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Low temperature sintering of iron deficient Z type hexagonal ferrites

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Abstract

Low temperature sintering of iron deficient hexagonal Co_2Z type ferrites is attempted to prepare a chip inductor for ultra high frequency uses. It should be attained below the melting point of silver (960 °C) used as the electrode material of the chip inductor. The best result is obtained for the sample with the composition $2.15Co_{0.6}Cu_{0.4}O{\cdot}3Ba_{0.79}Sr_{0.16}Bi_{0.05}O{\cdot}9.725Fe_2O_3$ sintered at 925 °C containing 0.5 wt.% of lithium bismuth oxide as a sintering additive. Its density and permeability reaches 5.0 g/cm^3 and 7, respectively. As a result, the impedance of the chip inductor also reaches 390 ohm at 2 GHz using this material.

Keywords: Milling; Sintering; Magnetic Properties; Ferrites; Chip inductors

1. Introduction

Recently, down-sizing of electronic devices has been required due to miniaturization and high frequency tendency of the electronic equipment. Then, multi-layered chip inductors have been applied their applications as magnetic devices. Until now, the chip inductors which are prepared by co-firing nickel ferrites with silver electrodes have been utilized as magnetic devices to meet these demands. Their use, however, is restricted below ∼200 MHz due to the so-called Snoek limit.

Then, the hexagonal ferrites known as Ferroxplana[1] (Z, Y or W type) have become candidates for the chip inductor materials which exceed Snoek's limit into the GHz region. Among these ferrites, Co_2Z ($2CoO{\cdot}3BaO{\cdot}12\,Fe_2O_3$) has the highest magnetic property. The preliminary studies by the present authors aimed at improving the magnetic properties of a Co_2Z compound, detailed elsewhere.[2] This study aims at lowering the sintering temperature of the Z type hexagonal ferrite for co-firing with silver electrode to prepare chip inductors. Usual sintering temperature of this ferrite, however, is sufficiently higher than the melting temperature of silver electrode (960 °C), namely, over 1250 °C. Some approaches were reported on this problem which tried to sinter Z type ferrites at ∼900 °C by adding abundant glassy additives.[3–5] The ferrites, however, revealed low permeability, less than 4, even when sintered at 950 °C. The impedance of the prepared chip inductor was 150 Ω at 2 GHz.[3]

This study adopts an iron deficient Z type hexagonal ferrite with composition $(2+3x)Co_{0.6}Cu_{0.4}O{\cdot}3Ba_{0.833(1-x)}Sr_{0.167(1-x)}Bi_xO{\cdot}(9.8-1.5x)Fe_2O_3$ as a starting material. Firstly, it was found effective to decrease iron content from the stoichiometric value 12 of Co_2Z to 9.8 for lowering sintering temperature.[2] Secondly, cobalt ions were partially replaced by copper ions, and barium ions were also partially replaced by strontium and bismuth ions. This process is based on the concept of decreasing sintering temperature of the ferrite as low as possible and of increasing the permeability as high as possible, based on the results already reported[2] in our preliminary experiment. In addition, calcined powders were pulverized as fine as possible using an organic surfactant and small amount of sintering aids were added to the powders

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during the pulverizing process. Finally, chip inductors were produced using these ferrite powders.

2. Experimental

Reagent-grade $BaCO_3$ (99.9% Furuuchi Chemicals, Tokyo, Japan), $SrCO_3$ (99.9% Furuuchi Chemicals), Bi_2O_3 (99.8% Shin Nihon Metal Chemicals, Kyoto, Japan), Co_3O_4 (96.25% CoO content Sumitomo Metal Mines, Tokyo, Japan), CuO (99.9%, Furuuchi Chemicals) and Fe_2O_3 (99.19% Toda Industries, Tokyo, Japan) were used as raw materials in the present study. These materials were weighed in molar ratios as $(2+3x)Co_{0.6}Cu_{0.4}O{\cdot}3Ba_{0.833(1-x)}Sr_{0.167(1-x)}Bi_xO{\cdot}(9.8-1.5x)Fe_2O_3$, where x was bismuth substitution ratio (A: $x=0$, B: $x=0.05$, C: $x=0.10$ and D: $x=0.15$). This composition was determined so as to satisfy the charge compensation caused by substitution of divalent barium and strontium ions with trivalent bismuth ions. Accordingly, trivalent iron ions were replaced by divalent cobalt and copper ions to compensate the excess charges caused by bismuth substitution. The weighed materials were mixed in a wet ball mill with yttria-toughed zirconia (YTZ) balls, and dried. The mixed powders were calcined at 1140 °C for 2 h, added with sintering aids such as Bi_2O_3 or $LiBiO_2$, ground in a ball mill for 40 h using iron balls of 2 mm in diameter in isopropyl alcohol containing an organic surfactant (Kusumoto Chemicals), mixed with 2% of poly vinyl butyl alcohol (PVB) as a binder and dried. These samples were pressed in a die at a pressure of 150 or 350 MPa and then sintered in air for 4 h at 900, 925 or 950 °C, respectively. The grain sizes of the powders and the sintered samples were evaluated by SEM observations. The true densities of the powders were determined by the pycnometer method. The magnetic properties of the powders were obtained by VSM (vibrating sample magnetometer) method. The lattice constant of the powders was estimated by XRD technique. The bulk density of the specimens was determined by the Archimedes method. The complex permeability $\mu=\mu'-\mu''$ (μ'' is a measure of loss: $Q=1/\tan\delta=\mu'/\mu''$) was measured by a Q-meter method using an impedance analyzer (YHP 4191 A, YHP Co. Ltd.) from 15 MHz to 1.8 GHz.

3. Results and discussion

Fig. 1 shows an SEM photograph of the calcined powder (C: $x=0.10$) ground in a ball mill for 40 h. As seen in the photograph, very fine grains were formed uniformly. The grain sizes were about 0.2 μm and the BET value was 7.6 m^2/g. Almost the same values were obtained for all other powders used in this experiment. Fig. 2 shows the surface of the sample C sintered at 950 °C. Uniform grains (about 1–2 μm) were observed, indicating that uniform grain growth occurred at 950 °C. Nearly the same grain growth was observed except the sample A without bismuth substitution.

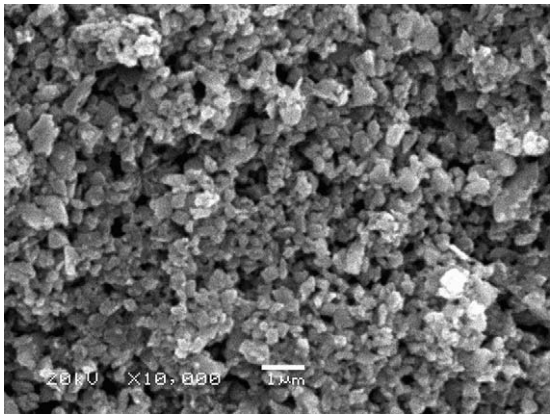

Fig. 1. SEM photograph of finely pulverized calcined powder.

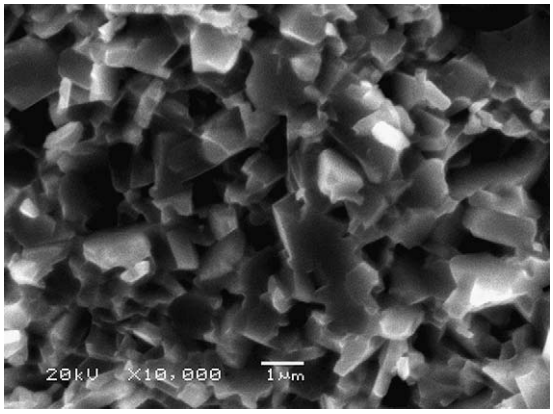

Fig. 2. SEM photograph of the fractured surface of the sample C sintered at 950 °C.

The true density of the samples was determined by the pycnometer method as shown in Fig. 3. It increases with increasing bismuth content probably due to heavy bismuth ion substitution and is a little larger than the theoretical density of the stoichiometric Z type hexagonal ferrite Co_2Z of 5.35 g/cm^3 in JCPDS data.

Figs. 4 and 5 show the magnetization at 25 °C and Curie temperature of the samples. The magnetization increases

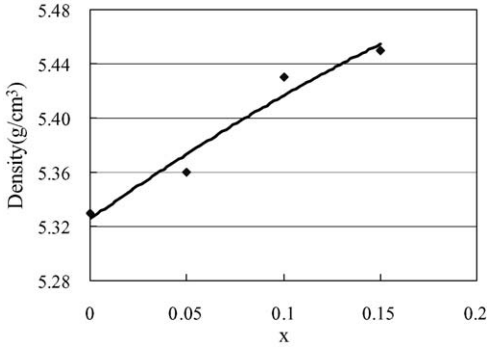

Fig. 3. Change of true density with bismuth substitution x.

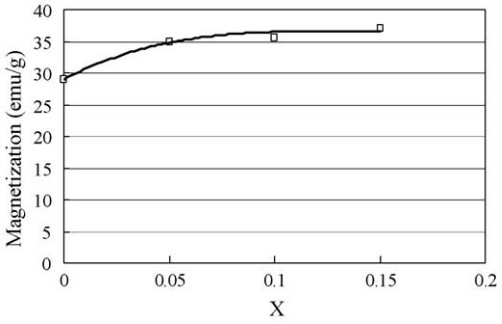

Fig. 4. Change of magnetization with bismuth substitution x.

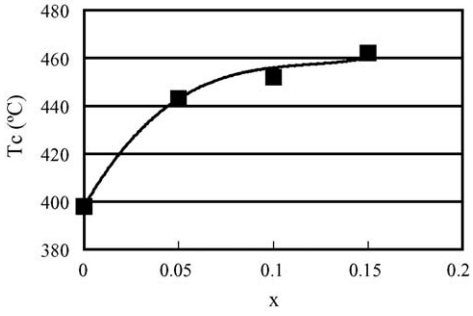

Fig. 5. Change of Curie temperature with bismuth substitution x.

from 30 to 37 emu/g with increasing bismuth substitution. However, the value of Co_2Z was 50 emu/g, which was considerably larger than these values. This fact may result from the fact that iron content decreased from the stoichiometric value 12–9.8. Also, the Curie temperature increases with bismuth substitution and is substantially higher than the value of Co_2Z of 410 °C except that of the unsubstituted sample.

The lattice constant a continuously increases with increasing bismuth substitution, as shown in Fig. 6 and the other lattice constant c was found invariant 5.216 nm independent of bismuth substitution. These results suggest that bismuth substitution was continuously attained.

Figs. 7 and 8 show the effects of forming pressure on the density and permeability of the sample C ($x = 0.10$) with 0.5 wt.% of Bi_2O_3 as a sintering aid, respectively. As seen, both density and permeability increase slightly

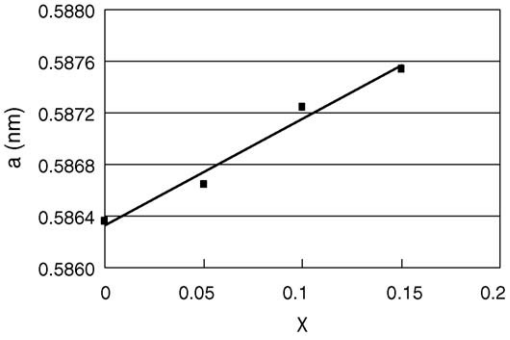

Fig. 6. Change of lattice constant a with bismuth substitution x.

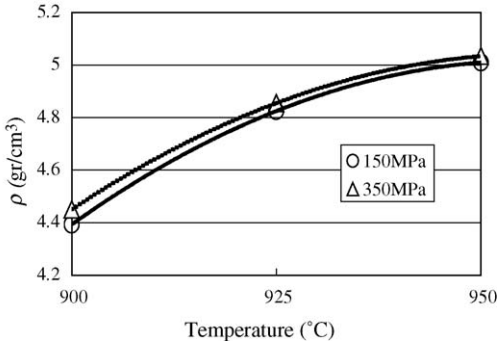

Fig. 7. Effect of forming pressure on the density of the sample C (Bi_2O_3 0.5 wt.%).

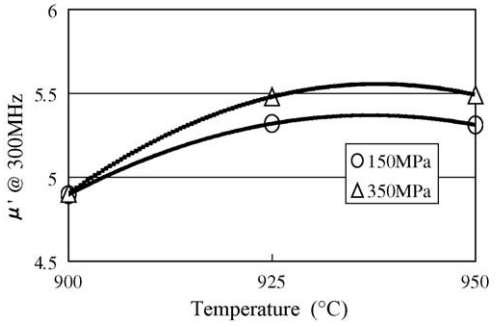

Fig. 8. Effect of forming pressure on the permeability of the sample C (Bi_2O_3 0.5 wt.%).

when the forming pressure increases from 150 to 350 MPa. Accordingly, the forming pressure is hereafter determined as 350 MPa. The preliminary experiment revealed that SLBO (stoichiometric lithium bismuth oxide: $LiBiO_2$, eutectic point 690 °C) addition was found most effective among Bi_2O_3, eutectic lithium bismuth oxide (0.08 Li_2O-0.92 Bi_2O_3 m.p. 690 °C) and SLBO. Then, SLBO was determined as the sintering aid. Fig. 9 shows the effect of SLBO amount on the density of the sample B. As seen in the figure, the optimum amount of SLBO additive was found to be 0.5 wt.% for densification of the sample. Fig. 10 shows the effect of SLBO amount on the permeability of the sample B. Also as seen, 0.5 wt.% addition of SLBO was found most effective. Accordingly, excess addition of SLBO additive over 0.5% is

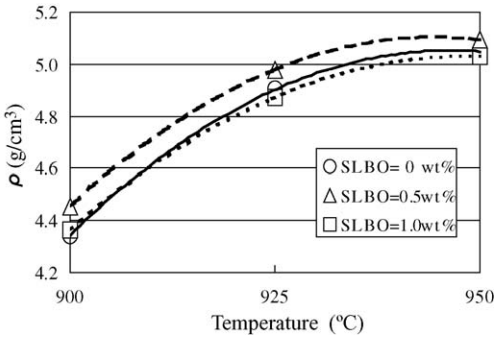

Fig. 9. Effect of SLBO amount on the density of the sample B.

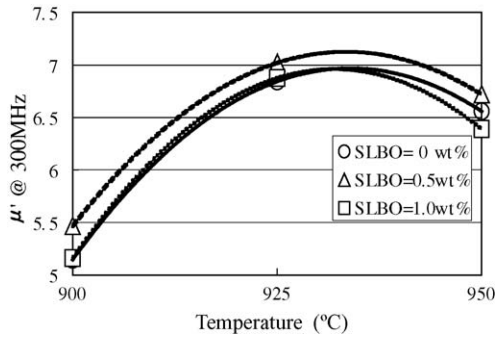

Fig. 10. Effect of SLBO amount on the permeability of the sample B.

found to decrease both density and permeability of the sample.

Fig. 11 shows the effect of bismuth substitution on the density of the samples sintered at 900, 925 or 950 °C containing 0.5 wt.% of SLBO. As seen, the density of the sample A without bismuth substitution is less than 4.0 g/cm^3, indicating that the sample A could not be densified sufficiently below 950 °C. On the other hand, the density of the other samples with bismuth substitution reached 5.0 g/cm^3 at 925 °C corresponding to 95% of theoretical density (5.36 g/cm^3) for sample B($x = 0.05$), as shown in Fig. 3. This fact indicates that bismuth substitution is most effective to lower the sintering temperature of ferrite of this type. As a result, it is suggested that these samples containing bismuth can be utilized as the chip inductor materials since the sintering temperature of 925 °C is sufficiently lower than the melting point of silver electrode of at 960 °C. Accordingly, the samples with bismuth substitution could be utilized as chip inductor materials. Fig. 12 shows the frequency dependence of complex permeability for the samples sintered at 925 °C. As seen, the permeability of the samples B and C reached 7 and 5, respectively, sufficiently high for the chip inductor material.

A multi-layered chip inductor (1608 type: 1.6 mm by 0.8 mm by 0.8 mm) was prepared by co-firing the above ferrite with silver electrodes. Fig. 13 shows the frequency dependence of its impedance. The impedance increases from 1 GHz and reaches maximum of 390 Ω at 2 GHz, which was

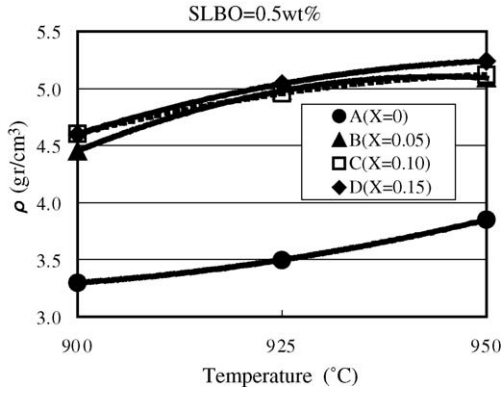

Fig. 11. Effect of bismuth substitution on the density of the samples.

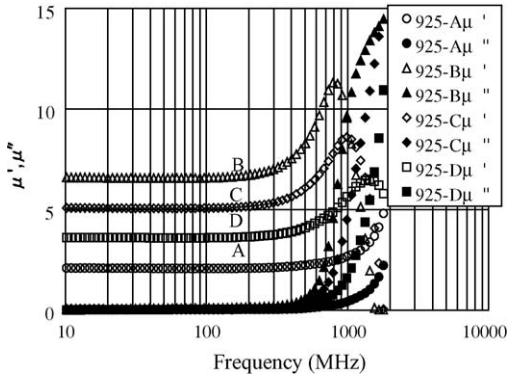

Fig. 12. Frequency dependence of complex permeability of the samples.

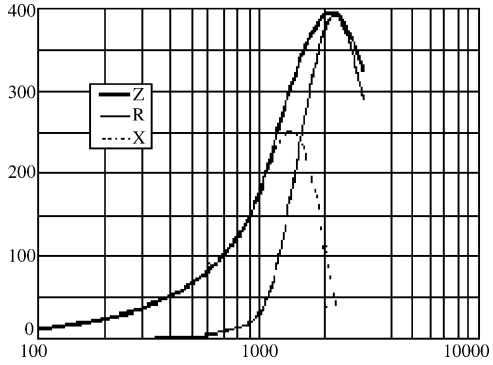

Fig. 13. Frequency dependence of the impedance of the chip inductor.

about 2.5 times larger than that was reported already[3] and sufficiently high for the noise filter application from 1 to 4 GHz.

4. Conclusions

Low temperature sintering of Z type hexagonal ferrites was attained by lowering iron content from the stoichiometric value, partially substituting cobalt ions by copper ions and incorporating bismuth ions. Finally, we could obtain a materials with density of 5.0 g/cm^3 and permeability of 7 at 300 MHz when sintered at 925 °C, using 0.5% SLBO as a sintering aid. Its density and permeability were sufficiently high and the sintering temperature of 925 °C was well below the melting temperature of silver electrode of 960 °C. A multilayered chip inductor could be prepared using this material. Its maximum impedance reached 390 Ω at 2 GHz, which was about 2.5 times larger than that was reported already[3] and sufficiently high for the noise filter application at UHF region.

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