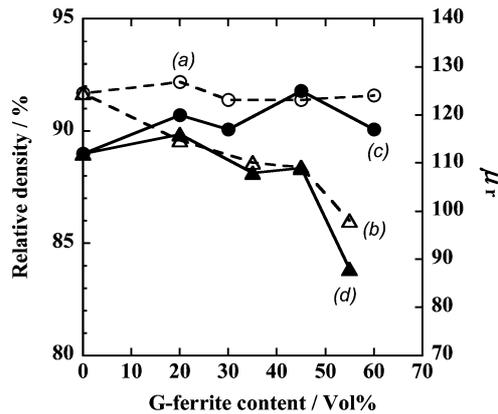


Fig. 11. Effect of G-ferrite content on relative density and μ_r changes of 10BST composite samples.

ferrite powder showed nearly the same density values irrespective of G-ferrite content, revealing that the G-6 ferrite powder would have a sintering characteristic similar to that of the F-ferrite powder. These considerations were supported by comparative microstructure observation of ferrite samples which consisted of 10 vol% F-ferrite and 90 vol% G-6 or G-8 ferrite powders and were sintered at 900°C for a shorter duration of 0 h (cooling just after reaching at 900°C). The reason why ferrite samples without the BST component were selected was to eliminate microstructure unclearness due to the presence of BST granules. As clearly shown in Fig. 12, the sample fabricated using the G-8 ferrite powder was characterized by the presence of loosely connected granules [Fig. 12(B)], whereas that fabricated using the G-6 ferrite powder demonstrated considerably different microstructure [Fig. 12(A)]. In addition to the different sintering behavior, it should be noted that their μ_r values tended to increase with an increasing content of the G-6 ferrite powder. In the previous section, we have mentioned that (1) the limited growth of ferrite grains, (2) the formation of non-magnetic secondary phases, or (3) a change in ferrite composition could reduce, independently or synergetically, the μ_r values of the present composite samples. Since such reduction of the μ_r values are essentially associated with a liquid phase formed during sintering, an amount of the liquid phase should be minimized and the regional extent over which the liquid phase can contribute to above changes should be also minimized to improve the resulting μ_r values. Therefore, improved μ_r values observed in 10BST composite samples fabricated by incorporating G-6 ferrite powders might be due to the limited extension of the liquid phase into ferrite granules. Thus, the μ_r value of 10BST composite sample increased from $\mu_r = 112$ for that fabricated from only fine ferrite powder to $\mu_r = 125$ for that fabricated using ferrite granules calcined at 600°C. This result suggested that the incorporation of ferrite granules combined with the optimization of process conditions could further improve μ_r values of the composite samples fabricated at a low-temperature sintering of 900°C.

4. Conclusions

NiCuZn ferrite-(Ba_{0.7}Sr_{0.3})TiO₃ (BST) composite ceramics with a BST content of up to 50 vol% were fabricated by sintering powder mixtures of each component at 900°C. The densification of the composite samples was improved as a combined result of using BST granules instead of a pulverized BST powder and adding an optimum amount of a low-temperature melting Bi₂O₃-

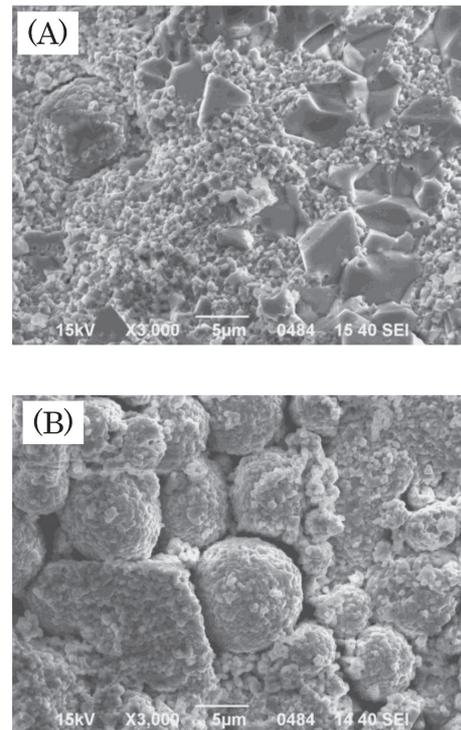


Fig. 12. SEM images of ferrite samples fabricated using (A) G-6 and (B) G-8 granules.

based oxide additive. Composite samples thus fabricated showed calculated ϵ_r values whereas their μ_r values were considerably reduced from calculated ones, particularly, for those with lower BST contents. From a detailed examination of the effect of Bi₂O₃-based oxide additives on the densification and μ_r of NiCuZn ferrite samples, the reduction of μ_r could be attributed to the formation of non-magnetic second phases and the compositional change of the ferrite phase in addition to the inhibited growth of ferrite grains, which were due to the reaction between ferrite and the additive during sintering.

Process modification was performed to improve the reduced μ_r values for the 10BST composite sample. It was found that the addition of Bi₂O₃-ZnO additive with the eutectic composition of as low as 1 wt% was enough to obtain a densified sample with a highest μ_r value. An attempt to incorporate granulated ferrite powders into the present 10BST composite system was also made in order to minimize the reduction of μ_r . The incorporation of ferrite granules calcined at 600°C (G-6 ferrite) resulted in the production of highly densified 10BST composite samples with improved μ_r values. The improvement of μ_r could be attributed to the lowering of the regional extent over which a liquid phase formed during sintering can contribute to the changes leading to the reduction of μ_r . Thus, a densified 10BST composite sample with $\mu_r = 125$ was fabricated by sintering compacted powder mixtures of G-6 and fine ferrites at 900°C.

References

- 1) H. Yang, H. Wang, L. Shui and L. He, *J. Mater. Res.*, **25**, 1803–1811 (2010).
- 2) H. Yang, Y. Lin, J. Zhu and F. Wang, *J. Mater. Sci.: Mater. Electron.*, **21**, 368–372 (2010).
- 3) K. Abe, N. Kitahara, M. Higuchi and J. Takahashi, *J. Ceram. Soc. Japan*, **117**, 944–949 (2009).
- 4) K. Abe, N. Kitahara, M. Higuchi and J. Takahashi, *Jpn. J.*

- Appl. Phys.*, **48**, 09KC04 (2009).
- 5) R. V. Petrov, A. S. Tatarenko, G. Srinivasan and J. V. Mane, *Microw. Opt. Technol. Lett.*, **50**, 3154–3157 (2008).
 - 6) C. A. F. Vaz, J. Hoffman, C. H. Ahn and R. Ramesh, *Adv. Mater. (Deerfield Beach Fla.)*, **22**, 2900–2918 (2010).
 - 7) D. R. Patil, S. A. Lokare, S. S. Chougule and B. K. Chougule, *Physica B*, **400**, 77–82 (2007).
 - 8) A. Testino, L. Mitoseriu, V. Buscaglia, M. T. Buscaglia, I. Pallecchi, A. S. Albuquerque, V. Calzona, D. Marré, A. S. Siri and P. Nanni, *J. Eur. Ceram. Soc.*, **26**, 3031–3036 (2006).
 - 9) K. Kamishima, Y. Nagashima, K. Kakizaki, N. Hiratsuka, K. Wanatabe, T. Mise, H. Naganuma and S. Okumura, *J. Phys. Soc. Jpn.*, **77**, 064801 (2008).
 - 10) K. Abe, Ph.D. Thesis, p. 50–64 (2010).
 - 11) L. Su, P. Liu, Y. He, J. Zhou, L. Cao, C. Liu and H. Zhang, *J. Alloys Compd.*, **494**, 330–335 (2010).
 - 12) L. Jia, H. Zhang, T. Li, Y. Liu, Q. Wen and J. Shen, *J. Appl. Phys.*, **107**, 09E309 (2010).
 - 13) L. Su, P. Liu, Y. He, C. Mu, J. Zhou, L. Cao, C. Liu, H. Zhang and G. Yao, *Mod. Phys. Lett. B*, **24**, 2869–2878 (2010).
 - 14) H. Zhang, H. Zhong, B. Liu, Y. Jing and Y. Liu, *IEEE Trans. Magn.*, **41**, 3454–3456 (2005).
 - 15) J. Mürbe and J. Töpfer, *J. Electroceram.*, **15**, 215–221 (2005).
 - 16) T. T. Ahmed, I. Z. Rahman and M. A. Rahman, *J. Mater. Process. Technol.*, **153–154**, 797–803 (2004).
 - 17) A. J. Moulson and J. M. Herbert, “Electroceramics”, 2nd ed., John Wiley & Sons Ltd., Chichester, (2003) pp. 469–505.
 - 18) T. Ota, J. Takahashi and I. Yamai, *Key Eng. Mater.*, **66–67**, 185–246 (1992).
 - 19) Phase diagrams for ceramists, *Amer. Ceram. Soc.*, **1**, 126 (1964).
 - 20) Phase diagrams for ceramists, *Amer. Ceram. Soc.*, **6**, 115 (1987).
 - 21) M. N. Rahaman, “Ceramic processing and sintering”, 2nd Ed., Marcel Dekker Inc., New York (2003) pp. 702–708.
 - 22) M. N. Rahaman, “Ceramic processing and sintering”, 2nd Ed., Marcel Dekker Inc., New York (2003) pp. 716–723.
 - 23) A. J. Moulson and J. M. Herbert, “Electroceramics”, 2nd Ed., John Wiley & Sons Ltd., Chichester (2003) pp. 82–85.
 - 24) J. Mürbe and J. Töpfer, *J. Electroceram.*, **16**, 199–205 (2006).
 - 25) S.-F. Wang, Y.-R. Wang, T. C. K. Yang, P.-J. Wang and C.-A. Lu, *J. Magn. Magn. Mater.*, **217**, 35–43 (2000).
 - 26) R. W. Rice, “Mechanical properties of ceramics and composites”, Marcel Dekker Inc., New York (2000) pp. 54–71.
 - 27) A. J. Moulson and J. M. Herbert, “Electroceramics”, 2nd Ed., John Wiley & Sons Ltd., Chichester (2003) pp. 492–505.