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Short communication

Effect of interface layer on dielectric and magnetic properties of 2–2 type $Ba_2Ti_9O_{20}$–$BaFe_{12}O_{19}$ composite ceramics

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Abstract

2–2 type $Ba_2Ti_9O_{20}$–$BaFe_{12}O_{19}$ composite ceramics were prepared by a tape casting method. Interface, dielectric and magnetic properties of prepared composite ceramics have been reported. Obvious interface diffusion between the dielectric and the ferrite has been observed by scanning electron microscopy and energy dispersive spectrometer. It was observed that the thickness of interface increased with increasing of sintering temperature. Compared with pure $Ba_2Ti_9O_{20}$ ceramic, relatively high dielectric constant and loss of the prepared composite have been obtained. Meanwhile, lower saturation and remnant magnetizations, and higher coercive field than that of pure $BaFe_{12}O_{19}$ ferrite has also been obtained. The dielectric constant of the prepared composites increased and then decreased, with increasing of sintering temperature accompanied with an opposite variation for the dielectric loss. At the same time, the saturation magnetization, the remnant magnetization and the coercive field decreased.
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Keywords: Ceramics; Casting; Interface; Dielectric; Magnetic

1. Introduction

Rapid development of emerging information and wireless technologies acquires ultrahigh performance of materials, which increases the complexity of issues related to noise suppression because of the wide noise frequency band (0.8–2 GHz) [1]. Multilayer chip LC filters consisted of a co-fired, multilayer structure of dielectric, ferrite and internal conductors have been a promising electromagnetic interference (EMI) device. Therefore, the co-firing between capacitor and inductor material is a fundamental process in fabricating perfect multilayer chip LC devices. And multilayer dielectric–ferrite composites have attracted much attention. Several composites, such as $BaTiO_3$–$Ni_{0.5}Zn_{0.5}Fe_2O_4$, $Bi_2(Zn_{1/3}Nb_{2/3})O_7$–$(Ni_{0.3}Cu_{0.1}Zn_{0.6}O)$–$(Fe_2O_3)_{0.8}$, $NiFe_2O_4$–$Pb(Zr_{0.52}Ti_{0.48})O_3$, $Pb(Zr_{0.52}Ti_{0.48})O_3$–garnet ferrite, and $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$–$(Ni_{0.2}Cu_{0.2}Zn_{0.6})Fe_2O_4$, have been successfully produced [2–6]. Among these composites, the dielectric system and magnetic material are not suitable for using in high-frequency range (0.8–2 GHz), because the dielectrics almost belong to the ferroelectricity group with a self-resonance frequency limit, or the ferrite with spinal structure exhibit a low cut-off frequency due to Snoek's limit, respectively. Some researchers developed composite ceramics composed of paraelectrics and hexagonal ferrites [7], and the co-fire behavior between dielectrics and ferrites has been reported. However, the effect of interface between two different materials on the dielectric and magnetic properties of the composites has not been researched.

In this paper, $Ba_2Ti_9O_{20}$ (B2T9), as a candidate for microwave dielectric ceramics because of its high dielectric constant and low loss, and $BaFe_{12}O_{19}$ (BF12) with a high cut-off frequency up to GHz [8], were chosen as dielectric and magnetic materials, respectively. The effect of interfacial characteristics between two different materials on the dielectric and magnetic properties of composite ceramics were studied.

2. Experimental

Analytical grade metal oxides were used to synthesis the dielectric of B2T9 and the ferrite of BF12 through solid state reaction. Then, the calcined B2T9 and BF12 powders were

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ground and mixed with binder, plasticizer, dispersant and solvent, respectively. After vacuumed, both slurries were tape-casted into dielectric and magnetic green sheets by doctor blade. The thickness of each green sheet was about 200 μm. Firstly, five dielectric layers were stacked. Then, five ferrite layers were stacked on the dielectric layers to obtain composite laminates. For comparison, ten layers of pure B2T9 and pure BF12 were stacked, respectively. And then, these laminates were treated by warm press at 80 °C under 160 MPa to obtain green pellets.

The polymers in the green pellets were burned out at 400 °C for 2 h by a very slowly heating speed of 0.5 °C/min. And then, all pellets were placed between two Al_2O_3 ceramic substrates with thickness of about 1 mm to avoid the defects from the mismatch in the sintering characteristics between the dielectric and the ferrite, and sintered at different temperatures for 4 h, 1350 °C for pure B2T9, 1270 °C for pure BF12, and 1250, 1300 and 1350 °C for B2T9–BF12.

X-ray diffraction (XRD, Panatical, Netherlands) and energy dispersive spectrometer (EDS, GENESIS-2000, EDAX, USA) were used to identify the composition of samples. The microstructure characteristics were observed using scanning electron microscopy (SEM, TM1000, Hitachi, Japan). The dielectric data were collected using Agilent E 4980. The magnetic properties were measured with vibrating sample magnetometer (VSM, BKY-4500, China).

3. Result and discussions

Fig. 1 illustrates SEM micrographs of the cross section of B2T9–BF12 ceramics were sintered at different temperature plots. When sintered at 1250 °C, many pores in the composite were generated due to the relatively high sintering temperatures for pure B2T9 and BF12 ceramics. When sintered at 1300 °C, a dense microstructure without pores was observed. Further increasing the temperature to 1350 °C, large number of pores is observed at the interface near the dielectric layer. Additionally, there is an interfacial reaction or diffusion occurred between the dielectric and the ferrite. With increasing of the temperature, the thickness of interface layer increased from ~15 to ~25 μm.

EDS was used to determine the compositions of interface as shown in Fig. 1. And the results are listed in Table 1. It can be seen that there are three types of cations included iron, barium and titanium at the interface. And the distribution of barium is relatively homogeneous, while iron and titanium have a wide diffusion range. The variation of atomic distribution around the interface indicates that new compounds or new phases may form during the co-firing.

Table 1
EDS results for the spots shown in Fig. 1.

Atom (%)	Spot				
	A	B	C	D	E
Fe	39.39	11.72	8.75	6.97	–
Ti	–	23.47	22.51	27.45	39.78
Ba	5.96	4.22	4.96	5.70	8.25
O	54.65	60.59	63.78	59.89	51.97

The structure of the composite can be accounted as two capacitors in series. The dielectric constant of the composite can be calculated with $K_C = 1(1/K_D + 1/K_F)$, where K_C, K_D and K_F represent the dielectric constants for composite, dielectric and ferrite, respectively [9,10]. As shown in Fig. 2, the dielectric constant has been found at 36 for B2T9 in this work. Mallick et al. confirmed that the dielectric constant of BF12 strongly depended on the sintering conditions but not more than 32 [11]. Thus, the dielectric constant of composite prepared in this paper should be lower than that of dielectric or ferrite. However, as shown in Fig. 2, the composite ceramics exhibit higher dielectric constant and loss than pure B2T9 at 1 MHz during the temperature of 30–80 °C, which may be attributed to the interfacial diffusion or the new phase during co-firing. Additionally, Vanderah et al. reported that BF12 exhibited some characteristics of semiconductor [12]. Under an alternative electric field, the interface polarization such as Maxwell–Wagner polarization between the dielectric and the ferrite may enlarge the dielectric constant [13]. During the sintering temperature range, a relatively high dielectric constant and a low dielectric loss are obtained when the composites were sintered 1300 °C. It is well known that pores in ceramics can lower the dielectric constant and increase the dielectric loss. As shown in Fig. 1, there are many pores in the ceramics sintered at 1250 and 1350 °C, which could decrease the dielectric constant and increase the dielectric loss. It is noted that the dielectric constant remains nearly a constant for all samples over a temperature range of 25–85 °C, and the dielectric loss is no more than 0.01. Especially, the composite sintered at 1300 °C has a high dielectric constant of 105, and a low loss of 0.006 at

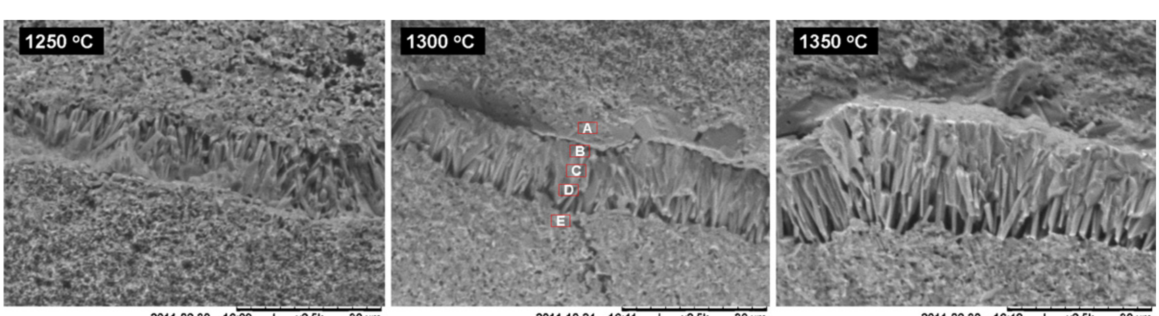

Fig. 1. SEM of B2T9–BF12 composite ceramics sintered at different temperatures.

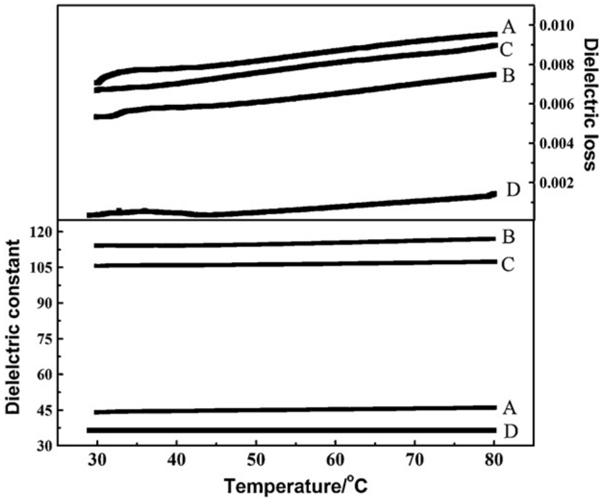

Fig. 2. Dielectric properties of B2T9–BF12 ceramics sintered at 1250 °C (A), 1300 °C (B) and 1350 °C (C) for 4 h, and B2T9 ceramic sintered at 1350 °C for 4 h (D).

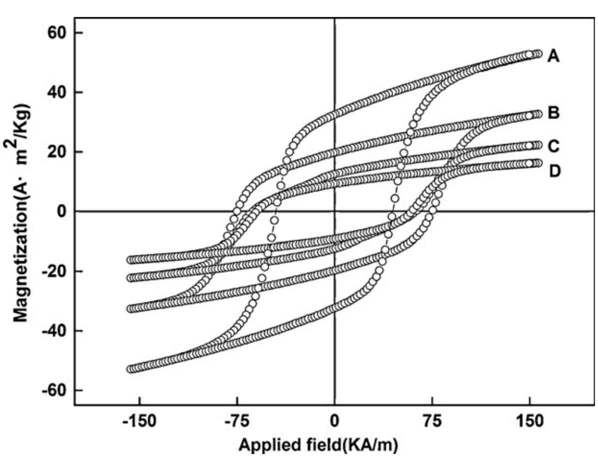

Fig. 3. Magnetic hysteresis loops of pure BF12 sintered at 1270 °C (A), B2T9–BF12 sintered at 1250 °C (B), 1300 °C (C), and 1350 °C (D).

room temperature. After calculated, the temperature coefficient of dielectric constant for all composites is no more than 0.01/°C, which is higher than that of pure BT, and increases with sintering temperature.

As shown in Fig. 3, typical magnetization hysteresis loops for pure BF12 and B2T9–BF12 ceramics can be observed. Due to the introduction of non-magnetic dielectric, the composite ceramics exhibit lower saturation magnetization (Ms) and remnant magnetizations (Mr) than that of pure ferrite, accompanied with higher coercive field (Hc). These variations in magnetization correspond with the fact that the individual ferrite grains act as the centers of magnetization and the non-magnetic dielectric material incorporates into the ferrite and break the magnetic circuit. In general, grain sizes increase and pores disappear simultaneously in ferrites with increase of sintering temperature, which would enhance Ms and Mr, and lower Hc [14]. And in dielectric–magnetic composite materials, the reduction of volume fraction for magnetic materials will decrease Ms and Mr, and increase Hc [2–4]. In this work, both Ms and Mr decrease with sintering temperature for the composites. As shown in Fig. 1, the interface thickness increases with sintering temperature, reducing the volume fraction of the ferrite. Thus, it could be proposed that this reduction of the volume fraction has larger influence than those arising from the enhancement of grain size on Ms and Mr with sintering temperature. And when the sintering temperature increases from 1250 to 1300 °C, the composite ceramics become compact, which decrease the Hc. Further increasing sintering temperature to 1350 °C, the Hc has an insignificant change, which may be attributed to the opposite effects of the interface thickness and the grain size on magnetic properties as above illustration. At last, the variation of magnetic properties depends strongly on the development of microstructure such as interface, grain size, etc.

4. Conclusions

The laminated composite ceramics of B2T9–BF12 were prepared using a tape-casting method. An obvious interface between two materials has been observed, and the thickness of the interface increases with sintering temperature. Both the dielectric constant and loss of the composites are larger than that of pure B2T9 due to the interface polarization between the dielectric and the ferrite. And the composites exhibit relatively low Ms and Mr and high Hc compared with pure BF. The dielectric and magnetic properties depend strongly on the development of microstructures such as interface, grain size and pores with sintering temperature. At last, further investigations such as the frequency dependence of dielectric and magnetic properties, reduction of loss, and etc. should be considered for high frequency applications.

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References

[1] Y. Tarusawa, K. Ohshita, Y. Suzuki, T.N. Nojima, T. Toyoshima, Experimental estimation of EMI from cellular base-station antennas on implantable cardiac pacemakers, IEEE Trans. Electromagn. Compat. 47 (2005) 938–950.

[2] C. Harnagea, L. Mitoseriu, V. Buscaglia, I. Pallecchi, P. Nanni, $BaTiO_3$–$(Ni_{0.5}Zn_{0.5})Fe_2O_4$ ceramic composites with ferroelectric and magnetic properties, J. Eur. Ceram. Soc. 27 (2007) 3947–3950.

[3] T.M. Peng, R.T. Hsu, J.H. Jean, Low-fire processing and properties of ferrite + dielectric ceramic composite, J. Am. Ceram. Soc. 89 (2006) 2822–2827.

[4] J.L. Chen, Z. Xu, S.B. Qu, X.Y. Wei, X.H. Liu, Electromagnetic properties of ferroelectric–ferrite ceramic composites, Ceram. Int. 34 (2008) 803–807.

[5] J.Y. Kim, J.H. Koh, J.S. Song, A. Grishin, Magnetically and electrically tunable devices using ferromagnetic/ferroelectric ceramics, Phys. Status Solidi B 241 (2004) 1714–1717.
[6] J. Shen, J. Zhou, B. Li, L. Li, Ferroelectric and dielectric properties of $[Pb(Ni_{1/3}Nb_{2/3})O_3–PbTiO_3]/[(Ni_{0.2}Cu_{0.2}Zn_{0.6})Fe_2O_4]$ composites, Mater. Lett. 60 (2006) 1071–1075.
[7] M. Wang, J. Chou, Z. Yue, L. Li, Z. Gui, Co-firing behavior of $ZnTiO_3$–TiO_2 dielectric/hexagonal ferrite composites for multi-layer LC filters, Mater. Sci. Eng. B 99 (2003) 262–265.
[8] G.H. Jonker, H.P.K. Wijin, P.B. Braun, Feroxplana, hexagonal ferromagnetic iron-oxide compounds for very high frequencies, Philips Technol. Rev. 18 (1956) 145–180.
[9] R. Wu, T. Zhao, P. Chen, J. Xu, X. Ji, Periodic layered waveguide with negative index of refraction, Appl. Phys. Lett. 90 (2007) 082506.
[10] S. Wang, C. Tang, T. Pan, L. Gao, Effectively negative refractive material made of negative permittivity and negative permeability bilayer, Phys. Lett. A 351 (2006) 391–397.
[11] K.K. Mallick, P. Shepherd, R.J. Green, Dielectric properties of M-type barium hexaferrite prepared by co-precipitation, J. Eur. Ceram. Soc. 90 (2007) 2045–2052.
[12] T.A. Vanderah, J.M. Loezos, R.S. Roth, Magnetic dielectric oxides: subsolidus phase relations in the $BaO:Fe_2O_3:TiO_2$ system, J. Solid State Chem. 121 (1996) 38–50.
[13] Z. Yu, C. Ang, Maxwell–Wagner polarization in ceramic composites $BaTiO_3–(Ni_{0.3}Zn_{0.7})Fe_{2.1}O_4$, J. Appl. Phys. 91 (2002) 794–797.
[14] Q. Yang, H. Zhang, Y. Liu, Q. Wen, Microstructure and magnetic properties of microwave sintered M-type barium ferrite for application in LTCC devices, Mater. Lett. 63 (2009) 406–408.