The microstructure and magnetic properties of Mg–Cu substituted W-type barium hexaferrites

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The W-type barium hexagonal ferrites BaMg2-xCu,xFe16O27, 0 \leq x \leq 1.4, were prepared by the ceramics process at 1270°C for 3 h, respectively. The X-ray diffraction (XRD) results revealed that the ferrites were single W-phase as Cu content (x) \leq 0.6, while the second phase (α-Fe2O3) began to occur when Cu content (x) \geq 0.8. Permanent magnetic properties of the magnets were measured by a B–H hysteresis curve measurements. The effects of the Cu content (x) on the permanent magnetic properties of the magnets were studied systematically. As a result, the remanence (Br) first increased with the increase of Cu content (x) and reached the maximum value of 402.4 mT at x = 0.6, then decreased when x continued to increase. Moreover, the intrinsic coercivity (Hc), magnetic induction coercivity (Hci) and maximum energy product ([BH]max) decreased obviously with the x increased.

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1. Introduction

The hexagonal ferrite s are magnetic ceramic materials and play an important role in many technological and industrial fields.1) The family of hexagonal ferrites can be classified on the basis of different chemical compositions and crystal structures. They are subdivided into six fundamental types: M, W, Y, X, Z and U.2) It has been reported that, the molecular unit of W-type barium hexagonal ferrites (BaMe2Fe16O27) is made of one R block and two S blocks. Meanwhile, the Fe3+ and Me2+ are much smaller ions and can occupy three different kinds of sites (A tetrahedral site, B octahedral site, the Lindquist Site, BaMg2- Me4+, Mn4+, etc. Recently, some success has been achieved with Cu substituted W-type barium hexaferrites (BaMg2-xCu,xFe16O27) with a composition of BaMg2-xCu,xFe16O27 (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4) were prepared by using the ceramics process. The starting materials used in the present study were BaCO3 (99% purity), Fe2O3 (99% purity), CuO (98% purity) and MgO (98% purity). The mixed powders of these starting materials were milled in water for 6 h with an angular velocity of 80 rpm and a ball-to-power weight ratio of 12:1. The mixtures of magnetic powders were dried at 393 K in a oven and calcined at a temperature of 1270°C in a muffle furnace for 2 h. Then, the mixtures were crushed in a vibration mill and wet-milled with additives (0.5 wt% CaCO3 + 1.0 wt% SrCO3 + 0.5 wt% SiO2 + 1.0 wt% Cr2O3 + 0.7 wt% H3BO3) for 2 h using a ball mill. Followingly, the calcined materials were pressed for cylinder magnets under 300 MPa with the condition of oriented magnetic field and sintered in 1200°C for 2 h.

The phase purity and composition of magnet powders were checked by X-ray diffraction (Cu-Kα). The microstructure of the magnets was observed using the scanning electron microscope (SEM) (model HITACHI S-4800). The permanent magnetic properties of the magnets were measured by applying B–H hysteresis curve measurements (Model MATS-2000, National Institute of Metrology of China).

2. Experimental procedures

W-type barium hexaferrites with a composition of BaMg2-xCu,xFe16O27 (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4) were prepared by using the ceramics process. The starting materials used in the present study were BaCO3 (99% industry purity), CuO (99% purity), Fe2O3 (98% purity) and MgO (98% purity). The mixed powders of these starting materials were milled in water for 6 h with an angular velocity of 80 rpm and a ball-to-power weight ratio of 12:1. The mixtures of magnetic powders were dried at 393 K in a oven and calcined at a temperature of 1270°C in a muffle furnace for 2 h. Then, the mixtures were crushed in a vibration mill and wet-milled with additives (0.5 wt% CaCO3 + 1.0 wt% SrCO3 + 0.5 wt% SiO2 + 1.0 wt% Cr2O3 + 0.7 wt% H3BO3) for 2 h using a ball mill. Followingly, the calcined materials were pressed for cylinder magnets under 300 MPa with the condition of oriented magnetic field and sintered in 1200°C for 2 h.

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3. Results and discussion

3.1 XRD analysis

Figure 1 shows the XRD patterns of BaMg2-xCu,xFe16O27 magnetic powders with different Cu content (x) from 0 to 1.4. The observed phase was identified with the position (2θ) and intensity of the X-ray diffraction lines of Lindquist Site, BaMg2-xCu,xFe16O27. JCPDS Card No. 78-0134. It can be seen from Fig. 1 that the ferrites are single W-phase as x \leq 0.6, however, the second phase (α-Fe2O3) is present when x \geq 0.8. This can be
attributed to some Cu$^{2+}$ ions enter into Fe$^{3+}$ sites and a portion of Fe$^{3+}$ forms Fe$_2$O$_3$.

The lattice constants $a$ and $c$ are calculated from the value of the interplanar spaces $d_{hkl}$ corresponding to $(110)$ peaks and $(116)$ peaks according to the following equation:

$$ d_{hkl} = \frac{h^2 + k^2 + l^2}{a^2 + c^2} \frac{1}{2}^{1/2} $$

The lattice constants $a$, $c$, and $c/a$ of the hexagonal ferrites BaMg$_2_x$Cu$_{x}$Fe$_{16}$O$_{27}$ magnetic powders with different Cu contents ($x$) from 0.0 to 1.6 are presented in Table 1. From it we can see that the lattice constant $a$ increases with the increase of Cu content ($x$), whereas the lattice constant $c$ decreases significantly.

In addition, Cu$^{2+}$ ions occupy B octahedral sites in W-type hexaferrites has been reported by D. M. Hemeda. The increase in $a$ may be due to the Cu$^{2+}$ ions substitute Mg$^{2+}$ ions in B sites and the radius of Cu$^{2+}$ (0.72 Å) is bigger than that of Mg$^{2+}$ (0.65 Å). The variation of lattice constant $c$ with $x$ is related to the decrease of Mg$^{2+}$ ions at A sites which decreasing the distance between the R block and S block in the direction of $c$-axis.

### 3.2 SEM analysis

Figure 2 and Fig. 3 show two typical scanning electron microscopy (SEM) morphologies of the BaMg$_{1.4}$Cu$_{0.6}$Fe$_{16}$O$_{27}$ magnet with different directions. Figure 2 reveals the morphology perpendicular to the pressing direction. It can be clearly observed from Fig. 2 that the magnet has formed the hexagonal structure, and has a uniform particle size ($D$) about 3 to 4 μm. Figure 3 reveals the morphology parallel to the pressing direction. From it we can confirm that the magnet has a platelet-like structure.

### 3.3 Magnetic properties

Figure 4 illustrates the effect of the Cu content ($x$) on the remanence ($B_r$) of the BaMg$_{2-x}$Cu$_x$Fe$_{16}$O$_{27}$ ($x = 0$–1.4) magnets. It can be seen that the $B_r$ firstly increases with the Cu content ($x$) increases and reaches the maximum value (402.4 mT) at $x = 0.06$, then decreases obviously when $x$ continues to increase. The
magnetic moment of Cu$^{2+}$ and Fe$^{3+}$ ions are 1.3 and 5 µB, while the Mg$^{2+}$ ions is non-magnetic. When $x$ increases from 0 to 0.6, the amount of Cu$^{2+}$ ions increases by substituting Mg$^{2+}$ at B octahedral sites, leading an increase in the net magnetic moment of the magnets. This increase of the net magnetic moment promotes the $B_t$ of magnets. White and Herman have reported that the substitution of Cu$^{2+}$ ions at B sites can leads to the Fe$^{3+}$ ions are forced to migrate from B to A sites. In addition, the decreasing of Mg$^{2+}$ content increases the amount of Fe$^{3+}$ ions at A sites and the magnetic moment of Fe$^{3+}$ (5 µB) is greater than Cu$^{2+}$ (1.3 µB). Therefore, as the $x$ increases from 0.6 to 1.4, the increase in contribution of Fe$^{3+}$ at A sites causes a decrease of net magnetic moment, which decreases the $B_t$ of magnets.

**Figure 5** indicates that the variation of the intrinsic coercivity ($H_{ci}$) and magnetic induction coercivity ($H_{cb}$) of BaMg$_{2-x}$Cu$_x$Fe$_{16}$O$_{27}$ magnets with different Cu contents ($x$). It can be observed that the $H_{ci}$ and $H_{cb}$ decrease with the increase of $x$. The observed decrease of $H_{ci}$ and $H_{cb}$ can be explained according to the cation distribution and exchange interaction. It is well known that the A–B interaction are stronger than A–A and B–B interactions, meanwhile, the Fe–O–Fe superexchange interaction are stronger than Fe–O–Cu superexchange interaction. The substitution of Mg$^{2+}$ by Cu$^{2+}$ at B sites leads to the Fe$^{3+}$ ions migrate from B to A sites, which weakened the strength of the A–B interaction. Therefore, as Cu content ($x$) increases, the $H_{ci}$ and $H_{cb}$ decreases. This is in agreement with the report by Eckelt and Bottger.

The variation of the maximum energy product ($\{(BH)_{max}\}$) of the BaMg$_{2-x}$Cu$_x$Fe$_{16}$O$_{27}$ magnets with different Cu content ($x$) is represented in Fig. 4. From it we can know that the $\{(BH)_{max}\}$ decreases from 31.4 kJ/m$^3$ ($x = 0$) to 14.6 kJ/m$^3$ ($x = 1.4$), which is decreased by 53.5%. This can be attributed to the variations of the remanence ($B_r$) and intrinsic coercivity ($H_{ci}$). As shown, the maximum energy product ($\{(BH)_{max}\}$) is the maximum area in the second quadrant of the hysteresis loop, which value is related to the multiplied by $B_t$ and $H_{ci}$. Hence, from Figs. 4–5 we can know that, the product of $B_t$ and $H_{ci}$ decreases, which leads to the decrease in $\{(BH)_{max}\}$.

**Figure 6** shows that two typical demagnetization curve of the BaMg$_{2-x}$Cu$_x$Fe$_{16}$O$_{27}$ magnets with a Cu content of (a) $x = 0.0$ and (b) $x = 0.6$, respectively. As can be seen from Fig. 6(a), the magnet with $x = 0.0$ indicates the magnetic properties, including the remanence ($B_r = 371.1$ kA/m), intrinsic coercivity ($H_{ci} = 181.7$ kA/m), magnetic induction coercivity ($H_{cb} = 176.4$ kA/m) and maximum energy product ($\{(BH)_{max}\} = 31.4$ kJ/m$^3$). As can be seen from Fig. 6(b), the magnet with $x = 0.6$ exhibits the magnetic properties, including the remanence ($B_r = 402.4$ kA/m), intrinsic coercivity ($H_{ci} = 146.7$ kA/m), magnetic induction coercivity ($H_{cb} = 136.6$ kA/m) and maximum energy product ($\{(BH)_{max}\} = 27.1$ kJ/m$^3$).

**4. Conclusions**

The W-type barium hexaferrites BaMg$_{2-x}$Cu$_x$Fe$_{16}$O$_{27}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4$) were prepared by the ceramics process with calcined at 1270°C for 3 h, respectively. The XRD and SEM showed that all the samples were typical W-type hexagonal structure, the second phase (α-Fe$_2$O$_3$) started to present...
when \( x \geq 0.8 \). The lattice constants \( a \) and \( c \) were calculated by using X-ray diffraction. It indicated that the lattice constant \( a \), increased with the increase in Cu content \( (x) \), although the lattice constant \( c \) deceased.

The permanent magnetic properties of the BaMg\(_{2}\text{Cu}_{x}\text{Fe}_{16}\text{O}_{27}\) \((x = 0–1.4)\) magnets were obtained by a \( B-H \) hysteresis curve measurements. The intrinsic coercivity \( (H_c) \), magnetic induction coercivity \( (H_{cb}) \) and maximum energy product \( (BH)_{\text{max}} \) of magnets decreased with the Cu content \( (x) \) increased. However, the remanence \( (B_r) \) of the magnets increased at first, reached to the maximum value \((402.4 \text{ mT})\) at \( x = 0.6 \) and then decreased. Meanwhile, at \( x = 0.6 \), other magnetic properties of the magnets were obtained, including intrinsic coercivity \( (H_{cj}) = 146.7 \text{ kA/m} \), coercivity magnetic induction \( (H_{cb}) = 136.6 \text{ kA/m} \) and maximum energy product \( (BH)_{\text{max}} = 27.1 \text{ kJ/m}^3 \).

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