Enhancement of Magnetization Intensity in Na- and K- β'' -Ferrites by Annealing in Chalcogen Atmosphere

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The enhancement of magnetization intensities in Na- and K- β'' -ferrites by annealing in a chalcogen (S, Se) atmosphere was studied. Although Na- and K- β'' -ferrites were changed to Na- and K- β -ferrites by annealing in a Se atmosphere ($P_{\text{Se}} = 31.4$ kPa) at 1073 K for 1 h, the high magnetization intensities of 50 and 63 μWbmk^{-1} respectively, were first obtained in Na- and K- β -ferrites. The enhancement of magnetization intensity is resulted from Se absorption into ionic conduction layer. It was indicated that Se atoms may occupy in two sites on the ionic conduction layer, because its TG curve showed two steps desorption process. K- β'' -ferrite annealed at 1273 K in a Se atmosphere decomposed to cubic spinel and $\alpha\text{-Fe}_2\text{O}_3$ phases, on the contrary, the K- β'' -ferrite annealed in a S atmosphere decomposed to only the cubic spinel phase.

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I. Introduction

β - and β'' -ferrites have a structure similar to that of β - and β'' -aluminas which are well known compounds for high ionic and protonic conductors. Over the past few decades a considerable number of studies have been made on the synthesis, the crystal structure, and ionic conductivities of β - and β'' -ferrites⁽¹⁾⁻⁽⁶⁾. These ion conductive ferrites have alternate stacking structure of ionic conduction layers and spinel blocks which have four cubic close-packed oxygen layers as shown in Fig. 1. However, the crystal structures of β - and β'' -ferrites show obvious differences in their symmetries. Namely, the β -structure is hexagonal ($P6_3/\text{mmc}$) while the β'' -structure is rhombohedral ($R\bar{3}\text{m}$). The chemical composition of β - and β'' -ferrites is approximately expressed as $\text{K}_{1+x}\text{Fe}_{11}\text{O}_{17}$ ($0 \leq x \leq 1$). β'' -ferrites is unstable, however, if divalent cation Me(II), such as Co^{2+} , Zn^{2+} , Cd^{2+} , are absent in the spinel block⁽⁷⁾⁻⁽⁹⁾. The chemical formula of a β'' -ferrite therefore is written as follows:

The magnetism of β - and β'' -ferrites is classified as either antiferro- or weak ferro-magnetism, because the uncounterbalanced magnetic moment in ferrimagnetic spinel blocks, which is about $25 \mu_B$, is nullified by antiferromagnetic superexchange interaction of O^{2-} ions in ionic conduction layers⁽¹⁰⁾⁻⁽¹²⁾.

Recently, a large number of studies have been made on the influence of hydration upon the electrical and magnetic properties of β'' -ferrites⁽¹³⁾⁽¹⁴⁾. According to these studies, hydrated β'' -ferrites show low ionic conductivities and high magnetization intensity up to $17 \mu\text{Wbmk}^{-1}$. It was clarified by neutron diffraction that this enhance-

ment of magnetization intensity is due to additionally induced ferromagnetic superexchange interaction by O^{2-} ion of H_2O or H_3O^+ which are introduced into the ionic conduction layer by hydration⁽¹²⁾. If the ions which have a different superexchange interaction with O^{2-} ion, are introduced into the ionic conduction layer, it is expected that β'' -ferrite may show the higher magnetization intensity.

Since chalcogen ions, especially S^{2-} and Se^{2-} ions, have a different superexchange interaction with O^{2-} ions⁽¹⁵⁾, they may enhance the magnetization intensity stronger than O^{2-} ion. Little attention has given,

Fig. 1 Schematic diagrams of (a) the β -ferrite and (b) the β'' -ferrite structures.

however, to the S and Se which would affect the magnetic properties of β'' -ferrites in the same manner as O^{2-} ions.

The purpose of this paper is to study the enhancement of magnetization intensities in β'' -ferrites by annealing in a chalcogen (S, Se) atmosphere.

II. Experimental Procedures

Single crystals of β'' -ferrite were prepared by a flux method. The composition of the flux powder mixture was 63 mol% Fe_2O_3 –37 mol% Na_2O and that of the sample powder mixture was $K_2O \cdot 5Fe_2O_3$, to which a small amount of CoO was added in order to stabilize the β'' -phase⁽¹³⁾. After the sample and flux powder mixture were weighed in the mole ratio of 1:5.5, the mixture was pressed into pellet. The pellet was placed in a Pt crucible and calcined at 1173 K for 10 h. After the sample was melted at 1573 K for 5 h, a single crystal was grown by decreasing the temperature to 1323 K at a cooling rate of 2 K/h. The crystals were extracted from the flux by hot dil. HNO_3 .

Since the as-grown β'' -ferrite crystals contained both K and Na, an ion exchanging treatment was carried out in order to obtain β'' -ferrites that contained only one kind of alkali ion by dipping the crystals in either molten Na or K nitrate for 24 h. Then Na- or K-exchanged crystals were annealed at 1073 or 1273 K in chalcogen atmosphere ($P_{\Sigma S} = 48.6$ kPa, $P_{\Sigma Se} = 31.4$ or 64.8 kPa) for 1 h, where $P_{\Sigma S}$ and $P_{\Sigma Se}$ mean total vapor pressure of S and Se vapor, respectively.

Magnetization curves were recorded by means of a vibrating sample magnetometer (VSM) in a maximum applied magnetic field of 1.2 MA/m at room temperature. The amount of chalcogen absorbed in compounds was determined by thermal gravity (TG) measurements up to 1273 K in an Ar atmosphere.

III. Results and Discussion

The single crystals extracted from flux have the platelet shape with dimensions of approximately $5 \times 5 \times 1$ mm.

The chemical formula of each Na and K exchanged crystals analyzed by EDX was as follows:

First of all, in order to clarify the phase of the exchanged single crystal, the single crystal was crushed into a powder, which was studied using XRD. Figure 2 shows the XRD patterns of the K-exchanged sample and those annealed in a Se atmosphere ($P_{\Sigma Se} = 31.4$ or 64.8 kPa) at 1073 or 1273 K for 1 h after K-exchanging. The XRD pattern of the K-exchanged crystal is indexed as a single β'' -phase. Although β and β'' phases give similar diffraction patterns, typical unique diffraction for β phase is (107), which enables to differentiate β phase from β'' phase, and one for β'' phase is (1011)⁽⁶⁾. Judging from this criteria, the samples annealed at 1073 K consisted mainly of

Fig. 2 X-ray diffraction patterns of the K- β'' -ferrite and that annealed at 1073 or 1273 K in Se atmosphere ($P_{\Sigma Se} = 31.4$ or 64.8 kPa) for 1 h.

the β -phase with a small amount of the cubic spinel phase, due to the appearance of the (107) reflection (indicated by the arrow in Fig. 2). The diffracted intensities from these phases were fairly independent of the partial pressure of Se. In contrast, the sample annealed at 1273 K has mainly α - Fe_2O_3 with residual β and spinel phases.

Figure 3 shows the transmission Laue photographs of the single crystal samples corresponding to the samples in Fig. 2. The Laue patterns of the samples annealed at 1073 K are similar to that of the K-exchanged crystal, except that a few reflections show streaks. In contrast, the sample annealed at 1273 K which is considered as an α - Fe_2O_3 phase from the XRD in Fig. 2, had already changed into a polycrystal. Then suitable annealing temperature was 1073 K.

Figure 4 shows the magnetization curves of the single crystal samples except for one annealed at 1273 K, which caused the decomposition of the sample into α - Fe_2O_3 . K-exchanged crystal showed antiferromagnetic-like magnetization curve. After annealing in a Se atmosphere with either $P_{\Sigma Se} = 31.4$ or 64.8 kPa at 1073 K, however, the K-exchanged crystal became magnetic crystal with a spontaneous magnetization of 63 and 44 $\mu Wbmkg^{-1}$ which were obtained by extrapolation. It is surprising that the high magnetization intensity of 63 $\mu Wbmkg^{-1}$, which is about fourth times higher than that of hydrated β'' -ferrite, is introduced by annealing in a Se atmosphere. This enhancement of magnetization intensity will be due to the invasion of Se atoms into the ionic conduction layer of β -ferrite which is derived from β'' -ferrite by annealing in a Se atmosphere.

Fig. 3 Laue photographs of (a) the K- β'' -ferrite, annealed at (b) 1073 K, $P_{\Sigma\text{Se}}=31.4$ kPa, (c) 1073 K, $P_{\Sigma\text{Se}}=64.8$ kPa, and (d) 1273 K, $P_{\Sigma\text{Se}}=31.4$ kPa for 1 h.

Fig. 4 Magnetization curves of the K- β'' -ferrite and that annealed at 1073 K in Se atmosphere ($P_{\Sigma\text{Se}}=31.4$ or 64.8 kPa) for 1 h.

Since it was already found in the K-exchanged crystals that the suitable annealing temperature for creating the β phase was 1073 K, the Na- β'' -ferrite was also annealed at 1073 K. Figure 5 shows the magnetization curves of the Na- β'' -ferrite single crystals annealed at 1073 K in a Se atmosphere. The Na-exchanged crystal shows antiferromagnetic-like magnetization curve. After annealing in a Se atmosphere with $P_{\Sigma\text{Se}}=31.4$ or 64.8 kPa at 1073 K, however, the Na-exchanged crystal became a magnetic crystal with spontaneous magnetization of 11 and 50 μWbmkg^{-1} , corresponding to the different levels of $P_{\Sigma\text{Se}}$. This is the first observation that β -ferrites exhibit the high magnetization intensities as high as 50 μWbmkg^{-1} .

The appearance of high magnetization intensities may be due to the absorption of Se atoms into the ionic conduction layers of the β -ferrite. The amount of Se absorbed in this layer was estimated from TG measurement of the desorption of Se.

Figure 6 shows the TG curves of the Na-exchanged single crystals annealed in a Se atmosphere ($P_{\Sigma\text{Se}}=31.4$ kPa) at 1073 K for 1 h which showed small enhancement of magnetization intensity of 11 μWbmkg^{-1} in Fig. 4. The magnetization and TG were measured with same crystals. Mass loss in the Na-exchanged crystals annealed in a Se atmosphere occurred at two temperature ranges from 460

Fig. 5 Magnetization curves of the Na- β'' -ferrite and that annealed at 1073 K in Se atmosphere ($P_{\text{Se}}=31.4$ or 64.8 kPa) for 1 h.

Fig. 6 TG curve of the Na- β'' -ferrite annealed at 1073 K in Se atmosphere ($P_{\text{Se}}=31.4$ kPa) for 1 h.

to 600 K and over 800 K. The desorption of Se from the ionic conduction layer occurred at the lower temperature of 600 K because the slight mass loss over 800 K was due to desorption of alkali element. It is important to mention that the desorption process of the Na-exchanged crystals annealed in a Se atmosphere occurred in two steps. It seems reasonably to say that the Se atoms will exist on two sites which have different bonding energy in ionic conduction layers because the onsets of each desorption process were 459 and 550 K, and the each amount of Se calculated from mass loss was 0.17 and 0.05 mol/f.u. Two step desorption process was already reported in hydrated β'' -ferrites. The onsets of each desorption process of Se were roughly same as those of H_2O which were ranging from 437 to 523 K and ranging from 523 to 623 K respectively⁽¹³⁾.

Fig. 7 X-ray diffraction patterns of the K- β'' -ferrite and that annealed at 1073 or 1273 K in S atmosphere ($P_{\text{S}}=48.6$ kPa) for 1 h.

Although Se content was very small and it requires further studies to clarify the quantitative relationship between the magnetization and the amount of Se, it is confirmed in this studies that Na- and K- β'' -ferrites annealed in a Se atmosphere change to Na- and K- β -ferrites and show the enhancement of magnetization which is resulted from absorption of Se.

Figure 7 shows XRD patterns of the K-exchanged β'' -ferrite single crystal and that annealed in a S atmosphere ($P_{\text{S}}=48.6$ kPa) at 1073 or 1273 K for 1 h after K-exchanging. The diffraction pattern of the sample annealed at 1273 K, shows that the sample was perfectly decomposed into the cubic spinel phase. The sample annealed at 1073 K contained a relatively large amount of cubic spinel phase. It is interesting to note that the β'' -ferrite annealed in a S atmosphere decomposed to the cubic spinel not to $\alpha\text{-Fe}_2\text{O}_3$ phase, which existed in the β'' -ferrite annealed at 1273 K in a Se atmosphere.

IV. Conclusion

The enhancement of the magnetization intensities in Na- and K- β'' -ferrites by annealing in a chalcogen (S, Se) atmosphere was studied. The high magnetization intensities of 50 and $63 \mu\text{Wbmkg}^{-1}$ were observed in Na- and K- β -ferrites derived from Na- and K- β'' -ferrites by annealing in a Se atmosphere at 1073 K for 1 h. This is the first observation that β -ferrites show such high magnetization intensities. Se atoms which induce the high magnetization intensity may be occupied in two sites because its TG curve showed two steps desorption process. Further

studies are needed to clarify the relationships between enhanced magnetization intensity and the amount of Se in Na- and K- β -ferrite.

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