論文の内容の要旨

磁場による 200 GHz 帯吸収体の共鳴周波数の制御

(Tuning of the resonance frequency of 200-GHz-band absorbers by magnetic fields)

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Abstract

1. Introduction

Epsilon iron oxide (ε-Fe_2O_3) is one of phases of Fe_2O_3, which can be obtained as a stable phase in nanometer-size region. It has been reported that millimeter wave absorption is exhibited at 182 GHz by zero-field ferromagnetic resonance due to its large magnetic anisotropy. In addition, it has reported that Fe^{3+} in ε-Fe_2O_3 can be replaced by other metal cations, with Al^{3+}, Ga^{3+}, In^{3+}-substitutions, and Ti^{4+}-Co^{2+} co-substitution result in lower resonance frequencies (35–182 GHz), and Rh^{3+}-substitution results in higher frequencies (182–222 GHz). As entering the IoT era, the usage of high frequency electromagnetic waves called millimeter wave (30–300 GHz) is spreading in the fields of wireless communication and sensing. Millimeter waves are expected to be used in the next generation of high speed wireless communication and 6G (or 7G), especially around 220 GHz, which is one of the "window of air", is important. Therefore, rhodium-substituted epsilon iron oxide (ε-$Rh_xFe_{2-x}O_3$), which is a millimeter-wave absorber in 220 GHz band, is interesting. It is known that the natural resonance frequency of magnetic materials, such as metal oxide magnets, shifts its frequency more than in the zero-field case with the application of a magnetic field. In the low-frequency region below 110 GHz, magnetic field effect has been known. By this principle, shifting the resonance frequency of millimeter-wave absorbers in the 220 GHz band is expected to be a meaningful use of this band, which has the highest frequency in the atmospheric window.

In this work, I report the synthesis of ε-$Rh_xFe_{2-x}O_3$ by sintering iron oxide hydroxide with rhodium hydroxide in a silica matrix, and the change in millimeter-wave absorption properties by applying an external magnetic field was measured by using terahertz time-domain spectroscopy (THz-TDS).

2. Millimeter wave absorption and magnetic field effect on ε-$Rh_xFe_{2-x}O_3$

The target compounds, ε-$Rh_xFe_{2-x}O_3$ nanomagnets, were synthesized by sol-gel method. Rhodium nitrate and β-iron hydroxide oxide were dissolved in pure water, and 25% NH_3 aq. and tetraethyl orthosilicate was added dropwise to form SiO_2 matrix around metal hydroxide. Then the mixture was stirred and the precursor was obtained by centrifuging the solution to separate and washed several times with water. After drying and grinding in a mortar, the precursors were obtained. The precursors were sintered for 4 h in the air, and then cooled down to room temperature. The sintered samples were added to a sodium hydroxide solution to remove the SiO_2 matrix, which was then washed and dried to obtain blackish brown powder samples **1** and **2**.

Transmission electron microscopy (TEM) images of the obtained samples **1** and **2** were taken and show that the obtained samples consisted with nanoparticles. X-ray powder diffraction (XRD) patterns of samples were measured using Cu Kα source (λ = 1.5418 Å). **1** and **2** consisted of epsilon phase (orthorhombic, $Pna2_1$) as a major phase and alpha phase (rhombohedral, $R\bar{3}c$) or gamma phase (cubic, $Fd\bar{3}m$) as a minor phase. The lattice volume of the epsilon phase of each sample was calculated from Rietveld analysis. Elemental analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) showed the concentrations of the Rh^{3+} ions in the whole sample for **1** and **2**. From the previously reported lattice parameters of ε-$Rh_xFe_{2-x}O_3$ and the result of Rietveld analysis for obtained samples, the formula of the epsilon phases of **1** and **2** were determined and it was found that **1** and **2** were obtained as a ε-$Rh_xFe_{2-x}O_3$.

To measure the natural resonance frequency and its magnetic field effect, transmission measurements in the millimeter wave region were performed using a THz-TDS system. The magnetic field was applied perpendicular to the surface of the pellet sample with installing a permanent magnet (3.5 kOe). The pellet sample was obtained by adding pressure to the powder. The magnetic field of 78 kOe was applied perpendicularly to the pellet sample using a superconducting magnet, and then the magnetic field was turned off to obtain magnetized pellets. The magnetized pellets were set in a sample holder, and the transmission spectra was measured. The absorption peaks were observed in 200 GHz-band for **1** and **2**. The permanent magnet was installed in the THz-TDS system, and THz pulse was irradiated from the N-pole side of the magnetized pellets under an external magnetic field (H_{ex}) generated from the permanent magnet, and the transmission spectrum was measured for two conditions: one where the external magnetic field is applied in the same positive direction as the magnetization (H_{ex} = +3.5 kOe), and one where the external magnetic field is applied in the opposite direction to the magnetization (H_{ex} = −3.5 kOe). In the case of H_{ex} = +3.5 kOe, the absorption peak shifts to the higher frequency side, while in the case of H_{ex} = −3.5 kOe, the peak shifts to the lower frequency side.

3. Qualitative ferromagnetic resonance simulation using Landau-Lifshitz-Gilbert equation

To understand the magnetic field effect on the millimeter wave absorption of **1** and **2**, the magnetization dynamics were analyzed using Landau-Lifshitz-Gilbert (LLG) equation:

$$\frac{d\boldsymbol{M}}{dt} = -\frac{\gamma}{1+\alpha^2}\boldsymbol{M}\times\boldsymbol{H}_{\mathrm{eff}} - \frac{\gamma\alpha}{(1+\alpha^2)M_S}\boldsymbol{M}\times(\boldsymbol{M}\times\boldsymbol{H}_{\mathrm{eff}})$$

where $\boldsymbol{M}$ is magnetization, γ is gyromagnetic constant, α is damping factor, M_s is saturation magnetization, and $\boldsymbol{H}_{\mathrm{eff}}$ is effective magnetic field, which is described by the vector summation of anisotropy field ($\boldsymbol{H}_a$), external magnetic field ($\boldsymbol{H}_{ex}$), and magnetic field of electromagnetic wave ($\boldsymbol{H}_{em}$). Here, the magnetization dynamics under the irradiation with an electromagnetic wave in a static magnetic field assuming was simulated assuming the external magnetic field value (-10 kOe ≤ H_{ex} ≤ +10 kOe) and other parameters. In the calculation, the magnetic field component of electromagnetic wave ($\boldsymbol{H}_{em}$) was set to be parallel to the *x*-axis, and the external magnetic field $\boldsymbol{H}_{ex}$ was applied in the z-axis direction.

In the present pellet samples, the direction of uniaxial magnetic anisotropy is assumed to be randomly distributed towards the hemisphere along the magnetic field direction in the magnetization process. By taking an average of random orientation, simulations showed that the resonance frequency (f_r) shifts higher frequency and lower frequency from the original value by applying external magnetic field of +3.5 kOe and −3.5 kOe respectively. The observed resonance frequency shifts of sample **1** and sample **2** qualitatively agree with the calculation.

4. Conclusion

In this study, it was observed that millimeter wave absorption by zero-field ferromagnetic resonance in sample **1** and **2** (ε-$Rh_xFe_{2-x}O_3$), which was 200 GHz band absorber. the resonance frequency shifted to higher frequency and lower frequency by applying external magnetic field of + 3.5 kOe and −3.5 kOe, respectively. The high-frequency millimeter waves absorbed by these materials are expected to be applied to various millimeter wave applications. In particular, 220 GHz is the highest frequency of "window of air" and is expected to be the carrier frequency for 6G or 7G wireless communications. In addition, the absorption frequency can be tuned by the applying of an external field as small as that generated by a coil current, and this was confirmed by LLG simulation qualitatively. Therefore, this study is expected to help to realize the application of millimeter-wave band isolators and circulators.