Synthesis and magnetic properties of Fe substituted hibonite

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We have investigated the synthesis conditions and magnetic properties of Fe substituted hibonite with initial compositions of CaAl_{12-x}Fe_xO_{19} (0 \leq x \leq 12) and CaAl_{10-x}Fe_xO_{19-\delta} (0 \leq x \leq 10). The Fe doped hibonite can be synthesized at a sintering temperature of 1300°C. The X-ray diffraction patterns of Fe substituted hibonite samples are in good agreement with the pattern of hibonite. The lattice parameter increased due to the difference between the radius of Al^{3+} and that of Fe^{3+}. The magnetization and Curie temperature of the best sample (CaAl_{2}Fe_{8}O_{19-\delta}) are 31 emu/g and 290°C, respectively.

Keywords: M-type, hexaferrite

1. Introduction

M-type ferrites (Ba, Sr, Pb)Fe_{12}O_{19} have high magnetization and coercivity, which leads to application as a permanent magnet. Consequently, M-type ferrites have long been the subject of intensive research.\(^1\)

Ca-based M-type ferrite is an attractive subject because of the rich resource of its Fe and Ca elements. Fe and Ca are widespread elements in minerals, as implied by the 4th and 5th largest Clarke numbers of Fe and Ca.\(^2\) However, there is no CaFe_{12}O_{19} phase in the CaO-Fe_{2}O_{3} diagram.\(^3, 4\) This Ca-based M-type ferrite can be stabilized only by the addition of a rare-earth element of La.\(^5-7\)

The crystal structure of M-type ferrite is similar to that of hibonite (CaAl_{12}O_{19}) except that the structure models are divided on the interpretation of the bipyramidal Al^{3+} ions.\(^9\) Figure 1 shows the crystal structure of CaAl_{12}O_{19} along [010] view direction. The unit cell contains two chemical formulas of CaAl_{12}O_{19} like M-type ferrite. To the best of our knowledge, the systematic substitution effect of Fe^{3+} for Al^{3+} of CaAl_{12}O_{19} has not been reported yet in spite of the similarity in the crystal structures.\(^9\)

In this study, we have investigated the synthesis conditions and magnetic properties of the Fe substituted hibonite.

2. Experimental procedure

Samples were prepared by a conventional ceramic method. We used CaCO_{3}, Al_{2}O_{3}, and \(\alpha\)-Fe_{2}O_{3} as starting materials. Before we mixed them, we heated Al_{2}O_{3} powder at 500°C for an hour in order to remove water molecules on the material. They were mixed in the desired proportions of CaAl_{12-x}Fe_xO_{19} (0 \leq x \leq 12) and CaAl_{10-x}Fe_xO_{19-\delta} (0 \leq x \leq 10) 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 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. 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). The chemical composition was examined by using a commercial electron probe micro analyzer (EPMA) (JEOL, JXA-8200).

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**Fig. 1** Crystal structure of hibonite along [010] view direction.
3. Results and discussion

Figure 2 shows the X-ray diffraction patterns of the sintered samples at 1300°C whose starting powder was mixed at the iron-substituted-hibonite chemical composition of Ca: Al: Fe = 1: (12 − x):x. The hibonite chemical composition sample (x = 0) exhibits the mixed phases of Al₂O₃, CaAl₄O₇, and CaAl₂O₄. The hibonite phase was formed by the substitution of Fe for Al at x ≥ 1. The diffraction peaks of the hibonite phase shifted to the low angle side with increasing the Fe content.

The (Al+Fe)/Ca ratio of twelve to one may be too large for the reaction to form the hibonite phase because the starting material of α-Fe₂O₃ remained at x ≥ 7 (iron rich compositions). In the same way, that of Al₂O₃ did not react at x ≤ 2 (aluminum rich compositions).

Figure 3 shows the lattice constants of the hibonite phase in the CaAl₁₂₋ₓFeₓO₁₉ (0 ≤ x ≤ 12) initial composition samples sintered at 1300°C. The lattice constants a and c were obtained using Cohen’s least square method. a and c gradually increased with the amount of Fe³⁺ ions.

Fig. 2 X-ray diffraction patterns of the CaAl₁₂₋ₓFeₓO₁₉ (0 ≤ x ≤ 12) initial composition samples sintered at 1300°C.

Fig. 3 Lattice constants of the CaAl₁₂₋ₓFeₓO₁₉ (1 ≤ x ≤ 11) initial composition samples sintered at 1300°C.
because the ionic radius of an Fe$^{3+}$ ion $\{\text{Fe}^{3+}\}$ is larger than that of an Al$^{3+}$ ion $\{\text{Al}^{3+}\}$: $\{\text{Fe}^{3+}\}$, HS$=0.49$ Å $>$ $\{\text{Al}^{3+}\}$, HS$=0.39$ Å at a tetrahedral site and $\{\text{Fe}^{3+}\}$, HS$=0.645$ Å $>$ $\{\text{Al}^{3+}\}$=0.535 Å at an octahedral site, where “HS” denotes the high spin configuration of electrons. 11) The dotted straight lines are connected between the lattice constants of the hibonite ($x=0$) and the typical M-type ferrite (SrFe$_{12}$O$_{19}$) in which the ionic radius of Sr is similar to that of Ca. Our results are close to these dotted lines, which implies that a linear relation exists between the lattice constant and the concentrations of the constituent elements (Vegard’s law).12)

Figure 4 shows the saturation magnetization ($M_S$) at room temperature, the Curie temperature ($T_c$), and the relative intensity $I_{(203)}/I_{(102)}$ of the Fe rich composition samples (CaAl$_{12-x}$Fe$_x$O$_{19}$; $x \geq 6$). The samples at $x<7$ had small magnetizations at room temperature in spite of the single crystallographic phase of hibonite. This fact reflects the small intrinsic magnetic moment and low $T_c$ due to the small amount of the iron cations. With increasing the iron content up to $x=10$, $M_S$ increased although the relative intensity of $\alpha$-Fe$_2$O$_3$ gradually increased. This increase of $M_S$ is due to the replacement of non-magnetic Al$^{3+}$ to magnetic Fe$^{3+}$ ions of magnetic hibonite phase in these samples. On the other hand, $M_S$ decreased with increasing the iron content above $x=10$. This is consistent with the fact that the diffraction peaks of hibonite became weak and finally disappeared at $x=12$.

The Curie temperature was increased by iron substitution. Because nonmagnetic Al$^{3+}$ ions were
replaced by magnetic $\text{Fe}^{3+}$ ions, the average superexchange interaction between magnetic $\text{Fe}^{3+}$ ions in the sample can operate. The increase of the amount of the iron cations and their interactions may lead to the rise of $T_C$: $T_C$ was increased up to $x=11$ even though $M_S$ was decreased from $x=10$ to $x=11$. This means that the magnetic hibonite phase was formed with excessive $\alpha-\text{Fe}_2\text{O}_3$ at $x=11$. The excess of $\alpha-\text{Fe}_2\text{O}_3$ at $x=11$ is also implied by the abrupt increase of $I_{(102)}^{\alpha-\text{Fe}_2\text{O}_3}/I_{(203)}^{\text{hibonite}}$ from $x=10$ to $x=11$ in Fig. 4. This result also suggests that the (Al+Fe)/Ca ratio of twelve to one is too large for the formation of the hibonite phase. This is consistent with the XRD result shown in Fig. 2.

These experimental results of CaAl$_{12-x}$Fe$_x$O$_{19}$ led us to the next experiments to decrease the (Al+Fe)/Ca ratio in iron-substituted hibonite. We changed the starting composition from CaAl$_{12-x}$Fe$_x$O$_{19}$ to CaAl$_{10-x}$Fe$_x$O$_{19-\delta}$ in order to prevent the excess of $\alpha-\text{Fe}_2\text{O}_3$ and to improve the magnetic properties.

Figure 5 shows the X-ray diffraction patterns of the sintered samples at 1300°C whose starting powder was mixed at the chemical composition of Ca:Al:Fe=1:(10-x):x. After we changed the starting composition from CaAl$_{12-x}$Fe$_x$O$_{19}$ to CaAl$_{10-x}$Fe$_x$O$_{19-\delta}$, peaks of hematite became weaker at the iron rich compositions.

Figure 6 shows the lattice constants of the CaAl$_{10-x}$Fe$_x$O$_{19-\delta}$ (0≤$x$≤9) initial composition samples sintered at 1300°C. The dotted straight lines are connected between the lattice constants of the hibonite ($x=0$) and SrFe$_{12}$O$_{19}$. The substitution-dependent variation of lattice constants ($\Delta a/\Delta x$ and $\Delta c/\Delta x$) of CaAl$_{10-x}$Fe$_x$O$_{19-\delta}$ at the Fe rich compositions is larger than that of CaAl$_{12-x}$Fe$_x$O$_{19}$ ($x<10$). In addition, the X-ray diffraction peaks of the remaining $\alpha-\text{Fe}_2\text{O}_3$ in CaAl$_{10-x}$Fe$_x$O$_{19-\delta}$ are weaker than those in CaAl$_{12-x}$Fe$_x$O$_{19}$ at the Fe rich compositions. These facts indicate that the substitution of $\text{Fe}^{3+}$ for $\text{Al}^{3+}$ in CaAl$_{10-x}$Fe$_x$O$_{19-\delta}$ is
more successful than in CaAl_{12-x}Fe_{x}O_{19}.

Figure 7 shows the saturation magnetization ($M_s$) at room temperature and the Curie temperature ($T_C$) and the relative intensity $I_r$ of the Fe rich composition samples. The iron-substitution dependence is similar to that of CaAl_{12-x}Fe_{x}O_{19} in Fig. 4. However, the value of $M_s$ was higher than that of CaAl_{12-x}Fe_{x}O_{19} composition samples. The maximum $T_C$ was 325°C for CaAl$_{10-x}$Fe$_x$O$_{19}$ at $x=9$. It should be noted that this maximum Curie temperature is higher than the maximum $T_C$ of CaAl$_{12}$Fe$_x$O$_{19}$ at $x=11$. The relative intensity $I_r$ is also lower than that in Fig. 4. These facts suggest that the starting material composition of Ca: Al: Fe=1: (10−x):x is more suitable for the synthesis of iron-substituted magnetic hibonite.

Table 1 shows the estimated chemical composition of the $x=8$ sample (CaAl$_2$Fe$_8$O$_{19}$) sintered at 1300°C. By the use of EPMA, we measured the compositions of 50 particles of this sample. The table shows the average composition. The elements of Ca, Al, and Fe were in the ratio 1: 1.75: 7.11. The ratio of Ca is slightly higher than the initial ratio of 1: 2: 8. This may be caused by the elution of the Ca-rich oxide (e.g., CaFe$_2$O$_4$ with melting point of 1216°C) on the sample grains.

4. Conclusion

Fe$^{3+}$ substituted hibonite-phase samples have been successfully synthesized by a conventional ceramic method with the modified initial chemical compositions of CaAl$_{10-x}$Fe$_x$O$_{19}$, XRD patterns of CaAl$_{10-x}$Fe$_x$O$_{19}$ sintered at 1300°C demonstrated the hibonite phase at 1≤$x$≤9. The lattice parameter increased with increasing Fe$^{3+}$ content. The maximum saturation magnetization was 31 emu/g at $x=8$ (CaAl$_{2}$Fe$_{8}$O$_{19}$). The Curie temperature rose up to 325°C with the replacement of Al$^{3+}$ ions by Fe$^{3+}$ ions.

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