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Microstructure and Magnetic Properties of La-Ca-Co Substituted M-Type Sr-Hexaferrites with Controlled Si Diffusion

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Abstract: La-Ca-Co substituted M-type Sr-hexaferrites ($\text{Sr}_{0.3}\text{Ca}_{0.4}\text{La}_{0.3}\text{Fe}_{9.8}\text{Co}_{0.2}\text{O}_{19-\delta}$) were prepared by a solid-state reaction using two different procedures, where the SiO_2 additive was mixed either before calcination (pre-Si) or after calcination (post-Si). At the same sintering temperature, smaller cell volumes and reduced saturation magnetization (M_s) values were obtained for samples processed with the pre-Si method than those with the post-Si method. This implied that the pre-Si method resulted in a greater degree of Si substitution into the M-type lattice and increased Fe extrusion out of the lattice. The grain growth behavior was controlled by the SiO_2 amount and sintering temperature. It was found that abnormal grains occur with a bimodal distribution in the 0.5 wt% SiO_2 samples sintered at 1240 °C, due to the increased critical driving force for growth caused by an increased amount of SiO_2 addition. The M_s and coercivity values were altered with the control of Si diffusion and abnormal grain growth. The control of the additive diffusion behavior is one of the important keys in the material design under same materials compositions.

Keywords: M-type hexaferrite; magnetic properties; microstructure; abnormal grain growth

1. Introduction

M-type (Ba, Sr)-hexaferrites are some of the most useful materials for permanent magnets [1]. Enhancing the magnetic and mechanical properties of these materials is economically important due to their widespread use across various global industries, such as consumer electronics and the electric automotive industry. Many studies have led to developments that have improved the intrinsic magnetic properties of Sr-hexaferrites, such as the saturation magnetization (M_s) and crystalline anisotropy, by compositional design with elemental substitutions [2–7]. Among these, La-, Ca-, and Co-substitution of the M-type Sr-hexaferrites (La-Ca-Co:SrM) is considered to be the most successful approach, leading to a significant enhancement in the crystalline anisotropy without reducing the M_s [4,8]. The resulting La-Ca-Co substituted M-type Sr-hexaferrites are thus high-grade ferrite magnets.

The coercivity (H_c) is dependent on the grain size of the La-Ca-Co:SrM permanent magnets [9–11]. Grain growth behavior involves the movement of interfaces, including grain boundary structures, by interface reactions. This behavior can be controlled by adding dopants to alter the diffusion of atoms into the materials [12–14], adjusting the sintering temperature [15], and changing the oxygen partial pressure [16–18]. Generally, it has been understood that dopants change the microstructure of ceramics by suppressing grain growth and increasing densification [19]. These additive elements can segregate at grain boundaries and form a secondary solid or liquid phase and suppress the migration of interfaces and grain boundaries by the solute drag and Zener effects [19,20]. In the grain growth

theory, grain growth behavior can be explained by the relationship between the critical driving force for grain growth (Δg_c) and the maximum driving force for grain growth (Δg_{max}) in the two-dimensional nucleation grain growth mechanism [20–30]. Phenomenologically, grain growth behavior is divided into normal grain growth (invariable distribution of relative growth sizes with sintering time) and abnormal grain growth (some large grains grow quickly) [17,20,22]. The grain growth type can be changed by the value of Δg_c relative to Δg_{max} during sintering [17,18,20,22]. The abnormal grain growth behavior can be calculated and explained exactly by the two-dimensional nucleation grain growth mechanism [22]. To the best of our knowledge, while a number of studies have analyzed the grain growth in M-type hexaferrites [6,23–27], no studies on La-Ca-Co:SrM grain growth have been reported. In the present study, the effects of SiO₂ additives on the grain growth in La-Ca-Co:SrM were investigated. There are many previous studies on Sr hexaferrites with addition of SiO₂ [12,31–34]. However, there has been no discussion of the position of Si elements regarding which Si element is in the lattice of grains or not.

The purpose of this study is to provide experimental support for the predicted effect of adding SiO₂ and to determine the conditions that suppress the diffusion of Si into the crystalline lattice of the Sr_{0.3}Ca_{0.4}La_{0.3}Fe_{9.8}Co_{0.2}O_{19-δ} (SCLFCO) system. The specific molar fraction of the elements in SCLFCO was selected concerning the previous works [3,7,8]. The selective diffusion of Si should be controlled in order to increase H_c without decreasing M_s .

2. Materials and Methods

SiO₂-doped La-Ca-Co:SrM samples were prepared by a conventional solid-state reaction that employed two different procedures, referred to as pre-Si and post-Si. In the pre-Si method, precursor powders of Fe₂O₃ (99%up, Kojundo Chemical Lab., Co., Ltd., Saitama Pre, Japan), SrCO₃ (99.9%, Kojundo Chemical Lab., Co., Ltd., Saitama Pre, Japan), La₂O₃ (99.9%, Sigma-Aldrich, St. Louis, MO, USA), CaCO₃ (99.9%, Sigma-Aldrich, St. Louis, MO, USA), and CoO (98%, Kojundo Chemical Lab., Co., Ltd., Saitama Pre, Japan) were weighed according to the target cation composition of Sr_{0.3}Ca_{0.4}La_{0.3}Fe_{9.8}Co_{0.2} and mixed together. Additionally, SiO₂ (99.9%) was added to the mixture at a dose of 1 wt% of the total precursor powder. The powder mixture was ball-milled in water for 24 h using a polypropylene jar and yttria-stabilized ZrO₂ balls with 3, 5, and 10 mm diameters. The dried slurry was calcined at 1100 °C in air for 4 h. The calcined powders were crushed, ball-milled in water for 24 h, dried, and pressed in a mold with a diameter of 15 mm at a pressure of 16.6 MPa to produce a disk-shaped green compact pellet. The pelletized samples were sintered in air at a temperature range of 1200–1250 °C for 2 h. During the sintering process, the heating rate was 5 °C/min and the samples were then furnace-cooled to room temperature.

In the post-Si method, the same amount of SiO₂ powder as used in the pre-Si method (1 wt% of total precursor powder) was added before the second ball-milling process after calcination, as opposed to being added before the first ball-milling process before calcination. The target composition and all the other processes were the same as in the pre-Si method.

The density of the sintered sample was calculated based on the weight and geometric dimensions of the disk-shaped sample. The phase of the sintered samples was characterized using X-ray diffraction (XRD, D8 Advance, Bruker) with a Cu-K α radiation source ($\lambda = 0.154056$ nm). The microstructures of the sintered samples were observed via field-emission scanning electron microscopy (FE-SEM, JSM-7610F, JEOL) of the fracture surfaces of the samples. Magnetization (M-H) curves of the sintered samples were measured using a vibrating sample magnetometer (VSM, 7410-S, Lake Shore) at room temperature with a sweeping magnetic field within ± 25 kOe.

3. Results and Discussion

Figure 1a–c show the XRD patterns of undoped (no-Si), pre-Si, and post-Si SCLFCO samples sintered at various temperatures. All no-Si SCLFCO samples were single phase M-type hexaferrites at all sintering temperatures (1200–1250 °C), with a hexagonal crystal structure and a space group of

P63/mmc. On the other hand, when 1 wt% SiO₂ was added, a secondary phase of Fe₂O₃ appeared in all of the samples sintered at 1200–1250 °C. Sharp peaks of Fe₂O₃ were found in the pre-Si samples at lower sintering temperatures, but were not observed in the post-Si samples. The substitution of Si into an Fe site could explain the appearance of an Fe₂O₃ solid phase. If Si diffused into the unit cell, then Fe would diffuse out and form Fe₂O₃.

Figure 1. XRD patterns of no-Si, pre-Si, and post-Si SCLFCO samples sintered at (a) 1200 °C, (b) 1225 °C, and (c) 1250 °C.

Table 1 shows the cell volume of the SCLFCO hexaferrites, calculated based on XRD patterns (Jade 6.0, V6.2.9200, MDI, Materials Data, Inc., USA). For each sintering temperature, the cell volume was the highest in no-Si samples and the lowest in pre-Si samples. The change in cell volume could be the result of Si substitutions in Fe sites, as the ionic size of Si^{4+} is smaller than that of Fe^{3+} [35]. In addition, the observation that cell volumes of the pre-Si samples are smaller than those of the post-Si samples at each sintering temperature implies that a larger amount of Si was substituted into the hexaferrite lattice in the pre-Si method than in the post-Si method.

Table 1. Densities and unit cell volumes of sintered samples.

Sintering Temperature	1 wt% SiO_2 Addition	Density, g/cm^3	Unit Cell Vol., $\text{\AA}^3$
1200 °C	no-Si	4.91	688.481
	post-Si	4.55	687.746
	pre-Si	4.78	687.518
1225 °C	no-Si	4.89	689.005
	post-Si	4.72	688.073
	pre-Si	4.89	687.707
1250 °C	no-Si	4.95	689.025
	post-Si	4.82	687.144
	pre-Si	4.93	686.250

The excess Fe atoms form the Fe_2O_3 secondary phase, which could inhibit grain growth based on the Zener effect, where the movement of the interface and grain boundary is suppressed by a secondary phase on the interface and grain boundary [19,20]. When Si is added, a liquid phase can form, the structures of the interface and grain boundary can change, and the growth rate of each grain can be altered [14,20,22,28–30].

Figure 2a–i display SEM micrographs of no-Si, pre-Si, and post-Si SCLFCO samples sintered at various temperatures. The effect of the sintering temperature on the average grain size of each sample type is insignificant. However, the average grain size significantly decreased as SiO_2 was added to all samples. The decrease in average grain size could be explained by the effect of Fe_2O_3 formation, as the Fe_2O_3 detected in the XRD patterns can suppress the migration of grain boundaries [19,20,24].

Figure 2. SEM micrographs of no-Si, pre-Si, and post-Si SCLFCO samples sintered at (a) 1200 °C, (b) 1225 °C, and (c) 1250 °C.

The H_c and other extrinsic properties may increase in samples with the addition of SiO_2 due to a decrease in the average grain size [31,32]. However, the intrinsic properties, such as M_s , could also be changed due to the diffusion of Si into the lattice. The unit cell volumes of the samples with SiO_2 addition were changed, as shown in Table 1. This phenomenon can be explained by the diffusion of Si into unit cells which changed the intrinsic properties. As shown in Table 2, the degree of change in the M_s in the pre-Si sample is larger than that in the post-Si sample. This could be due to the larger degree of Si substitution in the hexaferrite lattice in the pre-Si samples than that in the post-Si samples.

Table 2. M_s and H_c of sintered samples measured by vibrating sample magnetometer (VSM).

Sintering Temperature	1 wt% SiO_2 Addition	H_c , Oe	M_s , emu/g
1200 °C	no-Si	2272	68.01
	post-Si	3560	67.04
	pre-Si	3235	62.48
1225 °C	no-Si	2216	69.09
	post-Si	3581	65.37
	pre-Si	3293	63.26
1250 °C	no-Si	2298	68.16
	post-Si	3400	64.98
	pre-Si	3351	64.85

The microstructures in Figure 3 show that the coarsening behavior changes considerably with the addition of SiO_2 during sintering at 1250 °C. Here, all the samples were prepared with the pre-Si procedure but used different amounts of SiO_2 . The addition of 0.5 wt% SiO_2 caused an exaggerated, abnormal grain growth. In the samples with the addition of 1.0 and 2.0 wt% SiO_2 , the grain size decreased compared to the case of the undoped and 0.5 wt% SiO_2 -added sample. This cannot be explained with only the solute drag or Zener effects as the grain size should decrease due to these effects. According to the two-dimensional nucleation grain growth theory, abnormal grain growth can occur when the grain growth rate or migration of the interface is non-linear with Δg and is governed by the interface reaction [14,15,20,22,36–39]. In previous studies, the abnormal grain growth phenomenon was observed in hexaferrites and the results and analyses support the theory of a non-linear grain growth rate [6,23–27]. During the sintering of inorganic materials, grain growth occurs due to the difference in pressure induced by interface curvature and a decrease in the total interface energy [20]. The driving force for the growth of a grain is given by [20,22,39]:

$$\Delta g = 2\gamma V_m \left(\frac{1}{r^*} - \frac{1}{r} \right) \quad (1)$$

where γ = interface energy, V_m = molar volume, r = radius of the grain of interest, and r^* = critical grain radius or the radius of a grain that does not grow or shrink, and is similar to the average grain radius. Each grain has its own Δg and the largest grain has a Δg_{max} as schematically shown in Figure 4. Δg_c is the value that determines whether appreciable grain growth occurs in two-dimensional nucleation grain growth. The critical driving force for growth can be expressed by [22,39]

$$\Delta g_c = \left(\frac{\pi \sigma^2}{kTh} \right) \ln K^{-1} \propto \frac{\sigma^2}{h} \quad (2)$$

where σ = step free energy, h = height of the two-dimension nucleus, k = Boltzmann constant, T = absolute temperature, and K is a constant that accounts for the diffusion coefficient and the number of nuclei per unit area. According to Equation (2), Δg_c decreases as the sintering temperature increases and can be changed by altering the step free energy. The step free energy can be explained as the energy needed to form one layer and can be changed by the interface energy and structure [36]. Δg_c can be

altered by controlling the interface energy and structure among grains via changing temperature [15,23], adding a dopant [14,38], or changing the sintering atmosphere [16,17].

Figure 3. SEM micrographs of SCLFCO samples sintered at 1250 °C with varying amounts of SiO₂ additions using the pre-Si method: (a) No-Si, (b) 0.5 wt%, (c) 1.0 wt%, and (d) 2.0 wt%.

Figure 4. Schematic showing the growth rate of a crystal as a function of the driving force for diffusion (dashed lines) and a mix of diffusion and interface reaction control mechanisms (solid lines). (a) Plot of three mixed control curves for no-Si (0Si), 0.5 wt% SiO₂ (0.5Si), and 1.0 wt% SiO₂ (1.0Si) SCLFCO samples sintered at the same temperature. (b) Plots of three mixed control curves for 0.5 wt% SiO₂ SCLFCO samples sintered at 1220 °C, 1240 °C, and 1250 °C.

Figure 4 depicts the grain growth rate as a function of the Δg for diffusion (dashed line) and interface reactions (solid line) according the Equations (1) and (2). In the case of the no-Si sample sintered at 1250 °C, most grains can grow since the Δg of the grains is larger than the Δg_c for no-Si (Δg_c^{0Si}), as shown in Figure 4a. As the grain growth behavior changes with the addition of SiO₂, the Δg_c for appreciable grain growth increases when adding SiO₂. This is similar to the phenomenon observed when TiO₂ is added to sodium bismuth titanate [14]. As seen in Figure 4a, when 0.5 wt% SiO₂ was added using the pre-Si method (pre-0.5Si), $\Delta g_c^{0.5Si}$ increased but is still lower than the Δg_{max} . Therefore, some grains can grow rapidly and encroach on one another and Ostwald ripening can occur during the initial stage of sintering, where small grains are dissolved and absorbed into larger grains. Finally, grain growth stops in samples of pre-0.5Si. Figure 4a shows that as the amount of SiO₂ increases, Δg_c increases until it is greater than Δg_{max} , resulting in no grain growth in the initial stage of

sintering. The changes in the microstructure of samples with the addition of SiO_2 , as shown in Figure 3, are in line with the grain growth theory and are similar to previous studies on hexaferrites [24,26].

To confirm the non-linearity of the grain growth rate with Δg and understand the microstructural changes in samples with SiO_2 addition, the compacted powders of pre-Si samples with 0.5 wt% SiO_2 were sintered at various temperatures. The SEM images of these samples are shown in Figure 5. As seen in Figure 5b, a bimodal grain size distribution is observed in the sample sintered at 1240 °C; aside from a few grains that grew rapidly, most grains did not grow. No grain growth occurred in the samples sintered at 1200 °C and 1220 °C, resulting in a small grain size. In the grain growth theory, the Δg_c increases and the diffusion rate decreases as the sintering temperature decreases [20,22,39]. The pore and grain shape are dependent on the interface (grain boundary and surface) structure [20,21]. The anisotropy of grain and pore increases as the fraction of the atomically ordered interface increases [14,21]. The Δg_c increases as the fraction of the of the atomically ordered interface increases [14,18]. The spherical pore shape can explain that the anisotropy decreases and the Δg_c decreases as the sintering temperature increases.

Figure 5. SEM micrographs of 0.5 wt% SiO_2 pre-Si SCLFCO samples sintered at (a) 1250 °C, (b) 1240 °C, (c) 1220 °C, and (d) 1200 °C.

The slope of the dashed line in Figure 4b decreases as the diffusion rate and sintering temperatures decrease [22]. As the sintering temperature decreases from 1250 °C to 1240 °C, the Δg_c increases and is closer to, but still below, Δg_{max} . This results in an abnormal growth of a few grains with a Δg greater than $\Delta g_c^{1240\text{C}}$, while most grains cannot grow. Figure 4b indicates that as the Δg_c increases and the sintering temperature decreases, $\Delta g_c^{1220\text{C}}$ becomes larger than Δg_{max} . This results in no grain growth as none of the grains have a driving force for growth at the low sintering temperatures of 1200 °C and 1220 °C. The abnormal grain growth phenomena of SCLFCO can be explained by the grain growth theory and observed via the addition of SiO_2 and the change in sintering temperature. The grain growth mechanism of SCLFCO can be explained by the migration of the facet plane, consistent with previous studies [6,23–27].

The M-H curves of sintered samples are plotted in Figure 6a–c. The M_s and H_c values of these samples are presented in Table 2, where M_s is the magnetization value at $H = 25$ kOe. Comparing samples sintered at the same temperature, the no-Si samples have the largest M_s and the pre-Si samples have the smallest M_s . These results show that a Si substitution into an Fe site in the hexaferrite matrix deteriorates the magnetism. Pre-Si samples have a lower M_s value and a greater degree of substitution of Si than post-Si samples. However, the magnitude of the difference in M_s among these samples is highly dependent on the sintering temperature. At a sintering temperature of 1200 °C, the M_s of the

post-Si sample is closer to that of the no-Si sample than that of the pre-Si sample, as the driving force of Si diffusion into the interior of the grains in the post-Si sample is not high enough to produce an appreciable effect. At a sintering temperature of 1250 °C, the M_s of the post-Si sample is closer to that of the pre-Si sample than that of the no-Si sample. These data show that the Si atom has a significantly higher driving force for diffusion at 1225 °C than that at 1200 °C. The driving force for diffusion is high enough to achieve full diffusion of Si at 1250 °C. It can be assumed that there is a homogeneous distribution of Si in the pre-Si grains and the M_s values of pre-Si and post-Si samples are approximately the same. Concerning the H_c of the samples, it was found that the post-Si method is more effective than the pre-Si method, as higher H_c values were obtained for post-Si samples. However, both post-Si and pre-Si samples exhibit greatly enhanced values compared to no-Si samples. As shown in Figure 2, the average grain size between the samples prepared by pre-Si and post-Si methods is not significantly different. As previously mentioned, it was observed that Si substitution into Fe sites extrudes Fe out of the matrix and forms excess Fe_2O_3 , which prohibits grain growth. The H_c of the samples mostly depends on the grain size.

Figure 6. M-H curves of no-Si, pre-Si, and post-Si SCLFCO samples sintered at (a) 1220 °C, (b) 1225 °C, and (c) 1250 °C.

4. Conclusions

The grain growth behaviors and magnetic properties of SCLFCO systems with SiO₂ addition were investigated. Typically, when a dopant is added, the grain growth is suppressed by the solute drag and Zener effects. However, abnormal grain growth behavior of SCLFCO was observed by changing the sintering temperature and the amount of SiO₂ added. Thus, the grain growth behavior cannot be explained solely based on the solute drag and Zener effects. The effects of Si addition on the intrinsic magnetic property, M_s , were studied by changing the processing procedure. It was shown that Si can diffuse into the unit cell and change the intrinsic properties. At the same sintering temperature, the cell volumes of the pre-Si samples were smaller than those of the post-Si samples, which meant that a larger amount of Si was substituted into the hexaferrite lattice in the pre-Si method. The grain growth behavior of SCLFCO with SiO₂ addition can be explained by a two-dimensional nucleation grain growth mechanism with a non-linear relationship between the grain growth rate and the driving force for grain growth. As the amount of SiO₂ increases, the critical driving force for grain growth increases, which results in abnormal grain growth with a bimodal distribution in the 0.5 wt% SiO₂ samples sintered at 1240 °C. When more SiO₂ was added, the critical driving force was larger than the driving force for growth of all grains, which resulted in no grain growth in the initial stage of sintering. The growth mechanism of SCLFCO can be explained by the migration of the facet plane with the two-dimensional nucleation grain growth mechanism. The magnetic properties of M_s and H_c can be altered through the control of the Si addition process and the abnormal grain growth in hexaferrites.

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