Complex permittivity and permeability of Zn–Co substituted Z type hexaferrite prepared by citrate sol–gel process

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A series of Z type hexaferrite samples with composition \( \text{Ba}_{x}\text{Co}_{y}\text{Zn}_{1-x-y}\text{Fe}_{2}\text{O}_{4} \) (x varying from 0 to 2.0 in steps of 0.4) were prepared by a citrate sol–gel process. Samples were characterised by TG–DSC, X-ray diffraction, and scanning electron microscopy. Complex permittivity and permeability, and dielectric and magnetic losses were studied as a function of measurement frequency, composition, and annealing temperature. The dependence of natural resonant frequency on annealing temperature as well as on cobalt content was investigated in the range 100 MHz to 6 GHz. Reflection loss has been calculated as a function of frequency according to transmission line theory. BCT/545

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INTRODUCTION

The Z type ferrites are compounds of hexagonal structure, consisting of isotropic materials with spiral structure and the higher anisotropic materials developed by Jonker et al. in the late 1950s.1 The crystal structure of Z type hexaferrite is very complex: the unit cell, containing 140 atoms, belongs to the \( \text{P6}3\text{/mmc} \) space group, and can be considered as a superposition of four \( \text{S} \) blocks, two \( \text{T} \) blocks, and one \( \text{R} \) block. Because of their high dispersion frequency, Z type ferrites are considered to be candidate materials for commercial use in UHF (300 MHz to 3 GHz) components such as car phones, inductor cores, UHF communications devices, and electromagnetic wave absorbers.2

Extensive studies have been made of \( \text{Ba}_{x}\text{Co}_{y}\text{Zn}_{1-x-y}\text{Fe}_{2}\text{O}_{4} \) hexaferrite because of its unique magnetic properties. \( \text{Co}_{2}Z \) prefers the basal plane at room temperature following a transition to this from a cone of magnetisation at \(-53^\circ\)C, but it then undergoes a further change to magnetisation parallel to the c axis from \( 207^\circ\)C to the Curie point at \( 400^\circ\)C. According to Pullar et al.3 the Z phase forms at \( 1250^\circ\)C, and only after full crystallisation of the M and Y phases at \( 1000^\circ\)C; however, \( \text{Ba}_{x}\text{Co}_{y}\text{Fe}_{2}\text{O}_{4} \) spherical nanocrystals with grain sizes in the range 15–25 nm are reported to be synthesised at \( 750^\circ\)C by a stearic acid sol–gel method.4 Strontium ions were used to replace barium ions by Kimura et al.5,6 in order to improve the magnetic properties of \( \text{Co}_{2}Z \). Barium ions were partially substituted with lead ions by Zhang et al. to sinter \( \text{Co}_{2}Z \) hexaferrite at lower temperature.7 Various chemical methods have been proposed and proven to be effective in reducing the sintering temperature and achieving good properties for hexaferrites such as \( \text{BaM} \) and \( \text{Co}_{2}\text{W} \).8,9,10

To achieve homogeneity of ions at the atomic level in the precursor and to obtain Z type ferrite at lower temperature, the citrate sol–gel technique is used in the present paper to prepare a series of Z type \( \text{Ba}_{x}\text{Co}_{y}\text{Zn}_{1-x-y}\text{Fe}_{2}\text{O}_{4} \) hexaferrites. The effects of measurement frequency, sintering temperature, and composition on complex permeability and dielectric constant are also reported.

EXPERIMENTAL PROCEDURES

Ferrite powder preparation

Stoichiometric amounts of ferric citrate, barium carbonate, cobalt nitrate, and zinc nitrate were dissolved in an aqueous solution of citric acid at \( 80^\circ\)C to obtain a transparent and completely homogeneous solution. The solution was slowly evaporated until a highly viscous residue was formed, which was then heated at 120–140°C to produce a dried gel. The dried gel was preheated at 450°C for 5 h and then calcined from 600 to 1200°C for 5 h to obtain \( \text{Ba}_{x}\text{Co}_{y}\text{Zn}_{1-x-y}\text{Fe}_{2}\text{O}_{4} \) ferrite powder.

Structural characterisation

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were conducted on a Netzsch STA 449C thermal analysis system in air at a rate of 10 K min\(^{-1}\). Phase evolution in the preheated powders was analysed by means of X-ray diffractometry. Data collection was carried out on a Rigaku X–ray diffractometer using Cu K\( \alpha \) radiation in the range 2\( \theta \) = 10°–80°. Scanning electron microscopy (Jeol JSM 5610LV) was used to study grain morphology and average grain size.

1  TG–DSC curves of \( \text{Ba}_{x}\text{Zn}_{y}\text{Co}_{1-x-y}\text{Fe}_{2}\text{O}_{4} \) preheated at 450°C
and reflection coefficients of samples in the frequency range 0.1–6.0 GHz. Relative complex permeability and permittivity were calculated from the measured transmission and reflection coefficients using the theoretical formulas described by Vanzura et al.\textsuperscript{11} The Lichtenecker effective medium expressions were used to isolate intrinsic ferrite properties.

RESULTS AND DISCUSSION

Figure 1 shows DSC–TG curves from 20 to 1200°C for the ferrite precursor precalcined at 450°C for 5 h. A small exothermal peak with weight loss may be observed in the TG curve at 803.3°C, corresponding to decomposition of BaCO\textsubscript{3} and formation of BaM hexaferrite. The formation of barium ferrite (BM) can be expressed as follows

\[ \text{BaCO}_3 + 6\text{Fe}_2\text{O}_3 \rightarrow \text{BaFe}_{12}\text{O}_{19} \]

The decomposition of BaCO\textsubscript{3} has been reported to take place at 1055°C for pure carbonate.\textsuperscript{12} The fact that the temperature at which this reaction occurred was lower for the sample used here may be attributed to the larger surface area and larger surface free energy of the precursor prepared by the citrate sol–gel method. Another broad exothermal peak in the temperature range 900–1100°C, again with weight loss in the TG curve, may result from the formation of Z type. Neither exothermal nor endothermal peaks were observed in the DSC curve below 450°C, indicating that dehydration and removal of organics by oxidation occurred during the precalcination process. The initial weight loss in the TG curve corresponds to the loss of absorbed water in the precalcined precursor.

XRD patterns of the Ba\textsubscript{12}Co\textsubscript{2}Zn\textsubscript{12-x}Fe\textsubscript{2x}O\textsubscript{41} Z type hexaferrite samples formed by the citrate sol–gel route are shown in Fig. 2. These patterns show mixed peaks of BaCO\textsubscript{3} and γ-Fe\textsubscript{2}O\textsubscript{3}, and BaFe\textsubscript{12}O\textsubscript{19} (BaM) and γ-Fe\textsubscript{2}O\textsubscript{3} phases in

Microwave measurements

The Ba\textsubscript{12}Co\textsubscript{2}Zn\textsubscript{12-x}Fe\textsubscript{2x}O\textsubscript{41} ferrite powders were randomly dispersed in paraffin wax at a volume fraction of 25%. Dispersed powders were then die pressed to form hollow cylindrical samples with 3.04 mm inner diameter, 7.00 mm outer diameter, and 2.4 mm thickness. An HP8753E vector network analyser was used to measure the transmission

3 SEM micrographs of etched and sintered surfaces of Ba\textsubscript{12}Zn\textsubscript{12-x}Fe\textsubscript{2x}O\textsubscript{41}: a sintered at 1100°C, b sintered at 1200°C, c sintered at 1100°C and etched, d sintered at 1200°C and etched
the precursors annealed at 450 and 800°C respectively. In the case of calcining at 1100°C a mixture of Z type and BaM hexaferrite was present in the sample, and Z type hexaferrite was the only crystalline phase that could be detected by XRD in the sample annealed at 1200°C. In fact, the synthesis temperature of Z type hexaferrites is lower in the sol-gel process than in standard ceramic fabrication. Intermediate phases such as BaFe$_2$O$_4$ and other phases of barium iron oxide were not observed, in contrast to samples synthesised by the ceramic route. This indicates that the reaction is homogeneous and that the mixing of cations takes place at the atomic level, thus reducing the diffusion paths and enhancing volume diffusion of the various cations.

Figure 3 shows the microstructure of etched and sintered surfaces of Ba$_2$Co$_{3-x}$Zn$_x$Fe$_{12}$O$_{33}$ ferrite calcined at 1200 and 1100°C. The micrograph in Fig 3b indicates that the Z type ferrite particles sintered at 1200°C consist of homogeneous hexagonal shaped crystals, with a clear outline and an average size of 4–6 μm. The grain size of the sintered surface is about 2–3 μm larger than that of the etched surface, owing to the higher activity of the surface atoms. The increase in crystal grain size with annealing temperature was also observed for Z type hexaferrite.

The frequency dependence of $\varepsilon'$ and $\varepsilon''$ for all Ba$_2$Co$_{3-x}$Zn$_x$Fe$_{12}$O$_{33}$ ferrites calcined at 1000–1200°C is shown in Fig. 4. The complex dielectric constant shows no obvious variation in any of the samples sintered at 1000 or 1100°C. However, the values of $\varepsilon'$ and $\varepsilon''$ decrease with increasing frequency for the samples annealed at 1200°C. This is normal behaviour which has been observed in several ferrite systems$^{15-16}$ and can also be explained by the theory of Koops.$^{16}$ The sample with composition Ba$_2$Co$_{3-x}$Zn$_x$Fe$_{12}$O$_{33}$ calcined at 1200°C shows maximum values of $\varepsilon'$ and $\varepsilon''$ from 100 MHz to 60 GHz. The values of complex permittivity increase very slightly with annealing temperature for all samples, owing to the formation of larger numbers of Fe$^{3+}$ ions with increasing temperature. The higher values of complex permittivity for Ba$_2$Co$_{3-x}$Zn$_x$Fe$_{12}$O$_{33}$ annealed at 1200°C may be due to the significant contribution of Fe$^{3+}$ as well as Zn$^{2+}$ complexes to interfacial polarisation.

Figure 5 illustrates the frequency dependence of the real and imaginary parts of permeability for all samples annealed at 1000–1200°C in the range 0.1–60 GHz. The graphs show that $\mu'$ and $\mu''$ are dependent on measurement frequency as well as composition and annealing temperature. The higher the annealing temperature, the higher are $\mu'$ and $\mu''$, owing to the higher annealing temperature resulting in grain growth of Z type ferrite, an increase in density, and a decrease in the magnetic anisotropy of the sample. For all samples, $\mu'$ decreases almost monotonically with frequency, and this decrease is more rapid at low frequency (<1 GHz) than at high frequency (1 < f < 6 GHz). Very clear resonance phenomena stemming from natural resonance can be
observed in $\mu''$ spectra for the samples annealed at 1100 and 1200°C. The natural resonance frequency is dependent not only on composition but also on calcining temperature: the lower the zinc content and annealing temperature, the higher is the natural resonance frequency. In the case of the samples sintered at 1100°C, the natural resonance frequency was 1.44 GHz for Co$_{0.7}$Zn$_{0.3}$Z, 1.32 GHz for Co$_{0.8}$Zn$_{0.2}$Z, 1.20 GHz for Co$_{0.8}$Zn$_{0.2}$Z, 1.08 GHz for Co$_{0.8}$Zn$_{0.2}$Z, 0.98 MHz for Co$_{0.8}$Zn$_{0.2}$Z, and 0.84 MHz for Zn$_2$Z ferrite. However, for the samples sintered at 1200°C, the natural resonance frequencies were as follows: 1.44 GHz for Co$_{0.7}$Z, 1.20 GHz for Co$_{0.8}$Z, 1.08 GHz for Co$_{0.8}$Z, 0.98 MHz for Co$_{0.8}$Z, and 0.84 MHz for Zn$_2$Z hexaferrite. The increase in the natural resonance frequency with $x$ is a result of the anisotropy field increasing with cobalt content. The enhancement of the natural resonance frequency with decreasing annealing temperature may be attributed to the much smaller crystal grains (Fig.3), the increase in the anisotropy field, and the coexistence of BaM and Z type hexaferrite (Fig.2) as the annealing temperature decreases. According to Pullar et al., the natural resonance frequency of BaM ferrite is about 45 GHz. As a matter of fact, another resonance peak may be observed in the curve of $\mu''$ against frequency in addition to the one resulting from natural resonance for Co$_{0.7}$Z ferrite annealed at 1200°C (about 4 GHz) and all samples calcined at 1100°C (about 5 GHz). The reason for this extra peak is still far from clear and will be further investigated in future work. In materials with planar anisotropy, the natural ferromagnetic resonance (NMR) frequency will be governed by the anisotropy field $H_A$ and $H_D$, the resonance condition being given by

$$2\pi f_{\text{res}} = g(H_A H_D)^{1/2}$$

(1)

Literature values for $H_A$ and $H_D$ will therefore give an indication of the NMR frequency expected for the Co$_{0.7}$Z ferrite studied. For Ba$_{0.4}$Fe$_{12}$O$_{19}$, $H_A = 1035 \times 10^6$ Am$^{-1}$ and $H_D$ ranges from 1280 to 9000 Am$^{-1}$ (Ref. 2), resulting in $f_{\text{res}} = 13-34$ GHz. This is in agreement with the experimental result of 1.44 GHz. According to the theory of electromagnetism, for the ferrite with planar anisotropy and uniaxial anisotropy, $\mu_r$ can be described by the pair of equations

$$\mu_r = 1 + c_1(M_s/H_D) + c_2(M_s/H_D)$$

(2)

$$\mu_r = 1 + c(M_s/H_D)$$

(3)

where $c_1$, $c_2$ are constants and $H_D$, $H_A$ are the anisotropy fields. The equations demonstrate that the value of $\mu_r$ for planar anisotropic hexaferrite ($x=1/2$, 1/6, 2/6) is higher than that for uniaxial anisotropic hexaferrite ($x=0$, 4/6), which is also in agreement with the experimental results. Figure 6 shows the frequency dependence of dielectric loss and magnetic loss in the range 100 MHz to 6 GHz for
6 Frequency dependence of dielectric and magnetic losses in Ba$_2$Zn$_{0.5}$Co$_{1.5}$Fe$_{2.5}$O$_{11}$ calcined at a 1000°C, b 1100°C, c 1200°C

all samples. The dielectric loss shows no variation with frequency, with a small value about zero; the magnetic loss spectra are somewhat similar to the $\mu''$ spectra for all samples. There was also a maximum magnetic loss of around 1.5 at 6 GHz for Zn$_{1.5}$Co$_{0.5}$Z ferrite annealed at 1200°C.

According to transmission line theory, reflection loss (dB) is a function of normalised input impedance, expressed as

$$\text{Reflection loss} = 20 \log_{10}\left(\frac{|Z_{in}|}{|Z_{in} + 1|}\right)$$

Thus, the surface reflectance of an absorber is a function of six characteristic parameters, $f$, $d$, $\mu'$, $\mu''$, $\varepsilon'$, and $\varepsilon''$. It is

7 Calculated reflection losses in Ba$_2$Zn$_{0.5}$Co$_{1.5}$Fe$_{2.5}$O$_{11}$ wax composites sintered at 1200°C for 5 h: a $d=3$ mm, b $d=2$ mm
possible to evaluate the numerical values of the parameters from the condition of zero reflection. The values of reflection loss calculated using equation (4) for all samples annealed at 1200°C are shown in Fig. 7. The reflection loss is dependent on $f$ and $d$ as well as on composition. The higher the measuring frequency or absorber thickness, the higher is the reflection loss. There is a maximum reflection loss of about 18 dB at 6 GHz for Ba$_x$Co$_{3}$Zn$_{1-x}$Fe$_{2}$O$_{4x}$ annealed at 1200°C with $d=3$ mm.

CONCLUSIONS

A series of Ba$_x$Co$_{3}$Zn$_{1-x}$Fe$_{2}$O$_{4x}$ hexaferrites were prepared by the citrate sol–gel technique by processing at 1200°C for 5 h with precursors of ferric citrate, barium carbonate, and metal nitrates. The Z type hexaferrite particles fired at 1200°C were hexagonal, with an average size of 5±0 μm. The complex permittivity and permeability spectra of Ba$_x$Co$_{3}$Zn$_{1-x}$Fe$_{2}$O$_{4x}$ hexaferrites were measured using the transmission/reflection coaxial line method in the frequency range 0.1–6 GHz. The results show that $\mu'$ for all samples decreases with increasing frequency. The natural resonance phenomenon was observed in curves of $\mu''$ vs. $f$. The higher the zinc content or annealing temperature, the lower was the resonance frequency.

REFERENCES
