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Low temperature sintered magneto-dielectric ferrite ceramics with near net-shape derived from high-energy milled powders

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ABSTRACT

Nanosized $Ni_{0.70}Zn_{0.25}Co_{0.05}Fe_{1.90}Mn_{0.02}O_4$ ferrite ceramics were fabricated from high-energy ball milled powder mixtures with various ratios of Fe_2O_3/Fe as starting materials, in order to achieve magneto-dielectric materials with near net shape behavior for practical applications. The ferrite ceramics were obtained by sintering the milled powder compacts at 800 °C for 4 h, with a linear expansion of less than 4% as compared to the green pellets. The ceramics had an average grain size of less than 200 nm. The real part of relative permittivity decreases with increasing percentage of Fe_2O_3 used in the starting mixtures. The sample from the powder mixture with 50% Fe_2O_3 exhibits promising magneto-dielectric properties at frequencies of up to 90 MHz, which can be used for miniaturization of antennas at very high frequency (VHF) band.

1. Introduction

Due to their relatively large physical sizes, high frequency (HF, 2–30 MHz) and very high frequency (VHF, 30–90 MHz and 100–300 MHz) antennas have been desired to be miniaturized by antenna designers for more convenient applications [1–3]. Besides various electromagnetic miniaturization strategies, material loading has been acknowledged to be an effective way for such purpose. They are known as magneto-dielectric materials, with both the real permeability and permittivity to be much higher than those of free space [4–6]. Meanwhile, they have almost equal or close values of real permeability and permittivity, in order to maintain a good matching in impedance with the free space, so that electromagnetic waves would enter them without suffering reflection loss. Furthermore, the materials should have sufficiently low magnetic and dielectric losses over the desired working frequency ranges.

Noting the requirement of both magnetic and dielectric properties, only magnetic ceramics can be used. Because metallic magnetic materials do not exhibit proper dielectric characteristics, only ferrite ceramics are suitable candidates. Various ferrite ceramics have been developed to show promising magneto-dielectric performances [7–13]. Generally, pure ferrite ceramics are sintered at relatively high temperatures of ≥1200 °C, during which Fe^{2+} ions are formed that are retained after the sintering process. Owing to the presence of Fe^{2+} ions, the ferrites would have high electrical conductivity and thus high dielectric loss tangent. To solve this problem, it is necessary to use sintering aids to reduce the sintering temperature to be below 1200 °C. In this case, Bi_2O_3 has been demonstrated to be very effective for various ferrite ceramics. Ferrite ceramics with Bi_2O_3 sintering aid can be sintered very well without the formation of Fe^{2+} ions. In addition, matching permeability and permittivity can be realized by modifying magnetic

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properties of the ferrite ceramics [7–13].

It is well known that ceramic materials always experience dimensional shrinkage during the sintering process. Since the shrinkage is very sensitive to a number of processing parameters, such as composition of the materials, properties of starting materials, green density, sintering temperature and sintering time duration, it is very difficult to precisely control the sizes of the final products, which could however be an important consideration in practical antenna designs. To address this issue, we demonstrated a simple strategy that can be used to develop ferrite ceramics with near net shape characteristics. $Ni_{0.88}Zn_{0.07}Co_{0.05}Fe_{1.90}Mn_{0.02}O_4$ was selected as an example. The near net shape fabrication was achieved by optimization the composition of Fe and Fe_2O_3 in the precursor mixtures. During sintering process, the volume shrinkage caused by sintering was compensated by the expansion related to the oxidation of Fe to Fe_2O_3. More importantly, the ferrite ceramics with optimized composition exhibited promising magneto-dielectric properties, with almost equal real permeability and permittivity, as well as low magnetic and dielectric loss tangents, over 30–90 MHz. Interestingly, the ferrite ceramics could be obtained at a sintering temperature of as low as 800 °C, with an average grain size to be less than 200 nm.

2. Experiment

The ferrite composition selected in this study was $Ni_{0.88}Zn_{0.07}Co_{0.05}Fe_{1.90}Mn_{0.02}O_4$. Commercially available Fe (99+% purity, Aldrich Chemical Company Inc., USA), Fe_2O_3 (99% purity, Aldrich Chemical Company Inc., USA), MnO_2 (98% purity, Aldrich Chemical Company Inc., USA) and Co_3O_4 (99+% purity, Aldrich Chemical Company Inc., USA) powders, were used as starting materials. In this case, Fe was used to achieve near net shape fabrication, due to the oxidation of Fe to Fe_2O_3 during the sintering process. To optimize the content of Fe, ratios of $Fe_2O_3/(Fe+Fe_2O_3)$ were set to be 10%, 20%, 30% and 50%.

The starting materials were mixed by a high-energy ball milling for 12 h without using any liquid additives. The high-energy milling was conducted by using a Retsch PM400 type planetary ball milling system. A 250 ml tungsten carbide vial and 100 tungsten carbide balls with diameter of 10 mm were used as a milling medium. The milling speed was set at 200 rpm. The milled powders were then compacted and sintered at 800 °C for 4 h.

Two types of samples, namely disk (diameter of ~10 mm and thickness of ~1.5 mm) and coaxial cylinder (outer diameter of ~20 mm, inner diameter of ~10 mm and thickness of ~2.5 mm), were prepared. Disk samples were used for measurement of permittivity and DC resistivity, while cylinder samples were used for measurement of permeability.

Densification behaviors of the green pellets were monitored by using a Setaram Setsys 16/18 type dilatometer at a heating rate of 10 °C/min in air atmosphere. Phase compositions of the samples were analyzed using a Philips PW 1729 type X-ray diffractometer (XRD) with Cu K_α radiation. Grain size and grain morphology of the sintered samples were examined by using a JEOL JSM-6340 F type field emission scanning electronic microscope (FESEM). Densities of the ferrite ceramics were derived from the masses and dimensions of the samples.

DC resistances of the sintered samples were measured using a multimeter. DC resistivities of the samples were then calculated based the resistances and sample dimensions. The complex relative permeability and permittivity of the ceramics were measured using an Agilent E4991A RF impedance/materials analyzer over 1 MHz - 1 GHz. For the measurement of electrical and dielectric properties, the disk samples were coated with a room temperature drying Ag paste as electrodes.

3. Results and discussion

Fig. 1 shows linear shrinkage curve of the sample with 10% Fe_2O_3 in the starting mixture. With a certain degree of fluctuation, the sample starts to expand at about 650 °C, which is believed to be mainly caused by the volume expansion during the oxidation reaction of Fe to Fe_2O_3. In addition, owing to huge amount of heat from the exothermic reaction [14], the internal temperature of the sample increased sharply, thus resulting in the significant thermal expansion of the sample. From 650 °C to 850 °C, the expansion is very fast and almost linear, which slows down at about 850 °C. Such slow-down in expansion infers to the completion of the oxidation and starting of the sintering process. At about 1000 °C, the sample starts to shrink. Until 1200 °C, the about 25% expansion of the sample is still retained. Meanwhile, similar results have been observed for other samples with higher contents of Fe_2O_3 in the initial mixtures, with gradually smaller expansion due to the decreased level of Fe.

It is well known that sintering is a process of particle rearrangement and densification at high temperatures. The densification of green body inevitably leads to shrinkage of the ceramic sample. In present work, the volume expansion due to iron oxidation counteracts the shrinkage caused by the densification, so that the final dimensional change of the sintered sample is small when cool down to room temperature. The linear expansion magnitudes of the four samples are listed in Table 1, which are all less than 4%, exhibiting a good near net shape characteristic. According to sintering behaviors, all the samples were sintered at 800 °C for 4 h in this study.

Fig. 2 shows XRD patterns of the samples with different contents of Fe_2O_3 in the initial mixtures after sintering at 800 °C for 4 h. It is found that all the patterns can be indexed as spinel crystal structure, without any detectable second phase. This result implies that the Fe in the starting mixtures has been completely oxidized to Fe_2O_3 and phase pure ferrite is formed at the sintering temperature. At least, it is safe to state that the content of Fe in the samples is much less than the detection limit of the XRD equipment.

Cross-sectional SEM images of the four samples after sintering are shown in Fig. 3. The sample derived from the initial mixture with 10% Fe_2O_3 has an average grain size of >1 μm, while many grains exhibit an irregular shape. As the content of Fe_2O_3 is increased to 20%, the grain size is greatly reduced, with average grain size to be much smaller than 1 μm. Further increase in the

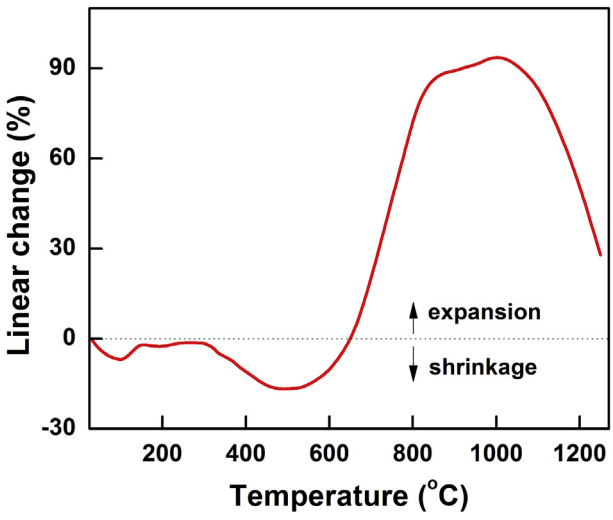

Fig. 1. Linear change of the 10%-Fe_2O_3 sample during sintering process.