Preparation and properties of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics [①]

ZHANG Hai-jun(张海军) [1], JIA Xiao-lin(贾晓林) [1], YAO Xi(姚　熹) [2], ZHANG Liang-ying(张良莹) [2]

(1. High Temperature Ceramics Institute, Zhengzhou University, Zhengzhou 450052, China;

2. Functional Materials Research Laboratory, Tongji University, Shanghai 200092, China)

Abstract: $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ (Z varies from 0. 0 to 1. 2 in step of 0. 4) microcrystalline glass ceramics were prepared by citrate sol-gel process at 1 200 ℃ in the system of $BaO-Fe_2O_3-CoO-ZnO-SiO_2$. The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) . The complex dielectric constant and complex permeability of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics were measured in the range of 0. 1 − 6. 0 GHz by transmission/ reflection coaxial line method. The natural resonance phenomenon was observed in μ'' spectra for all the $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics, which was closely affected by the substitution of Zn^{2+} ion.

Key words: $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$; microcrystalline glass ceramics; sol-gel; complex dielectric; complex permeability

CLC number: TM 277　　　　　　　　　　　**Document code:** A

---

1 INTRODUCTION

Microcrystalline glass ceramics are those materials bearing the major characteristic of both glass and ceramics, and essentially a nano-crystallline or a micro-composite with glass matrix, which are good for hydrophone detectors, pyroelectric detectors, microwave absorbers, and frequency agile microwave electronic devices. Many methods were used to prepare such kinds of materials, sol-gel in-situ precipitation process was probably the most versatile method to prepare the microcrystalline glass ceramics [1-5]. The main advantage of this method was that the raw components mixed at molecular level, high homogeneity could be achieved and the solid-state reaction was lowered obviously. The composition of the final product could also be accurately controlled. And the sol-gel process can avoid the formation of unwanted stray phases which result in the glass ceramics with pure microcrystallites in wide range of concentration.

$Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}$ hexaferrite is considered to be a candidate material for commercial use in ultra high frequency(0. 3 − 3. 0 GHz) implements such as car telephones because of its higher dispersion frequency, and has been extensively studied in many articles for its unique magnetic properties [5-9]. When glass was added to $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}$ hexaferrite, the sintering temperature of this material will be low and it is easy to obtain dense and fine microstalline, which makes it has better chemical and physical com-patibility with silicon substrate and optical fiber, and therefore has better adaptation to microelectronics and optoelectronics.

In this paper, the citrate sol-gel in-situ precipitation process is used to prepare a series of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics. The effect of composition and frequency on complex permeability and complex dielectric constants of Z-type microcrystalline glass ceramics are studied.

2 EXPERIMENTAL

The raw materials utilized in the present paper were barium carbonate, ferric citrate, cobalt nitrate, zinc nitrate, citrate acid and tetraethyl silicate (TEOS) . A stoichiometric amount of ferric citrate and barium carbonate was dissolved in a citric acid aqueous solution at 80 ℃. Then a stoichiometric amount of cobalt nitrate and zinc nitrate was added, and after complete mixing, a homogenous transparent solution was achieved within a few seconds. These solution were slowly evaporated until a highly viscous colloid was formed which was then mixed with tetraethyl silicate precursor to get the gel. The gel heated in a temperature range of 120 − 140 ℃ for 24 h to get a dried gel. Finally, the dried gel precursor was preheated at 450 ℃ for 5 h and subsequently calcined at 1200 ℃ for 5 h to obtain $Ba_2Zn_{2-Z}Co_ZFe_{28}O_{46}/SiO_2$ microcrystalline glass ceramics powder.

The identification of the crystalline phase after heat treatment was carried out on a RAX-10 X-ray powder diffractometer using Cu K_α radiation. Micrographs were taken by a JSM-5610LV scanning electron microscope (SEM). A network analyzer (HP8753E) was employed to determine the values of ε', ε'', μ' and μ'' in the frequency range of 0. 1－6. 0 GHz by using reflection/ transmission technique. The intrinsic ferrite properties were isolated by the Lichtenecker effective medium expressions.

3 RESULTS AND DISCUSSION

The XRD patterns of $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics and $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$ ferrite synthesized by the citrate sol-gel route at 1 200 ℃ are shown in Fig. 1. The mixtures of Z-type ($Ba_3Co_2Fe_{24}O_{41}$, JCPDS: 19－0097) and M-type ($BaFe_{12}O_{19}$, JCPDS: 43－0002) phase are found in the microcrystalline glass ceramics annealed at 1 200 ℃ for 5 h (see Fig. 1(a)), however, only pure Z-type is detected in the $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$ ferrite calcined at 1 200 ℃ by XRD (see Fig. 1(b)), which shows that it is much more difficult to crystallize pure Z-type hexaferrite phase from $BaO-Fe_2O_3-ZnO-CoO-SiO_2$ system than that from $BaO-Fe_2O_3-ZnO-CoO$ system.

Figs. 2(a) and (b) show the microstructures of eroded surface of $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics and the $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$ ferrite annealed at 1 200 ℃, respectively. It is indicated that the $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$ particles in $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics are global-shaped with an average size of 0. 3 μm, however, the pure Z-type ferrite particles are hexagonal-shaped crystals, with an even size of 3－4 μm on average. This shows that
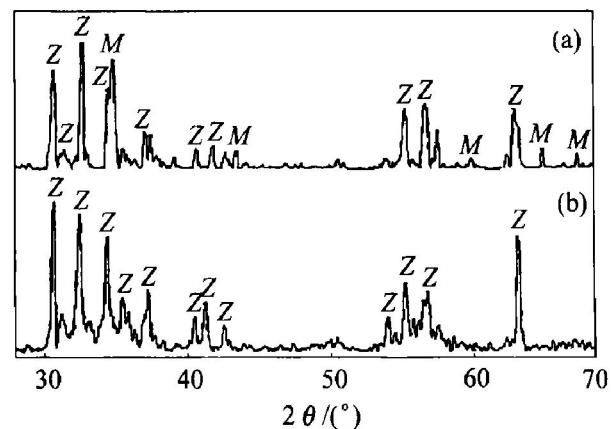

Fig. 1 X-ray diffraction patterns of precursors heated at 1 200 ℃ for 5 h(Z= 1. 2)
(a) —$Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}/SiO_2$;
(b) —$Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$

SiO_2 glass effectively impedes the growth of $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$ crystallite particles in $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics, which seem to echo Refs. [10, 11] that silicon enriched in the grain boundaries plays a role in grain-growth inhibition.

Fig. 3 illustrates the frequency dependence of real part and imagine part of dielectric constant for all $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics. Samples sintered at 1 200 ℃ are found to exhibit the least dielectric dispersion. This behavior is quite similar to that observed by Ref. [12] and can be explained on the basis of the many-body interactions. Owing to the disordered structure of the grain boundaries, the polarisation is due to discontinuous hopping of charges, electrons or ions, between localized states as a result of many-body interactions between its constituent parts. The content of Zn^{2+} and Co^{2+} has no clear effect on the value of ε' and ε'', and ε'' is small in the whole range of measuring frequencies.
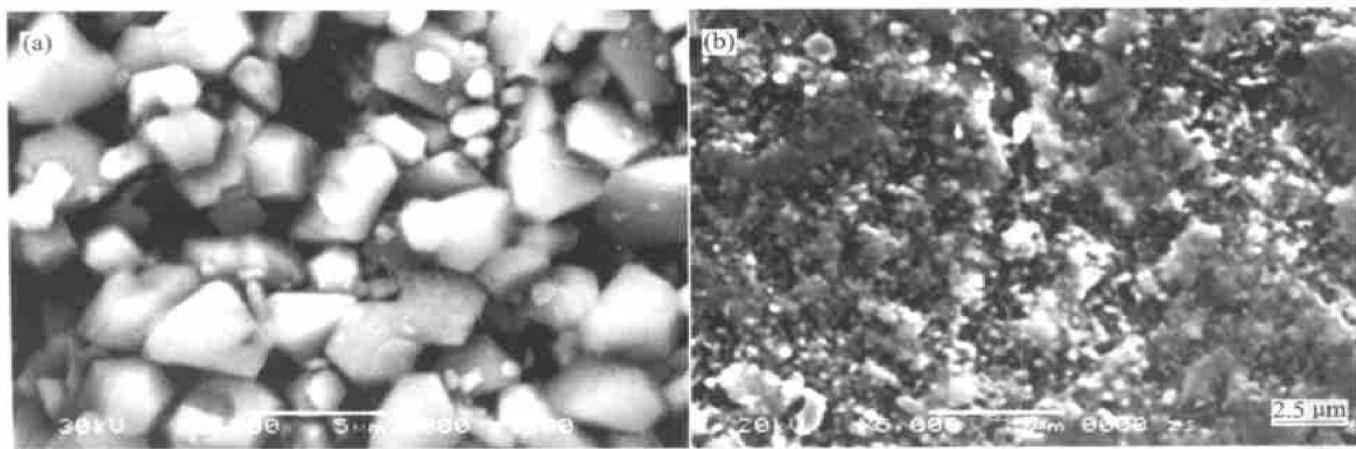
Fig. 2 SEM photograph of eroded surface of $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics and pure $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$ ferrite sintered at 1 200 ℃ for 5 h
(a) —$Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}/SiO_2$; (b) —$Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$
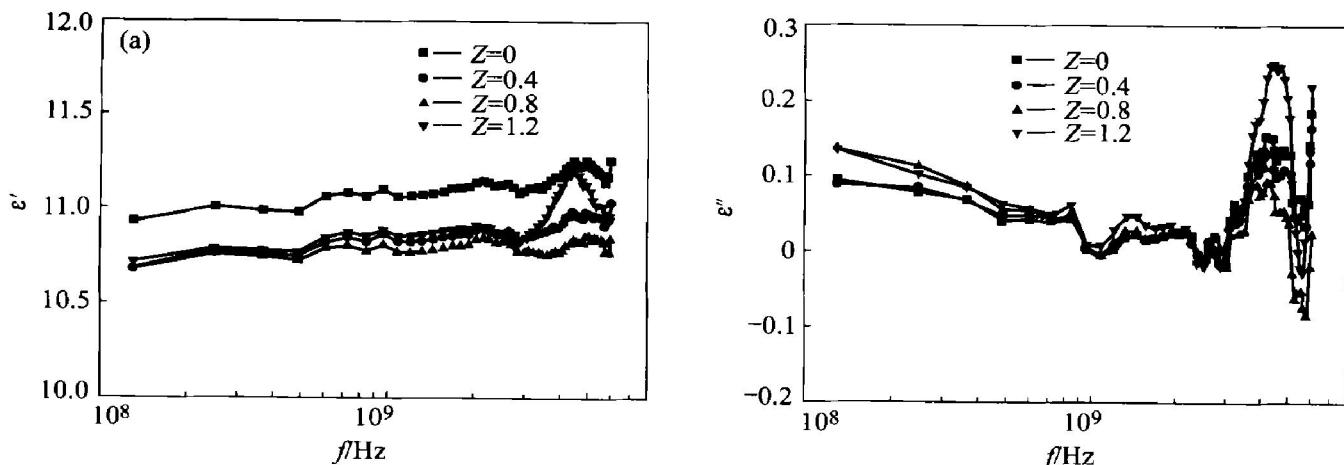
Fig. 3　Frequency dependence of complex dielectric constant of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$
(a) —Real part of permittivity; (b) —Imaginary part of permittivity

Fig. 4 shows the frequency dependence of the real part and imaginary part of permeability of all samples annealed at 1 200 ℃ in the range from 0. 1 — 6. 0 GHz. The real part of permeability μ' almost decreases monotonically with increasing frequency, and this decrease is more rapid for the samples with higher zinc content than those with lower zinc content. The decrease in μ' is attributed to zinc loss due to evaporation, which increases with increasing zinc content. Zinc loss results in compositional and structural changes. The domain wall has the tendency to get pinned to the lattice imperfections thus created. At high frequencies the unpinning of the domain walls which form the imperfections cannot keep pace with the rapidly changing magnetic field resulting in the decreased value of μ'. The content of Zn^{2+} and Co^{2+} markedly affects the values of μ' for all samples at lower frequency, and the more the Zn^{2+} content is, the higher μ' is. The increase in the zinc content increases the grain size and density[13], and decreases the anisotropy, which result in an increase in the value of μ'.

It also can be noticed that an obvious peak due to natural resonance phenomenon appears in μ'' spectra, in which resonance frequency shifts toward higher frequency with increasing Co^{2+} content. And the natural resonance frequency (f_{res}) equals 848, 968 MHz, 1. 08 and 1. 44 GHz for samples with $Z=1.2$, 0. 8, 0. 4 and 0, respectively. In materials with planar anisotropy the natural resonance frequency is governed by the rotational stiffness of the magnetization within the ab plane as well as the stiffness out of the ab plane. The resonance condition is given by

$$2\pi f_{res} = \gamma \sqrt{H_\theta H_\varphi} \tag{1}$$

Literature values of H_φ and H_θ will therefore give an indication of natural resonance frequency expected for hexaferrite studied here. For Co_2Z, $H_\theta = 1.035 \times 10^6$ A·m^{-1} and H_φ ranges from 1 280 to 9 000 A·m^{-1}[13], which results in $f_{res}=1.3-3.4$

GHz. That is in agreement with the experiment result of 1. 44 GHz. The natural resonance frequency of these ferrites moving to lower frequency with increasing Zn^{2+} content can be ascribed to the decreasing anisotropy field of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}$ ferrite as the Zn^{2+} content increases.

Fig. 5 shows the frequency dependence of dielectric loss and magnetic loss in the range of 0. 1 — 6. 0 GHz for all $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}$ samples. This indicates that the dielectric loss is small and the contents of Zn^{2+}, Co^{2+} have no obvious influence on the value of dielectric loss for all samples. The magnetic loss spectra are similar to that of μ'' spectra for all samples. As can be seen in Fig. 5, μ''/μ' is observed to increase with increasing zinc content as well as frequency. The samples with smaller zinc content exhibiting lower loss values are due to the defects, which results from zinc loss and influence of the wall movement is insignificant. And the sample annealed at 1 200 ℃ with the composition $Z=1.2$ shows the largest magnetic loss with f_{res} of about 1. 2 at 6. 0 GHz.

According to the transmission line theory, the reflection coefficient (dB) is a function of six characteristic parameters as f, d, μ'_r, μ''_r, ε'_r and ε''_r, where f, d, μ_r and ε_r are the frequency of electromagnetic wave, the thickness of the absorber material, the relative complex permeability and permittivity, respectively. The reflection coefficients can be calculated by these six parameters. The calculated microwave reflection coefficients of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics with $d=3.2$ mm in frequency range of 0. 1—6. 0 GHz are shown in Fig. 6. It can be seen that reflection loss increases with increasing frequency for all samples, and the higher the thickness of absorber material is, the higher the reflection loss is. In the case of $d=3.0$ mm, the sample annealed at 1 200 ℃ with the composition $Z=0.8$ shows the largest calculated reflection loss at 6. 0 GHz with a
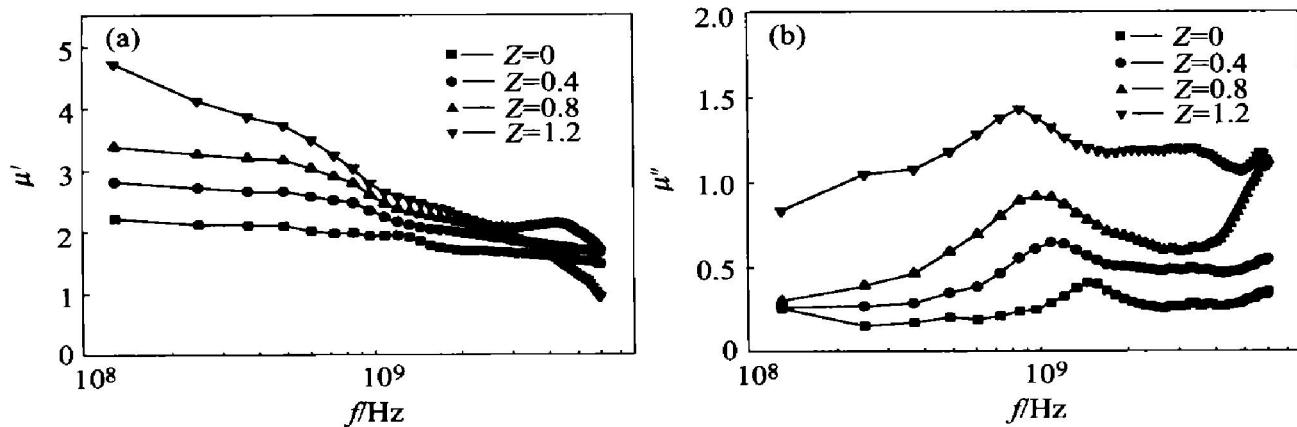
**Fig. 4** Frequency dependence of complex permeability of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$
(a) —Real part of permittivity; (b) —Imaginary part of permittivity
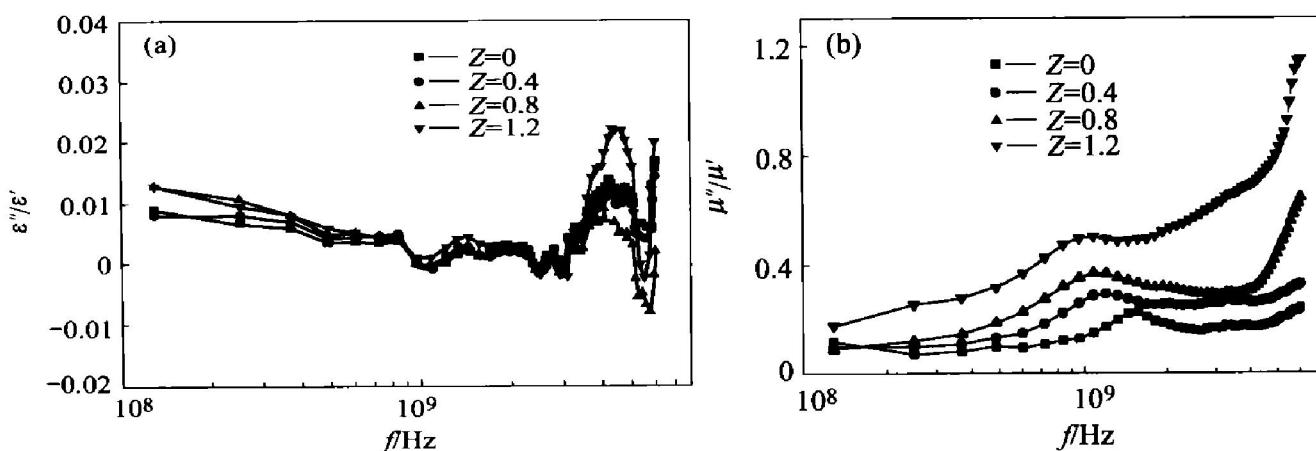
Fig. 5 Frequency dependence of dielectric and magnetic loss of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$
(a) —Dielectric loss; (b) —Magnetic loss
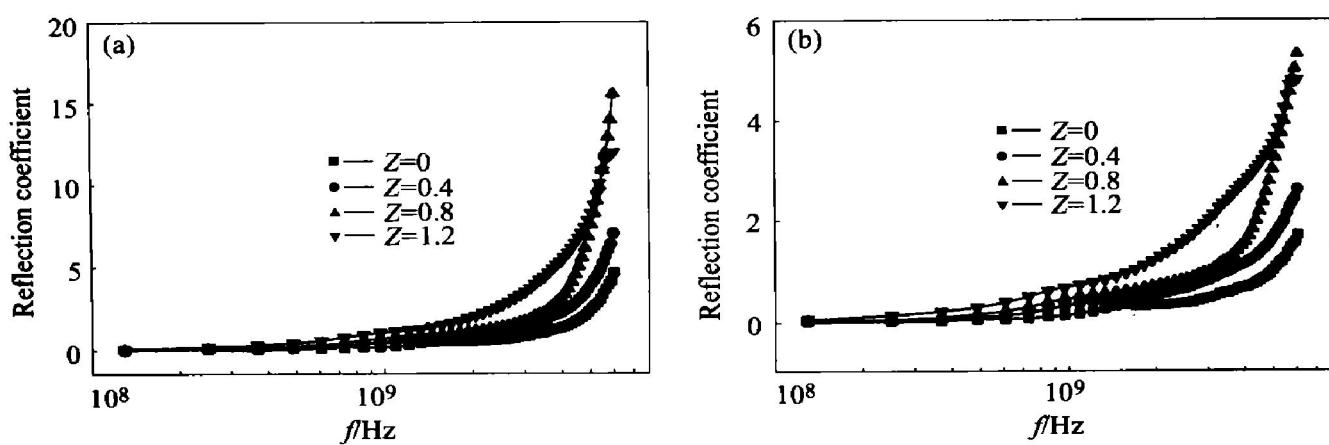
Fig. 6 Calculated reflection loss of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$-wax composite
(a) —1 200 ℃, 3 mm; (b) —1 200 ℃, 2 mm

value of about 16 dB.

4 CONCLUSIONS

A series of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics were prepared by citrate sol-gel technique at 1 200 ℃ for 5 h. $Ba_3Zn_{1.2}Co_{0.8}Fe_{24}O_{41}$

crystallite particles in $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics are global-shaped with an even size of 0.3 μm. The complex dielectric constants and dielectric loss only show little variation with frequency in the entire measuring frequencies, and the real part of permeability of all samples decreases with increasing frequency. The natural resonance phenomenon is observed in $μ''$ —f_{res} curve, the more the

zinc ion content is, the lower the resonance frequency is. The values of complex permeability of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ microcrystalline glass ceramics are composition dependent. The largest calculated reflection loss of $Ba_3Zn_ZCo_{2-Z}Fe_{24}O_{41}/SiO_2$ is about 16 dB in the case of $d = 3.0$ mm.

REFERENCES

[1] Kui Y, Xi Y, Weiguang Z, et al. Structural and electrical characters of sintered Ba-Ti-Al-Si ferroelectric glass-ceramic prepared from sol-gel derived powders [J]. Japanese Journal of Applied Physics, 1997, 36A (7): 4369 - 4376.

[2] Kui Y, Xi Y, Weiguang Z, et al. Preparation and properties of barium titanate glass-ceramics sintered from sol gel derived powders[J]. Journal of Materials Science, 1997, 32(14): 3659 - 3665.

[3] Kui Y, Xi Y, Weiguang Z, et al. Effects of glass elements on the structural evolution of in situ grown ferroelectric perovskite crystals in sol-gel derived glass-ceramics [J]. Journal of Materials Research, 1997, 12(4): 1131 - 1140.

[4] ZHANG Pei-xin, LIN Rong-yi, YAN Jia-qiang. Crystallization on SiO_2-Al_2O_3-CaO-Fe_2O_3 glass ceramic[J]. The Chinese Journal of Nonferrous Metals, 2000, 10(5): 752 - 756.

[5] ZHANG Hong-guo, LI Long-tu, WU Ping-gui, et al. Investigation on structure and properties of low-temperature sintered composite ferrites[J]. Materials Research Bulletin, 2000, 35(13): 2207 - 2215.

[6] Wohlfarth E P. Ferromagnetic Materials[M]. Amsterdam, New York, Oxford: North-holland Publishing Company, 1982. 414 - 416.

[7] Pullar R C, Bhattacharya A K. The synthesis and characterization of the hexagonal Z ferrite, $SrCo_2Fe_{24}O_{41}$, from a sol-gel precursor[J]. Materials Research Bulletin, 2001, 36(7 - 8): 1531 - 1538.

[8] Kimvra O, Matsumoto M, Sakakara M. Enhanced dispersion frequency of hot-pressed Z-typed magnetoplumbite ferrite with the composition $2CoO \cdot 3Ba_{0.5}Sr_{0.5}O \cdot 10.8Fe_2O_3$[J]. Journal of the American Ceramics Society, 1995, 78(10): 2857 - 2860.

[9] Zhang H G, Zhou J, Yue Z X. Investigation of low-temperature sintering of Pb-modified Co_2Z hexaferrite[J]. Materials Science and Engineering B, 1999, 65(3): 184 - 186.

[10] Chien Yung-Tsen, Ko Yung-Chao. The effect of silica characterization on the microstructure of $BaFe_{12}O_{19}$ ferrites[J]. Journal of Materials Science, 1990, 25(3): 1711 - 1714.

[11] Yamamoto H, Mitsuoka T. Effect of CaO and SiO_2 additives on magnetic properties of $SrZn_2$-W type hexagonal ferrite[J]. IEEE Transcations on Magnetics, 1994, 30(6): 5001 - 5007.

[12] ZHANG Xiu-cheng, ZHAO Zhen-sheng, FENG Ze-kun. Study of complex permittivity of microwave ferrite absorbent[J]. Journal of Functional Materials, 1995, 26(3): 251 - 254.

[13] Smit J, Wijn H P J. Ferrites[M]. Eindhoven: Philips Technical Library, 1959. 221 - 82.

(Edited by LONG Huai-zhong)