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<Paper>

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 $CaAl_xFe_{y-x}O_{19-\delta}$ ($1 \leq x \leq 3$, $5 \leq y \leq 9$) and $CaAl_xFe_{8-x}O_{19-\delta}$ ($0.5 \leq x \leq 1.6$) sintered at 1200–1300ºC. 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 1250ºC. The best magnetic hibonite was magnetized at 75.0 A·m²/kg at T = 5 K and $\mu_0 H$ = 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 330ºC, 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.[1-3] In spite that pure M-type $CaFe_{12}O_{19}$ phase does not exist in the CaO-Fe_2O_3 diagram,[4-6] the M-type phase becomes stable with the addition of a rare-earth element of lanthanum to $CaFe_{12}O_{19}$.[7,8] The optimum synthesis condition of the (Ca,La)-based M-type ferrite with the highest magnetization was recently clarified.[9]

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.[10]

We previously reported the study of synthesis and magnetic properties of Fe substituted hibonite.[11] In this report, we changed initial composition from $CaAl_{12-x}Fe_xO_{19}$ to $CaAl_{10-x}Fe_xO_{19-\delta}$ in order to prevent the excess of α–Fe_2O_3 and to improve the magnetic properties. But it was insufficient to optimize synthesis conditions because α-Fe_2O_3 still remained in the magnetic samples of $CaAl_{10-x}Fe_xO_{19-\delta}$.

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_2O_3, and α-Fe_2O_3 as starting materials. First, Al_2O_3 powder was heated at 500ºC for an hour in order to remove water molecules on the material. The starting materials were mixed in the desired proportions of $CaAl_xFe_{y-x}O_{19-\delta}$ ($1 \leq x \leq 3$, $5 \leq y \leq 10$) and $CaAl_{8-x}Fe_xO_{19-\delta}$ ($6.4 \leq x \leq 7.5$) 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 900ºC 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 1100–1400ºC 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).

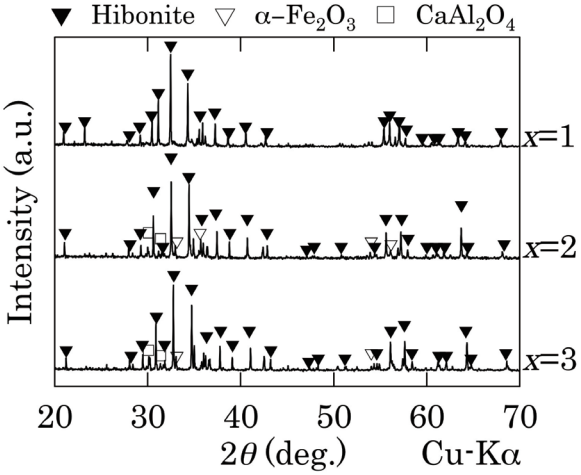

Fig. 1 X-ray diffraction patterns of initial composition samples of $CaAl_xFe_{y-x}O_{19-\delta}$ ($1 \leq x \leq 3$, y = 8) sintered at T_S = 1300ºC.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the Ca:Al:Fe = 1:x:y–x ($1 \le x \le 3$, $y = 8$) composition samples sintered at T_S = 1300ºC. 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-Fe_2O_3 and $CaAl_2O_4$ 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 ($1 \le x \le 3$, $5 \le y \le 9$). 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 $CaAl_xFe_{y-x}O_{19-\delta}$ ($1 \le x \le 3$, $5 \le y \le 12$) sintered at T_S = 1300ºC, where M_S was estimated from the magnetization measurements at $-2\ \mathrm{T} \le \mu_0 H \le 2\ \mathrm{T}$. 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-Fe_2O_3 and $CaAl_2O_4$.

These experimental results of $CaAl_xFe_{y-x}O_{19-\delta}$ 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 $CaAl_xFe_{8-x}O_{19-\delta}$ ($0.5 \le x \le 1.6$) 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 $T_S \le 1225$ºC, suggesting the lowest limit of T_S for the formation of the single phase of hibonite.

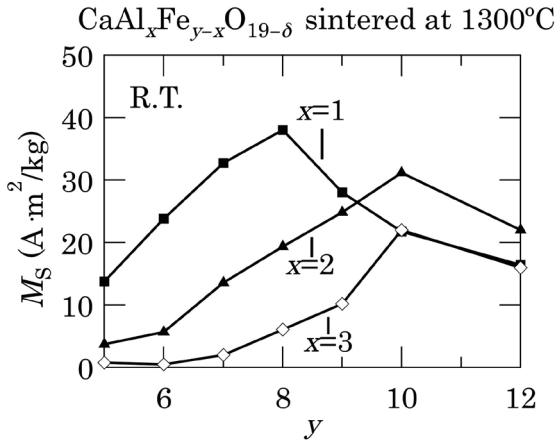

Fig. 2 Room-temperature saturation magnetization of initial composition samples of $CaAl_xFe_{y-x}O_{19-\delta}$ ($1 \le x \le 3$, $0 \le y \le 12$) sintered at T_S = 1300ºC.

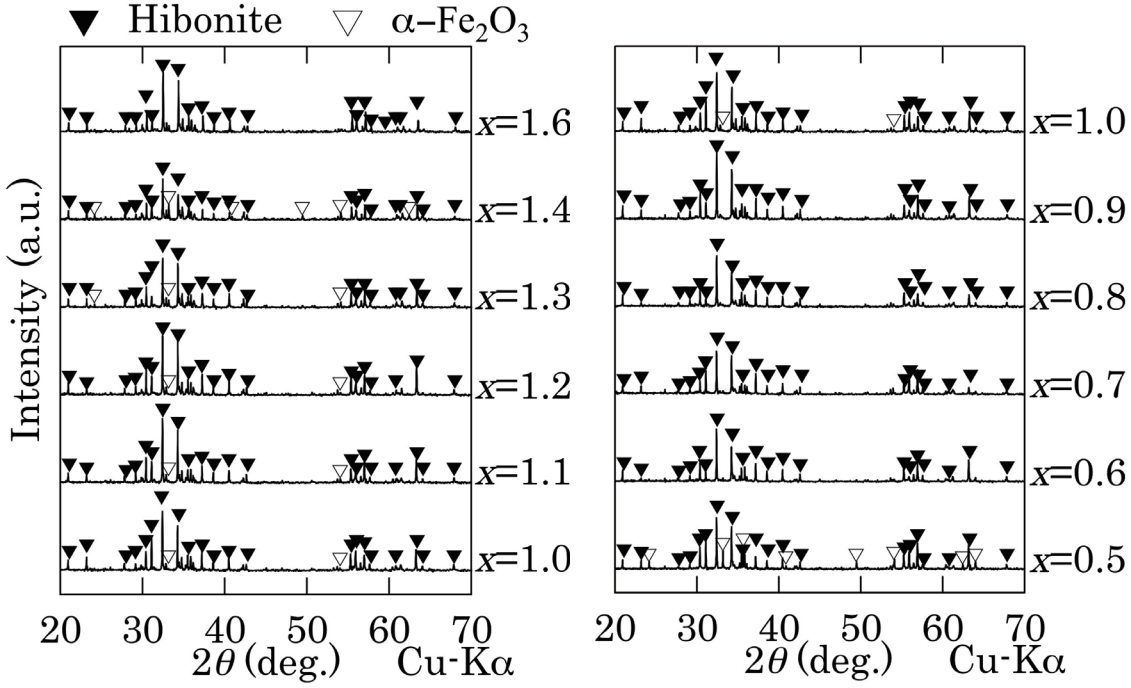

Fig. 3 X-ray diffraction patterns of initial composition samples of $CaAl_xFe_{8-x}O_{19-\delta}$ ($0.5 \le x \le 1.6$) sintered at T_S = 1250ºC.

Figure 4 shows the lattice constants of the hibonite phase in initial composition samples of $CaAl_xFe_{8-x}O_{19-\delta}$ ($0.5 \leq x \leq 1.6$) sintered at T_S = 1250ºC. The lattice constants of a and c were obtained by the use of Cohen's least square method.[12] Both a and c became maximum at x = 0.6, which is in agreement with the above-mentioned x_{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 $r[Al^{3+}]$.

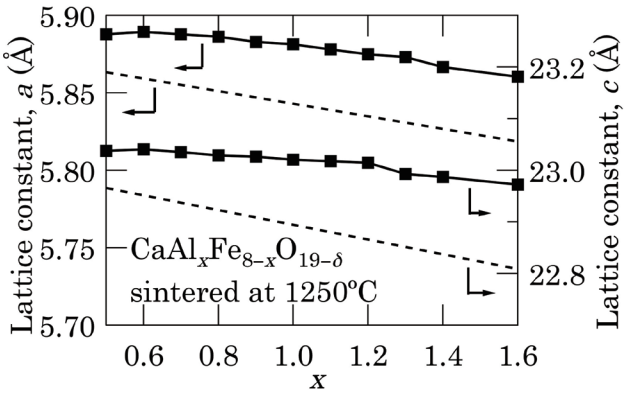

Fig. 4 Lattice constants of initial composition samples of $CaAl_xFe_{8-x}O_{19-\delta}$ ($0.5 \leq x \leq 1.6$) sintered at T_S = 1250ºC. Dotted lines are connected between lattice constants of $CaAl_{12}O_{19}$ at x = 8 and those of $SrFe_{12}O_{19}$ (instead of $CaFe_{12}O_{19}$ that does not exist) 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 $I^{\alpha-Fe_2O_3}_{(102)}/I^{hibonite}_{(203)}$ of initial composition samples of $CaAl_xFe_{8-x}O_{19-\delta}$ ($0.5 \leq x \leq 1.6$). With decreasing x from 1.6, T_C was linearly increased up to 330ºC 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 1250ºC 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 α–Fe_2O_3. The sample with x = 0.6 had the maximum M_S of 44 A·m²/kg and the highest T_C of 330ºC.

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 $CaFe_2O_4$ 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 $Ca_{1.4}Al_{0.8}Fe_{10.7}O_{18.6}$. 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 $Ca_{0.88}La_{0.12}Fe_{8.80}Al_{1.01}O_{15.8}$ was about 350ºC.[13] 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

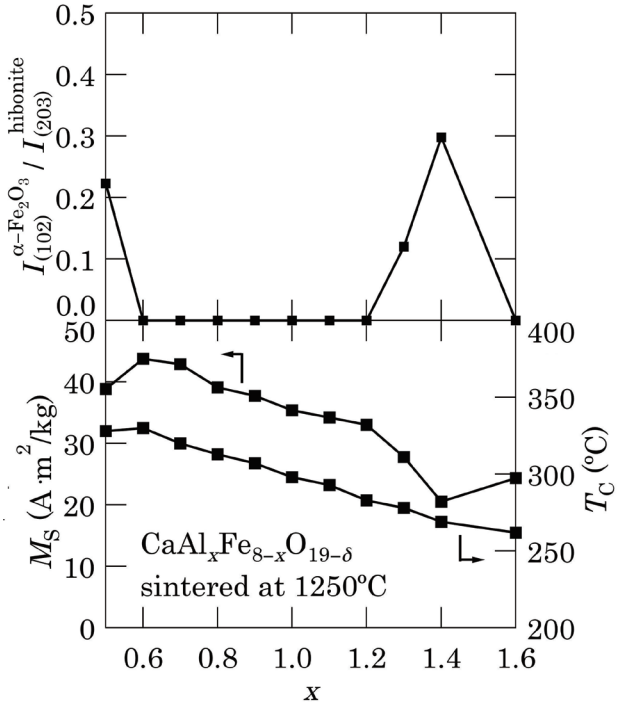

Fig. 5 Room-temperature saturation magnetization (M_S) and Curie temperature (T_C) of initial composition samples of $CaAl_xFe_{8-x}O_{19-\delta}$ ($0.5 \leq x \leq 1.6$) sintered at T_S = 1250ºC. Intensity ratio of α-Fe_2O_3 (102) plane to hibonite (203) plane is also shown.

are similar between $Ca_{1.4}Al_{0.8}Fe_{10.7}O_{18.6}$ and $Ca_{1.05}La_{0.14}Fe_{10.5}Al_{1.20}O_{18.8}$, which may cause the similarity in the Curie temperature.

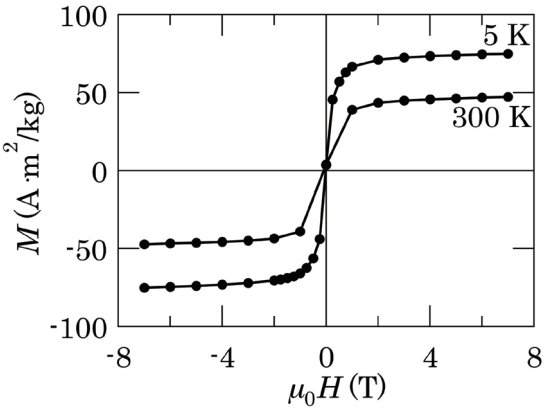

Fig. 6 Magnetization curves at T = 5 K and 300 K for sample at x = 0.6 sintered at T_S = 1250°C.

Figure 6 shows the magnetization curves at T = 5 K and 300 K for the sample with x = 0.6 sintered at T_S = 1250°C. Gradual increase of magnetization was observed above $\mu_0 H$ > 2 T. At the maximum external magnetic field of $\mu_0 H$ = 7 T, the magnetizations at T = 5 K and 300 K are 75.0 A·m^2/kg and 47.3 A·m^2/kg, respectively. The magnetization at T = 5 K corresponds to the magnetic moment per formula unit of 13.1 μ_B/f.u.

We would like to discuss the magnetic structure of the best magnetic hibonite in our study. The magnetic structure of this iron-substituted hibonite can be similar to that of the M-type ferrite because the crystal structure of hibonite is similar to that of the M-type ferrite. The M-type ferrite has a collinear magnetic structure where eight of the Fe^{3+} cations are antiparallel to the other four Fe^{3+} cations. The total magnetic moment of the M-type ferrite is equivalent to four Fe^{3+} cations (20 μ_B).

Here, the chemical formula of the best magnetic hibonite is estimated to be $Ca_{1.4}Al_{0.8}Fe_{10.7}O_{18.6}$. Albanese demonstrated that Al^{3+} cations in $BaAl_xFe_{12-x}O_{19}$ tend to occupy the up-spin 12k site at $x \leq 1$.[14] Also, the estimated chemical formula with the excess of Ca^{2+} cations suggests that Ca^{2+} replaces O^{2-} (possibly in the R-block), which can produce vacancy at a small cation site due to the local electroneutrality (the Pauling principle). Therefore, we can assume that the magnetic hibonite has the collinear magnetic structure where the up-spin-sites contain 0.8 Al^{3+} and 0.5 vacancy. Then, 6.7 Fe^{3+} cations are antiparallel to the other four Fe^{3+} cations. The total magnetic moment of the magnetic hibonite becomes equivalent to 2.7 Fe^{3+} cations (13.5 μ_B). This value is close to the experimental result of 13.1 μ_B/f.u. at T = 5 K and $\mu_0 H$ = 7 T.

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^{2+}-Ti^{4+} for Fe^{3+} in $BaFe_{12}O_{19}$ can progressively break the collinearity of the magnetic structure of $BaFe_{12-2x}Co_xTi_xO_{19}$ at x > 0.7 although the overall behavior remains ferrimagnetic.[15] 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 (= 12–2×0.7) 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·m^2/kg at T = 5 K and $\mu_0 H$ = 7 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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