

Impacts of heat treatment on the microstructure and magnetic properties of LaPr-Co substituted M-type CaSr hexaferrite

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The M-type hexaferrite $\text{Ca}_{0.4}\text{Sr}_{0.3}(\text{La}_{0.8}\text{Pr}_{0.2})_{0.3}\text{Fe}_{11.76}\text{Co}_{0.24}\text{O}_{19}$ was synthesized by the solid-state reaction method. The effects of calcination temperature and sintering temperature on the microstructural and magnetic properties have been carefully investigated. The X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and a permanent magnetic measuring system were used to investigate the microstructure and magnetic properties of the samples. Single-phase hexaferrite patterns are observed for the hexaferrite magnetic powders at different temperatures from 1210 to 1270 °C for 2 hrs. The FE-SEM images of the magnets show that the hexagonal structures have been formed in the magnets, and the grains in the magnets are distributed evenly. With the increase of calcination temperature, the remanence (B_r) and maximum energy product $[(BH)_{\max}]$ increase from 1210 °C to 1270 °C, while the magnetic induction coercivity (H_{cb}) and intrinsic coercivity (H_{ci}) increase from 1210 °C to 1250 °C, and then decrease when the calcination temperature ≥ 1250 °C. With the increase of sintering temperature, the remanence (B_r) and maximum energy product $[(BH)_{\max}]$ increase from 1180 to 1200 °C, while the magnetic induction coercivity (H_{cb}) and intrinsic coercivity (H_{ci}) increase from 1180 to 1195 °C, and then decrease when the calcination temperature ≥ 1195 °C.

Key words: M-type hexaferrite, Calcination temperature, Sintering temperature, X-ray diffraction, Magnetic properties.

Introduction

M-type hexaferrites are one of the most utilized magnetic materials in permanent magnets due to their large magnetocrystalline anisotropy, moderate energy product, high Curie temperature, excellent chemical stability, high corrosion, high density and low cost [1]. For M-type hexaferrites, it is well known that Fe^{3+} ions occupy five distinct sites such as one tetrahedral site ($4f_1$), three octahedral ($2a$, $12k$ and $4f_2$) and one bipyramidal site ($2b$) [2].

It is an effective method to modify the magnetic properties of M-type hexaferrites by the ion substitution. There are two effective methods for ion substitution. The first one is the single ion substitution for Sr^{2+} or Ba^{2+} ions [3] or Fe^{3+} ions [4]. Due to their similar radii, rare earth metal ions, such as La^{3+} [3], Nd^{3+} [5], Sm^{3+} [6], and Pr^{3+} [7], prefer to substitute partly Sr^{2+} or Ba^{2+} ions. The transition metal ions, such as Cr^{3+} [4], Co^{2+} [8], Mn^{3+} [9], Al^{3+} [10], and Bi^{3+} [11], prefer to substitute Fe^{3+} ions [4, 8–11]. The second one is ion combinations, such as $\text{La}^{3+}\text{-Zn}^{2+}$ [12], $\text{La}^{3+}\text{-Cu}^{2+}$ [13], $\text{La}^{3+}\text{-Co}^{2+}$ [14], Zr-Mn [15], $\text{Mn}^{2+}\text{-Zn}^{2+}$ [16], and $\text{Ce}^{3+}\text{-Co}^{2+}$ [17].

It has been reported that the microstructure and magnetic properties of the M-type hexaferrites are influenced by the heat treatment temperatures [18–20]. In this work, La^{3+} and Pr^{3+} ions are chosen to substitute Sr^{2+} ions, and Co^{2+} ions are chosen to substitute the Fe^{3+} ions. The LaPr-Co substituted M-type CaSr hexaferrite has been synthesized by the solid-state reaction method. We have carefully investigated the effects of calcination temperature and sintering temperature on the microstructural and magnetic properties.

Experimental Procedure

The M-type hexaferrite $\text{Ca}_{0.4}\text{Sr}_{0.3}(\text{La}_{0.8}\text{Pr}_{0.2})_{0.3}\text{Fe}_{11.76}\text{Co}_{0.24}\text{O}_{19}$ was prepared by the solid-state reaction method. The starting powders of CaCO_3 , SrCO_3 , La_2O_3 , Pr_6O_{11} , Fe_2O_3 and CoO , all 99% pure, were weighted in accordance with the ratios of the chemical composition. The starting powders were wet-mixed in a ball mill at a rotate speed of 80 rpm for 8 hrs. After that, the mixed powders were dried in a drying oven in the air, and then calcined in a muffle furnace in air. Next, the calcined powders were shattered to particles by a vibration mill, and then wet-milled with suitable additives (0.6 wt% CaCO_3 , 0.3 wt % SrCO_3 , 0.2 wt % SiO_2 , 0.2 wt% $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_7)_2$) for 16 hrs in a ball-mill. At the final step, the finely milled slurry was pressed into cylindrical pellets under 310 MPa in the magnetic

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field of 800 kA/m. The compacted pellets were sintered in a muffle furnace in air. For the samples to study the influence of calcination temperature, the mixed powders were firstly calcined at 1210 °C, 1230 °C, 1250 °C, and 1270 °C for 2 hrs, respectively, and then all the compacted pellets were sintered at 1185 °C for 1.5 hrs. For the samples to study the influence of sintering temperature, all the mixed powders were firstly calcined at 1270 °C for 2 hrs, and then the compacted pellets were sintered at 1180 °C, 1185 °C, 1190 °C, 1195 °C, and 1200 °C for 1.5 hrs, respectively.

The phase compositions and structure of the magnetic powders were identified by using a PANalytical X'Pert Pro diffractometer in continuous mode with Cu K α radiation in the range of $2\theta = 20\text{--}80^\circ$. The images of the surface of the sintered pellets were observed by FESEM (Hitachi S-4800, Japan). Magnetic properties of the sintered pellets at room temperature were measured by a permanent magnetic measuring system (NIM-2000HF, made by the National Institute of Metrology of China).

Results and Discussions

XRD patterns for the magnetic powders calcined at different temperatures from 1210 to 1270 °C for 2 hrs are shown in Fig. 1. The diffraction peaks of the hexaferrite phase are indexed on the basis of hexagonal magnetoplumbite crystal structure with space group $P6_3/mmc$ (JCPDS card no. 80-1198). Single-phase hexaferrite patterns are observed for the hexaferrite magnetic powders at different temperatures from 1210 to 1270 °C for 2 hrs.

The lattice constants c and a are calculated from the XRD data by using the following relation [21]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \times \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

where d_{hkl} is the inter-planer spacing value, and h , k and l are corresponding Miller indices. Fig. 2 shows the change of lattice parameters c and a of the magnetic powders as a function of calcination temperature. It is clear that the lattice parameter c first decreases with the calcination temperature increases from 1210 °C to 1250 °C, and when the calcination temperature ≥ 1250 °C, the lattice parameter c increases. While compared with the lattice parameter c , the variation of

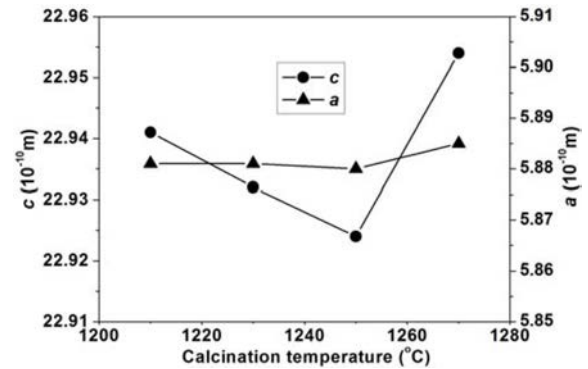


Fig. 2. Lattice parameters c and a of the magnetic powders as a function of calcination temperature.

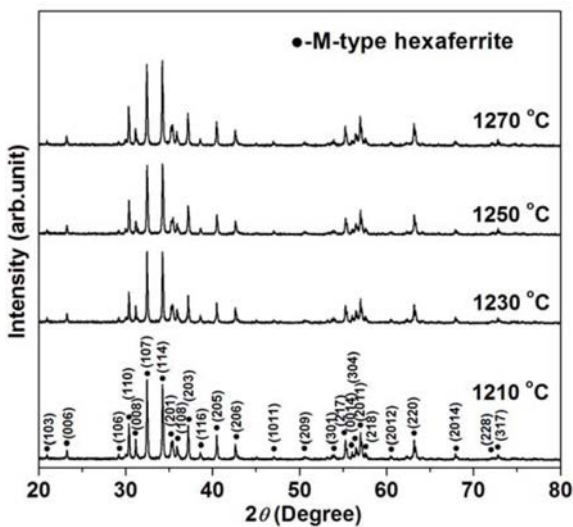


Fig. 1. X-ray diffraction patterns for the magnetic powders calcined at various temperatures from 1210 to 1270 °C for 2 hrs.

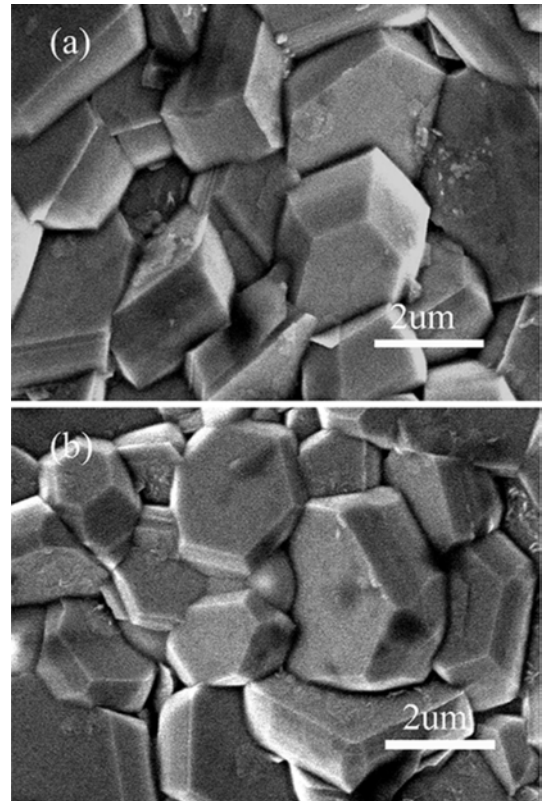


Fig. 3. Representative FESEM micrographs of the magnets made from the magnetic powders calcined at (a) 1210 °C, and (b) 1250 °C for 2 hrs, and sintered at 1185 °C for 1.5 hrs.

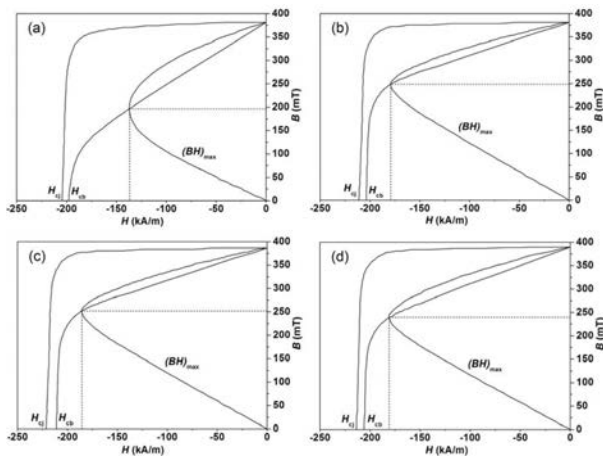


Fig. 4. Demagnetizing curves for the magnets made from the magnetic powders calcined at (a) 1210 °C, (b) 1230 °C, (c) 1250 °C, and (d) 1270 °C for 2 hrs, and sintered at 1185 °C for 1.5 hrs.

Table 1. Magnetic properties of the magnets made from the magnetic powders calcined at (a) 1210 °C, (b) 1230 °C, (c) 1250 °C, and (d) 1270 °C for 2 hrs and sintered at 1185 °C for 1.5 hrs.

Calcination temperature (°C)	B_r (mT)	H_{cb} (kA/m)	H_{cj} (kA/m)	$(BH)_{max}$ (kJ/m ³)
1210	381.4	197.8	204.5	27.5
1230	384.7	203.6	211.2	28.0
1250	386.5	210.9	221.6	28.3
1270	389.7	205.9	213.7	28.7

the lattice constant a is not substantial in the calcination temperature range.

Fig. 3(a) and 3(b) show the representative FE-SEM micrographs of the magnets made from the magnetic powders calcined at 1210 and 1250 °C, respectively, and sintered at 1190 °C. As seen from Fig. 3, the hexagonal structures have been formed in the magnets, and the grains in the magnets are distributed evenly.

Fig. 4 shows the demagnetizing curves for the magnets made from the magnetic powders calcined at 1210 °C, 1230 °C, 1250 °C, and 1270 °C for 2 h, and sintered at 1185 °C for 1.5 hrs. The remanence (B_r), intrinsic coercivity (H_{cj}), magnetic induction coersivity (H_{cb}) and maximum energy product [$(BH)_{max}$] were extracted from the demagnetizing curves and listed in Table 1. Fig. 5 and Fig. 6 show the influence of calcination temperature on the remanence (B_r) and maximum energy product [$(BH)_{max}$], magnetic induction coersivity (H_{cb}) and intrinsic coercivity (H_{cj}) of the magnets sintered at 1185 °C, respectively. As seen from Fig. 5, it is clear that with the increase of calcination temperature, the value of B_r increases from 381.4 mT at 1210 °C to 389.7 mT at 1270 °C. In the basic structure of M-type hexaferrite, the Fe^{3+} ions are distributed on

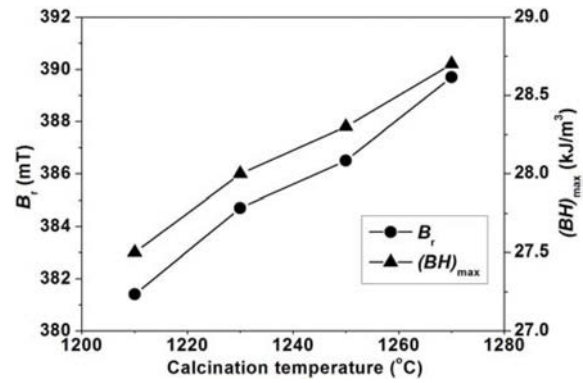


Fig. 5. Influence of calcination temperature on B_r and $(BH)_{max}$ of the magnets sintered at 1185 °C for 1.5 h.

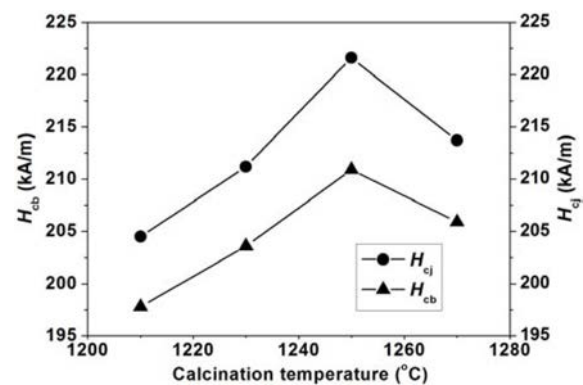


Fig. 6. Influence of calcination temperature on H_{cj} and H_{cb} of the magnets sintered at 1185 °C for 1.5 hrs.

five different interstitial sites: one bipyramidal site 2b (upward spin), one tetrahedral site 4f₁ (downward spin), three octahedral sites 2a (upward spin), 4f₂ (downward spin), 12k (upward spin). The magnetic moments of Fe^{3+} ions in the hexagonal ferrite are arranged collinearly because of super-exchange interaction. Tenaud et al. [22] have reported that in the La-Co substituted M-type strontium ferrites, most of Co^{2+} is substituted for Fe^{3+} in the octahedral 2a and 4f₂ sites, and a valence change of some Fe^{3+} to Fe^{2+} appears at 2a sites. If the amount of Fe^{3+} ions that change into Fe^{2+} ions is x , the stoichiometric formula will be changed into $Ca_{0.4}Sr_{0.3}(La_{0.8}Pr_{0.2})_{0.3}(Fe^{3+})_{11.76-x}(Fe^{2+})_xCo_{0.24}O_{19}$. As the calcination temperature increases from 1210 to 1270 °C, the increase in B_r may be attributed to the enhancement of Fe^{3+} -O- Fe^{3+} super-exchange interaction between 2b and 12k sites.

From Fig. 6, it is observed that the increase of calcination temperature, H_{cj} and H_{cb} increase from 197.8 and 204.5 kA/m at 1210 °C to 210.6 and 221.6 kA/m at 1250 °C, respectively, and then begin to decrease when the calcination temperature ≥ 1250 °C. The variation of the coercivity has the same trend as that reported by Ketov et al. [23] and Nga et al. [24]. For the magnets, further grain growth will not occur during sintering because the coarsening of grain has already taken place at higher calcination temperature

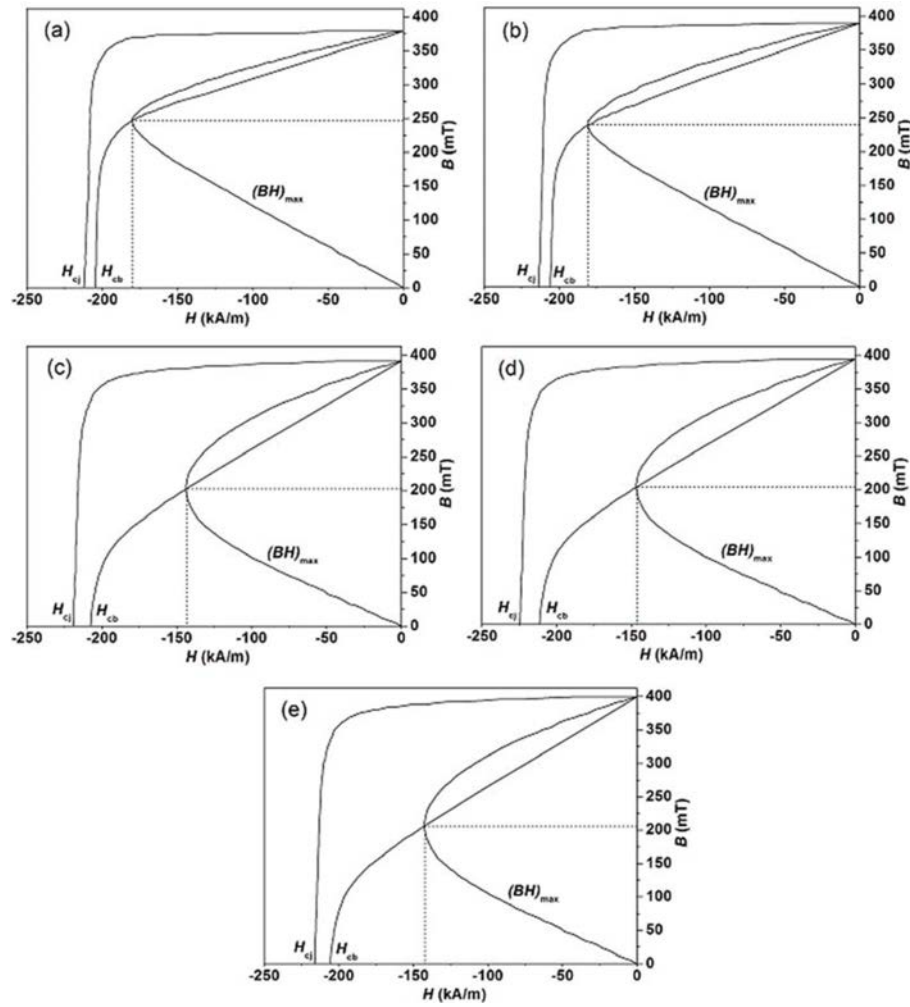


Fig. 7. Demagnetizing curves for the magnets made from the magnetic powders calcined at 1270 °C for 2 hrs and sintered at (a) 1180 °C, (b) 1185 °C, (c) 1190 °C, (d) 1195 °C, and (e) 1200 °C for 1.5 hrs.

Table 2. Magnetic properties of the magnets made from the magnetic powders calcined at 1270 °C for 2 hrs and sintered at (a) 1180 °C, (b) 1185 °C, (c) 1190 °C, (d) 1195 °C, and (e) 1200 °C for 1.5 hrs.

Sintering temperature (°C)	B_r (mT)	H_{cb} (kA/m)	H_{cj} (kA/m)	$(BH)_{max}$ (kJ/m ³)
1180	379.0	204.5	212.3	27.3
1185	389.7	205.9	213.7	28.7
1190	391.9	207.4	219.1	29.0
1195	394.9	211.4	224.7	29.4
1200	399.7	205.6	216.2	29.8

[25]. It is seen that the average grain size of the magnets is bigger than the critical size of 650 nm reported by Zi et al. [26] for the single domain magnetic particle. In the present work, the average grain size of the magnets is higher than 3.0 μm . Thus, the grains of the magnets are the multi-domain structures. The change of the coercivity could be ascribed to crystallinity improvement and the grain growth with increasing the calcination temperature.

As observed from Fig. 5, $(BH)_{max}$ increases from 27.5 kJ/m³ at 1210 °C to 28.7 kJ/m³ at 1270 °C. The maximum energy product of the M-type ferrites can be estimated by the product between the remanence (B_r) and magnetic induction coercivity (H_{cb}). Thus, the maximum energy product has the same feature as B_r as shown in Fig. 5.

Fig. 7 shows the demagnetizing curves for the magnets made from the magnetic powders calcined at 1270 °C for 2 hrs, and sintered at 1180 °C, 1185 °C, 1190 °C, 1195 °C, and 1200 °C for 1.5 hrs. The remanence (B_r), intrinsic coercivity (H_{cj}), magnetic induction coercivity (H_{cb}) and maximum energy product $[(BH)_{max}]$ were extracted from the demagnetizing curves and listed in Table 2. Fig. 8 and Fig. 9 show the effects of sintering temperature on the remanence (B_r) and maximum energy product $[(BH)_{max}]$, magnetic induction coercivity (H_{cb}) and intrinsic coercivity (H_{cj}) of the magnets made from the magnetic powder calcined at 1270 °C, respectively. It can be seen from Fig. 8 and Table 2 that B_r increases with the increase of sintering temperature from 1180 to 1200 °C. The result is in agreement with that reported by Sharma et al. [25].

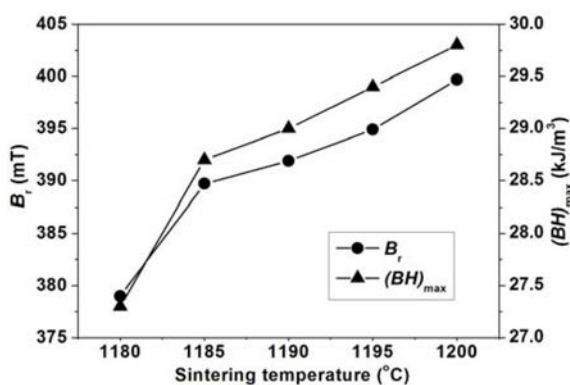


Fig. 8. Effects of sintering temperature on B_r and $(BH)_{max}$ of the magnets made from the magnetic powders calcined at 1270 °C for 2 h.

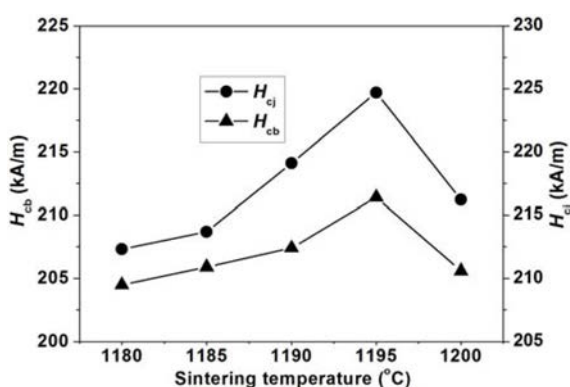


Fig. 9. Effects of sintering temperature on H_{cj} and H_{cb} of the magnets made from the magnetic powders calcined at 1270 °C for 2 hrs.

As seen from Fig. 9, it is clear that with the increase of sintering temperature, H_{cb} and H_{cj} increase from 204.5 and 212.3 kA/m at 1180 °C to 211.4 and 224.7 kA/m at 1195 °C, respectively, and then decrease when the sintering temperature ≥ 1195 °C. When the sintering temperature ≤ 1195 °C, the solid phase reaction is not complete, and the grain coarsening does not occur [27]. At the sintering temperature = 1195 °C, the solid phase reaction is complete, and the values of H_{cb} and H_{cj} reach to the maximum values. When the sintering temperature ≥ 1195 °C, the coarser grains occur which leads to the decrease of H_{cb} and H_{cj} [25].

It is clear from Fig. 8 that $(BH)_{max}$ increases with increasing the sintering temperature from 1180 to 1200 °C. The maximum energy product is the maximum area in the second quadrant of the hysteresis loop, and thus the values of the remanence (B_r) and magnetic induction coercivity (H_{cb}) will have their influence on it. The changing trend of $(BH)_{max}$ of the magnets is in agreement with that of B_r as shown in Fig. 8.

Conclusions

In the present work, the M-type hexaferrite with

nominal compositions of $\text{Ca}_{0.4}\text{Sr}_{0.3}(\text{La}_{0.8}\text{Pr}_{0.2})_{0.3}\text{Fe}_{11.76}\text{Co}_{0.24}\text{O}_{19}$ were prepared the solid-state reaction method. We have carefully investigated the effects of calcination temperature and sintering temperature on the microstructural and magnetic properties. The major findings of this work were listed in the following:

1. The XRD results exhibit that the single-phase hexaferrite patterns are observed for the hexaferrite magnetic powders at different temperatures from 1210 to 1270 °C for 2 hrs. The FE-SEM images show that the hexagonal structures have been formed in the magnets, and the grains in the magnets are distributed evenly.

2. With the increase of calcination temperature, B_r and $(BH)_{max}$ increase from 1210 °C to 1270 °C, while H_{cj} and H_{cb} increase from 1210 °C to 1250 °C, and then decrease when the calcination temperature ≥ 1250 °C.

3. With the increase of sintering temperature, B_r and $(BH)_{max}$ increase from 1180 to 1200 °C, while H_{cj} and H_{cb} increase from 1180 to 1195 °C, and then decrease when the calcination temperature ≥ 1195 °C.

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