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Low temperature firing of Co_2Y–NiCuZn ferrite composites

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Abstract

Hexagonal structure magnetoplumbite ferrites have revealed a higher dispersion frequency than that of nickel ferrites because of the magnetoplumbite's magnetic anisotropy. The magnetoplumbite ferrite densification temperature always exceeds 1000 °C and the initial low temperature firing permeability of magnetoplumbite ferrites with added glass is too low (μ_i = 2–4). Therefore, it is desirable to develop a material that has a higher permeability at above 300 MHz and can be densified at temperatures below 900 °C. The Bi_2O_3–B_2O_3–ZnO–SiO_2 (BBSZ) glass addition effects on the densification and magnetic properties of Co_2Y–NiCuZn ferrite composites with various Co_2Y/NiCuZn ferrite ratios were investigated. The densification of Co_2Y–NiCuZn ferrite composites was enhanced by the addition of glass at low sintering temperatures (<900 °C) due to the liquid phase sintering. Co_2Y–NiCuZn ferrite composites with 4 wt% BBSZ glass sintered at 900 °C show a relative density above 90%, a high-initial-permeability of 5–6, a quality factor of above 30 in the 200–300 MHz frequency and a resonance frequency above 1 GHz, which can be used in high frequency multilayer chip inductors.
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Keywords: B. Composites; Hexagonal ferrites; NiCuZn ferrites; Low temperature firing

1. Introduction

The most commonly used materials in inductors for high-frequency applications are NiCuZn ferrites [1], or non-magnetic materials such as low-temperature cofired ceramics [2]. The non-magnetic materials are used for high-frequency applications because NiCuZn ferrites (ferroxcube) typically exhibit severe property changes above 200 MHz due to the Snoek limit [3]. The maximum quality factor frequency in chip inductors made of non-magnetic material is over 500 MHz. However, the quality factors at frequencies around 200–300 MHz are much lower than those at higher frequencies [2]. Because chip inductors are prepared by winding a wire around a non-magnetic material core it is necessary to have a larger number of coil winding turns to obtain the desired inductance; thus limiting miniaturization. Therefore, it is desirable to develop a low temperature firing (below 950 °C) magnetic material that has a higher quality factor than non-magnetic materials at 200–300 MHz, for use in making high frequency multilayer chip inductors. Magneto-plumbite ferrites with hexagonal structures have revealed a higher dispersion frequency than NiCuZn ferrites, which can be used in high frequency applications [4–8]. Among those ferrites, the Co_2Y ferrite 2(BaO)·2(CoO)·6(Fe_2O_3) has good magnetic properties (such as permeability and quality factors) above 200 MHz [9,10]. However, the densification temperature of Co_2Y ferrites always exceeds 1000 °C and the initial permeability of low temperature fired Co_2Y ferrites with glass addition is too low (μ_i = 2–4), which limit its application in multilayer chip inductors. Improved ceramic densification at low temperatures can be achieved by chemical processing, adding glass flux and using starting materials with smaller particle sizes. Of the above methods, lowering the sintering temperature through glass addition is the most effective and least expensive technique. However, glass addition often results in magnetic properties degradation due to the low-permeability additive dilution effect or the chemical reaction between the glass and ferrites to form a low-permeability phase [11,12]. Therefore, choosing a suitable glass flux that can reduce the sintering temperature below 900 °C without significantly degrading the Co_2Y ferrite magnetic properties is important for high frequency multilayer chip magnetic device fabrication. Our previous studies found

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that that Bi_2O_3–B_2O_3–ZnO–SiO_2 (BBSZ) glass can be successfully used to lower the densification temperatures of microwave dielectric ceramics and ferrites [13–17]. Zn substitution can promote the saturation magnetization (M_s), and hence increase the permeability of Co_2Y ferrites [18]. The Cu for Co and Bi for Ba substitution can promote Y-type ferrite densification at low temperatures [19–21]. The previous study observed that $2(Ba_{1-x}Bi_xO)\cdot 2(Zn_yCo_{0.8-y}Cu_{0.2}O)\cdot 6(Fe_{2-x/3}Zn_{x/3}O_3)$ with $x = 0.1$ and $y = 0.4$ sintered at 1050 °C showed a relative density of 94%, a high initial permeability of 4.5, a quality factor (Q) of 50 [22].

The objective of this study was to develop a low temperature fired Co_2Y–NiCuZn ferrite composite with high permeability by changing the composite compositions using different ratios of NiCuZn ferrites and Co_2Y ferrites to increase the initial permeability and adding BBSZ glass to lower the sintering temperature. The effects of BBSZ glass addition and the NiCuZn ferrite and Co_2Y ferrite ratios on the densification behaviors, micro-structures and magnetic properties of Co_2Y–NiCuZn ferrite composites were investigated.

2. Experimental procedures

Co_2Y ferrites with a composition of $2(Ba_{0.9}Bi_{0.1}O)\cdot 2(Zn_{0.4}$-$2(Zn_{0.4}Co_{0.4}Cu_{0.2}O)\cdot 6(Fe_{1.87}Zn_{0.13}O_3)$ [22] were prepared from reagent-grade $BaCO_3$, Bi_2O_3, $SrCO_3$, Co_3O_4, CuO, ZnO and Fe_2O_3. These ferrites were mixed and then calcined at 1000 °C for 2 h. NiCuZn ferrites with a composition of $(Ni_{0.28}Cu_{0.12}Zn_{0.6}O)$–$(Fe_2O_3)_{0.99}$ were prepared from reagent-grade NiO, CuO, ZnO and Fe_2O_3, mixed and then calcined at 740 °C for 2 h. High purity Bi_2O_3, ZnO, H_3BO_3, and SiO_2 powders were weighed according to the 35%Bi_2O_3–27%H_3BO_3–6%SiO_2–32%ZnO (in mole%) composition to produce BBSZ glasses. The powders were mixed, dried and melted at 1000 °C for 30 min. The melt was then quenched in water to form glass. The glass transition temperature of BBSZ glass was about 560 °C. The glass was powdered homogeneously (the specific surface area was about 6.5 m^2/g) and then mixed with 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites powder at 0–4 wt% proportion to obtain the NiCuZn–Co_2Y ferrite composite + BBSZ glass powder. The 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites powder with 0–4 wt% glass and Co_2Y ferrites + 4 wt% glass powders with different amounts of NiCuZn ferrite powders (the Co_2Y ferrite and NiCuZn ferrite ratios = 80/20 and 90/10) were milled for 24 h in acetone using yttria-stabilized tetragonal zirconia polycrystal (YTZ) balls. The powders were dried in an oven and then mixed with PVA for granulation. The powders were dry-pressed at 180 MPa into pellets and toroidal bodies. These specimens were then debindered at 500 °C and sintered at 850–950 °C for 2 h.

Thermal shrinkage was measured using a dilatometer (Netzsch DIL 420C). The densities of the sintered samples were determined using the Archimedean method. The true densities for the BBSZ glass of 6.70 g/cm^3, the Co_2Y ferrite of 5.45 g/cm^3, and NiCuZn ferrite of 5.2 g/cm^3 measured using a pycnometer (Micromeritics, AccuPyc 1340) were used to calculate the theoretical densities of the sintered samples using the mixture rule. The crystalline phase identification was determined using X-ray diffractometry (Dandong Fangyuan, DX-2700, Sandong, China) with Cu Kα radiation. The microstructure was observed using scanning electron microscopy (Hitachi S4100). The magnetic properties (initial permeability (μ_i) and quality factor (Q)) were measured using an LCR meter (YHP 4291A, YHP Co., Ltd.).

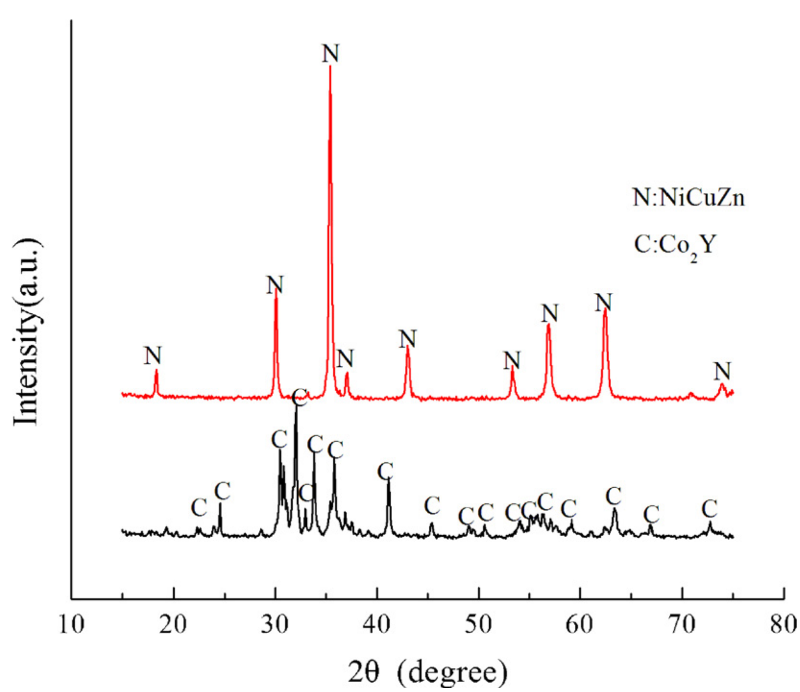

Fig. 1. XRD patterns of the calcined Co_2Y and NiCuZn ferrites.

3. Results and discussion

Fig. 1 shows the XRD patterns of the calcined Co_2Y and NiCuZn ferrites. It indicates that pure Co_2Y ferrites (ICDD 44-0206) and NiCuZn ferrites (ICDD 22-1086) without other secondary phase were obtained. Fig. 2 shows the XRD patterns of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites powder with 0–4 wt% BBSZ glass sintered at 950 °C. No phases other than Co_2Y and NiCuZn ferrites were found, indicating no significant chemical reactions occurred during sintering.

Fig. 3 shows the shrinkage curves and shrinkage rates of NiCuZn ferrites, Co_2Y ferrites added with 4 wt% glass and 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites added with 0 and 4 wt% glass. The shrinkage and shrinkage rate of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites were lower than those of Co_2Y ferrites. This can be explained by the lower onset shrinkage temperature and higher densification rate of Co_2Y ferrites than NiCuZn ferrite, as shown in Fig. 3, which resulted in the formation of large densified Co_2Y aggregates before the densification onset of NiCuZn ferrite. The densified Co_2Y aggregates may act as a densification constraint to inhibit the densification of NiCuZn ferrite during sintering. For the Co_2Y–NiCuZn ferrites composites, the onset shrinkage temperature decreased from 800 °C to 700 °C and the shrinkage rate in the temperature range between 750 °C and 850 °C increased significantly as the glass addition was increased from 0 to 4 wt%. The relative densities of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites sintered at 950 °C as a function of the addition of BBSZ glass are shown in Fig. 4. Note that the relative density increased from 87.8% to 90.8% as the BBSZ glass content was increased from 0 wt% to 4 wt%. These results indicate that BBSZ glass can effectively promote Co_2Y–NiCuZn ferrite composite densification. Because the addition of excess glass into the Co_2Y–NiCuZn ferrite composite will degrade the magnetic properties, a fixed glass addition of 4 wt%, which can promote the relative density of the Co_2Y–NiCuZn ferrites composite above 90%, was used to investigate the ratio effects between NiCuZn ferrite and Co_2Y ferrite on the densification behaviors, micro-structures and magnetic properties of Co_2Y–NiCuZn ferrite composite. Fig. 5 shows the relative densities of the samples with Co_2Y:NiCuZn ferrite = 80:20 and 90:10 added with 4 wt% glass at various sintering temperatures. The sintered density increased with increasing sintering temperature and reached above 90% as the sintering temperature was raised above 900 °C. Moreover, the sintered density decreased as the addition of NiCuZn ferrite increased, indicating the addition of NiCuZn ferrite suppressed the densification of Co_2Y–NiCuZn ferrite composite.

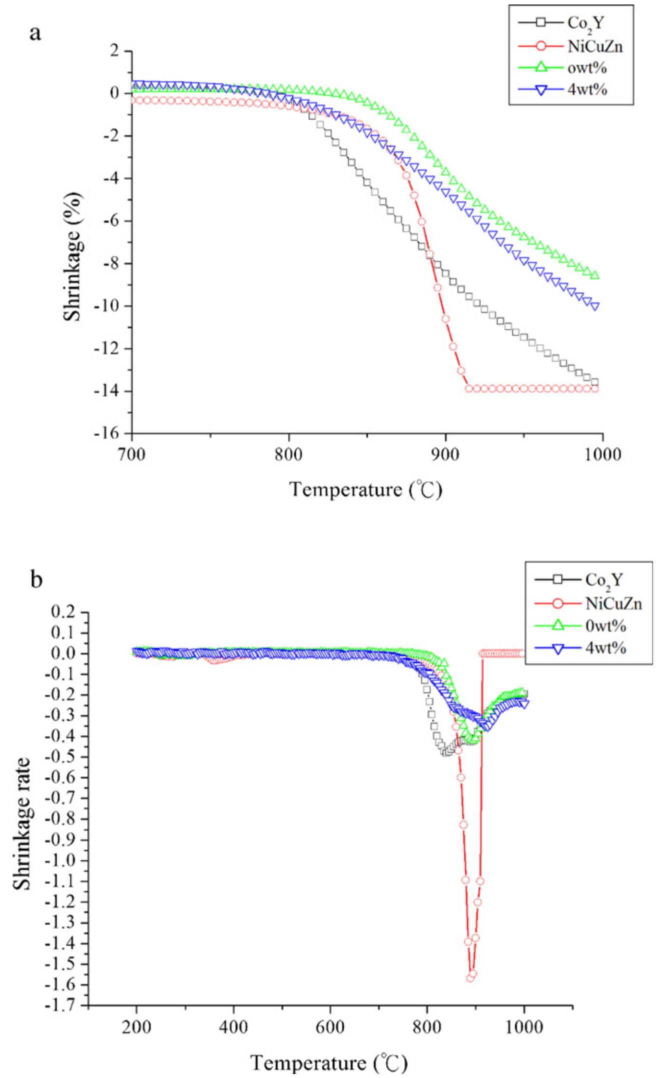

Fig. 3. Shrinkage curves (a) and shrinkage rates (b) of NiCuZn ferrites, Co_2Y ferrites added with 4 wt% glass and 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites added with 0 and 4 wt% glass.

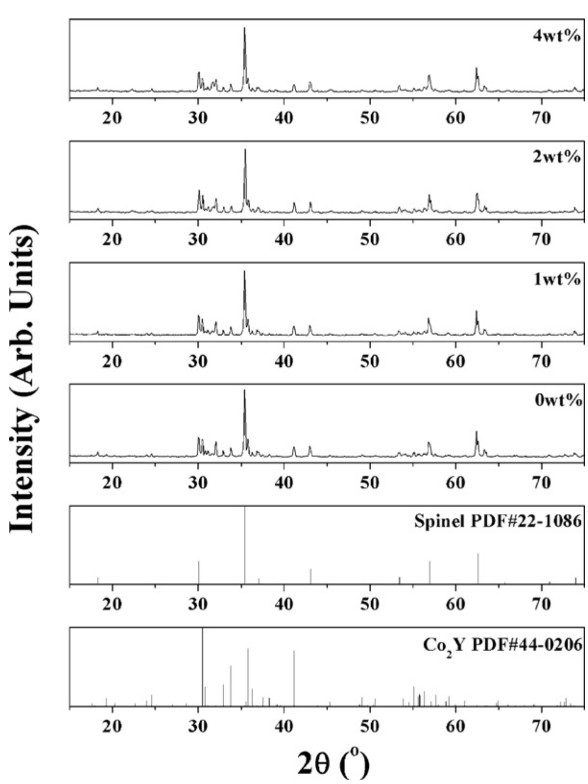

Fig. 2. XRD patterns of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites powder with 0–4 wt% BBSZ glass sintered at 950 °C.

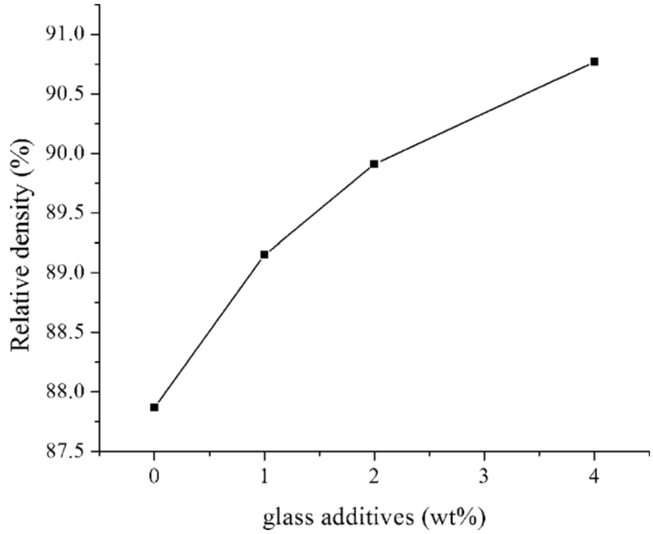

Fig. 4. Relative densities of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites sintered at 950 °C as a function of the addition of BBSZ glass.

Fig. 6 shows the microstructures of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites added with 0 and 4 wt% glass sintered at 950 °C. This indicates that the number of pores decreased but no significant grain growth was observed as the glass addition was increased from 0 wt% to 4 wt%. Fig. 7 shows the microstructures of samples with Co_2Y:NiCuZn ferrite = 90:10 added with 4 wt% glass sintered at various temperatures. The grain size and sintered density increased significantly with increasing sintering temperature. At the same sintering temperature, the sample with Co_2Y:NiCuZn ferrite = 90:10 exhibited more dense and uniform microstructures compared with the sample with Co_2Y:NiCuZn ferrite = 80:20 (not shown), which is consistent with the relative density results observed in Fig. 5.

The glass addition effect on the initial permeability of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites sintered at 950 °C is shown in Fig. 8. The initial permeability of 50 wt%/50 wt%-

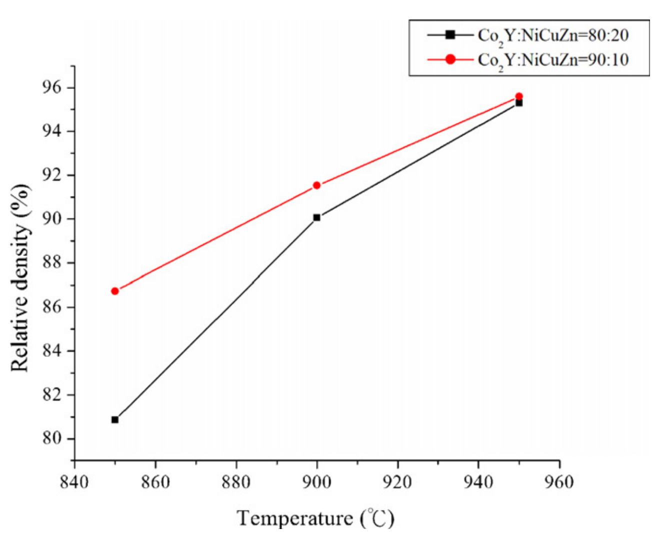

Fig. 5. Relative densities of the samples with Co_2Y:NiCuZn ferrite = 80:20 and 90:10 added with 4 wt% glass at various sintering temperatures.

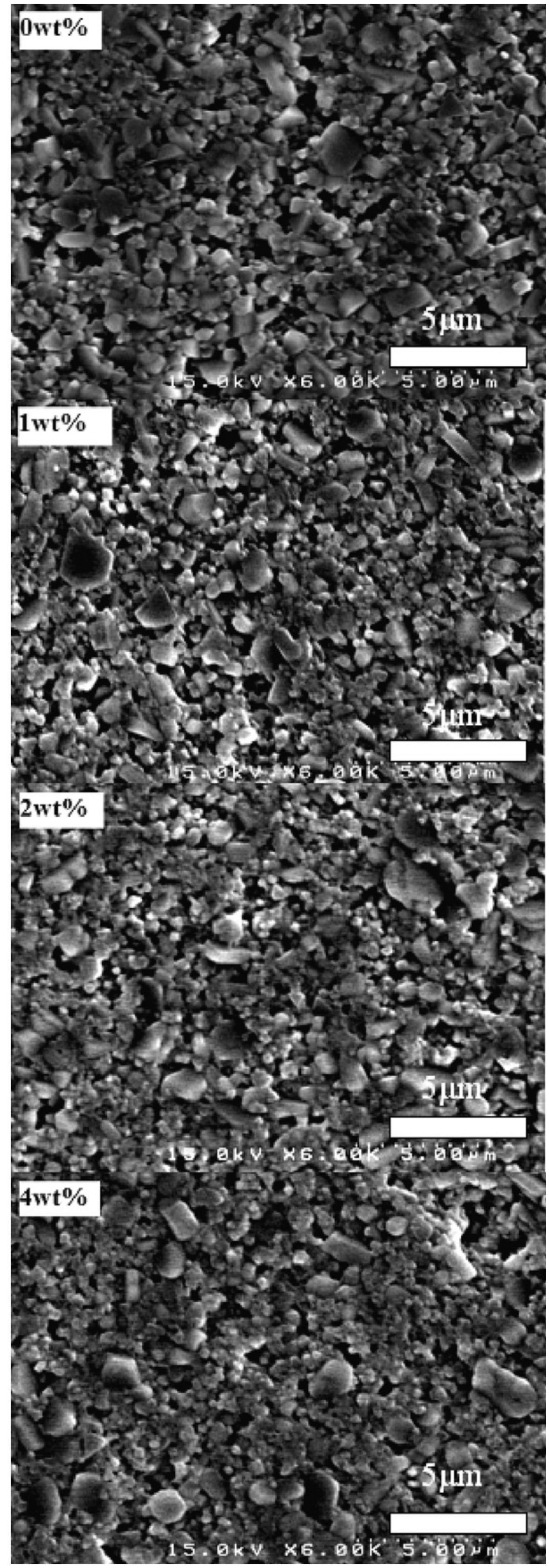

Fig. 6. Microstructures of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites added with 0 and 4 wt% glass sintered at 950 °C.

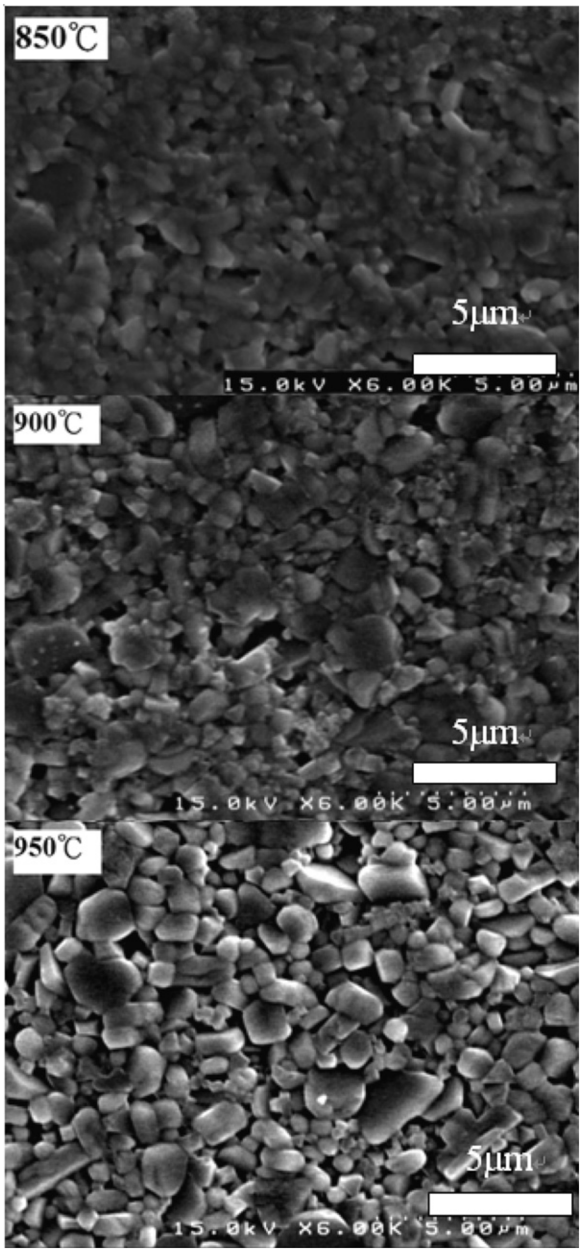

Fig. 7. Microstructures of samples with Co_2Y:NiCuZn ferrite = 90:10 added with 4 wt% glass sintered at various temperatures.

NiCuZn/Co_2Y ferrites composite reached 10–13 and increased with increasing glass addition due to the increase in the relative density, as shown in Fig. 4. Note that the resonance frequencies of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites added with various amounts of glass occurs at about 100–200 MHz, which is much higher than the resonance frequencies of the low temperature fired NiCuZn ferrite (10–50 MHz), but still cannot be used in radio frequency devices operating in a frequency of above 300 MHz. Qu et al. [23] investigated the effect of different NiCuZn ferrite and Co_2Y ferrite ratios on the magnetic properties of low temperature fired Co_2Y–NiCuZn ferrite composite prepared using the co-precipitation method and observed that the initial permeability reached 14–30 but the resonance frequencies were all below 200 MHz because the compositions were within the NiCuZn ferrite-rich.

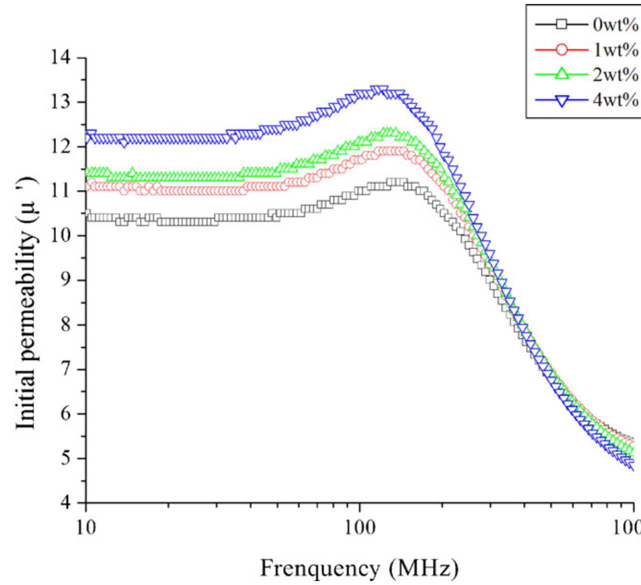

Fig. 8. Glass addition effect on the initial permeability of 50 wt%/50 wt%-NiCuZn/Co_2Y ferrites sintered at 950 °C.

The Co_2Y to NiCuZn ferrite ratio and sintering temperature effects on the initial permeability are shown in Fig. 9. The changes in magnetic properties were strongly influenced by the addition of NiCuZn ferrite and the sintering temperature. As expected, the initial permeability of the composites increased with increasing NiCuZn ferrite content. The initial permeability of the ferrites is strongly dependent on the density and grain size developed during sintering. The initial permeability of the ferrites increased as the sintering temperature increased from 850 to 950 °C. This may be the result of the increase in grain size and density, as shown in Figs. 5 and 6. The samples sintered at 950 °C showed a lower resonance frequency than the ferrites sintered at 850 °C and 900 °C (Fig. 6). The model for natural

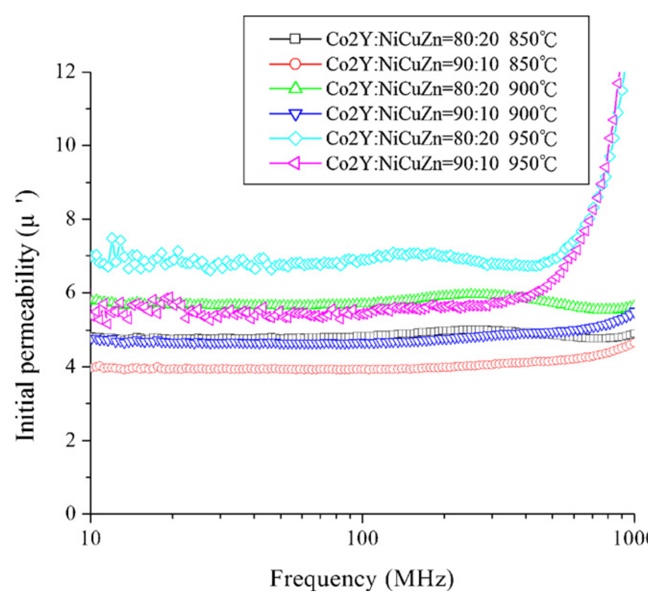

Fig. 9. Co_2Y to NiCuZn ferrite ratio and sintering temperature effects on the initial permeability.

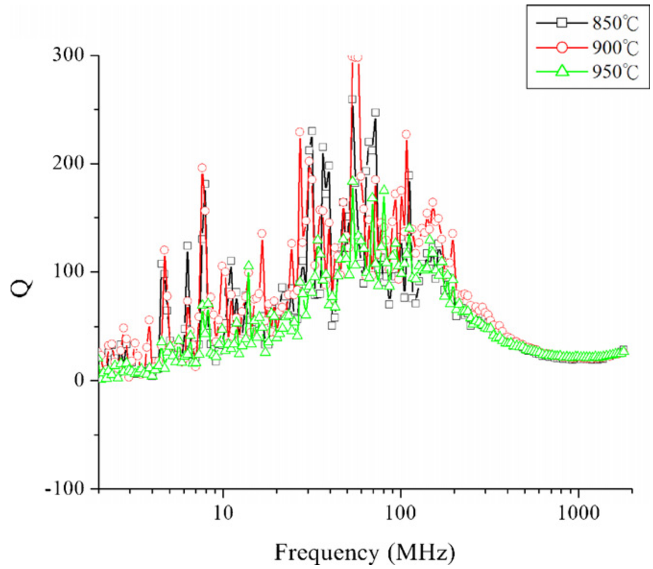

Fig. 10. Sintering temperature effect on the Q value of the samples with Co_2Y:NiCuZn ferrite = 90:10.

magnetic resonance frequency of ferrites with planar anisotropy predicts the resonance frequency to be [3]

$$f_{\text{res}} = \frac{\gamma H_a}{2\pi},$$

where γ is the gyromagnetic ratio, H_a is the effective anisotropy field, and f_{res} is the natural resonance frequency of ferrites. The above equation indicates that the natural resonance frequency depends on the effective anisotropy field. Imperfections such as the second phase and pores will induce local demagnetizing fields, which will add to the magnetocrystalline anisotropy field and may raise the resonance frequency [24]. As the sintering temperature was raised from 850 °C to 950 °C, the amount of pores in the ferrites decreased and the grain size increased. Therefore, the resonance frequency of the ferrites decreased as the sintering temperature was increased from 850 °C to 950 °C as a consequence of the decrease in demagnetizing field (Fig. 9). The sintering temperature effect on the Q value of the samples with Co_2Y:NiCuZn ferrite = 90:10 are shown in Fig. 10. The maximum Q values occurred at about 60–100 MHz and the Q values were all above 30 in the 200–300 MHz frequency. Note that Co_2Y–NiCuZn ferrite composites with 4 wt% BBSZ glass sintered at 900 °C showed a relative density above 90%, a high-initial-permeability of 5–6, a quality factor of above 30 in the 200–300 MHz frequency and a resonance frequency above 1 GHz, which can be used in high frequency multilayer chip inductors.

4. Conclusions

A low temperature (below 900 °C) fired microwave ferrite with high permeability can be obtained by adding 10–20 wt% NiCuZn ferrite into Co_2Y ferrite to increase the initial permeability and 4 wt% BBSZ glass to lower the sintering temperature. No significant chemical reactions occurred between the NiCuZn ferrite, Co_2Y ferrite and BBSZ glass during sintering. Co_2Y–NiCuZn ferrite composites with 4 wt% BBSZ glass sintered at 900 °C showed a relative density above 90%, a high initial permeability of about 5–6, a Q value of above 30 in the 200–300 MHz frequency and a resonance frequency of above 1 GHz, which can be a good candidate material for high frequency multilayer chip inductors.

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