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Crystalline phases and magnetic properties of Cu–Bi–Zn co-doped Co_2Z ferrites

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ABSTRACT

The effects of Cu, Bi and Zn substitutions on the crystalline phase and magnetic properties of hexagonal ferrites with a composition of $3(Ba_{1-x}Bi_xO)$•$2(Co_{1-y}Cu_yO)$•$12(Fe_{2\text{-}(x/4)}Zn_{(x/4)}O_3)$ were investigated. The results showed that the addition of Bi and Zn can significantly promote Z phase formation. The Z phase may be triggered to decompose into U and W phases resulting from the evaporation of Bi and segregation of Co-rich ferrites at high sintering temperatures for samples with large amounts of Bi and Zn. The initial permeability decreased with increasing x value because the Bi substitution promoted Z phase decomposition into U and W phases.

1. Introduction

Magnetoplumbite ferrites with a hexagonal structure exhibit a higher dispersion frequency than nickel ferrites, because of the magnetic anisotropy of the magnetoplumbite [1]. Among those ferrites, the Co_2Z ferrite $3(BaO)$•$2(CoO)$•$12(Fe_2O_3)$ had the best magnetic properties (such as permeability and quality factor) above 200 MHz [2,3]. However, the saturation magnetization (M_s) of Co_2Z is slightly low, only 51 emu/g at room temperature. Zn substitution can promote M_s, and hence increasing the permeability [4]. The phase formation temperature of Co_2Z ferrite prepared using the solid state reaction method is as high as 1250–1300 °C due to its complex structure [5]. The substitution of Cu for Co and Bi for Ba can promote the formation of Z-type ferrite at a low temperature [6]. However, to our best knowledge, there is no study on the effects of Cu–Bi–Z co-doping on the crystalline phase and magnetic property of Co_2Z ferrite.

The main objective of this study was to investigate the effects of Cu, Bi and Zn substitutions on the crystalline phase, microstructure and magnetic properties of hexagonal ferrites with a composition of $3(Ba_{1-x}Bi_xO)$•$2(Co_{1-y}Cu_yO)$•$12(Fe_{2\text{-}(x/4)}Zn_{(x/4)}O_3)$. The relationships between the chemical compositions, crystalline phases, micro-structures and magnetic properties of Co_2Z ferrite are presented.

2. Experimental procedures

The hexagonal ferrites with composition of $3(Ba_{1-x}Bi_xO)$•$2(Co_{1-y}Cu_yO)$•$12(Fe_{2\text{-}(x/4)}Zn_{(x/4)}O_3)$ were prepared from reagent-grade $BaCO_3$, Bi_2O_3, $SrCO_3$, Co_3O_4, CuO, ZnO and Fe_2O_3, which were mixed and then calcined at 1250 °C for 2 h. The calcined powders were milled for 48 h using YTZ balls. The powders were dried in an oven with PVA then added for granulation. The powders were dry-pressed at 110 MPa into toroidal bodies. These specimens were then debindered at 500 °C and sintered at 1300 °C for 2 h. The densities of the sintered samples were determined using the Archimedean method. The crystalline phase evolution was characterized using an X-ray diffractometer with a Cu Kα (Siemens, D5000). The microstructures of the sintered samples were examined using scanning electron microscopy (SEM) (Hitachi, S-4100) and field emission transmission electron microscope (FEI, Tecnai G2 F20). Energy dispersive spectroscopy (EDS) was used to compare the grain and grain boundary compositions. The initial permeability was measured using an LCR meter (YHP 4291B, YHP Co., Ltd.) from 1 MHz to 1.8 GHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples with $x = 0$ and $y = 0.2$–0.3 after calcination at 1250 °C. The Co_2Y phase was accompanied by a significant BaM phase as the main phases in the sample without Bi and Zn addition. A minor Co_2Z phase was observed only in $y = 0.3$, suggesting that the increase in Cu addition can enhance Co_2Z phase formation. This is in accordance with the observation of Wang et al. [7] who reported that the Co_2Z phase formation temperature can be reduced by partial substitution of Co with Cu ions in $Ba_3Co_{2-x}Cu_xFe_{24}O_{41}$. In the case of the sample with $x = 0.1$ and $y = 0$, the Co_2Z phase was predominant with a small amount of Y and U phase. This indicates that the addition of Bi and Zn can significantly promote Z phase formation. As the y value (Cu addition) increased from 0 to 0.2 and 0.3 for the samples with $x = 0.1$–0.2, the Y phase was not detected and only U and W phases were observed as the secondary phases accompanied with the decrease in Co_2Z phase (Figs. 2 and 3). This is supported by the finding observed by Kračunovska and Töpfer [8] who reported that the decomposition of Co_2Z phase at high temperature led to the appearance of W phase as minor component besides Z phase, implying that the

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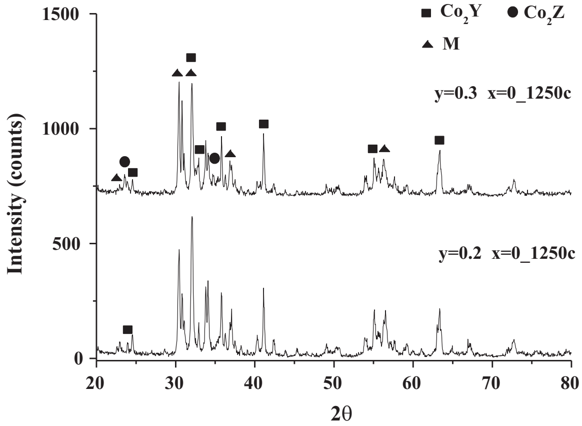

Fig. 1. XRD patterns of the samples with $x = 0$ and $y = 0.2$–0.3 after calcination at 1250 °C.

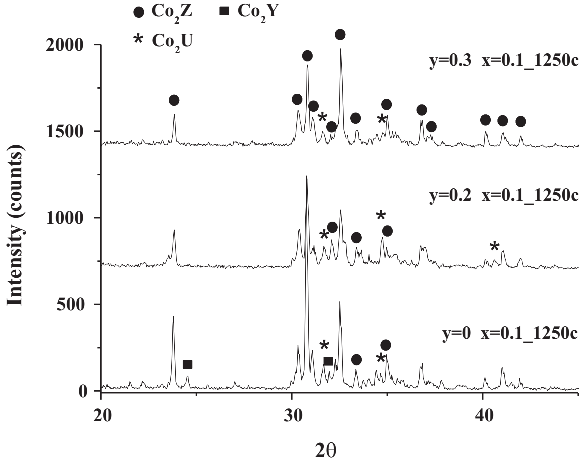

Fig. 2. XRD patterns of the samples with $x = 0.1$ and $y = 0$–0.3 after calcination at 1250 °C.

temperature stable range of the Co$_2$Z phase was narrowed by the Cu substitution. Table 1 is a summary of the crystalline phases for the samples calcined at 1250 °C for 2 h.

Table 2 is a summary of the crystalline phases for samples sintered at 1300 °C for 2 h. For the sample with $x = 0$ after sintering, the main crystalline phases changed from M + Y (after calcination) to Z + Y and Z phase increased as y increased from 0.2 to 0.3

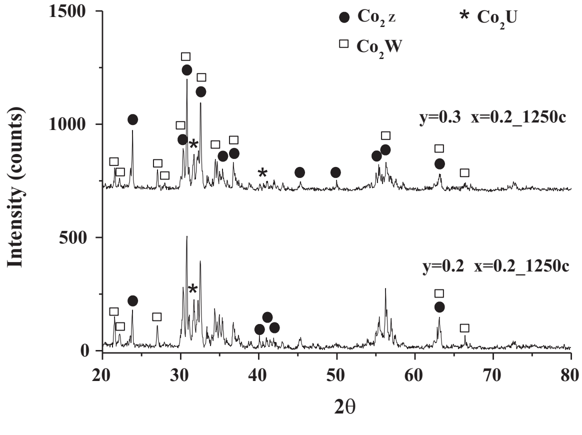

Fig. 3. XRD patterns of the samples with $x = 0.2$ and $y = 0.2$–0.3 after calcination at 1250 °C.

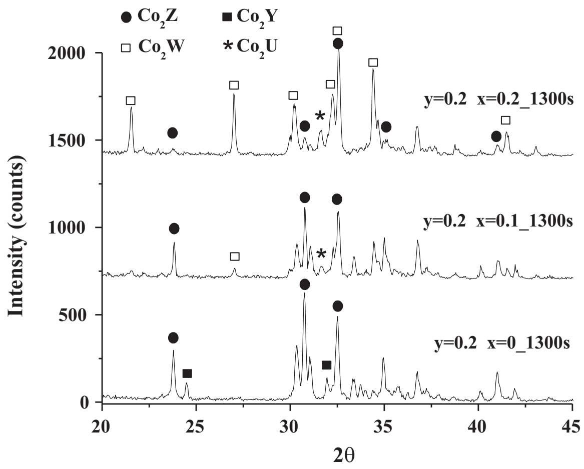

Fig. 4. XRD patterns of the samples with $y = 0.2$ and $x = 0$–0.2 after sintering at 1300 °C for 2 h.

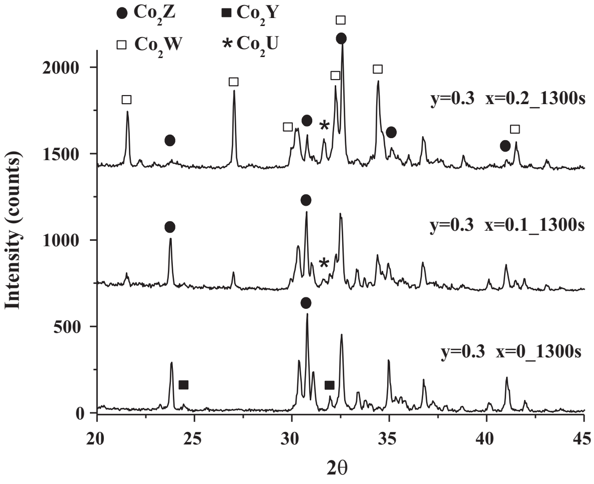

Fig. 5. XRD patterns of the samples with $y = 0.3$ and $x = 0$–0.2 after sintering at 1300 °C for 2 h.

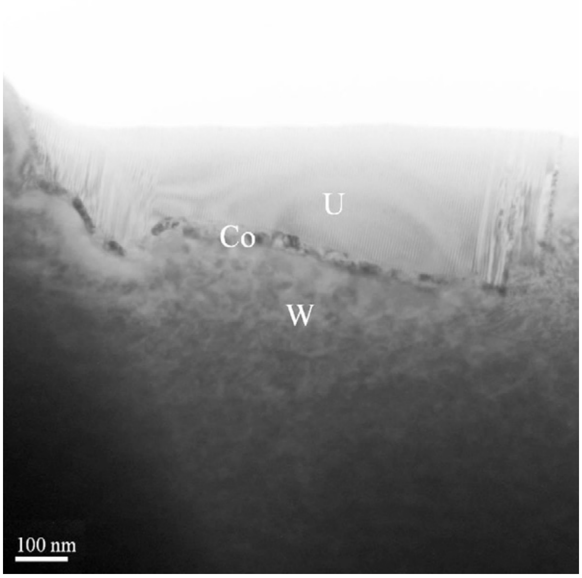

Fig. 6. TEM micrograph of the sample with $x = 0.2$ and $y = 0.2$ sintered at 1300 °C.

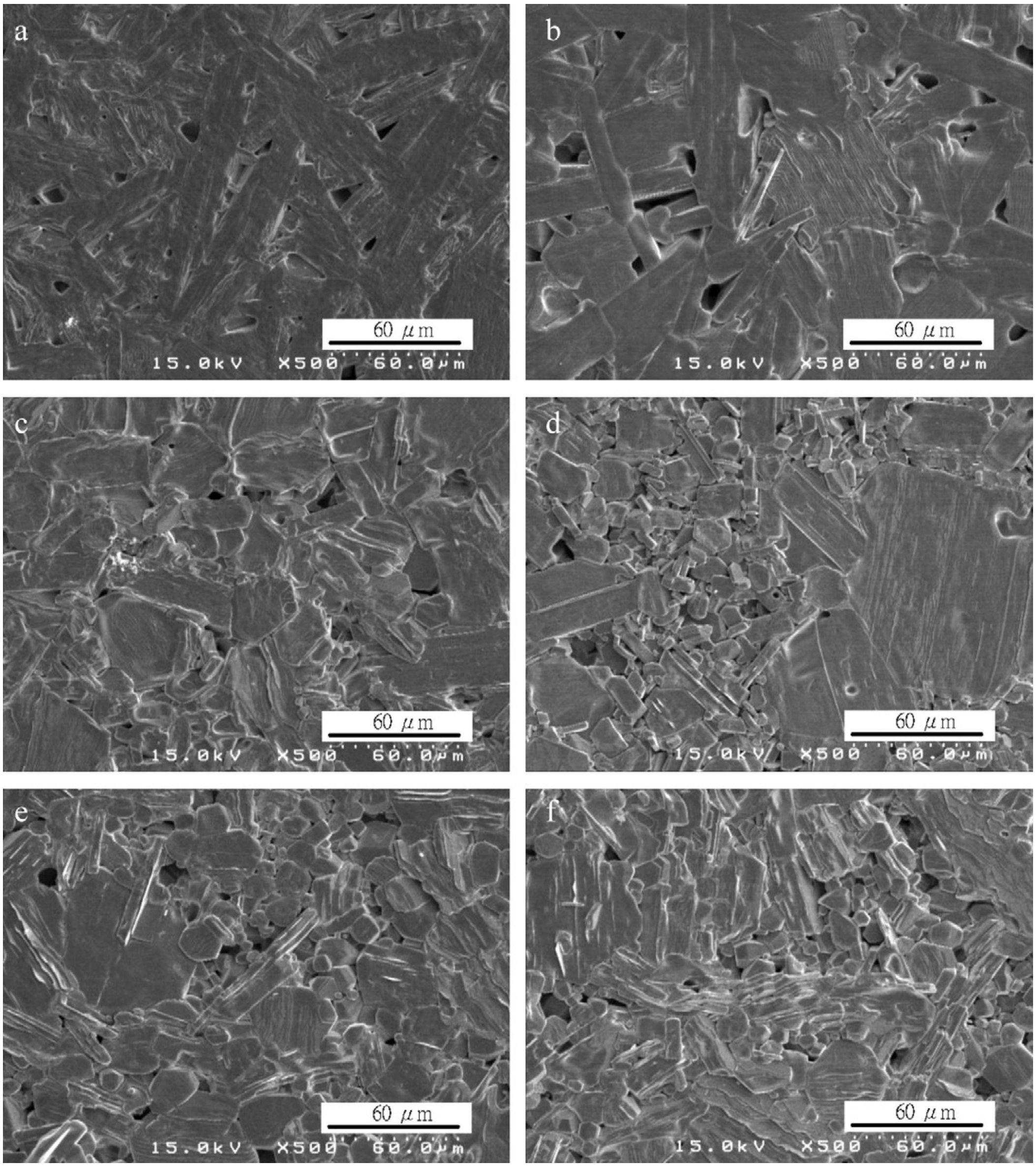

Fig. 7. SEM micrographs of the samples sintered at 1300 °C (a) $x=0$, $y=0.2$; (b) $x=0$, $y=0.3$; (c) $x=0.1$, $y=0.2$; (d) $x=0.1$, $y=0.3$; (e) $x=0.2$, $y=0.2$; (f) $x=0.2$, $y=0.3$.

(Figs. 4 and 5). As the x value increased from 0 to 0.1 and 0.2, the Z + W phases and W phase became the main crystalline phases, respectively (Figs. 4 and 5), suggesting that the addition of Bi and Zn may promote Z phase decomposition, leading to the formation of W phase.

Table 1
Summary of the crystalline phases for the samples calcined at 1250 °C for 2 h.

y value	$x=0$	$x=0.1$	$x=0.2$
0.2	M + Y	Z+ (U)	Z + W+ (U)
0.3	M + Y+ (Z)	Z+ (U)	Z + W+ (U)

( ): minor

Table 2
Summary of the crystalline phases for samples sintered at 1300 °C for 2 h.

y value	$x=0$	$x=0.1$	$x=0.2$
$y=0.2$	Z + Y+ <M>	Z + W+ (U)	W + (Z + U)
$y=0.3$	Z+ <Y + M>	Z + W+ (Y + U)	W + (Z + U)

( ): minor; < >: trace.

Fig. 6 shows a TEM micrograph of the sample with $x=0.2$ and $y=0.2$ sintered at 1300 °C. Table 3 shows the quantitative analysis of the chemical compositions corresponding to Fig. 6 from EDS analysis. These results are based on the XRD, EDS and TEM analyses, indicating that Co-rich ferrites segregated along the interface between the U and W phases. The Bi content in the Co-rich ferrites, U and W phases were all very low, which may be due to the vaporization of Bi ions during sintering. Therefore, the Z phase may be triggered to decompose into U and W phases resulting from the

Table 3
Quantitative analysis of the chemical compositions corresponding to Fig. 6 from EDS analysis.

Element	U region (at%)	Co region (at%)	W region (at%)
Ba	8.910	2.748	5.117
Bi	0.165	0.392	0.104
Co	1.927	52.122	6.210
Cu	1.097	1.854	1.432
Zn	0.850	0.546	2.446
Fe	87.048	42.334	84.689

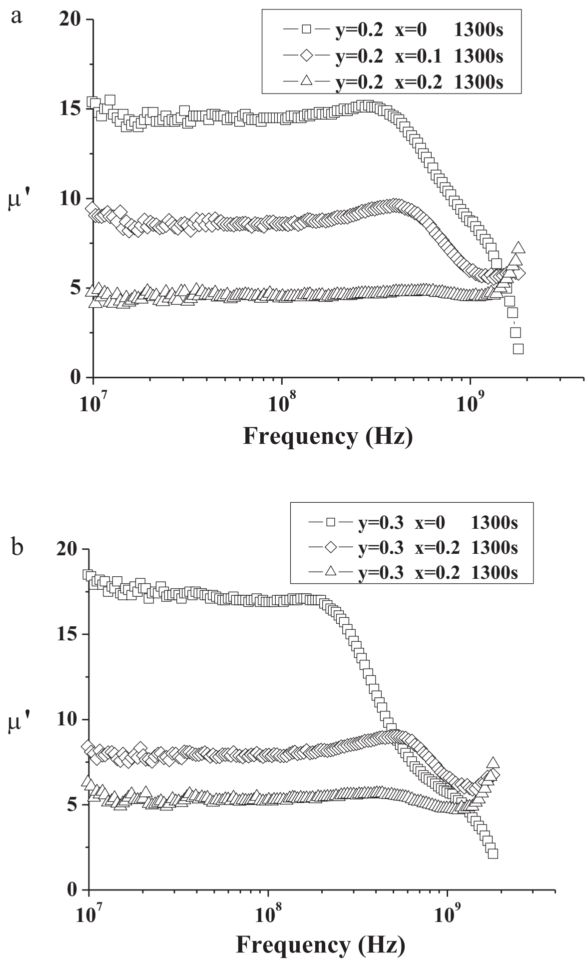

Fig. 8. Frequency dependence of initial permeability for the samples sintered at 1300 °C (a) $y = 0.2$ and (b) $y = 0.3$.

evaporation of Bi and segregation of Co-rich ferrites at high sintering temperature for the samples with large amounts of Bi and Zn.

Fig. 7 shows SEM micrographs of the samples sintered at 1300 °C. It indicates that the grain size increased slightly with increasing Cu substitution (y value) and the grain shape changed from rod-like to hexagonal plate as x increased from 0 to 0.1 and 0.2 due to the main crystalline phase changing from Z phase to W phase. This is in good agreement with the fact that Kračunovska and Töpfer [9] found Co_2Z grains with preferential growth in one direction and with the inclusion of both Y- and W-type ferrites for the $Ba_3Co_2Fe_{24}O_{41}$ ceramics after sintering at 1330 °C for 4 h. No significant difference in density among the samples was observed based on the SEM micrographs. The densities of the samples with different compositions sintered at 1300 °C were all between 4.9 and 5.0 g/cm^3.

The permeability (μ) of hexagonal polycrystalline ferrites can be expressed by [10]

$$\mu - 1 = \frac{8\pi M_s}{3H_a}$$

where M_s is the saturation magnetization, H_a is the anisotropic field. Zn substitution will promote the permeability through increasing M_s and decreasing H_a. It is well known that the initial permeability of hexagonal polycrystalline ferrite depends mainly on the crystalline phase and the initial permeability of the Z phase is higher than that for the U or W phase [11]. The substitution of Bi may degrade the permeability due to the promotion of Z phase decomposition into U and W phases. The effect of Zn and Bi on the magnetic properties is competitive in the Bi–Zn co-doped hexagonal ferrites [12]. Fig. 8 shows the frequency dependence of initial permeability for the samples sintered at 1300 °C. As the Cu substitution increased from $y = 0.2$ to 0.3, the initial permeability increased due to the increase in grain size (Fig. 7) [7]. For the samples with $y = 0.2$ and 0.3, the initial permeability decreased with increasing x value. The amount of Z phase decreased with the increase in x value, as shown in Table 2, suggesting that the initial permeability of the samples co-doped with Cu–Bi–Zn was determined using the crystalline phase.

4. Conclusions

(1) Cu and Bi substitutions can enhance Co_2Z phase formation.
(2) The Z phase may be triggered to decompose into U and W phases resulting from the evaporation of Bi and segregation of Co-rich ferrites at high sintering temperature for samples with large amounts of Bi and Zn.
(3) The initial permeability for samples co-doped with Cu–Bi–Zn was determined using the crystalline phase. The initial permeability decreased with increasing x value because Bi substitution promoted Z phase decomposition into U and W phases.

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