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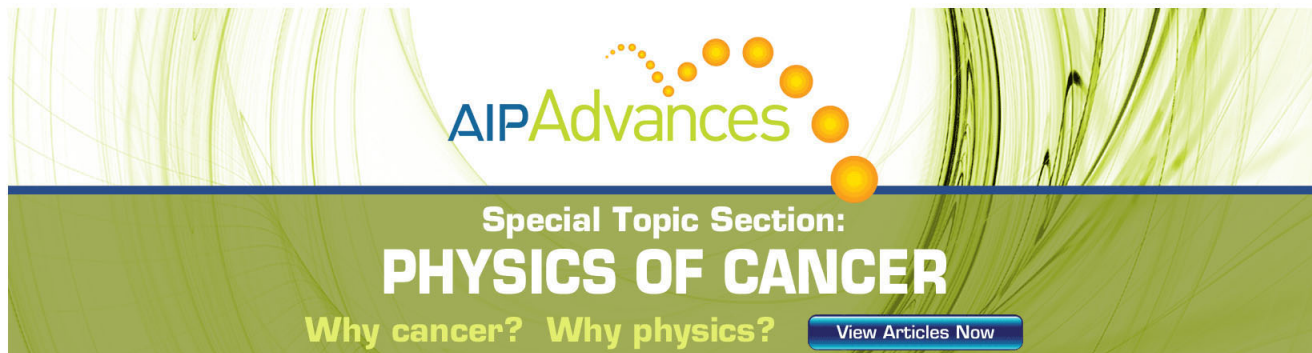
Magnetic and microwave absorption properties of *W*-type Ba(Zn$_x$Co$_{1-x}$)$_2$Fe$_{16}$O$_{27}$ hexaferrite platelets

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W-type barium hexaferrite platelets Ba(Zn$_x$Co$_{1-x}$)$_2$Fe$_{16}$O$_{27}$ ($0.1 \leq x \leq 0.9$) were prepared by a chemical coprecipitation route. The results of field-emission scanning electronic microscopy showed that the grains were regular hexagonal platelets with sizes from 0.5 to 1.5 μm. With increasing x, the coercivity decreased, whereas the saturation magnetization increased. Microwave absorption properties were investigated in the frequency range of 8–12 GHz. An optimal reflection loss (-24.8 dB) reached at 10 GHz for $x = 0.5$ with a thickness of 2 mm. These results indicated that our samples might be a potential candidate for permanent magnets and microwave absorption materials. © *2011 American Institute of Physics*. [doi:10.1063/1.3559538]

I. INTRODUCTION

W-type barium hexaferrite (BaM$_2$Fe$_{16}$O$_{27}$), where M is divalent cation, was discovered in 1980 in the Philips' research laboratories.[1] Owing to appropriate magnetic properties, excellent chemical stability and low cost, more and more attention has been devoted in the past decades.[2–7] It possesses high coercivity and large magnetic energy product. The merits mentioned earlier have made it be used as permanent magnets, recording heads, and components in high-frequency microwave devices.[8–12]

The crystal structure of *W*-type BaM$_2$Fe$_{16}$O$_{27}$ hexaferrite can be viewed as a stacking cubic spinel (S = Fe$_6$O$_8^{2+}$) and hexagonal (R = BaFe$_6$O$_{11}^{2-}$) blocks built in the form RSSR*S*S* [where an asterisk (*) denotes 180° rotation around the hexagonal *c*-axis].[13] The O^{2-} ions exist as close-packed layers, one Ba^{2+} ion is found replacing an O^{2-} ion in R block, the Fe^{3+} ions are distributed in five different interstitial sublattices.

W-type BaFe$_2$Fe$_{16}$O$_{27}$ ferrite containing two Fe^{2+} ions possesses a 10% higher saturation magnetization than that in corresponding *M*-type hard magnetic ferrites, and the energy product may be 20% higher at room temperature. However, it is rather difficult to control the Fe^{2+} concentration, resulting in instability of BaFe$_2$Fe$_{16}$O$_{27}$ performance. In order to overcome this difficulty, we select a combination of stable Co^{2+} and Zn^{2+} instead of Fe^{2+} to improve the thermal stability and properties. Because the magnetic and microwave absorption properties depend strongly on the size and shape of the particles, several techniques have been attempted to fabricate *W*-type ferrites, including the sol-gel method,[14,15] the solid-state method,[16,17] and the salt-melting/mechanical

ball-milling method.[18] Moreover, *W*-type hexaferrites form generally at very high temperatures ($>$1350 °C) by conventional techniques, leading to microstructure coarsening and small coercivity. It is well known that the chemical coprecipitation method is usually used to synthesize magnetic oxides due to its simplicity and well control of grain size.

In this paper, single-phase *W*-type Ba(Zn$_x$Co$_{1-x}$)$_2$Fe$_{16}$O$_{27}$ (BZCFO) hexagonal platelets with relatively homogeneous size were prepared by an improved chemical coprecipitation method. In this processing, ammonium oxalate monohydrate was used as a precipitator instead of alkali to control the nucleation and growth of particles. As a result, the grain size, shape, magnetic and microwave absorption properties were successfully controlled.

II. EXPERIMENTAL PROCEDURE

A series of *W*-type barium hexaferrites with the formula Ba(Zn$_x$Co$_{1-x}$)$_2$Fe$_{16}$O$_{27}$ platelets was prepared by chemical coprecipitation method. All starting materials were of high-purity compounds. First, Ba(NO$_3$)$_2$, Zn(NO$_3$)$_2$, Co(NO$_3$)$_2$·6H$_2$O, and Fe(NO$_3$)$_3$·9H$_2$O were stoichiometricly dissolved in de-ionized water by gentle heating; Then, the aqueous mixture was slowly poured into the (NH$_4$)$_2$C$_2$O$_4$·H$_2$O solution and stirred for several minutes using a magnetic stirrer. The gelatinous precipitates were filtered and washed several times using de-ionized water until the *p*H value of the solution became neutral. The dried powders were sintered at 500 °C for 8 h in air, and then sintered at 1100 °C for 8 h in air. Finally, the obtained powders were pressed into pellets with Φ10 mm$\times$2 mm under a pressure of 20 MPa and sintered at 1200 °C for 24 h in air.

The crystal structure was characterized by x-ray diffractometer (XRD, Philips designed, X'pert PRO type) with Cu *K*α radiation (wavelength $\lambda = 1.54056$ Å). The morphology of grains was investigated by field-emission scanning

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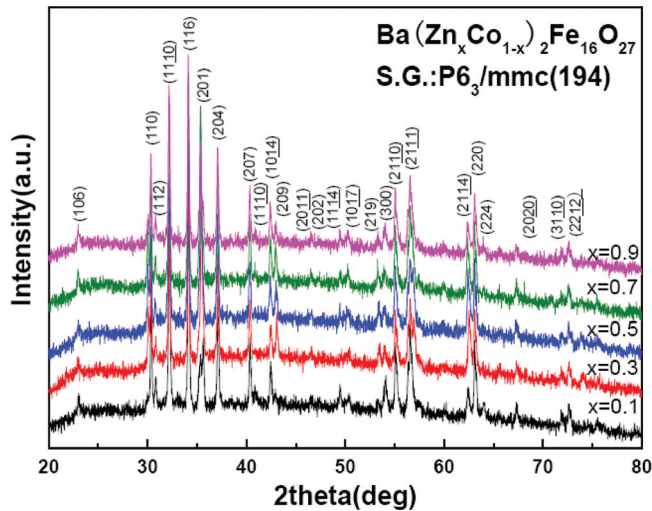
FIG. 1. (Color online) XRD patterns for the $Ba(Zn_xCo_{1-x})_2Fe_{16}O_{27}$ hexaplatelets.

electronic microscopy (FE-SEM). Fourier transform infrared (FTIR) spectroscopy was undertaken with a Nicolet Magna-IR 550 FTIR spectrometer. Magnetization measurements were performed using a vibrating-sample magnetometer accompanied in Quantum Design physical properties measurement system. The reflection loss (RL) measurements were carried out using HP8720ES vector network analyzer.

III. RESULTS AND DISCUSSION

XRD patterns of $Ba(Zn_xCo_{1-x})_2Fe_{16}O_{27}$ ($x = 0.1$, 0.3, 0.5, 0.7, and 0.9) samples can be well indexed on the basis of a hexagonal crystal unit cell with a space group of $P6_3/mmc$ in Fig. 1. The lattice parameters a and c are calculated as listed in Table I. It is obvious that the lattice constants a and c decrease with increasing Zn^{2+} contents and decreasing Co^{2+} contents. This variation of lattice parameters a and c can be explained on the basis of the ionic radii of substituted ions where the ionic radius of Co^{2+} is 0.082 nm and that of Zn^{2+} is 0.074 nm. The values in Table I are similar to the other reports for W-type barium hexaferrites.[19,20]

Typical FE-SEM images are shown in Fig. 2. It is clearly seen that the grains are regular hexagonal platelets with rather homogenous grain sizes between 0.5 and 1.5 μm. Further, the shape and diameters of most the grains are almost independent of the composition x.

TABLE I. The values of the lattice parameters a, c, c/a ratio, coercivity H_c, and saturation magnetization M_s at different Zn content x for the $Ba(Zn_x Co_{1-x})_2Fe_{16}O_{27}$ hexaplatelets.

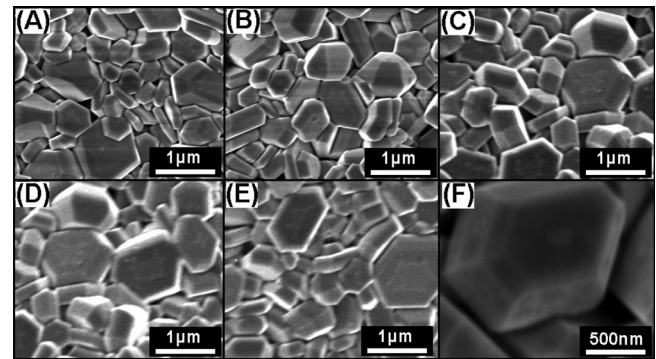| x	a (Å)	c (Å)	c/a	M_s (emu/g)	H_c (Oe)
0.1	5.991	33.19	5.54	80.9	1508
0.3	5.976	33.07	5.53	82.9	1277
0.5	5.943	32.96	5.55	85.8	1064
0.7	5.926	32.89	5.55	89.5	843
0.9	5.894	32.68	5.54	92.8	585

FIG. 2. FE-SEM micrographs of BZCFO platelets: (A) $x=0.1$, (B) $x=0.3$, (C) $x=0.5$, (D) $x=0.7$, and (E) $x=0.9$ (F) A higher-magnification view of (E).

To investigate the magnetic properties of the samples, the magnetic hysteresis loops are measured. The $M(H)$ loops for the $Ba(Zn_xCo_{1-x})_2Fe_{16}O_{27}$ ($x = 0.1$, 0.3, 0.5, 0.7, and 0.9) at 300 K are shown in Fig. 3. It is clear that BZCFO hexagonal platelets exhibit enhanced saturation magnetization (M_s) values with increasing x. A maximum M_s comes out to 92.8 emu/g at room temperature for $x = 0.9$, the results in detail are summarized in Table I. These results can be explained that the variation of tetrahedral–octahedral super-exchange interactions due to the high concentration of non-magnetic Zn^{2+} ions. It is well known for W-type hexaferrite that there are five different interstitial sublattices, that is, three spins-up (2a, 12k, and 2b) and two spins-down ($4f_1$ and $4f_2$) sublattices. It was previously reported that[21,22] for W-type hexaferrite the divalent ions (Zn^{2+} and Co^{2+}) are usually distributed among the tetrahedral ($4f_1$) and octahedral ($4f_2$) sites of the S block. Hence the substitution non-magnetic Zn^{2+} ions for magnetic Co^{2+} ions at $4f_1$ and $4f_2$ sites results in the enhancement of the total magnetic moments according to the Gorter model.[23]

The coercivity for a ferrimagnet can be reflected by coercivity field H_c. The obtained values of H_c for our samples are listed in Table I. It is found that value of H_c gradually decreases when Zn^{2+} ion content x instead of Co^{2+} ion
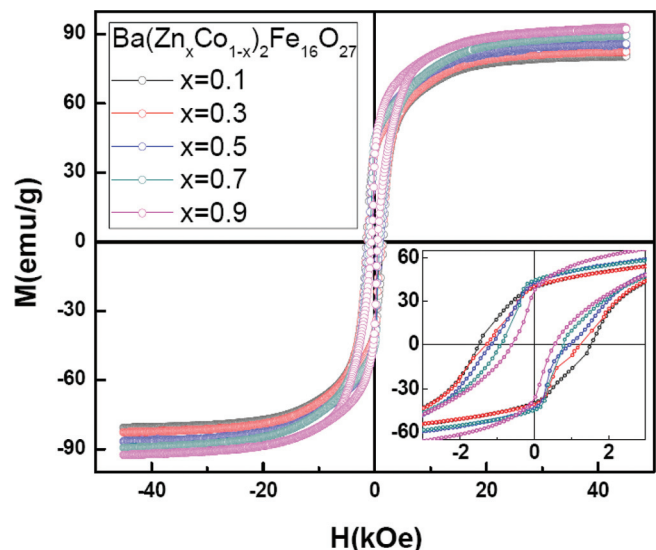

FIG. 3. (Color online) Room-temperature M–H hysteresis loops of BZCFO platelets for different compositions, the inset exhibits M–H loops on a larger scale.
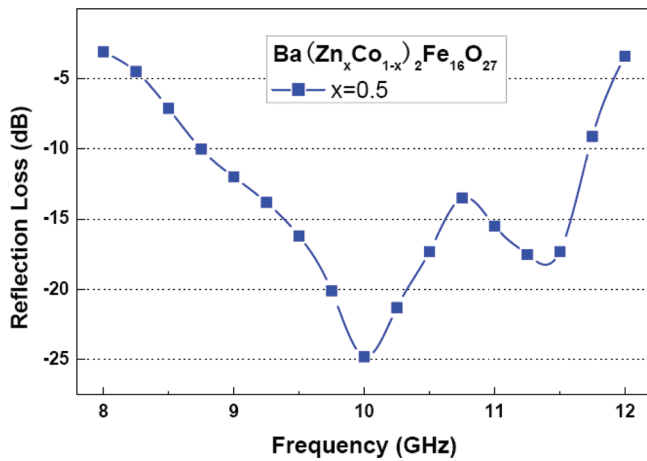
FIG. 4. (Color online) The frequency dependence of the RL of BZCFO/wax composition for x=0.5 with 2 mm thickness.

increases. There are two possible reasons for the above-mentioned variation of H_c. On the one hand, the coercivity for the disordered particles in W-type hexaferrite can be estimated through the following formula[24]:

$$H_c = 0.64 \frac{K_1}{M_s}, \qquad (1)$$

where K_1 is the magnetocrystalline anisotropy constant and M_s is the saturation magnetization. The decrease of the coercivity with increasing x may be contributed to the decreasing Co^{2+} ion contents, as substitution of nonmagnetic Zn^{2+} ions on strong planar magnetic Co^{2+} ions will lead to the decrease of magnetocrystalline anisotropy constant K_1 of BZCFO hexaferrite. On the other hand, the value of M_s gradually increases with an increasing Zn^{2+} ion content x based on the previous discussions, whereas the values of H_c and M_s basically accord with the inverse relation. Therefore, the increase of M_s will also result in the decrease of H_c.

The samples for the RL measurements were prepared by uniformly mixing BZCFO powders with wax, and the weight ratios were fixed at 4:1. The mixtures for microwave absorption measurements were molded into a rectangle ($20 \times 10 \times 2$ mm^3) to fit the waveguide sample holders well. Figure 4 shows the frequency dependence of the optimal RL of BZCFO/wax mixture for $x = 0.5$ with 2 mm thickness. It can be seen that there exist two RL peaks in the frequency range from 8 to 12 GHz. The first RL peak at 10 GHz is due to magnetic loss, the maximum value of RL reaches -24.8 dB. The second RL peak around 11.4 GHz is assigned to dielectric loss, the maximum value of RL reaches -18.2 dB. It is worth noting that the overlap of the first and second peaks results in broader absorption band, the absorption bandwidth (RL<-10 dB) reaches 3.9 GHz, exhibiting that appropriate substitution Zn^{2+} ions for Co^{2+} ions can widen absorption bandwidth of BZCFO. This property might make it promising in wide-band microwave absorption materials.

IV. CONCLUSIONS

A chemical coprecipitation method was used to prepare W-type BZCFO hexaferrites. The XRD results showed that all the derived samples were pure phase. FE-SEM results exhibited that the grains were regular hexagonal platelets with grain sizes from 0.5 to 1.5 μm. The variations of magnetic properties could be explained by the substitution nonmagnetic Zn^{2+} ions for magnetic Co^{2+} ions at $4f_2$ sites. The maximum value of RL is -24.8 dB and the absorption bandwidth (RL<-10 dB) reaches 3.9 GHz.

ACKNOWLEDGMENTS

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