Journal of Magnetism and Magnetic Materials 322 (2010) 819–823

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Low temperature fired Ni–Cu–Zn ferrite with $Bi_4Ti_3O_{12}$

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ARTICLE INFO

Article history:
Received 14 September 2009
Received in revised form
29 October 2009
Available online 14 November 2009

Keywords:
Ni–Cu–Zn ferrite
$Bi_4Ti_3O_{12}$ ceramic
LTCC
Magnetic property
Dielectric property

ABSTRACT

The Ni–Cu–Zn ferrites with different contents of $Bi_4Ti_3O_{12}$ ceramics (1–8 wt%) as sintering additives were prepared by the usual ceramic technology and sintered at 900 °C to adapt to the low temperature co-fired ceramic (LTCC) technology. The magnetic and dielectric properties of the ferrite can be effectively improved with the effect of an appropriate amount of $Bi_4Ti_3O_{12}$. For all samples, the ferrite sintered with 2 wt% $Bi_4Ti_3O_{12}$ has relatively high density (98.8%) and permeability, while the ferrite with 8 wt% $Bi_4Ti_3O_{12}$ has relatively good dielectric properties in a wide frequency range. The influences of $Bi_4Ti_3O_{12}$ addition on microstructure, magnetic and dielectric properties of the ferrite have been discussed.

1. Introduction

With the miniaturization of electronic devices, the Ni–Cu–Zn ferrite is extensively used in multi-layer chip inductors (MLCI) because it has excellent magnetic properties in the radio frequency (RF) range, high electrical resistivity, good chemical stability, and can be densified at temperatures lower than 950 °C when co-fired with Ag (inner conductors material) [1–4]. For the Ni–Cu–Zn ferrite, the magnetic properties can be easily adjusted by compositional modification (changing the content of NiO, CuO and ZnO), but it is difficult to take the dielectric properties into consideration simultaneously. If the dielectric properties can be effectively improved on the premise of low loss of the permeability, the ferrite has the potential application in the multi-layer electromagnetic interference filter (EMIF) as the material for both inductor layer and capacitor layer. It is helpful to simplify the process of device fabrication, reduce cost, and adapt to the development of low temperature co-fired ceramic (LTCC) technology. To solve above problem, proper sintering additives are requisite. The Bi_2O_3 is commonly used to promote grain growth and improve the densification degree of the ferrite sintered at low temperature [4–6], but its improvement effect on the dielectric properties is limited. Hence, the ceramics with low melting point and good dielectric properties will be a good choice as sintering additives. Ferroelectric $Bi_4Ti_3O_{12}$ (BIT) ceramic can meet above requirements due to its high dielectric constant, high Curie temperature, low melting point and liquid phase sintering [7,8]. In this work, the Ni–Cu–Zn ferrites with different BIT contents were synthesized by solid-state reaction at 900 °C. The influence of BIT content on the microstructures, magnetic and dielectric properties of the sintered ferrites has been investigated.

2. Experiment

The Ni–Cu–Zn ferrite samples were prepared by standard double sintering ceramic method. The $Ni_{0.60}Cu_{0.24}Zn_{0.16}Fe_2O_4$ (NCZF) was prepared through solid-state reaction using analytical grade NiO, CuO, ZnO and Fe_2O_3 as raw materials. These basic oxides were mixed and wet-milled for 12 h and pre-sintered at 850 °C for 2 h. The BIT was prepared through solid-state reaction using analytical grade Bi_2O_3 and TiO_2 and pre-sintered at 770 °C. The above two pre-sintered powders were mixed with mass ratio of BIT/NCZF (x)=0%, 1%, 2%, 4% and 8%, and then wet-milled for 12 h. The mixtures were dried, mixed with 10 wt% poly(ethylene glycol) binder, sieved through 0.15 mm mesh and pressed at 5 MPa to the shape of toroids ($Ø18 \times 8\ mm^2$) and pellets (Ø18 mm) with 2–3 mm thickness. The toroids and pellets were final sintered at 900 °C in air for 3 h to yield the final samples.

The phase structures of the samples were investigated by X-ray diffractometer (XRD, RINT2000, Rigaku Co.) with CuKα radiation. The microstructures on the cross section of the samples were examined by scanning electron microscope (SEM, JEOL JSM-6490). The bulk densities were measured by the Archimedes method. The low frequency permeability was measured by the precision LCR meter (Agilent 4284A) in the range of 20 Hz–1 MHz. Complex permeability, permittivity, and dielectric loss tangent were measured by the impedance analyzer (HP4291B) in the frequency range of 1 MHz–1.8 GHz.

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doi:10.1016/j.jmmm.2009.11.010

3. Results and discussion

The XRD patterns for the samples with 0, 4, and 8 wt% BIT, and BIT powder sintered at 900 °C are shown in Fig. 1. The single-phase spinel structure has never changed by adding a small amount of BIT. The main peaks of BIT phase can be observed in the XRD pattern of the sintered sample when the addition amount of BIT is up to 8 wt%. The lattice parameters, theoretical densities (D_x), and relative densities of all samples are given in Table 1. The theoretical density of the sample without BIT is calculated using the formula [9]:

$$D_x = ZM/NV, \tag{1}$$

where Z is the number of the nearest neighbors, M is the molecular weight, N is Avogadro's number, and V is the unit cell volume as determined from X-ray analysis. The theoretical densities of the samples containing BIT are calculated using the formula [10]:

$$D_x = (W_1 + W_2)/[(W_1/D_1) + (W_2/D_2)], \tag{2}$$

where W_1 and W_2 are the weight percentage of the NCZF and BIT with densities D_1 and D_2, respectively.

The SEM micrographs of the cross sections for the samples with 0, 1, 2, and 8 wt% BIT are shown in Fig. 2a–d, respectively. The sample without BIT (Fig. 2a), having fine and uniform crystal grains, presents porous in the microstructure. For the sample with 1 wt% BIT (Fig. 2b), some extremely large grains appear and the inhomogeneity in its microstructure is responsible for the obvious decrease in density, comparing with the sample without BIT. With increasing the BIT content in some degree, the grain growth and microstructural densification are significantly promoted. When the BIT addition reaches 2 wt%, the sintered body of the sample (Fig. 2c) has relatively larger grain size (approximately 5–15 μm) and less open pores. For the sample with 8 wt% BIT (Fig. 2d), it is observed that most grains, compared with that in the sample with 2 wt% BIT, show a decrease in size and abnormal growth.

Here, we associate the magnetic properties of the samples with the microstructure by means of the magnetic circuit model [11], and the static permeability μ_s is expressed as

$$\mu_s = \frac{\mu_i(1+(\delta/D))}{1+\mu_i(\delta/D)}, \tag{3}$$

where μ_i is intrinsic static permeability of materials without defects, δ is the thickness of the grain boundaries, and D is the average grain size. The ratio δ/D can be calculated approximately

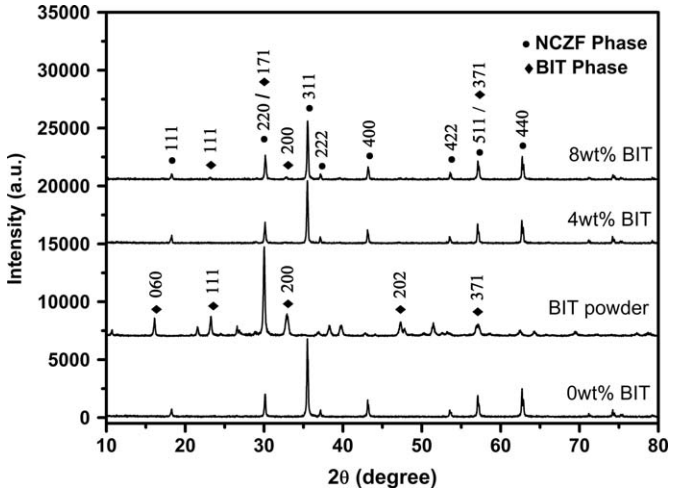

Fig. 1. X-ray diffraction patterns for the samples with 0, 4, and 8 wt% BIT, and BIT powder sintered at 900 °C.

Table 1
Lattice parameters, theoretical densities (D_x), relative densities (%), and the static permeability (μ') of the samples with different addition amounts of BIT.

BIT/NCZF (wt%)	Lattice parameters	D_x (g/cm^3)	%Density	μ' (200 Hz)
0	a=8.377	5.349	97.7	19.70
1	a=8.377	5.367	94.1	33.54
2	a=8.376	5.386	98.8	73.13
4	a=8.379	5.415	98.7	68.76
8	a=8.374	5.490	98.0	47.67

using the formula [12]:

$$\frac{\delta}{D} = \left(\frac{\rho_{d,i}}{\rho_d}\right)^{1/3} - 1, \tag{4}$$

where $\rho_{d,i}$ and ρ_d are the theoretical density and the measured density of the materials, respectively. As shown in Fig. 3, the dashed curve is obtained with the formula (3) using 93.19 as the fitted value of μ_i. The dots denote the samples with the static permeability measured at 200 Hz (listed in Table 1). It is noticed that the dots representing the samples with 1, 2, and 4 wt% BIT are close to the dashed curve, but the measured static permeability of the other two samples are obviously below the calculated values, especially for the sample without BIT. The above discrepancies appeared in the samples with 0 and 8 wt% BIT are derived from the method used for calculating the ratio δ/D. As known, the magnetization process of polycrystalline ferrite can be characterized as superposition of domain wall motion and spin rotation [13]. When the grain size is in a range of 1–10 μm, the permeability is almost proportional to the average grain size and the contribution of domain wall motion is significant. But the domain wall will gradually disappear if the grain size is close to a critical value. Globus and Duplex had pointed out that the grain size less than 0.2 μm led to pure rotation permeability [14]. The sample without BIT has many fine grains less than 1 μm, so the contribution of spin rotation should be taken into account. In this case, it is inaccurate to calculate the ratio δ/D by the formula (4). For the samples containing BIT, we approximately replace the measured density of the ferrite phase with that of the sample. When the formula (4) is used, there will be more obvious deviation in the sample with relatively higher BIT addition, such as 8 wt%.

For all samples, variations of the real and imaginary permeability with frequency are shown in Figs. 4 and 5, respectively. The real permeability increases rapidly with the increase of the BIT content at first, and reaches its peak value in the sample with 2 wt% BIT, and then gradually decreases when the BIT adding amount increases from 2 to 8 wt%. Considering the contribution of the domain wall motion which becomes more important with increasing sintered density, grain size, and homogeneity in microstructure of ferrite [15–17], the permeability increases with BIT addition increasing from 0 to 2 wt% due to obvious growth of grain, and its decrease with BIT addition increasing from 2 to 8 wt% is attributed to two factors: first, the excess content of BIT suppresses grain growth of the ferrite, thus leading to formation of heterogeneous particles (shown in Fig. 2d) and decrease in density, and, second, magnetic dilution caused by surplus non-magnetic BIT. As shown in Fig. 4, the peak value of the imaginary permeability shifts to lower frequencies with BIT addition increasing from 0 to 2 wt%, and decreases gradually with BIT addition increasing from 2 to 8 wt%. The evident shift which is companied with the increase of the permeability conforms to the Snoek's law [18]. The decrease of the above peak value from 2 wt% sample to 8 wt% sample is closely related to the decrease of ferrite grain size [19].