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Low-temperature-fired NiCuZn ferrites with BBSZ glass

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ABSTRACT

Addition of BBSZ (27% Bi_2O_3, 35% H_3BO_3, 6% SiO_2, and 32% ZnO in mol%) glass has been used to enhance densification and improve the magnetic properties of low-temperature-fired NiCuZn ferrites. It was found that the BBSZ glass did not form a visible second phase in our testing range. However, the densification and microstructure of the ferrites were initially very sensitive to the BBSZ glass content. Even a slight increase in BBSZ glass content from 0.25 to 0.5 wt% was sufficient to change the ferrite samples from not being well sintered with a uniform microstructure and very small grain size to a typical bimodal, inhomogeneous microstructure. It proved to be better to add more BBSZ glass than the critical content to obtain the appropriate microstructure and magnetic properties. In this study, a ferrite sample with 0.75 wt% BBSZ glass gave the best performance in terms of densification, microstructure, permeability, and *Q*-factor characteristics.

1. Introduction

Low-temperature-fired NiCuZn ferrites are the most important magnetic materials used in multilayer chip inductors or LC filters because of their high permeability in the RF frequency region, high electrical resistivity, and environmental stability [1–5]. In their applications, the sintering temperature of the NiCuZn ferrites should be decreased to around 900 °C to permit co-firing with a silver internal electrode. In recent years, many investigations have been carried out with a view to lowering the sintering temperature and improving the magnetic properties of NiCuZn ferrites, for example by choosing different preparation methods or conditions, optimizing the compositions of the ferrites, adding different sintering aids to the ferrites, etc. [6–10]. In these investigations, ferrites prepared by the conventional solid-state reaction method proved to be the most suitable for volume-production of multilayer chip devices, although this method has some deficiencies. It is necessary to lower the sintering temperature of the ferrites by the addition of a sintering aid. To date, many sintering aids, such as Bi_2O_3, MoO_3, PbO, and V_2O_5, have been incorporated into NiCuZn ferrites to lower the sintering temperature. Among these sintering aids, Bi_2O_3 has been considered as the most effective for NiCuZn ferrites [11]. However, it has also been found that Bi_2O_3 accelerates silver diffusion in multilayer chip devices. It is known that BBSZ glass does not react with silver electrodes and can be successfully used to densify microwave dielectric ceramics [12]. Nevertheless, to the best of our knowledge, no study on the effects of BBSZ glass on low-temperature-fired NiCuZn ferrites has hitherto appeared in literature. In this work, BBSZ glass was added to NiCuZn ferrites as a sintering aid, and the influences of BBSZ glass on densification, microstructure, and magnetic properties of the NiCuZn ferrites were investigated.

2. Experimental procedure

A NiCuZn ferrite with a composition of $(NiO)_{0.4}(ZnO)_{0.4}(CuO)_{0.2}(Fe_2O_3)_{0.95}$ was prepared by the conventional solid-state reaction method. Analytical grade Fe_2O_3, NiO, ZnO, and CuO were weighed according to the formula and mixed in a ball mill. After drying, the powder was calcined at 800 °C for 2 h to obtain the spinel phase. Different contents of BBSZ glass between 0 and 2 wt% were then added to samples of the calcined powder and the mixtures were further milled in ball mills. Following the addition of PVA, the milled powders were granulated and pressed into toroidal and disk-shaped samples, which were sintered in air at 900 °C for 3 h. To prepare BBSZ glass, high-purity Bi_2O_3, H_3BO_3, SiO_2, and ZnO were weighed according to the composition 27% Bi_2O_3/35% H_3BO_3/6% SiO_2/32% ZnO (in mol%). The powders were mixed, dried, and melted at 1000 °C for 1 h. The melt was then quenched in water to form BBSZ glass.

Bulk density was calculated by measuring the dimensions and weight of the disk-shaped samples. Linear shrinkage was calculated by comparing the diameters of the sintered and pressed samples. Phase formation was confirmed by X-ray diffraction (XRD). Micrographs of fractured cross-sections of the samples were obtained using a scanning electron microscope (SEM). The permeability and *Q*-factor spectra were measured using an Agilent4285 LCR meter

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within the frequency range 100 kHz–30 MHz. Saturation magnetizations were measured using a BHV-525 vibrating sample magnetometer (VSM).

3. Results and discussion

XRD patterns of the samples without and with maximum BBSZ glass content were obtained and are shown in Fig. 1. A single-phase spinel structure was observed for the two samples, which meant that either the BBSZ glass did not form a visible second phase or the content of BBSZ or of the components derived therefrom was too low to be detected in our testing range.

The bulk density and linear shrinkage of the samples sintered at 900 °C are shown in Fig. 2. As expected, the introduction of BBSZ glass significantly improved the densification of the samples. Both bulk density and linear shrinkage increased markedly with increase in BBSZ glass content from 0 to 0.5 wt%, and then reached the maximum at 0.75 wt% BBSZ glass. Thereafter, bulk density and linear shrinkage displayed slight decreases on further increase in BBSZ glass content. Fig. 3 shows micrographs of sintered samples

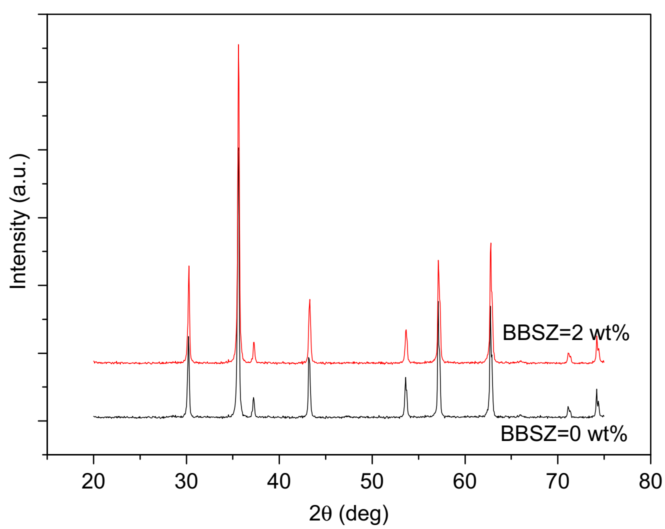

Fig. 1. X-ray diffraction patterns of the samples without and with maximum BBSZ glass content.

with different BBSZ glass contents. It was observed that little if any grain growth occurred for the glass-free sample. The average grain size increased slightly with 0.25 wt% BBSZ glass, but some point contacts between the grains were still seen. However, when the BBSZ glass content was increased to 0.5 wt%, a dual microstructure appeared with both small grains and some large grains. Thereafter, the samples displayed relatively large and even average grain size on further increase in BBSZ glass content. It is known that the BBSZ glass forms a liquid-phase layer during sintering. This provides an environment that facilitates the so-called liquid-phase sintering process. In liquid-phase sintering, the mechanisms related to densification and grain growth may be categorized into three types: (1) diffusion of the constituent atoms in the ferrite latticezero or an insufficient amount of liquid phase present at grain boundaries; (2) solution–reprecipitation processa thin layer of BBSZ glass-rich liquid phase to surround/wet all grains; (3) diffusion of atoms through the BBSZ glass-rich liquid layeran excessive amount of BBSZ glass. These three different mechanisms have different grain growth kinetics and account for the various trends in the microstructure mentioned above [13].

Figs. 4 and 5 show the real permeability and *Q*-factor spectra of the samples sintered at 900 °C. The permeability was strongly influenced by bulk density, microstructure, and saturation magnetization, and hence by BBSZ glass content. Starting with a permeability of about 42 for a glass-free sample with an average grain size of less than 0.8 μm and around 82% theoretical density, permeability gradually increased with increase in glass content and reached a maximum of about 163 with 0.75 wt% BBSZ glass. Thereafter, higher BBSZ glass contents led to a decrease in permeability.

Fig. 6 shows the saturation hysteresis loops of each of the samples. It can be seen that saturation magnetization first increased due to the increased degree of crystallization, but then decreased due to the non-magnetic BBSZ glass, weakening the contribution to the magnetization of the ferrite. However, the variation of saturation magnetization was so small that its influence on permeability was inconspicuous. The fact that the sample with 0.75 wt% BBSZ glass attained the maximum permeability can be mainly attributed to its having the largest average grain size and highest bulk density. The subsequent decrease in permeability can be mainly attributed to decrease in average grain size. Furthermore, slight decreases in bulk density and saturation magnetization also had some contributions. At the same time, the *Q*-factor displayed a

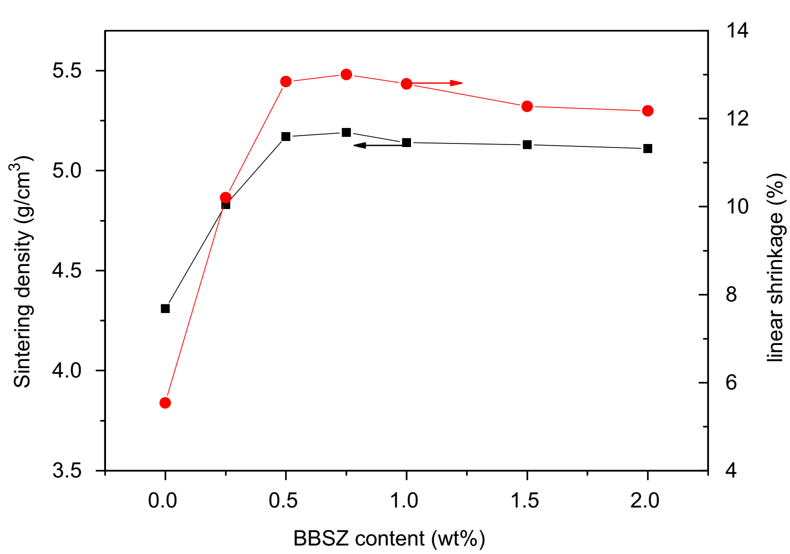

Fig. 2. Variations in density and linear shrinkage with BBSZ glass content.