Resonance Frequency Tuning of a 200 GHz Band Absorber by an External Magnetic Field

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The effect of the external magnetic field on the millimeter-wave absorption of rhodium-substituted epsilon iron oxide, ε-Rh$_{0.13}$Fe$_{1.87}$O$_3$ (1) and ε-Rh$_{0.19}$Fe$_{1.81}$O$_3$ (2) nanomagnets, is investigated. Terahertz time-domain spectroscopy (THz-TDS) shows that 1 and 2 display a zero-field ferromagnetic resonance (the so-called natural resonance) at 201 GHz with a linewidth of 20 GHz and at 210 GHz with a linewidth of 30 GHz, respectively. The ferromagnetic resonance is measured under an external magnetic field ($H_{ex}$). Applying $+3.5$ kOe parallel to the remnant magnetization and $-3.5$ kOe antiparallel to the remnant magnetization shifts the resonance frequency at 201 GHz in 1 by $+6$ and $-4$ GHz and that in 2 by $+4$ and $-4$ GHz, respectively. Simulations of the ferromagnetic resonance using the Landau–Lifshitz–Gilbert model reproduce the magnetic field-induced shifts of the resonance frequencies. The 220 GHz band millimeter wave is the highest frequency with a high transparency for “atmospheric windows” and is expected to be a carrier frequency for sixth-generation mobile communication systems (6 G) or 7 G. This study may help realize applications for millimeter-wave isolators, circulators, or shutters.

1. Introduction

As the society enters the internet of things (IoT) era, the usage of high-frequency electromagnetic waves, called millimeter waves (30–300 GHz), is spreading to wireless communication and sensing fields. Examples of millimeter-wave usage include the communication protocols of wireless gigabit (WiGig), automotive millimeter-wave radars, advanced driver assistance systems (ADASs), and noncontact biomonitoring technologies.$^{[15-31]}$ In addition, millimeter waves hold promise in next-generation mobile communication systems (6 G) and 7 G (Beyond 5 G).$^{[6,7]}$ In particular, 94, 140, and 220 GHz are important frequencies with a high transparency, which are called atmospheric windows. These frequencies are suitable for carrier electromagnetic waves.

From the perspective of electromagnetic environment protection, electromagnetic wave absorbers are important to suppress electromagnetic interference or noise countermeasures. Although magnetic materials absorb electromagnetic waves by magnetic loss, the resonance frequencies of common magnetic materials such as ferrite and magnetic metal are low.$^{[8-13]}$ In addition, the resonance frequencies of hard ferrites such as hexagonal ferrites$^{[14-16]}$ are limited to lower frequencies compared with the expected frequencies for 6 G or 7 G applications.

Epsilon iron oxide (ε-Fe$_3$O$_4$) nanomagnets are attractive because they have been reported to exhibit a large coercive field and high-frequency millimeter-wave absorption at 182 GHz by zero-field ferromagnetic resonance (the so-called natural resonance).$^{[17-48]}$ Metal-substituted epsilon iron oxide (ε-$M_x$Fe$_{2-x}$O$_3$: $M = A^3^+$, Ga$^{3+}$, and In$^{3+}$) and Ti$^{4+}$–Co$^{2+}$ cosubstituted series, ε-(TiCo)$_x$Fe$_{2-x}$O$_3$, exhibit zero-field ferromagnetic resonance over a wide frequency range of 35–182 GHz. Rhodium-substituted epsilon iron oxide, ε-Rh$_{x}$Fe$_{2-x}$O$_3$, shows even higher resonance frequencies above 182 GHz by increasing the Rh/Fe ratio.$^{[27,28]}$ Consequently, ε-Rh$_{x}$Fe$_{2-x}$O$_3$ holds promise as a millimeter-wave absorber because electromagnetic waves of 6 G or 7 G should use high-frequency millimeter-wave bands, especially around 220 GHz. From the viewpoint of industrial applications, tuning the resonance frequency by the magnetic field effect is important. Herein, we use terahertz time-domain spectroscopy (THz-TDS) to examine the effect of the magnetic field on ε-Rh$_{x}$Fe$_{2-x}$O$_3$, which is a 220 GHz-band millimeter-wave absorber.

2. Results and Discussion

2.1. Materials

Figure 1a shows the synthesis of ε-Rh$_{x}$Fe$_{2-x}$O$_3$ nanomagnets. This synthetic route differs from our previously reported methods.$^{[27,28]}$ Rhodium nitrate (0.9 mmol (1), 1.2 mmol (2)) and iron oxide hydroxide (28.9 mmol (1), 25.6 mmol (2)) were...
dissolved in 1.64 L of distilled water, and 76.7 mL of 25% ammonium aqueous solution was added dropwise while stirring at 70°C. Next, tetraethyl orthosilicate (TEOS) (0.41 mol) was added dropwise. The mixture was stirred at 75°C (1) or 60°C (2) for 20 h. The precipitates were obtained by adding 96 g (1) or 82 g (2) of ammonium sulfate to the solution. Then the precipitates were separated by centrifugation and washed several times with water. After drying at 60°C and grinding the precipitates in a mortar, the precursors were obtained. The precursors were sintered in air at 1140°C (1) or 1120°C (2) for 4 h. The sintered samples were added to a sodium hydroxide solution with a concentration of 6 mol dm⁻³ and stirred at 70°C for 24 h to remove the SiO₂ matrix. Finally, they were washed and dried to obtain blackish brown powder samples 1 and 2.

Transmission electron microscopy (TEM) images of the obtained samples showed that the samples consisted of nanoparticles with sizes of d ≈ 14.0 ± 5.6 nm (1) and 14.7 ± 6.1 nm (2) (Figure 1b). These particle sizes are smaller than those previously synthesized by the sol–gel method, d = 19–32 nm.[28] Powder X-ray diffraction (XRD) patterns were measured using a Rigaku Ultima IV (Cu Kα source, λ = 1.5418 Å) (Figure 1c and S1, Table S1, Supporting Information). 1 consisted of 93 wt% of ε-iron oxide (orthorhombic, Pna₂₂₁) and 7 wt% of α-iron oxide (rhombohedral, R₃c). The lattice constants of ε-iron-oxide were a = 5.1052(4) Å, b = 8.7961(7)Å, c = 9.4667(5)Å, and V = 425.11(5) Å³. 2 consisted of 83 wt% of ε-iron oxide and 17 wt% of γ-iron oxide (cubic, Fd3m). The lattice constants of ε-iron oxide in 2 were a = 5.1110(5) Å, b = 8.7996(9) Å, c = 9.4624(7) Å, and V = 425.57(7) Å³. The XRD patterns were analyzed by Rietveld analyses. The Rh³⁺ occupancies in ε-iron oxide in 1 were 0% at the A site, 3% at the B site, 24% at the C site, and 0% at the D site, while those in 2 were 0% at the A site, 0% at the B site, 38% at the C site, and 0% at the D site. These results indicated that substitution preferentially occurred at the C site.

Elemental analyses by inductively coupled plasma mass spectroscopy showed that the concentrations of the Rh³⁺ ions in the entire sample, [Rh][[Rh]+[Fe]], were 0.080 and 0.12 for 1 and 2, respectively. By combining these Rh ratios and the previously reported lattice volumes of ε-RhₓFe₂₋ₓO₃, α-RhₓFe₂₋ₓO₃, and γ-RhₓFe₂₋ₓO₃,[28] the formulas of the epsilon phases were ε-Rh₀.₁₃Fe₁.₈₇O₃ (1) and ε-Rh₀.₁₉Fe₁.₈₁O₃ (2).

2.2. Millimeter-Wave Absorption and the Effect of the Magnetic Field

The zero-field ferromagnetic resonance and ferromagnetic resonance under an external magnetic field were measured using a
THz-TDS system (Figure 2a). Powder samples were pressurized to obtain pellet samples, which were placed in a sample holder of our own design. A strong magnetic field was applied in the out-of-plane direction of the pelleted samples using a superconducting magnet. Then the magnetic field was turned off to obtain magnetized pellets. A THz pulse was irradiated from the N-pole side of the magnetized pellets under an external magnetic field \((H_{ex})\) of ±3.5 kOe. The reason why ±3.5 kOe was used in the present experiment was that this value was the maximum magnetic field of typical coil magnets, which would be used for designing devices such as magnetic field-controlled isolators and circulators in the millimeter-wave region.

The transmission spectra were measured under two conditions: an external magnetic field \((H_{ex})\) applied parallel to the remnant magnetization \((H_{ex} = 0)\) and an external magnetic field applied antiparallel to the remnant magnetization \((H_{ex} = -3.5 \text{ kOe})\). Figure 2b shows the results for 1. In the case of \(H_{ex} = +3.5 \text{ kOe}\), the absorption peak at 201 GHz shifted by +6 GHz (207 GHz), while in the case of \(H_{ex} = -3.5 \text{ kOe}\), the peak shifted by −4 GHz (197 GHz). Figure 2c shows the results for 2. The absorption peak at 210 GHz shifted by +4 GHz (214 GHz) for \(H_{ex} = +3.5 \text{ kOe}\), while the peak shifted by −4 GHz (206 GHz) for \(H_{ex} = -3.5 \text{ kOe}\). Table 1 lists the observed values of the resonance frequency, peak shift, and the full width at half maximum (FWHM), and the Section S2, Supporting Information, describes the spectral analyses. It should be noted that \(\alpha\)- and \(\gamma\)-phases do not possess absorption in the millimeter-wave region, and thus, the \(\alpha\)-phase in 1 and \(\gamma\)-phase in 2 do not affect the resonance behavior.

| \(H_{ex}\) [kOe] | Resonance frequency [GHz] | Resonance frequency shift [GHz] | FWHM [GHz] |
|----------------|--------------------------|---------------------------------|------------|
| 0             | 201                      | −                              | 20         |
| 1             | +3.5                     | 207                            | +6         | 22         |
| −3.5          | 197                      | −4                             | 23         |
| 0             | 210                      | −                              | 30         |
| 2             | +3.5                     | 214                            | +4         | 33         |
| −3.5          | 206                      | −4                             | 28         |

Figure 2. a) Schematic of the setup for ferromagnetic resonance measurements using THz-TDS, which consists of GaAs photoconductive antennas, an emitter and detector with Si lenses, and 1550 nm fiber lasers. b,c) Millimeter-wave absorption spectra of b) 1 and c) 2 measured with magnetized pelleted samples under \(H_{ex} = +3.5 \text{ kOe}\) (red), 0 kOe (green), and −3.5 kOe (blue).
2.3. Mechanism of the Magnetic Field Effect

We simulated the magnetization dynamics to understand the effect of the magnetic field on the millimeter-wave absorption of 1 and 2. The magnetization dynamics with the irradiation of electromagnetic wave under an external magnetic field was simulated using a Landau–Lifshitz–Gilbert (LLG) equation.

\[
\frac{dM}{dt} = -\frac{\gamma}{1 + \alpha^2} M \times H_{\text{eff}} - \frac{\gamma \alpha}{(1 + \alpha^2) M_s} M \times (M \times H_{\text{eff}})
\]

where \( M \) is the magnetization, \( \gamma \) is the gyromagnetic constant, \( \alpha \) is the damping factor, \( M_s \) is the saturation magnetization, and \( H_{\text{eff}} \) is the effective magnetic field described by the vector

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**Figure 3.** Simulation of the magnetic resonance using the LLG equation. \( \theta \) is the polar angle and \( \phi \) is the azimuthal angle. a) Distribution of the magnetization direction illustrated on the unit spheres. In the powdered pellet sample, the magnetization direction is randomly distributed (red dots on the unit sphere). After the pellet sample are magnetized using a superconducting magnet, the magnetization direction is distributed only toward the upper hemisphere in a random manner. b) Magnetic resonance spectra for selected \( \theta \) angles of 10°, 30°, and 80°, and the total averaged spectrum. c) (left) Calculated ferromagnetic resonance spectra under an external magnetic field \( (H_{\text{ex}}) \) from 0 (black line) to +10 kOe (red lines) and to −10 kOe (blue lines) from the average of 5000 randomly selected orientations. It is noteworthy that a shift in the resonance frequency \( (f_r) \) is not observed in a nonmagnetized sample because summing the shifts caused by the magnetization along the +z and −z directions cancels. (right) Shift of \( f_r \) versus \( H_{\text{ex}} \) value plot.
summation of anisotropy field \( (H_a) \), external dc magnetic field \( (H_{dc}) \) along \( \pm z \)-axis direction, and ac magnetic field of the electromagnetic wave \( (H_{em} = H_0 \cos(\omega t)) \) parallel to the \( x \)-axis. The following parameters were used in the simulation: \( \gamma = 2.8025 \times 10^{10} \) s\(^{-1} \) T\(^{-1} \), \( \alpha = 0.05 \), \( M_s = 1 \), \( H_s = 70 \) kOe, \( -10 \) kOe \( \leq H_{ac} \leq +10 \) kOe, and \( H_0 = 0.1 \) kOe. Here, \( \gamma \) and \( H_s \) are defined from the following equations, \( \gamma = \frac{g \mu_B}{h} \) and \( H_s = f_i / \gamma \), where \( g \) is g factor of electron, \( \mu_B \) is Bohr magneton, and \( h \) is Dirac constant. \( \alpha \) and \( H_0 \) are defined to reproduce the measurement result, and \( M_s \) is a normalized value. Supporting Information provides details of the calculations (Figure S4, Supporting Information).

In the pelletized samples, the direction of \( H_s \) was assumed to be randomly distributed (Figure 3a). The simulations used the average of the random orientation (Figure 3b). The resonance frequency shifted by +5 and –6 GHz from the original value upon applying an external magnetic field of +3.5 and –3.5 kOe, respectively (Figure 3c). The observed resonance frequency shifts of 1 (–4 and +6 GHz) and 2 (–4 and +4 GHz) were reproduced by the calculations.

Although the effect of the magnetic field on the resonance frequency is known in the low-frequency region below 110 GHz, such as yttrium–iron–garnet, hexagonal ferrite, and spinel ferrite,\(^{[49-56]} \) the effect of the magnetic field on materials above 200 GHz for 6 G or 7 G applications is yet to be reported.

3. Conclusion

We observed millimeter-wave absorption by the zero-field ferromagnetic resonance in 1 and 2 at 201 and 210 GHz, respectively. Applying an external magnetic field of +3.5 and –3.5 kOe shifted the resonance frequency in 1 by +6 and –4 GHz, respectively. Similarly, the resonance frequency of 2 shifted +4 and –4 GHz by applying +3.5 and –3.5 kOe, respectively. The high-frequency millimeter waves absorbed by these materials have potential in various millimeter-wave applications. The highest frequency of the atmospheric windows, 220 GHz, is expected to be a carrier frequency for 6 G or 7 G wireless communications. In addition, the absorption frequency can be tuned by applying an external field, which can be generated by a coil current. This study may help realize applications for millimeter-wave isolators or circulators as well as shutters for circularly polarized millimeter waves.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

beyond 5G, epsilon iron oxides, ferromagnetic resonances, magnetic field effects, millimeter wave absorptions

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