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Low-loss insulating-conductive ceramic composite with giant permittivity and high permeability using glass phase as separating layer

Ruoyang Ma[1], Bin Xiao[1], Ning Ma, Piyi Du*

State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

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Abstract

The control of dielectric loss in insulating-conductive ceramic composites is of great significance for the enhancement of the comprehensive performance of next-generation devices. In this work, a low-activity precursor co-sintering method was proposed to prepare low-loss $BaTiO_3$(BTO)/$Ni_{0.5}Zn_{0.5}Fe_2O_4$(NZFO) ceramic composite by using $2PbO–B_2O_3$(PBO) glass as insulating layer. XRD and SEM were used to reveal the phase composition and the morphology of the composite. Results showed that the conductive networks can be successfully cut off by PBO glass separating layer inside the composite $(1-x)$BTO/xNZFO where x is the molar fraction of NZFO ferrite, giving rise to decreased dielectric loss in a wide compositional range between $x=0.1$–0.7 while retaining considerable effective permittivity and initial permeability. Excess amount of PBO glass is not favorable for the formation of separating layer due to the chemical reactions occurring between the constituent phases and the glass phase; meanwhile, accompanied by the decrement in dielectric loss, the initial permeability of the composite decreases linearly with increasing PBO content.

Keywords: B. Grain boundary; C. Electrical conductivity; Ceramic composite; Initial permeability; Dielectric loss

1. Introduction

Multi-functional materials are promising candidate for the miniaturization of next-generation electronic devices due to their excellent comprehensive performance, such as simultaneous appearance of giant permittivity and high permeability [1–3], or novel coupling effect occurring between the constituent phases [4–6]. As a typical multi-functional material, multi-field susceptible ferroelectric/ferromagnetic ceramic composites that are sensitive to both electric and magnetic fields are becoming attractive and expected to be used in unprecedented novel devices to reduce production cost, save space occupation and improve device efficiency [7–10]. Therefore, it is of great interest to explore new ceramic composites with improved performance from the perspective of practical applications.

One typical material in the above-mentioned material family is $BaTiO_3$(BTO)/$(Ni,Zn)Fe_2O_4$(NZFO) ceramic composite, in which the barium titanate (BTO) is a typical ferroelectric material exhibiting giant permittivity, and the nickel zinc ferrite (NZFO) is a typical ferrimagnetic material widely used in microwave devices. Limited by the composite law, the volume fraction of the NZFO phase should be elevated as high as possible in order to obtain larger permeability in BTO/NZFO ceramic composite. However, with the enhancement of magnetic properties, the dielectric properties of the composite will be reversely undermined, characterized by a tremendous increment in dielectric loss above the percolation threshold (f_c) when the NZFO phase forms conductive networks. As is known, the unwanted increment in dielectric loss is mainly ascribed to the remarkable increase in the electrical conductivity of the composite, and is quite distinct especially in low frequency region [11]. It has also been revealed that in conventionally sintered BTO/NZFO ceramic composite, the conductive NZFO particles tend to connect with each other

*Corresponding author.
E-mail address: dupy@zju.edu.cn (P. Du).
[1]These authors contributed equally.

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when its volume fraction reaches about 55–65%, which is considered as the actual percolation threshold (f_c) for sol–gel derived BTO/NZFO system [12]. In percolative insulating-conductive composite, there exists a contradiction when the composite is composed of a nonmagnetic phase and a magnetic phase. On one hand, when the volume fraction of the magnetic phase is below the percolation threshold, the initial permeability of the composite is no larger than 10. For this reason, the volume fraction of the magnetic phase should be increased so as to enhance the magnetic properties of the composite. On the other hand, if the volume fraction of the magnetic phase is loaded far above the percolation threshold, such as 80–90%, the percolation of conductive phase inevitably leads to high dielectric loss arising from the contribution of dc conductivity, thus seriously prohibiting the practical applications of such percolative composite in electromagnetic devices [11,13]. Although some attempts have been carried out to solve the problem of high dielectric loss for the composite above f_c, the obtained results is still far from satisfactory, because the dielectric loss is usually larger than 0.3–0.5 [14,15]. Ideally, the dielectric loss of the composite should be as small as possible, but it is difficult to achieve this goal for insulating-conductive composite in practice.

A possible method to decrease the dielectric loss of such insulating-conductive ceramic composite is to introduce a high-resistance phase into the ceramic body to enwrap the conductive particles so that the conductive networks can be cut off and the transportation of charge carriers can be suppressed [16–18]. However, if the insulting phase, which generally turns out to be a glass phase, is co-sintered with the ceramic composite in situ in the sintering stage at high sintering temperature, the formation of impurity phase is almost inevitable as the glass phase will diffuse into the crystal lattice of the constituent phases and react with them chemically [19,20]. This effect is not favorable for the obtainment of high-performance composite with stable properties. Also, the occurrence of impurity phases brings undesirable complexity to the system as a result of uncontrollable phase composition and conductivity inhomogeneity, hence any theoretical analysis regarding these systems will become quite complicated.

Considering that the dielectric loss of insulating-conductive composites above the percolation threshold is mainly contributed by leakage current in low frequency region, it is an effective way to suppress the transportation of charge carriers across the grain boundaries by introducing a high-resistance glass separating layer. In this context, the chemical reactions between the glass and the constituent phases should be minimized. Herein, we demonstrate an effective method to prepare low-loss insulating-conductive ceramic composite by co-sintering low-activity composite precursor and subsequently added glass phase. The results revealed that the method can be potentially applied to prepare low-loss ferroelectric-ferromagnetic ceramic composite in which the glass phase acts only as physical separating layer without engendering any impurity phases, hence can reduce the low-frequency dielectric loss of the composite efficaciously. The minimum dielectric loss obtained in this work is 2–5 times smaller than that of conventionally sintered samples over a wide compositional range between $x=0.1$–0.7, and the magnetic properties of as-prepared composite are still applicable.

2. Material and methods

The $(1-x)BaTiO_3$(BTO)/$xNi_{0.5}Zn_{0.5}Fe_2O_4$(NZFO) ($x=0$–1) ceramic composite with $2PbO–B_2O_3$(PBO) glass separating layer were prepared by a sol–gel in situ process and a low-activity precursor co-sintering process. Here, x is the molar fraction of NZFO ferrite, varying from 0 to 1. The details of the sol–gel process have been reported elsewhere [21]. The composite precursor derived from the sol–gel process was pre-sintered at 850 °C for 1.5 h first, then sintered at 1280 °C for 12 h in powder state. Afterward, 10 wt% PBO glass powder was mixed with the composite powder precursor (with different molar ratio of BTO to NZFO) uniformly. Then, adequate amount of PVA (5 wt%) was added into the mixed powder for granulation and molding. The samples were eventually pressed into annular shape, averagely 20 mm in outer diameter, 10 mm in inner diameter and 1–2 mm in height. In the co-sintering stage, the samples were sintered at 1150 °C for 3 h, then cooled down to room temperature naturally. While investigating the effect of PBO content on the properties of BTO/NZFO composite, the co-sintering temperature was designed to be 1100 °C (duration of 3 h), decreased by 50 °C as there was an increment in PBO content up to 20 wt% so as to make sure the samples did not melt severely, while the other parameters were maintained the same.

The constituent phases of the composite were determined by a RIGAKUD/MAX-C type X-ray diffractometer (XRD, Cu Kα, $\lambda=0.1540562$ nm) between 10–80° with a step width of 0.02° and a scanning speed of 4°/min. The microstructure was observed by a SIRION-type field emitting scanning electron microscope (SEM, produced by Japan FEI Corporation). Silver electrodes were coated on both sides of the samples before the measurement of dielectric properties. The effective permittivity, dielectric loss and electrical conductivity of the composite were measured by Agilent 4292A precision impedance analyzer (HP4294A-LRC) between 40 Hz and 15 MHz. The effective permeability was measured by Agilent 16451B precision impedance analyzer (Palo Alto, CA) between 100 kHz and 110 MHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(1-x)$BTO/xNZFO ($x=0$–1) ceramic composite with 10 wt% PBO glass acting as separating layer prepared by the co-sintering method as described in the experimental section. It can be seen that the major phases formed in the composite are tetragonal BTO phase (with negligible amount of hexagonal BTO phase) and spinel NZFO phase, as can be well identified by their characteristic diffraction peaks. The peak intensity of BTO and NZFO phase increases clearly with the increment in their molar fraction in the composite. No extra peaks that are related to the PBO phase or any other impurity phases were observed within the same measurement accuracy.