Functional intermetallic compounds in the samarium–iron system

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Abstract

Magnetism of intermetallic compounds SmFe2, SmFe3, Sm6Fe23, and SmFe7 were studied in detail using single crystals and the use of these materials has been discussed. SmFe2 and Sm6Fe23 have cubic magnetocrystalline anisotropy and the easy axis of magnetization in the [111] direction. SmFe2 has giant negative magnetostriction that can be used for microactuator or ultrasonic generator. SmFe3 has a relatively large saturation moment and uniaxial anisotropy, which are promising for application as a perpendicular magnetic recording medium. Large saturation magnetization and extremely large magnetocrystalline anisotropy of SmFe7 seem promising as an absorber in the frequency range of milliwave as well as a high performance permanent magnet.

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1. Introduction

Discovery of high performance permanent magnet materials has promoted the improvement of electrical equipments and contributed much to energy saving. If new permanent magnet with higher performance is discovered, the energy efficiency of the electrical equipments will be further improved. Intermetallic compounds composed of rare earth and iron have attracted renewed attention since the innovative discovery of the high performance permanent magnet, Nd2Fe14B [1]. Extensive studies have been conducted to search for new materials in the binary and ternary systems with rare earth and iron. Among the rare earth and iron systems, the Sm–Fe system is interesting because a high performance hard magnetic material such as Sm2Fe14N1 was found in this system [2]. In the Sm–Fe system, the existence of stoichiometric compounds with compositions of Sm2Fe17 (Th2Zn17-type), SmFe3 (PuNi3-type), SmFe2 (MgCu2-type), and Sm6Fe23 (Th6Mn23) has been reported [3,4]. Although the magnetism of Sm2Fe17 has been studied thoroughly using single crystal specimen [5], magnetism of other compounds has not been clarified because of the difficulty in obtaining single crystal specimens. It is widely accepted that the magnetic properties of ferromagnetic materials strongly depend on their crystallographic direction. In addition, polycrystalline specimens often contain secondary phases, which prevent the investigation of intrinsic magnetic properties. In order to understand the magnetism in detail, further studies on single crystalline specimens have been expected. Moreover, since the phase diagram of the Sm–Fe system is incomplete, there is a high possibility that a new phase might be found in this system.

We succeeded in growing single crystals of SmFe2, SmFe3, and Sm6Fe23 for the first time using a modified flux method. Their crystallographic and magnetic properties have been evaluated [6–9]. Furthermore, in the process of crystal growth, we discovered a new phase with a composition of SmFe7. Its crystallographic and magnetic properties have been characterized in detail [10,11]. In this paper, we summarize and compare the magnetic properties of SmFe2, SmFe3, Sm6Fe23, and SmFe7 from the standpoint of potential application.

2. Experiment

Single crystals were grown with a modified flux method using samarium as a flux [12]. After arc-melting an appropriate amount of samarium (99.9%) and iron (99.9%), the mixture (~30 g) was placed in a BN-coated alumina crucible. The crucible was further sealed in a quartz ampoule with Ar gas (460 Torr) after evacuating to 5 × 10^-5 Torr. The mixture was heated over the dissolution temperature of the mixture...
(900–1050 °C) using an electric furnace. After being held at that temperature for 0.5–6 h, it was slowly cooled to 700–850 °C, and then the quartz ampoule was cooled to room temperature. The composition ratio of Sm/Fe in the starting mixture, cooling temperature range, and the cooling rate were 1–2.33, 950–700 °C, and 0.1–4 °C per hour, respectively.

The chemical composition of the crystals was determined by electron-probe microanalysis using wavelength dispersive spectrometers, an inductively coupled plasma atomic emission spectrometer, and an auger electron spectroscopy. The crystal structure was characterized by using single-crystal X-ray diffraction with a four-circle-goniometer and X-ray powder diffraction using Cu Kα radiation. The crystal structure was refined by the Rietveld method using the X-ray diffraction data. The crystallographic directions were determined by the X-ray Laue back-reflection method. Magnetization was measured by a vibrating sample magnetometer and a SQUID magnetometer on disk-shaped crystals. Magnetocrystalline anisotropy was characterized using a torque magnetometer. Magnetostriiction measurements were performed by an optical technique [13].

3. Results and discussion

Single crystals were grown on the samarium flux, which covered the bottom of the crucible. The crystals could be removed without applying any mechanical stress since the Sm flux changed into oxide powder by oxidation after a few days in the ambient atmosphere. The composition of the crystal could be controlled by changing the composition of raw materials, the composition ratio of the raw materials to the Sm flux, and the growth conditions, such as the cooling temperature range and the cooling rate. Fig. 1 shows the photographs of as-grown crystals of SmFe₂, SmFe₃, Sm₆Fe₂₃, and SmFe₇. All of the as-grown crystals have natural habits with metallic luster. The shape of as-grown crystals reflects their crystal structures. The crystal with cubic (SmFe₂), hexagonal (SmFe₃), or tetragonal (SmFe₇) structure have the shape of an octahedron, hexagonal plate, or rectangular parallelepiped, respectively. Crystal structure and lattice parameters of these crystals are listed in Table 1. In particular, the structure of SmFe₇ is very similar to the structure of Nd₂Fe₁₄B and Sm₂Fe₁₄Nₓ.

Fig. 2 shows the magnetic-field dependence of magnetization measured for SmFe₂, SmFe₃, Sm₆Fe₂₃, and SmFe₇ crystals in the specific crystallographic directions at 300 K. It is seen that SmFe₂ and Sm₆Fe₂₃ have easy and hard axes of magnetization in the [111] and [100] directions, respectively, suggesting that they have a negative cubic magnetocrystalline anisotropy constant K₁. SmFe₃ has an easy axis of magnetization in the direction parallel to the c-axis of hexagonal crystal, indicating that the hexagonal anisotropy constants satisfy

![Fig. 1. Photographs of as-grown crystal (a) SmFe₂, (b) SmFe₃, (c) Sm₆Fe₂₃, and (d) SmFe₇.](image-url)
the condition of $K_1^0_0$ and $K_2^0_0$. Moreover, the large difference observed for the magnetization curves measured along the $c$-axis and the $c$-plane suggests the existence of a significantly large anisotropy field along the $c$-axis. On the other hand, SmFe$_7$ has the easy axis of magnetization in the [100] direction of tetragonal crystal and a considerably large saturation magnetization. The large difference observed for the magnetization curves in the [001] and the [100] directions indicates the existence of a giant magnetocrystalline anisotropy.

Fig. 3 shows the temperature dependence of the magnetization measured for SmFe$_2$ and SmFe$_3$ crystals in a field of 10 kOe applied parallel to the specific crystal directions. In the case of SmFe$_2$ (Fig. 3(a)), the magnetization is the greatest in the [111] direction above 195 K; however, the magnetization is the largest in the [110] direction at temperatures between 5 and 195 K. This is confirmed by the angular dependence of magnetization shown in the inset of the figure. These results indicate that the easy axis of magnetization changes from the [110] direction to the [111] direction at 195 K. On the other hand, as shown in Fig. 3(b) and its inset, SmFe$_3$ has maximum magnetization in the direction parallel to the $c$-axis at temperatures above 160 K, while the magnetization is the largest in the direction that makes an angle of about 30° from the $c$-axis below 160 K. These results are consistent with the fact that SmFe$_3$ satisfies the conditions of $K_1^0_0$ and $K_1^K_2^0_0$. The easy axis of magnetization of SmFe$_3$ tilts by 30° from the $c$-axis for temperatures below 160 K. Although the crossover of the easy axis of magnetization was observed the [100] direction of tetragonal crystal and a considerably large saturation magnetization. The large difference observed for the magnetization curves in the [001] and the [100] directions indicates the existence of a giant magnetocrystalline anisotropy.
Magnetic properties of SmFe$_2$, SmFe$_3$, Sm$_6$Fe$_{23}$ and SmFe$_7$ crystals at 300 K

|         | $M_s$ (emu/g) | $T_C$ (K) | Magnetocrystalline anisotropy constants (erg/cc) | Easy direction of magnetization | $H_A$ (kOe) |
|---------|---------------|-----------|-------------------------------------------------|-------------------------------|-------------|
| SmFe$_2$ | 59.8          | 670       | $K_1 = -5.1 \times 10^6$                         | [111]                         | 12          |
|         |               |           | $K_2 = 1.7 \times 10^6$                         |                               |             |
| SmFe$_3$ | 80.7          | 640       | $K_1 = -2.4 \times 10^6$                         | $c$-axis                      | 72          |
|         |               |           | $K_2 = 2.2 \times 10^6$                         |                               |             |
| Sm$_6$Fe$_{23}$ | 64.4       | 442       | $K_1 = -2.7 \times 10^6$                         | [111]                         | 6           |
|         |               |           | $K_2 = 6.3 \times 10^5$                         | Circular cone$^a$             |             |
| SmFe$_7$ | 136           | 602       | $K_1 = -8.7 \times 10^7$                         | [100]                         | 110         |
|         |               |           | $K_2 = 1.4 \times 10^7$                         |                               |             |
|         |               |           | $K_3 = -2.7 \times 10^6$                         |                               |             |

$^a$ Easy direction of magnetization at low temperature.

for SmFe$_2$ and SmFe$_3$ crystals, no change was observed for the crystals of SmFe$_7$ and Sm$_6$Fe$_{23}$.

Spontaneous magnetization $M_s$, Curie temperature $T_C$, anisotropy constants, and anisotropy field $H_A$ obtained from the magnetization and torque measurements [6–11] are listed in Table 2. Among the compounds studied in this study, SmFe$_2$, SmFe$_3$, and SmFe$_7$ have remarkable magnetic properties. Fig. 4 shows the magnetic-field dependence of the magnetostriction constants measured for a SmFe$_2$ crystal at 300 K. It is seen that SmFe$_2$ has giant negative magnetostriction and the magnetostriction constant $\lambda_{111}$ obtained by extrapolating the data to infinite magnetic-field is $-2.01 \times 10^{-3}$. This extremely large value, which is the largest in the compounds with a negative magnetostriction constant, means that the displacement of 10 $\mu$m can be made when a SmFe$_2$ crystal with a length of 10 mm is used. Therefore, SmFe$_2$ is a promising material as a microactuator and a high power ultrasonic generator. Furthermore, if SmFe$_2$ with giant negative magnetostriction can function together with a giant positive magnetostrictive material, such as Tb$_{1-x}$Dy$_x$Fe$_2$ [14–16], the use of the magnetostrictive materials must be further developed.

SmFe$_3$ has a relatively large saturation magnetization and uniaxial anisotropy at the room temperature. Although attempts have been made to use SmFe$_3$ as a permanent magnet material because of its relatively large theoretical $(BH)_{\text{max}}$ of 19 MGOe, there is little hope of success in this attempt because the value is considerably smaller than that of commercial high performance magnets. However, when the magnetic properties of SmFe$_3$ are considered from the standpoint of magnetic recording material, it seems to have high potential as a material that could be used for the perpendicular magnetic recording media. When the values $K_1 = 2.4 \times 10^6$ J/m$^3$ $(=2.4 \times 10^7$ erg/cm$^3$) and $0.836$ Wb/m$^2$ $(=80.7$ emu/g) are used, the condition $K_1 > (M_s^2/2\mu_0)$ for the perpendicular magnetization is satisfied. Moreover, SmFe$_3$ crystal has a shape of hexagonal plate, suggesting that the growth rate in the $c$-plane is larger than that in the $c$-axis. Therefore, when the thin film of SmFe$_3$ is fabricated using a deposition technique such as sputtering, $c$-plane might be parallel to the substrate, and then a thin film with perpendicular magnetization might be obtained.

On the other hand, SmFe$_7$ has very large saturation magnetization and extremely large anisotropy field at 300 K. In particular, its anisotropy field and Curie temperature are superior to those of Nd$_2$Fe$_{14}$B. Theoretical $(BH)_{\text{max}}$ can be estimated for SmFe$_7$ using the relation $H_A = 4\pi M_s^2$, which is deduced for a single domain particle when the condition $K_1 > 2\pi M_s^2$ is satisfied and the field is applied to the easy direction of magnetization. $(BH)_{\text{max}}$ of $347$ kJ/m$^3$ $(=43.6$ MGOe) was obtained using the value of $M_s$ at 300 K. SmFe$_7$ appears to be a promising material as a high performance permanent magnet. However, in spite of the excellent magnetic properties, SmFe$_7$ has a serious drawback for practical applications. As shown in Table 2, the easy direction of magnetization is not parallel to the [001] direction (or $c$-axis) but in the (001) plane. It is well accepted that materials with uniaxial anisotropy are suitable for permanent magnet material. Therefore, control of the easy direction of magnetization is necessary for a practical application. It is commonly accepted that the magnetic properties of intermetallic compounds in the system of rare earth and iron are improved by the substitution of non-magnetic elements for the iron. We investigated the effect of a non-magnetic aluminum substitution in the Sm$(Fe_{1-x}Al_x)_{17}$ system. Fig. 5 shows the
aluminum content dependence of the magnetism and the magnetocrystalline anisotropy constant $K_1 + 2K_2$, which determines the easy direction of magnetization when $K_1 < 0$. Anisotropy constants were determined by magnetization measurements at 300 K. The saturation magnetization does not show any change for a very small Al substitution. However, a large Al substitution decreased the saturation magnetization. On the other hand, although the magnitude of $K_1 + 2K_2$ was decreased to almost zero by the Al substitution, it was unsuccessful in changing the easy axis of magnetization because of the limitation in the Al composition. It seems necessary to take into consideration the substitution for Sm as well as the substitution for iron to change the easy axis of magnetization.

In the study on hard magnetic properties, it has also been revealed that SmFe$_7$ has a great potential as a material for an electromagnetic wave absorber that can be used at an extremely high frequency. It is well accepted that the permeability of high frequency magnetic materials is suppressed by the Snoek’s limit, which is due to the natural resonance caused by the electromagnetic wave under the presence of the anisotropy field $H_A$. In general, the resonance frequency is given by $f_r = (\gamma/2\pi)H_A$, where $\gamma$ is the gyromagnetic ratio. However, when the precession of the magnetization vector occurs by moving out of the basal plane and the anisotropy fields satisfy the condition $H_{A1} \gg H_{A2}$, in which $H_{A1}$ determines the preferred plane of magnetization and $H_{A2}$ defines the preferred direction in the basal plane, then the resonance frequency is given by $f_r = (\gamma/2\pi)(H_{A1}/H_{A2})^{1/2}$ [17]. The anisotropy of SmFe$_7$ applied to this case. Since the $H_{A1}$ and $H_{A2}$ are given by $-2K_1/M_s$ and $-16K_2/M_s$, respectively, to the first approximation, the resonance frequency is given by $f_r = (2\gamma/\pi M_s)(2K_1K_2)^{1/2}$. When the values listed in Table 2 are substituted in the equation, $f_r \approx 230$ GHz is obtained for SmFe$_7$. SmFe$_7$ is, therefore, considered to be a promising material as an electromagnetic wave absorber in an extremely high frequency range up to D band.

4. Conclusions

Magnetism of intermetallic compounds SmFe$_2$, SmFe$_3$, Sm$_6$Fe$_{23}$, and SmFe$_7$ were studied in detail using single crystals grown by a modified flux method. SmFe$_2$ and Sm$_6$Fe$_{23}$ have the easy axis of magnetization in the [111] direction of a cubic crystal. Extremely large negative magnetostriction of SmFe$_2$ can be used practically as a material for a high performance microactuator or ultrasonic generator. SmFe$_3$ has a relatively large saturation moment and the easy axis of magnetization in the direction parallel to the c-axis of a hexagonal crystal. Since the saturation moment and the anisotropy constants satisfy the condition of perpendicular magnetization, SmFe$_3$ seems promising for an application as a next generation perpendicular magnetic recording medium. SmFe$_7$ has large saturation magnetization and extremely large magnetocrystalline anisotropy, which are suitable for an application as a high performance permanent magnet material. In addition, SmFe$_7$ has strong planer anisotropy, which is similar to ferroxplanas that have been used as a high frequency magnetic material. SmFe$_7$ seems promising as a high performance electromagnetic wave absorber in the frequency range of milliwave.

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