Optimum conditions for synthesizing Fe substituted hibonite

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We investigated the synthesis conditions and magnetic properties of Fe substituted hibonite with initial compositions of CaAl$_{12}$Fe$_x$O$_{19}$ (1 ≤ x ≤ 3, 5 ≤ y ≤ 9) and CaAl$_{12}$Fe$_y$O$_{19}$ (0.5 ≤ x ≤ 1.6) sintered at 1200–1300°C. The optimum conditions for synthesizing the best magnetic hibonite were found to be the initial composition of Ca:Al:Fe = 1:0.6:7.4 and the sintering temperature of 1250°C. The best magnetic hibonite was magnetized at 75.0 A m$^{-2}$/kg at $T_s$ = 5 K and $\mu_0H$ = 7 T. This magnetic moment can be interpreted with a model of the collinear magnetic structure. The Curie temperature of the best magnetic hibonite was 330°C, which was the highest among those of iron-substituted hibonite samples.

Keywords: M-type, hexaferrite

1. Introduction

Ca-based M-type ferrite has been attracting a lot of interest because the other alkaline-earth-based M-type ferrites (Ba, Sr)Fe$_{12}$O$_{19}$ have been used as a permanent magnet for a long time. In spite that pure M-type CaFe$_{12}$O$_{19}$ phase does not exist in the CaO-Fe$_2$O$_3$ diagram, the M-type phase becomes stable with the addition of a rare-earth element of lanthanum to CaFe$_{12}$O$_{19}$. The optimum synthesis condition of the (Ca, La) based M-type ferrite with the highest magnetization was recently clarified.

Resources of rare-earth elements are, however, limited in comparison with those of the other elements of calcium, iron, and oxygen. Therefore, it is desirable to avoid the use of rare-earth elements in the material.

On the other hand, the crystal structure of M-type ferrite is similar to that of hibonite (CaAl$_{12}$O$_{19}$). Therefore, instead of lanthanum, aluminum can stabilize the M-type structure even with iron elements. This approach is consistent with "element strategy" because aluminum, calcium, iron, and oxygen are abundant elements in Earth's crust.

We previously reported the study of synthesis and magnetic properties of Fe substituted hibonite. In this report, we changed initial composition from CaAl$_{12-x}$Fe$_x$O$_{19}$ to CaAl$_{10-x}$Fe$_x$O$_{19}$ in order to prevent the excess of α-Fe$_2$O$_3$ and to improve the magnetic properties. But it was insufficient to optimize synthesis conditions because α-Fe$_2$O$_3$ still remained in the magnetic samples of CaAl$_{10-x}$Fe$_x$O$_{19}$.

In this study, we have investigated the optimum synthesis conditions and magnetic properties of Fe substituted hibonite in order to produce a rare-earth-free Ca-based ferromagnet.

2. Experimental procedure

Samples were prepared by a conventional ceramic method. We used CaCO$_3$, Al$_2$O$_3$, and α-Fe$_2$O$_3$ as starting materials. First, Al$_2$O$_3$ powder was heated at 500°C for an hour in order to remove water molecules on the material. The starting materials were mixed in the desired proportions of CaAl$_{12}$Fe$_x$O$_{19}$ (1 ≤ x ≤ 3, 5 ≤ y ≤ 10) and CaAl$_{10-x}$Fe$_x$O$_{19}$ (6.4 ≤ x ≤ 7.5) in a ball-milling pot for 24 h. The mixed powder was pressed into a disk shape. The disk was pre-sintered in air at 900°C for 5 h. The sintered sample was pounded in a mortar and then ground into fine powder using a planetary ball mill for 10 minutes at 1100 rpm (Fritsch, P-7 Premium line). The powder was pressed into a disk shape again. The disks were heated at 1100–1400°C for 5 h. X-ray diffraction (XRD) analysis with Cu-Kα radiation was performed to characterize the crystalline samples. The magnetic properties were measured by using a vibrating sample magnetometer (Tamakawa TM-VSM2130HGC and superconducting quantum interference device (SQUID) magnetometers (Quantum Design MPMS-XL). The chemical composition was examined through energy dispersive X-ray analysis (EDX).

![X-ray diffraction patterns of initial composition samples of CaAl$_{12}$Fe$_x$O$_{19}$ (1 ≤ x ≤ 3, y = 8) sintered at $T_s$ = 1300°C.](image)
3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the Ca:Al:Fe = 1:x:y−x (1 ≤ x ≤ 3, y = 8) composition samples sintered at T_s = 1300º C. The sample with the initial composition at x = 1 and y = 8 showed the single hibonite phase. The diffraction pattern of hibonite is almost identical to that of Sr-based M-type ferrite. The other samples of x = 2 and 3 contained minority phases of α-Fe2O3 and CaAl2O4 although the main phase was that of hibonite. This situation is same for other starting composition samples with Ca:Al:Fe = 1:x:y−x (1 ≤ x ≤ 3, 5 ≤ y ≤ 9). But the single hibonite phase was observed only for the sample at x = 1 and y = 8.

Figure 2 shows the room-temperature saturation magnetization (M_s) of initial composition samples of CaAl_xFe_y−xO_19−δ (1 ≤ x ≤ 3, 0 ≤ y ≤ 12) sintered at T_s = 1300ºC, where M_s was estimated from the magnetization measurements at −2 T ≤ μ_0H ≤ 2 T. The sample at x = 1 and y = 8 had the highest M_s among these samples. This is consistent with the fact that the sample at x = 1 and y = 8 contained no minority phases of α-Fe2O3 and CaAl2O4.

These experimental results of CaAl_xFe_y−xO_19−δ strongly suggest that the suitable (Al+Fe)/Ca ratio is 8 for the formation of the iron-substituted magnetic hibonite. This led us to the next experiments to determine the optimum Al:Fe ratio so as to synthesize the best magnetic hibonite with the highest magnetization and the highest Curie temperature.

Figure 3 shows the X-ray diffraction patterns of initial composition samples of CaAl_xFe_8−xO_19−δ (0.5 ≤ x ≤ 1.6) sintered at T_s = 1250ºC. The maximum iron substitution amount corresponds to x_{max} = 0.6 where the secondary phase of hematite was not left. Here, the sintering temperature T_s was decreased to 1250ºC from 1300ºC because the samples sintered at T_s = 1300ºC showed the secondary hematite phase at x < 1.0. High T_s can remove iron and calcium elements from the hibonite structure with high concentration of Fe^{3+}, possibly due to a low melting point of CaFe_2O_4. On the other hand, the single hibonite phase was not observed for the samples at T_s ≤ 1225ºC, suggesting the lowest limit of T_s for the formation of the single phase of hibonite.

![X-ray diffraction patterns of initial composition samples of CaAl_xFe_8−xO_19−δ](image)

Fig. 3 X-ray diffraction patterns of initial composition samples of CaAl_xFe_8−xO_19−δ (0.5 ≤ x ≤ 1.6) sintered at T_s = 1250ºC.
Figure 4 shows the lattice constants of the hibonite phase in initial composition samples of CaAl$_{12}$Fe$_{8-x}$O$_{19}$, ($0.5 \leq x \leq 1.6$) sintered at $T_b = 1250^\circ$C. The lattice constants of $a$ and $c$ were obtained by the use of Cohen’s least square method. Both $a$ and $c$ became maximum at $x = 0.6$, which is in agreement with the above-mentioned $x_{\text{max}}$. The maximum lattice constants at $x = 0.6$ implied that Fe$^{3+}$ ions maximally replaced Al$^{3+}$ ions in the hibonite structure because the ionic radius of an Fe$^{3+}$ ion $r[Fe^{3+}]$ is larger than that of an Al$^{3+}$ ion $r[Al^{3+}]$.

![Lattice constants of initial composition samples of CaAl$_{12}$Fe$_{8-x}$O$_{19}$, ($0.5 \leq x \leq 1.6$) sintered at $T_b = 1250^\circ$C. Dotted lines are connected between lattice constants of CaAl$_{12}$O$_{19}$ at $x = 8$ and those of SrFe$_{12}$O$_{19}$ (instead of CaFe$_{12}$O$_{19}$ that does not exist) at $x = 0$, where a conversion of $x = 8x' / 12$ is employed for CaAl$_{12-x}$Fe$_{x}$O$_{19}$ due to the change of (Al+Fe)/Ca from 12 to 8.](image)

Fig. 4 Lattice constants of initial composition samples of CaAl$_{12}$Fe$_{8-x}$O$_{19}$, ($0.5 \leq x \leq 1.6$) sintered at $T_b = 1250^\circ$C. Dotted lines are connected between lattice constants of CaAl$_{12}$O$_{19}$ at $x = 8$ and those of SrFe$_{12}$O$_{19}$ (instead of CaFe$_{12}$O$_{19}$ that does not exist) at $x = 0$, where a conversion of $x = 8x' / 12$ is employed for CaAl$_{12-x}$Fe$_{x}$O$_{19}$ due to the change of (Al+Fe)/Ca from 12 to 8.

Figure 5 shows the room-temperature saturation magnetization ($M_s$), the Curie temperature ($T_C$) and the relative intensity $I_{(102)} / I_{(311)}$ of initial composition samples of CaAl$_{12}$Fe$_{8-x}$O$_{19}$, ($0.5 \leq x \leq 1.6$). With decreasing $x$ from 1.6, $T_C$ was linearly increased up to $330^\circ$C at $x = 0.6$ and then slightly decreased at $x = 0.5$. This $x$ dependence of $T_C$ is comparable to the variation of the lattice constants as shown in Fig. 4. The highest $T_C$ strongly suggests that the sample with $x = 0.6$ sintered at $1250^\circ$C contains the maximum amount of iron cations in the hibonite structure. Also, $M_s$ was basically increased with decreasing $x$ from 1.6 to 0.6 except that $M_s$ deviated from this linear tendency at $x = 1.4$ and 1.3 because of the formation of a minority phase of $\alpha$-Fe$_2$O$_3$. The sample with $x = 0.6$ had the maximum $M_s$ of 44 A m$^2$/kg and the highest $T_C$ of $330^\circ$C.

The EDX analysis of the sample with $x = 0.6$ provides the result of Ca:Al:Fe = 1.00±0.04 : 0.62±0.04 : 7.81±0.23 (average value ± one sigma estimation). The composition of Fe is slightly larger than the initial amount, which may be caused by low-melting-point calcium-iron oxides such as CaFe$_2$O$_4$ that can be eluted off from the hibonite grain. The chemical formula of this sample can be expressed as CaAl$_{0.6}$Fe$_{7.8}$O$_{13.6}$ where the composition ratio of oxygen is estimated from the charge balance with the concentration of Ca$^{2+}$, Al$^{3+}$, and Fe$^{3+}$ cations. The form of this chemical formula is much different from the reference materials of hibonite (CaAl$_{12}$O$_{19}$) and M-type ferrite (SrFe$_{12}$O$_{19}$).

On the other hand, the $x$ dependences of the lattice constants are similar to the dotted lines connected between lattice constants of CaAl$_{12}$O$_{19}$ and those of SrFe$_{12}$O$_{19}$ as shown in Fig. 4. This fact suggests that the framework of the hibonite structure is maintained even in the change of (Al+Fe)/Ca ratio. The crystal structure consists of a close-packed framework of large ions (Ca$^{2+}$ and O$^{2-}$) with intervening small ions (Al$^{3+}$ and Fe$^{3+}$). Therefore, we can assume that the total number of large ions (Ca$^{2+}$ and O$^{2-}$) in the hibonite structure is kept at 20 ($= 1+19$). Based on this assumption, the chemical formula of the sample with $x = 0.6$ is estimated to be Ca$_{1.4}$Al$_{0.6}$Fe$_{10.7}$O$_{18.6}$. The total number of Al$^{3+}$ and Fe$^{3+}$ cations becomes 11.5 that is smaller than 12.

This picture can be applied to the case of Al-substituted (Ca,La)-based M-type ferrite. Shigemura et al. recently reported that the Curie temperature of Ca$_{0.68}$La$_{0.12}$Fe$_{8.80}$Al$_{1.01}$O$_{18.8}$ was about $350^\circ$C. This chemical formula can be converted to Ca$_{1.05}$La$_{0.14}$Fe$_{10.5}$Al$_{1.20}$O$_{18.8}$ on the assumption that the total number of large ions (Ca$^{2+}$, La$^{3+}$, and O$^{2-}$) is kept at 20. The estimated amounts of Fe$^{3+}$ in chemical formulas

![Chemical formula of the sample with $x = 0.6$ sintered at 1250$^\circ$C.](image)
are similar between Ca$_{1.4}$Al$_{0.8}$Fe$_{10.7}$O$_{18.6}$ and Ca$_{1.05}$La$_{0.14}$Fe$_{10.5}$Al$_{1.26}$O$_{18.8}$, which may cause the similarity in the Curie temperature.

Figure 6 shows the magnetization curves at $T = 5\,\text{K}$ and $300\,\text{K}$ for the sample with $x = 0.6$ sintered at $T_S = 1250\,\text{C}$. The slight difference between the experimental result and the estimated value can be caused by the deviation from the collinear magnetic structure. In fact, Batlle et al. pointed out that the substitution of Co$^{3+}$-Ti$^3+$ for Fe$^{3+}$ in BaFe$_{12}$O$_{19}$ can progressively break the collinearity of the magnetic structure of BaFe$_{12.2}$Co$_{0.8}$Ti$_{0.9}$ at $x > 0.7$ although the overall behavior remains ferrimagnetic. In our case, the collinearity of our sample can be also weakened because the estimated amount of the Fe$^{3+}$ cations in our sample is close to this threshold of 10.6 ($=12-2x0.7$) and our sample does not contain magnetic Co$^{2+}$ cations. The high-field susceptibility of our sample is relatively high as shown in Fig. 6, suggesting the weakened collinearity.

Therefore, our result is consistent with the previous studies of M-type ferrite.

4. Conclusion

We have successfully synthesized Fe$^{3+}$ substituted hibonite-phase samples by a conventional ceramic method. The optimum synthesis conditions of the best magnetic hibonite are found to be the initial composition of Ca:Al:Fe = 1:0.6:7.4 and the sintering temperature of 1250°C. The magnetization of the best magnetic hibonite was 75.0 A$^2$/kg at $T = 5\,\text{K}$ and $\mu_0H = 7\,\text{T}$. This magnetic moment can be basically interpreted with the model of the collinear magnetic structure. The Curie temperature of the best magnetic hibonite was 330°C, which is the highest among those of iron-substituted hibonite samples.

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