Journal of the European Ceramic Society 23 (2003) 715–720
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Low-temperature sintering and high frequency properties of Cu-modified Co_2Z hexaferrite

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Received 28 November 2001; received in revised form 24 April 2002; accepted 4 May 2002

Abstract

The low temperature sintering behaviors and high frequency properties of Cu-modified Co_2Z hexaferrites have been investigated. Normally, Cu-modified Co_2Z hexaferrite is difficult to be sintered at temperature lower than 1150 °C. By adding a small amount of sintering aid Bi_2O_3, Cu-modified Co_2Z ceramics with high density (more than 95% theoretical density) have been prepared successfully after sintering below 900 °C. The microstructures and properties are significantly influenced by the sintering temperature, the amount of Bi_2O_3 addition, as well as Cu content. The modified hexaferrite ceramics sintered at 900 °C, exhibited excellent high frequency properties, such as high initial permeability up to 6.6, high quality factor more than 30, high resistivity over 10^9 Ω cm and good thermal stability. The experimental results show that these materials have a great potential as soft magnetic media for high frequency MLCIs applications.

Keywords: $Ba_3Co_2Fe_{24}O_{41}$; Ferrites; Magnetic properties; Sintering

1. Introduction

The revitalization of low temperature co-fired ceramics technology started in the beginning of the 1990's, such as surface mounting devices (SMD) have been developed rapidly with the development of ceramic electronics and information technology. As one of the most important SMD, multilayer chip inductors (MLCIs) made from soft ferrites become more and more miniaturized and integrated, and this requires that the soft ferrites should be co-fired with internal contact materials. Considering the conductivity and cost, pure silver is the most suitable internal contact material. Therefore, to realize the co-firing of ferrites and Ag internal electrode under 900 °C has been the main problem. By now, low-temperature sintered Ni–Cu–Zn ferrites have been commercially used for manufacturing MLCIs.[1,2] However, the spinel ferrite has a low cut-off frequency below 300 MHz, which can not be used into the hyper-frequency region (300–800 MHz).

Co_2Z ($Ba_3Co_2Fe_{24}O_{41}$) as one of the planar hexagonal ferrites discovered between 1952 and 1996 by Philips, is magnetically soft at room temperature, whose Curie point is 400 °C.[3,4] Co_2Z hexaferrite presents a much high permeability and ferromagnetic resonance up to the GHz region[5,6] with high thermal stability, and this brings it into the microwave region useful for inductor cores and uhf communication.[7] But, normally, due to its complex crystalline structure,[8–10] the Z-type phase formation and sintering temperature of Co_2Z is as high as 1300 °C by a conventional ceramic method. By partial substitution of Co with Cu ions in $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ reported in our previous paper,[11] the Z-type phase formation and sintering temperatures have been reduced to 1100–1180 °C. In order to further decrease the sintering temperature to realize co-firing with internal contact silver for MLCIs applications, appropriate sintering aid (Bi_2O_3) was introduced into this system, and the hexaferrite could be sintered below 900 °C to achieve highly dense ceramics. In this paper, the low-temperature sintering behaviors of Cu-substituted Z-type hexaferrite were studied, and the influences on the microstructures and eletromagnetic properties have been discussed.

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PII: S0955-2219(02)00157-7

2. Experimental procedures

$Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ powders were synthesized by the citrate precursor method, where $X = 0.00$, 0.10, 0.20, 0.30, 0.40, 0.50 and 0.60 respectively. Iron citrate, cobalt acetate, barium acetate, copper acetate and citric acid were used as raw materials. Metallic salts with stoichiometric quantities according to the formula of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ were dissolved in an aqueous solution with appropriate amount of citric acid. After heating at 60–80 °C for 2 h, some ammonia water was added into the solution until the solution was neutral or slightly alkaline (pH = 7–8). Then, the transparent homogeneous solution was heated at 95–135 °C and a dried gel-citrate precursor was developed. After heat-treating the gel between 1100 and 1200 °C for 6 h, Cu-modified and pure Co_2Z powders in Z-type phase were obtained.[11] The resulting $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ powders were then mixed with different amounts of sintering aid Bi_2O_3 and milled, dried, pressed under a pressure of about 40 000 N/m^2 with 5 wt.% polyvinyl alcohol as the lubricant. The pressed pellets ($\phi = 10$ mm, $t = 1$ mm) and toroidal samples ($\phi_{outer} = 20$ mm, $\phi_{inner} = 10$ mm, $t = 3$ mm) were then sintered at 860–950 °C for 6 h in the air.

Phase structures of the powders and ceramics were determined by a Rigaku diffratometer using Fe $K\alpha$ radiation in the region of $2\theta = 25$–85°. The magnetic measurements were carried out using a LDJ 9600 vibrating-sample magnetometer. Scanning electron microscopy (SEM) was used to observe the morphologies of the sintered specimens. Density has been determined by the Archimede's method. The frequency behaviors for the ceramics were measured using a Hewlett Packard HP4291B RF impedance analyzer from 1MHz to 1.8GHz at room temperature and various temperatures ranging from −35 to 135 °C. The DC resistivity measurements were carried on a Hewlett Packard HP4140B using silver paste contacts.

3. Results and discussion

3.1. Sintering behavior of Cu-modified Co_2Z with Bi_2O_3 addition

In our previous study,[11] the sintering behaviors of Cu-modified Co_2Z hexaferrites without any sintering aid were investigated and it has been found difficult to be sintered below 1150 °C. In order to promote densification of the Cu-modified Co_2Z hexaferrite, various amount of Bi_2O_3 were added as a sintering aid. Fig. 1 presents the influence of Bi_2O_3 on the sintering behaviors of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$). It can be seen that, with 1 wt.% Bi_2O_3 the density of specimen reaches 4.80 g/cm^3 (<90% of relative density) at 950 °C. With 2 wt.% Bi_2O_3, density of the specimen increases to 5.05 g/cm^3 (94.7%). While Bi_2O_3 is more than 3 wt.%, the specimens are easily sintered even at the temperature as low as 860 °C. It is reported that the melting point of Bi_2O_3 is 824 °C.[12] Therefore, it is considered that the improved densification is resulted from the formation of liquid phase during the sintering. Highly dense hexaferrite ceramics could be achieved with sufficient amount of sintering aid of 3–4 wt.% Bi_2O_3, even at low temperature below 900 °C.

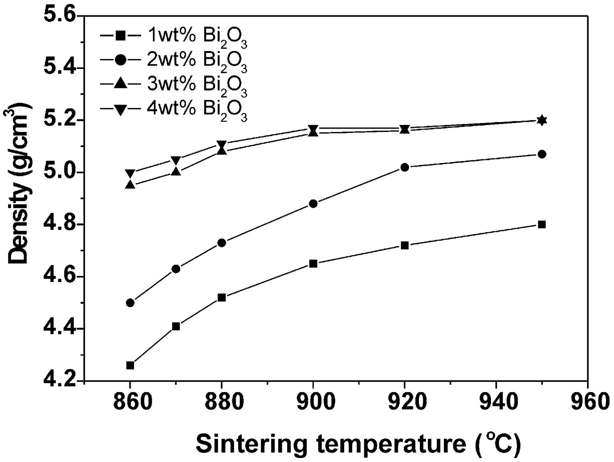


Fig. 1. Density as a function of sintering temperature for the $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) hexaferrites doped with various amount of Bi_2O_3.

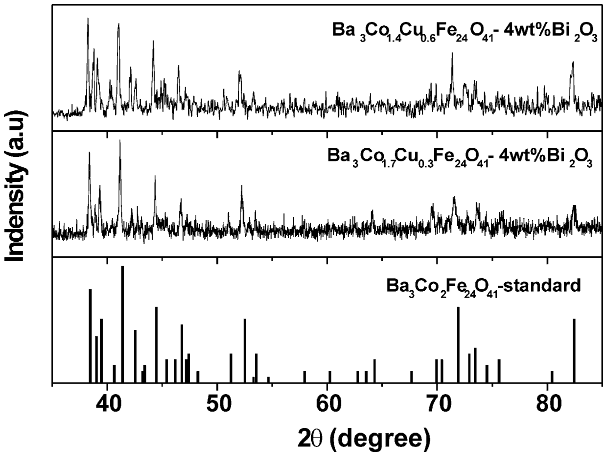


Fig. 2. X-ray diffraction patterns of the specimens of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$ and 0.6) hexaferrites with 4 wt.% Bi_2O_3 sintered at 900 °C.

3.2. Phase identification and microstructures of the sintered specimens

The ceramic specimens doped with Bi_2O_3 were examined by X-ray diffraction at room temperature. The XRD patterns of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$ and 0.6) hexaferrites doped with 4 wt.% Bi_2O_3 sintered at 900 °C are shown in Fig. 2. In Fig. 3 the XRD patterns for $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.6$) hexaferrites doped with 4 wt.% Bi_2O_3 sintered at different temperatures (860,

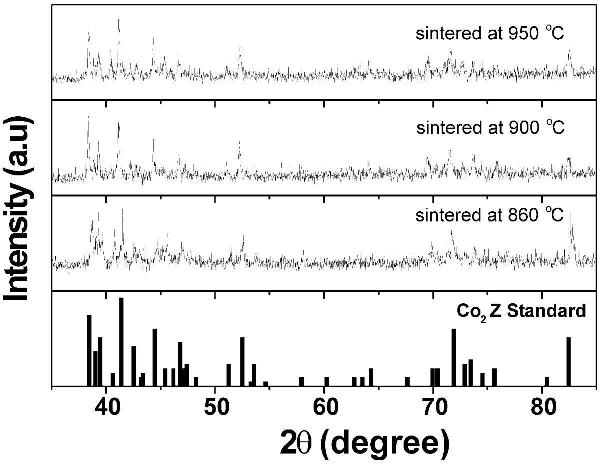


Fig. 3. X-ray diffraction patterns of the specimens of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.6$) hexaferrites with 4 wt.% Bi_2O_3 sintered at different temperatures.

900 and 950 °C) are also presented. It can be found that all the specimens still preserve the original single Z-type structures without any other second phase. That indicates the Z-type phases of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ hexaferrites with addition of Bi_2O_3 are rather stable when sintering at temperatures between 860 and 950 °C.

Fig. 4 shows the microstructures of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) ceramics sintered at 900 °C with different amount of Bi_2O_3. From the fraction images of the specimens, it can be seen that the pore ratio decreases with the increasing amount of Bi_2O_3, and high dense ceramics with few pore were obtained with enough sintering aid above 3 wt.% Bi_2O_3. This is consistent with the result shown in Fig. 1. The ceramics have homogeneous fine-grained microstructures with hexagonal platelet grains of 0.5 μm in thickness and up to 2.0 μm in diameter.

Fig. 5 gives the SEM images of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) ceramics with 4 wt.% Bi_2O_3 sintered at 920 and 950 °C, respectively. It seems that the density increased further with higher sintering temperature, but no significantly grain growth was found. The average grain sizes for the ceramics are still in the range of 2.0–2.5 μm in diameter.

3.3. Magnetization characterization of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ferrites doped with Bi_2O_3

Magnetization measurements of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) ferrite doped with various amount of Bi_2O_3 were carried out with a maximum field up to 20 KOe.

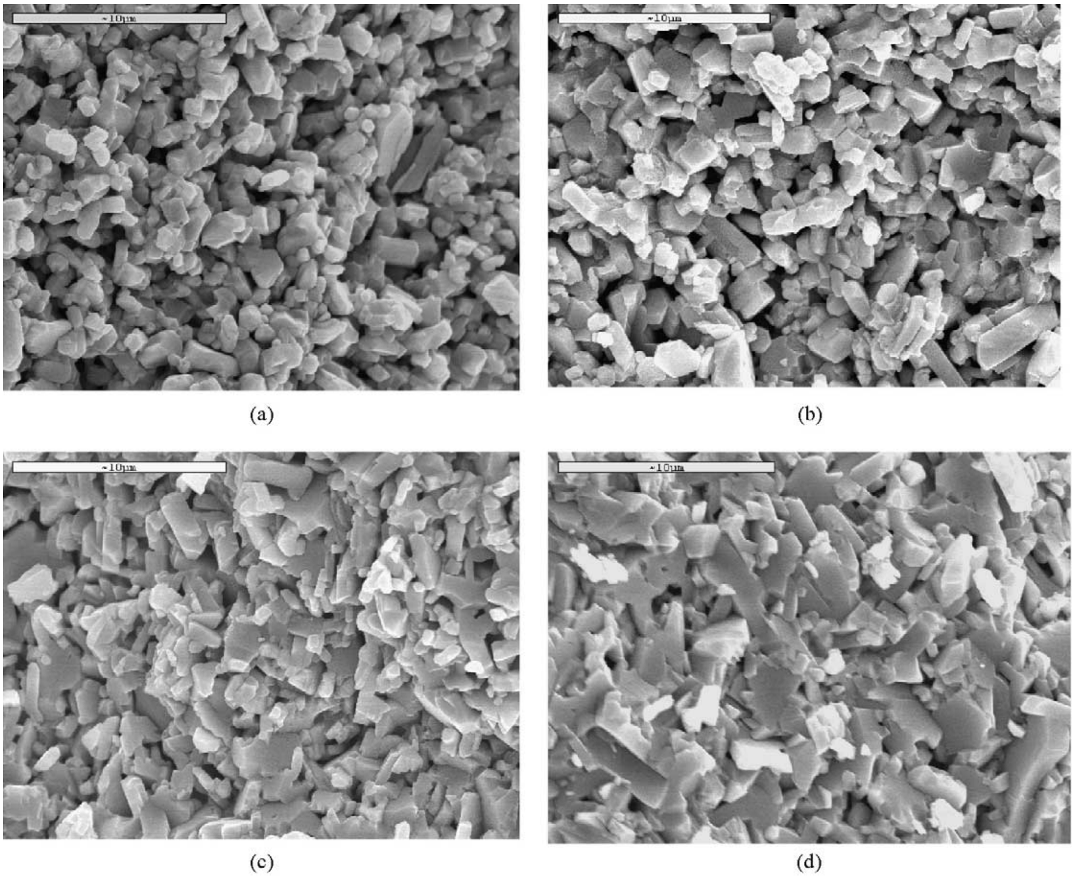
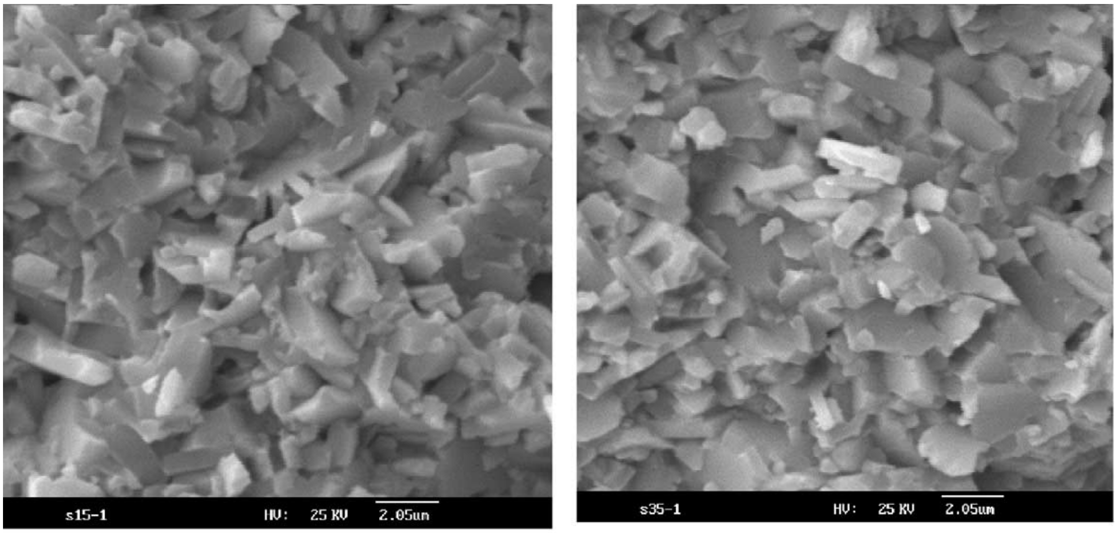

(a) (b)
(c) (d)

Fig. 4. SEM photographs of the $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) hexaferrite ceramics sintered at 900 °C doped with (a) 1 wt.% Bi_2O_3 (b) 2 wt.% Bi_2O_3 (c) 3 wt.% Bi_2O_3 (d) 4 wt.% Bi_2O_3.



(a) (b)

Fig. 5. SEM photographs of the $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) hexaferrite ceramics with 4 wt.% Bi_2O_3 after sintering at (a) 920 °C (b) 950 °C.

The magnetization data such as specific saturation magnetization (σ_s), remanent magnetization (σ_r) and coercivity (H_c) are listed in Table 1. No significant change in the value of coercivity for $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) ferrites was found due to the addition of Bi_2O_3, while a little drop (<2%) both in specific saturation magnetization and remanent magnetization were observed as shown in Table 1, which is attributed mainly to the introduction of non-magnetic material of Bi_2O_3. In principle, it seems that the addition of sintering aid in this case has less influence on the magnetization of low-temperature sintered $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ferrites.

3.4. High frequency properties of the low-temperature sintered specimens

The effect of Bi_2O_3 on the high frequency properties of low temperature sintered Cu-modified Co_2Z were investigated. Fig. 6 shows the initial permeability as a function of frequency for the $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) specimens sintered at 900 °C with various amount of Bi_2O_3. The initial permeability raises up with the increasing amount of Bi_2O_3, and the specimens with 4 wt.% Bi_2O_3 exhibits higher initial permeability of 4.8. It indicates that the magnetic permeability seems to be sensitive to the amount of Bi_2O_3 addition. From the SEM images of $Ba_3Co_{2-x}CuxFe_{24}O_{41}$ ($X = 0.3$) hexaferrite doped with different amount of Bi_2O_3 sintered at 900 °C (Fig. 4), they have almost the same grain size, while their pore ratios are different. Allegri[13] has reported that the magnetic permeability of Z-type hexaferrite is insensitive to grain size but seems to depend on porosity (or density). As discussed above, the improved densification has been achieved with more addition of Bi_2O_3. Therefore, the increased initial permeability may be mainly attributed to the increase of density as shown in Fig. 1.

Table 1
Magnetization data of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) ferrites with different amount of Bi_2O_3

Bi_2O_3 content (wt.%)	σ_s (emu/g)	σ_r (emu/g)	H_c (Oe)
0	49.66	6.93	99.38
1	49.27	6.89	98.99
2	49.13	6.90	98.54
3	49.04	6.84	99.26
4	48.71	6.80	98.34

The sintering temperature can also influence the properties of the ceramics. Fig. 7 shows the initial permeability spectra of the $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) hexaferrites sintered at different temperatures (870, 890,

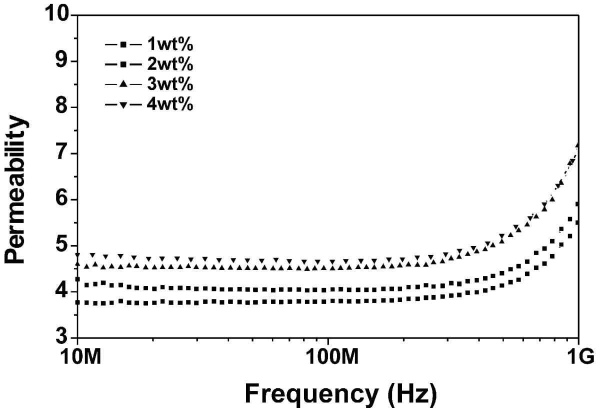


Fig. 6. Initial permeability as a function of frequency for $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X = 0.3$) hexaferrite ceramics sintered at 900 °C with various amount of Bi_2O_3.

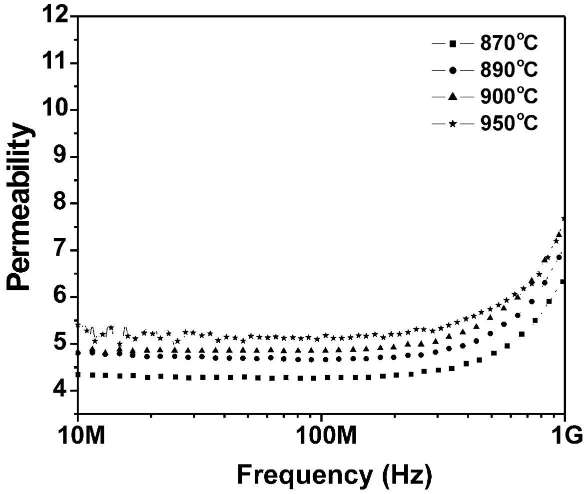


Fig. 7. Initial permeability as a function of frequency for $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X=0.3$) hexaferrite ceramics with 4wt.% Bi_2O_3 sintered at different temperatures.

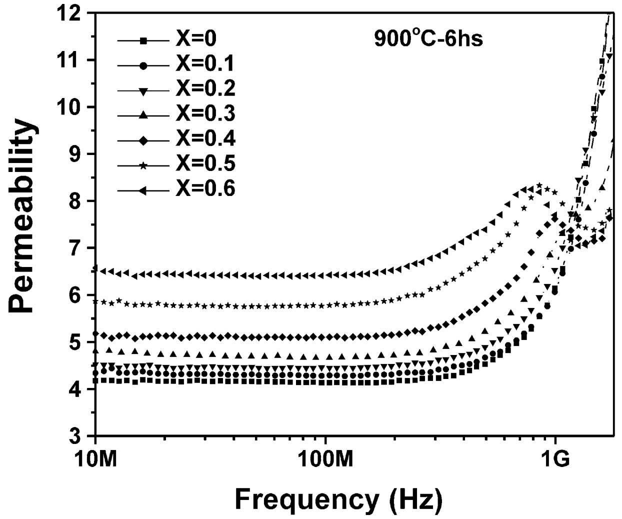


Fig. 8. Influence of Cu-content on permeability via frequency for the specimens of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ ($X=0\sim0.6$) hexaferrite sintered at 900 °C.

900 and 950 °C, respectively). The value of initial permeability goes up from 4.3 to 5.2 with elevated sintering temperatures, which is attributed to the enhanced density and the slight grain growth. This behavior is similar to that of the high-temperature sintered samples reported previously.[11]

The effects of Cu-content (X) on the high frequency properties of the low temperature sintered $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ hexaferrite were investigated. Table 2 summarizes the density (D), average grain size (G), initial permeability (μ_i), quality factor (Q), DC electric resistivity (ρ), cut-off frequency (f_r), and specific temperature coefficient of permeability (α_T) of the Cu-modified Co_2Z ($X=0\sim0.6$) sintered at 900 °C.

The measured spectra of the initial permeability for the Cu-modified Z-type hexaferrite with different Cu-content are shown in Fig. 8. It can be seen clearly from the figure that the initial permeability increases from 4.2 to 6.6 as Cu-content changes from 0 to 0.6. There are many factors that affect the initial permeability value of Z-type hexaferrite, such as ceramic density, grain size, the saturation magnetization and so on. As well known, the initial permeability is proportional to the squared saturation magnetization. In fact, the saturation magnetization of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ has been measured to increase as Cu-content changes from 0 to 0.6 in our previous paper.[11] So in this case, the main reason responsible for the improvement of permeability of the low temperature sintered Cu-modified Co_2Z hexaferrites is the increase in the saturation magnetization induced by Cu substitution. These results reveal that the high initial permeability can be obtained by increased Cu content.

Table 2
The properties data of low-sintering $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ hexaferrites ($X=0\sim0.6$)

X	0	0.1	0.2	0.3	0.4	0.5	0.6
Density (g/cm^3)	5.10	5.12	5.15	5.17	5.16	5.18	5.20
Grain size (μm)	1.8	2.0	2.0	2.0	2.0	2.2	2.2
Initial permeability	4.2	4.4	4.5	4.8	5.3	5.8	6.6
Quality factor (300 MHz)	60	50	50	45	40	35	30
Resistivity ($10^9\Omega$ cm)	4.5	3.0	3.7	2.8	1.8	1.3	1.1
Cut-off frequency (Hz)	1.8G	1.8G	1.8G	1.7G	1.6G	1.5G	1.4G
Temperature coefficient (10^{-6}/°C)	2.7	1.6	2.1	3.3	4.0	1.9	3.7

The natural ferromagnetic resonance (cut-off) frequency of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ hexaferrites is determined to vary from 1.4 to 1.8 GHz, which shifts to lower frequency with increasing Cu-subsitution. That means Cu-substitution will cause a drop in the cut-off frequency.

The specific temperature coefficient of permeability, which is another important factor for MLCI applications, was calculated from the following equation, $\alpha_T = (\mu_{T2} - \mu_{T1})/\mu_i\mu_i(T_2 - T)$, where μ_{T1} and μ_{T2} are the permeability at temperature T_1 and T_2, respectively, and μ_i is the initial permeability at 25 °C. According to the requirement of MLCIs application, α_T is expected to be less than 8×10^{-6}/°C. It has been found that the Curie temperature of $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$ largely depends on the Cu content X and increases with X. Therefore the Cu-modified Z-type hexaferrites possess higher Curie temperature than that of pure Co_2Z (400 °C). The high Curie temperature will lead to a good thermal stability of permeability. As shown in Table 2, the α_T for all the specimens ($X=0\sim0.6$) are less than 4×10^{-6}/°C, meeting the requirement for manufacturing the high frequency MLCIs.

An adequate DC resistivity of the hexaferrite is also required in MLCIs manufacturing so as to avoid "creeping" while electroplating, which may do great harm to the quality of components. Usually, if DC electrical resistivity is less than 10^8 Ω cm, it will hardly fit the requirement. Whereas, as shown in Table 2, the low-temperature sintered Cu-modified Z-type ferrites prepared by this method show high DC resistivity above 10^9 Ω cm, which is much more preferable for either practical production or for the reliability of the components.

4. Conclusions

In summary, using the Cu-substituted Co_2Z hexaferrites powders prepared by citrated precursor method, highly dense ceramics could be successfully obtained after sintering at a low temperature under 900 °C by adding suitable amount of Bi_2O_3 as a sintering aid. The ceramics sintered at 900 °C for 6 h, have fine uniform microstructures with the average grain size of 2 μm in diameter. The initial permeability of the low-temperature sintered hexaferrite increases with increased sintering temperature because the higher density at higher sintering temperature leads to a higher initial permeability. On the other hand, copper content has significant influences on the electromagnetic properties, including initial permeability, quality factor, DC resistivity and cut-off frequencies. The low-temperature sintered Cu-substituted Co_2Z hexaferrites ($Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$, $X = 0 \sim 0.6$) exhibit excellent electromagnetic properties, such as high initial permeability up to 6.6, high resistivity above 10^9Ω cm, and high cut-off frequency above 1.4 GHz. The results indicate that the low-temperature sintered Cu-substituted Co_2Z hexaferrites ($Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$) are very promising materials for MLCIs application.

Acknowledgements

This work was supported by "863" high technology Research and Development project of China (grant No. 2001AA325020) and the National Natural Science Foundation of China (grant No. 59995523)

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