**ε-Iron Oxide Exhibiting High-Frequency Millimeter Wave Absorption**  
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**Abstract**  
This review article describes the large coercive field and high frequency millimeter wave absorption of ε-Fe$_2$O$_3$. In 2004, we obtained pure ε-Fe$_2$O$_3$ phase by a particular chemical synthesis method for nanosize particles, a combination method of reverse-micelle and sol-gel techniques. This ε-Fe$_2$O$_3$ exhibits a huge coercive field of 20 kOe at room temperature. In addition, its physical properties can be widely controlled by substituting the iron cations with other metal cations. In this paper, the synthesis, crystal structure, magnetic properties, and especially, the millimeter wave absorption properties of ε-Fe$_2$O$_3$ and metal substituted ε-M$_x$Fe$_{2-x}$O$_3$ (M = Al and Ga) are presented. ε-Fe$_2$O$_3$ and ε-M$_x$Fe$_{2-x}$O$_3$ based magnets have the possibility as millimeter wave absorbers for the future high-speed wireless communications.

**Key Words:** ε-Fe$_2$O$_3$, Iron oxide, Hard magnet, Millimeter wave

**I. INTRODUCTION**  
Maghemite (γ-Fe$_2$O$_3$) and hematite (α-Fe$_2$O$_3$) of iron oxide Fe$_2$O$_3$ are commonly observed in nature and have been extensively studied [1-8]. γ-Fe$_2$O$_3$ has been used in magnetic recording tapes or magnetic fluids, while α-Fe$_2$O$_3$ is widely known as red-dye. In the case of bulk Fe$_2$O$_3$, γ-Fe$_2$O$_3$ is known to transform to α-Fe$_2$O$_3$ with increasing temperature. By chemical synthesis of Fe$_2$O$_3$ nanoparticles, our group obtained a pure phase of ε-Fe$_2$O$_3$ (Fig. 1a) [9-11]. Its crystal structure is totally different from those of γ-Fe$_2$O$_3$ or α-Fe$_2$O$_3$. In 2004, we reported that ε-Fe$_2$O$_3$ has an extremely large coercive field ($H_c$) of 20 kOe at room temperature, which is the largest among metal oxide-based magnets (Fig. 1b).

Another interesting feature of ε-Fe$_2$O$_3$ is that it shows a spin reorientation phenomenon at 115 K [12-15]. From these unique magnetic properties, various experimental researches, such as Mössbauer studies, neutron diffraction studies, X-ray magnetic circular dichroism studies, etc. have been conducted to date [16-18]. Moreover, we have reported that ε-Fe$_2$O$_3$ exhibits high frequency millimeter wave absorption at 182 GHz [19], which is due to zero-field ferromagnetic resonance. The absorption frequency was widely changed by metal substitution of Fe$^{3+}$ ions [19-21].

Fig 1. (a) Phase transformation of Fe$_2$O$_3$ and crystal structures of γ-Fe$_2$O$_3$, α-Fe$_2$O$_3$, and ε-Fe$_2$O$_3$. (b) Magnetization versus external magnetic field curve of ε-Fe$_2$O$_3$ at 300 K exhibiting an $H_c$ value of 20 kOe, adapted from ref [9].
II. SYNTHESIS

ε-Fe₂O₃ and metal substituted ε-Fe₂O₃ (ε-MₓFe₂–xO₃, M = Al and Ga) nanoparticles are synthesized by chemical methods such as combination of reverse-micelle and sol-gel techniques, sol-gel method, and impregnation method using mesoporous silica [9,10,19-24]. Here, the combination method of reverse-micelle and solgel methods is described (Fig. 2a). In the reverse-micelle step, two reverse-micelle systems are formed by cetyl trimethyl ammonium bromide (CTAB) and 1-butanol as surfactant in n-octane solvent. One reverse-micelle system contains aqueous solution of Fe(NO₃)₃ and Ba(NO₃)₂ with addition of Al(NO₃)₃ or Ga(NO₃)₃ for metal substituted series, and the other contains NH₃ aqueous solution. These two microemulsion systems are mixed under rapid stirring, and tetraethoxysilane (C₂H₅O)₄Si is successively added to this solution. This forms SiO₂ matrix around the MₓFe₂–x(OH)₆ nanoparticles to obtain the precursor nanoparticles. The precipitation is separated by centrifugation and sintered in air at 1000°C for 4 hours. The SiO₂ matrix is removed by stirring in NaOH solution at 60°C for 24 hours. With this synthesis method, rod-shaped ε-MₓFe₂–xO₃ is obtained due to the effect of Ba²⁺ ions, which adsorb on particular planes of ε-Fe₂O₃ as morphology control agent, inducing growth towards one direction (Fig. 2b). Spherical nanoparticles can also be obtained without the use of Ba(NO₃)₂ (Fig. 2c).

Fig. 2 (a) Synthesis scheme of ε-MₓFe₂–xO₃. (b) TEM image of rod-shaped ε-Ga₀.₄₃Fe₁.₅₇O₃ adapted from ref [24] and (c) spherical ε-Ga₀.₄₀Fe₁.₆₀O₃ adapted from ref [20].

III. CRYSTAL STRUCTURE

ε-Fe₂O₃ has an orthorhombic crystal structure (a= 5.1019 (3) Å, b= 8.7807 (6) Å, c= 9.4661 (5) Å), categorized in Pnma2₁ space group with spontaneous polarization [12]. There are four different Fe³⁺ sites, Feₐ, Fe₇, Fe₈, and Fe₉, where Feₐ, Fe₇, and Fe₈ are octahedral, and Fe₉ is tetrahedral coordination (Fig. 1a). The bond lengths of Fe and O are 1.87 – 2.43 Å for Feₐ – O, 1.73 – 2.38 Å for Fe₇ – O, 1.86 – 2.21 Å for Fe₈ – O, and 1.74 – 1.94 Å for Fe₉ – O, indicating largely distorted coordination geometries around Feₐ and Fe₉ sites. The Al substituted and Ga substituted samples also have the same orthorhombic crystal structure. Rietveld analyses of the X-ray diffraction patterns showed that non-magnetic Al³⁺ ions and Ga³⁺ ions selectively occupy the Fe₉ site among the four iron sites (Table I). This site selectivity is understood by the smaller ion radius of Al³⁺ (0.535 Å) and Ga³⁺ (0.620 Å) compared to Fe³⁺ (0.645 Å) [25]. The Al³⁺ and Ga³⁺ ions prefer to occupy the smaller tetrahedral Fe₉ site than the octahedral Feₐ, Fe₇, and Fe₈ sites.

IV. MAGNETIC PROPERTIES

ε-Fe₂O₃ shows spontaneous magnetization at a Curie temperature (T_C) of about 500 K. At room temperature, ε-Fe₂O₃ shows a huge magnetic hysteresis loop as shown in Fig. 1b. The H_c value of ε-Fe₂O₃ at 300 K is 20 kOe. The magnetic structure has been investigated using molecular field theory, which indicated that ε-Fe₂O₃ is a ferrimagnet, where Fe₇ and Fe₈ sites have positive sublattice magnetizations, and Feₐ and Fe₉ sites have negative sublattice magnetizations (Fig. 3a) [26]. This result was consistent with the experimental results from neutron diffraction measurements and Mössbauer spectroscopy measurements [14,18], and was also consistent with first-principles calculation results [27].
Table I Substitution ratios (%) of each Fe site for \( \varepsilon \)-Ga\(_x\)Fe\(_{2-x}\)O\(_3\) and \( \varepsilon \)-Al\(_x\)Fe\(_{2-x}\)O\(_3\) [19,20].

<table>
<thead>
<tr>
<th></th>
<th>( x )</th>
<th>( \text{Fe}_A )</th>
<th>( \text{Fe}_B )</th>
<th>( \text{Fe}_C )</th>
<th>( \text{Fe}_D )</th>
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<tr>
<td>Ga substitution</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
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<td>0</td>
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<tr>
<td></td>
<td>0.29</td>
<td>0</td>
<td>0</td>
<td>13</td>
<td>45</td>
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<tr>
<td></td>
<td>0.40</td>
<td>0</td>
<td>0</td>
<td>17</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>0</td>
<td>8</td>
<td>21</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>0</td>
<td>9</td>
<td>28</td>
<td>98</td>
</tr>
<tr>
<td>Al substitution</td>
<td>0.06</td>
<td>3</td>
<td>0</td>
<td>-2</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>0.09</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>17</td>
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<tr>
<td></td>
<td>0.21</td>
<td>0</td>
<td>3</td>
<td>8</td>
<td>30</td>
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<td></td>
<td>0.30</td>
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<td>2</td>
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<td></td>
<td>0.40</td>
<td>12</td>
<td>1</td>
<td>14</td>
<td>52</td>
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By increasing the Ga\(^{3+}\) and Al\(^{3+}\) substitution ratio, change of the magnetic properties was observed. The field-cooled magnetization curves under an external magnetic field of 10 Oe showed that the \( T_C \) value decreased from 500 K \((x = 0)\) to 448 K \((Al, x = 0.40)\) and 324 K \((Ga, x = 0.67)\) with the increase of substitution. As for the \( H_c \) value at 300 K, it decreased from 22.5 kOe \((x = 0)\) to 10.2 kOe \((x = 0.40)\) with Al substitution, and saturation magnetization \((M_s)\) value increased. Similarly, with Ga substitution, the \( H_c \) value decreased to 2.1 kOe \((x = 0.67)\) and \( M_s \) value increased (Fig. 3b). These changes in the magnetic properties can be explained by the metal replacement of Fe\(^{3+}\) magnetic ions \((3d^5, S = 5/2)\) by non-magnetic Al\(^{3+}\) ions \((3d^0, S = 0)\) or Ga\(^{3+}\) ions \((3d^{10}, S = 0)\). As mentioned previously, \( \varepsilon \)-Fe\(_2\)O\(_3\) is a ferrimagnet with positive sublattice magnetizations at Fe\(_B\) and Fe\(_C\) sites and negative sublattice magnetizations at Fe\(_A\) and Fe\(_D\) sites. With the substitution of Fe\(_D\) site Fe\(^{3+}\) ions with non-magnetic ions, the total magnetization increases, leading to the increase of \( M_s \) value. In addition, the non-magnetic ions reduce the superexchange interaction between the magnetic sites, resulting in a decrease of \( T_C \) [26].

V. HIGH-FREQUENCY MILLIMETER WAVE ABSORPTION

The millimeter wave absorption spectra of \( \varepsilon \)-Ga\(_x\)Fe\(_{2-x}\)O\(_3\) and \( \varepsilon \)-Al\(_x\)Fe\(_{2-x}\)O\(_3\) are shown in Fig. 4. The absorption properties in the millimeter wave region were measured using two methods. Free space electromagnetic wave absorption measurement system was used for the lower frequency region \((V\text{-band; } 50-75\text{ GHz, and } W\text{-band; } 75-110\text{ GHz})\). Ga substituted samples \((x = 0.61 - 0.29)\) were measured in this region, and the powder samples were filled in \(30\text{mmφ} \times 10\text{ mm}\) quartz cell with fill ratios of \(ca\.\) 40%. As the \( x \) value decreased, the absorption frequency shifted higher, i.e., 64 GHz \((x = 0.54)\), 73 GHz \((x = 0.47)\), 84 GHz \((x = 0.40)\), 88 GHz \((x = 0.35)\), and 97 GHz \((x = 0.29)\). In the case of
x = 0.67, 0.22, and 0.15 Ga substituted samples, the absorption peaks exceed the measurement range (50–110 GHz). Therefore, hand-made apparatuses for the range of 27–40 GHz and 105–142 GHz were prepared to confirm the absorption frequencies of these materials. As a result, the sample for x = 0.67 showed an absorption peak at 35 GHz, and the absorption frequencies of x = 0.22 and 0.15 were observed at 115 GHz and 126 GHz, respectively.

For the measurement of higher frequency range, terahertz time domain spectroscopy (THz-TDS) measurement system was used. Al substituted samples were measured in this region, and the powder samples were filled in 8 mm × 8 mm × 8 mm paper containers with fill ratios of ca. 30%. The electromagnetic wave absorption spectra are shown in Fig. 4 with red lines. Absorption peaks were observed at 112 GHz (x = 0.40), 125 GHz (x = 0.30), 145 GHz (x = 0.21), 162 GHz (x = 0.09), 172 GHz (x = 0.06), and 182 GHz (x = 0). Similar to the Ga substituted series, the f_r value decreased with Al substitution, consistent with the behavior of the H_c value (Fig. 3c).

The mechanism of the observed millimeter wave absorption is explained as the following. Generally, when electromagnetic wave is irradiated into a ferromagnet under zero magnetic field, zero-field ferromagnetic resonance (natural resonance) occurs. The bulk magnetization is tilted away from the magnetic easy-axis by the magnetic component of the electromagnetic wave, and precession of the magnetization occurs around the easy-axis due to gyromagnetic effect. Resonance absorption is observed when this precession frequency coincides with the electromagnetic wave frequency [28]. This resonance frequency (f_r) is proportional to the magnetocrystalline anisotropy (H_K) and can be expressed as f_r = (ν / 2π)H_K, where ν is the gyromagnetic ratio. If the sample is consisted of randomly oriented particles with uniaxial magnetic anisotropy, the H_K value is proportional to H_c. Therefore, electromagnetic wave absorption at high frequencies is expected with insulating materials exhibiting large coercivity, which is the case for ε-Fe_2O_3 based magnets.

![Absorption Spectrum](image)

Fig. 4 Millimeter wave absorption spectra of ε-Ga_xFe_2-xO_3 (blue lines) and ε-Al_xFe_2-xO_3 (red lines) at room temperature. For Ga substituted x = 0.22 and 0.15, the dotted lines represent the experimental data and the solid lines are eye guides.

**VI. CONCLUSION**

In this article, millimeter wave absorption properties of ε-Fe_2O_3 and metal substituted ε-Fe_2O_3 (ε-M_xFe_2-xO_3, M = Al and Ga) were described along with the synthesis, crystal structure, and magnetic properties. The Al^{3+} and Ga^{3+} ions selectively substituted the tetrahedral sites of the crystal structure, increasing the magnetization and decreasing the coercive field. This leads to the tuning of the resonance frequency of millimeter wave absorption, since the resonance frequency is proportional to the magnetic anisotropy of the material. By Al substitution and Ga substitution, ε-Fe_2O_3 based magnets absorbed millimeter waves covering a wide range of 35 – 182 GHz. Therefore, it has the potential as millimeter wave absorbers for the next generation wireless communications to prevent electromagnetic wave interference problems. Furthermore, this material is based on chemically stable iron oxide Fe_2O_3, encouraging the possibility for industrial applications.
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