Preparation of novel potassium, lanthanum-iron oxides and their magnetic properties

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We have investigated the synthesis conditions, and the magnetic properties of M-type ferromagnetic potassium, lanthanum-iron oxides. The samples were prepared by solid-state-reaction. It is found that a new M-type ferrite can be effectively synthesized at 1275°C from the starting materials pulverized with a planetary ball mill. The magnetic transition temperature of the sample is 440°C which is quite close to that of the magnetoplumbite-type ferrite. EPMA compositional analysis for this new M-type ferrite shows the composition ratio of K : La : Fe = 0.75 : 0.90 : 18.58. From this result, the chemical formula of the magnetoplumbite phase in this sample is estimated to be $K_{0.45}La_{0.55}Fe_{12}O_{19}$.

Key words: potassium, lanthanum, magnetoplumbite, $LaFe_{12}O_{19}$

1. INTRODUCTION

The hexagonal ferrites, $MFe_{12}O_{19}$ ($M = Ba, Sr, Pb$) with the magnetoplumbite structure are well-known ferromagnetic iron-oxides for ceramic permanent magnetic materials at present. They have high saturation magnetization, high resistance, high chemical stability and high Curie temperatures. Their coercive field strength can be adjusted for a wide range of applications [1]. A basic feature of hexagonal magnetoplumbite structures is a layer of relatively large O^{2-} and M^{2+} ions arranged essentially in close-packed fashion, that is, each large ion is surrounded by six other large ions in the plane. The close-packed layers form two kinds of blocks, one is a spinel block and the other is an R block as shown in Fig. 1. In the spinel block, a transition metal cation is located at an octahedral site with six oxygen ligands or at a tetrahedral site with four oxygen ligands. Another close-packed large ion layer has a Ba^{2+} ion substituted for every fourth O^{2-} ion, which gives an ordered 1:3 ratio of alkaline earth metal cation to oxygen anion. When this Ba-O type layer is sandwiched between two oxygen layers, the total three layers become an R block. A transition metal cation just on the site with five oxygen ligands, which produce a uniaxial ligand field. Other sites between the Ba-O type and oxygen layers in the R block are octahedral. The hard magnetic properties of the M-type ferrites come from this magnetocrystalline anisotropy of Fe^{3+} at the R block in the magnetoplumbite structure.

Because of their significance for industrial applications, several forms of substitutions in hexagonal ferrites have been tried with the aim to improve hard magnetic properties [2-6]. Some experiments used rare-earth ions such as La substitution for Ba, Sr or Pb [7-9].

In the 1970's Lotgering [10] reported a remarkable increase of anisotropy $LaFe_{12}O_{19}$ which contains Fe^{2+} ions. Few investigations of this compound, however, have been carried out due to difficulties in preparing this iron-oxide. Kupferling et al. set out that $LaFe_{12}O_{19}$ was prepared by three different methods (mechanical

Fig. 1 Crystal structure of M-type ferrites. An asterisk denotes that the block is turned for 180° around c-axis.[11]

alloying, coprecipitation and sol-gel) [12]. Since La-hexaferrite phase is only stable between 1360 and 1390°C, in order to form this phase, a heat treatment within this temperature range and then a rapid quenching to room temperature were performed for these three samples. Nevertheless, these specimens contained $LaFeO_3$ and $\alpha-Fe_2O_3$ phases together with $LaFe_{12}O_{19}$ phase. So, it is extremely difficult to obtain single-phase $LaFe_{12}O_{19}$.

In this study, taking into account the ionic radius and the charge balance of the elements, a new M-type ferrite with substitution of trivalent La^{3+} and monovalent K^+ for divalent Ba^{2+} , Sr^{2+} , Pb^{2+} is prepared by a solid-state-reaction. We have investigated the synthesis conditions and the magnetic properties of M-type potassium, lanthanum-iron oxides.

2. EXPERIMENTAL PROCEDURE

The samples were prepared by a solid-state-reaction. K_2CO_3 (Wako; 99.5%), $\alpha-Fe_2O_3$ (JFE Chemical; 99.6%) and La_2O_3 (Wako; 99.5%) reagents were mixed in order to give the composition of $K_{0.5}La_{0.5}Fe_{12}O_{19}$ by using a

mortar or a planetary ball mill (Fritsch, P-7 premium line). The mixed powder was pressed into a disk. The disk was put in a platinum crucible, being covered with KCl powder in order to prevent the evaporation of potassium ions. It was sintered at 1275°C in air. The crystal structure was studied with X-ray diffraction (Rigaku RINT Ultima3). The magnetization was measured by using a vibrating sample magnetometer (VSM; Tamakawa TM-VSM2130HGC) and a superconducting quantum interference device magnetometer (SQUID; Quantum Design MPMS-XL). The compositional analysis data of the sample was obtained with an electron probe micro analyzer (EPMA; JEOL JXA-8200).

3. EXPERIMENTAL RESULT AND DISCUSSION

Figure 2 shows the X-ray diffraction pattern of the sample with the initial composition at K : La : Fe = 0.5 : 0.5 : 12. In this X-ray diffraction pattern, diffraction peaks of $\text{KFe}_{11}\text{O}_{17}$ and M-type ferrite, $\alpha\text{-Fe}_2\text{O}_3$, and LaFeO_3 phases were observed. As $\text{KFe}_{11}\text{O}_{17}$, $\alpha\text{-Fe}_2\text{O}_3$ and LaFeO_3 are nonferromagnetic, they give no contribution to spontaneous magnetization. However, there is a possibility that M-type ferrite is ferromagnetic. In order to investigate this possibility, magnetization of this sample was measured.

Fig. 2 X-ray diffraction pattern for the sample with the initial composition at K : La : Fe = 0.5 : 0.5 : 12.

Figure 3 shows the magnetization curve at 300 K of the sample with the initial composition of K : La : Fe = 0.5 : 0.5 : 12. The sample is clearly ferromagnetic and the magnetization at 70 kOe is 23.1 emu/g. Although the majority phase is antiferromagnetic $\text{KFe}_{11}\text{O}_{17}$, a small amount of the minority magnetoplumbite phase gives rise to the total magnetization. Therefore, we can expect that the magnetization of this magnetoplumbite phase is comparable with that of the conventional magnetoplumbite $\text{BaFe}_{12}\text{O}_{19}$.

Figure 4 shows the temperature dependence of magnetization at 5 kOe for this ferromagnetic sample. The magnetic transition temperature was 440°C, which is quite close to that of the magnetoplumbite-type ferrite ($T_C = 450^\circ\text{C}$ for $\text{BaFe}_{12}\text{O}_{19}$) [13]. No other anomaly was observed in this M-T curve from 50 to 600°C. $\alpha\text{-Fe}_2\text{O}_3$

Fig. 3 the magnetization curve at 300 K of the sample with the initial composition of K : La : Fe = 0.5 : 0.5 : 12.

Fig. 4 The temperature dependence of magnetization at 5 kOe for the sample with the initial composition of K : La : Fe = 0.5 : 0.5 : 12.

is a weak ferromagnetic substance originating from Dzyaloshinskii–Moriya interaction. However, this effect did not contribute to the total magnetization since this weak ferromagnet has very weak saturation magnetization of about 1 emu/g at RT. This result indicates that the magnetism of the sample originates from a new M-type ferrite with lanthanum and potassium ions. Nonetheless, the specimen contains $\text{KFe}_{11}\text{O}_{17}$, $\alpha\text{-Fe}_2\text{O}_3$ and LaFeO_3 , as shown in Fig. 2, which are not ferromagnetic. It is known that LaFeO_3 is easily synthesized at 1000°C [14]. Most of K_2CO_3 reagents seemed to react with $\alpha\text{-Fe}_2\text{O}_3$ to form $\text{KFe}_{11}\text{O}_{17}$. Thus, unreacted $\alpha\text{-Fe}_2\text{O}_3$ remained in the product. It should be noted that La_2O_3 and K_2CO_3 did not react with each other. For this reason, it needs to improve the solid-state-reaction activity of $\alpha\text{-Fe}_2\text{O}_3$ in order to involve both lanthanum and potassium ions to form a new iron-based oxide. If the surface area of particles is increased, the solid-state-reaction activity will be improved since the reaction paths between

particles depends on the contact surface area. So, we want to pulverize the starting materials of α -Fe₂O₃ and the others more strongly.

Figure 5 shows x-ray diffraction patterns of the sample with the initial composition at K : La : Fe = 0.5 : 0.5 : 12 prepared from the starting materials pulverized with the planetary ball mill. The sample prepared from the starting materials milled for 10 min. shows the diffraction peaks of the majority magnetoplumbite phase and the minority KFe₁₁O₁₇ and α -Fe₂O₃ phases. Therefore, the magnetoplumbite phase is effectively synthesized by pulverization of the starting materials. The samples prepared from the starting materials milled for 15 and 30 min. do not show the diffraction peaks of KFe₁₁O₁₇. The intensity of magnetoplumbite phase is strengthened and that of α -Fe₂O₃ phase is decreased with increasing pulverization time of the starting materials. In other words, the volume fraction of magnetoplumbite phase increases and that of α -Fe₂O₃ phase reduces with the application of milling to the starting materials.

Fig. 5 X-ray diffraction patterns of the sample with the composition at K : La : Fe = 0.5 : 0.5 : 12 prepared from the starting materials pulverized with a planetary ball mill.

Table 1 shows the magnetizations of the samples prepared from different starting materials. The saturation magnetization increases with decreasing the amounts of KFe₁₁O₁₇ and α -Fe₂O₃ phases, which indicates that the ferromagnetic property is caused by the magnetoplumbite phase.

Table. 1. The magnetizations of the samples prepared from different starting materials.

Milling process	Magnetization [emu/g]
Mortar	23.1
1000 rpm, 10 min	54.5
1000 rpm, 15 min	59.6
1000 rpm, 30 min	60.5

Figure 6 shows a SEM photo of the sample prepared from the starting materials milled for 15 min. The SEM result clearly indicates the existence of two different particles. We set the measuring point A on a typical hexagonal particle, and the measuring point B on a relatively small spherical particle. The chemical compositions at the measuring points A and B were studied by EPMA. The obtained EPMA compositional analysis data of measuring point A are K : La : Fe = 0.75 : 0.90 : 18.58. The measuring point B only contains iron and oxygen, so this particle seems to be α -Fe₂O₃. From these results, the composition of the magnetoplumbite phase in this sample is estimated to be K_{0.45}La_{0.55}Fe₁₂O₁₉₋₂₀.

Fig. 6 SEM photo of the sample prepared from the starting materials milled for 15 min.

4. SUMMARY

We have investigated the synthesis conditions, and the magnetic properties of M-type ferromagnetic potassium, lanthanum-iron oxides. The samples were prepared by a solid-state-reaction. K₂CO₃, α -Fe₂O₃ and La₂O₃ reagents were mixed in order to give the composition of K_{0.5}La_{0.5}Fe₁₂O₁₉ by using a mortar or a planetary ball mill. In the X-ray diffraction pattern of the sample prepared from the mortar-mixed starting materials with the initial composition at K : La : Fe = 0.5 : 0.5 : 12, diffraction peaks of KFe₁₁O₁₇ and M-type, α -Fe₂O₃, and LaFeO₃ phases are observed. From the magnetization curve at 300 K of the sample, the specimen is clearly ferromagnetic and the magnetization at 70 kOe was 23.1 emu/g. The magnetic transition temperature of the sample is 440°C which is quite close to that of the magnetoplumbite-type ferrite. No other anomaly is observed in the M-T curve from 50 to 600°C. This result indicates that the magnetism of the sample originates from a new M-type ferrite with lanthanum and potassium ions. Next, we pulverized the starting materials of α -Fe₂O₃ and the others more strongly. The sample prepared from the starting materials milled for 10, 15 and 30 min. shows the diffraction peaks of the majority magnetoplumbite phase. The saturation magnetization increases with decreasing the amount of KFe₁₁O₁₇ and α -Fe₂O₃ phases, which indicates that the ferromagnetic property is caused by the magnetoplumbite phase. The obtained EPMA compositional analysis data of a hexagonal particle are

K : La : Fe = 0.75 : 0.90 : 18.58. From this result, the composition of the magnetoplumbite phase in this sample is estimated to be $K_{0.45}La_{0.55}Fe_{12}O_{19-20}$.

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