Magnetic and dielectric properties of $R\mathrm{Fe_2O_4}$, $R\mathrm{Fe}M\mathrm{O_4}$, and $R\mathrm{GaCuO_4}$ (R=Yb and Lu, M=Co and Cu)

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The magnetic and dielectric properties have been investigated for the isostructural oxides of $R\mathrm{Fe_2O_4}$, $R\mathrm{Fe}M\mathrm{O_4}$, and $R\mathrm{GaCuO_4}$ (R=Yb and Lu, M=Co and Cu). The magnetization measurements for $R\mathrm{Fe_2O_4}$ showed ferrimagnetic ordering at ~250 K. This system also exhibited large dielectric constants of ~10 000–30 000 at around room temperature, which is attributable to the charge-ordering-induced ferroelectricity, as was proposed in our recent paper. The magnetic transition temperatures are lowered to ~45–90 K for $R\mathrm{Fe}M\mathrm{O_4}$. Magnetic ordering is not found for $R\mathrm{GaCuO_4}$. ac magnetic susceptibility measurements indicate that magnetic ordering becomes short-ranged by the substitution at the Fe site. The overall characteristic behavior of the magnetic properties is explained in terms of the change of a spin value as well as the dilution of magnetic interactions. Although the ac dielectric measurements show the existence of polar regions in each material, the dielectric constants below 300 K become smaller in the order of $R\mathrm{Fe_2O_4}$, $R\mathrm{FeCoO_4}$, $R\mathrm{FeCuO_4}$, and $R\mathrm{GaCuO_4}$. From the analysis of the dielectric dispersion, the distribution of the fluctuation time of polar regions is wider in $R\mathrm{FeCoO_4}$, $R\mathrm{FeCuO_4}$, and $R\mathrm{GaCuO_4}$ than in $R\mathrm{Fe_2O_4}$; a coherent motion of polar regions is suppressed in the substituted systems. By comparison to the results from the magnetic measurements, the dielectric properties are discussed in connection with a charge transfer between the transition-metal 3*d* orbitals, consistently with the proposed mechanism of the ferroelectricity in $R\mathrm{Fe_2O_4}$.

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I. INTRODUCTION

The rare earth-iron oxide system, $R\mathrm{Fe_2O_4}$, has a rhombohedral crystal structure (space group $R\bar{3}m$).[1,2] The structure consists of an alternating stacking of triangular lattices of rare earth, iron, and oxygen ions. As the Fe ions have an average valence of 2.5+, an equal amount of the Fe^{2+} and Fe^{3+} ions coexist on the same lattice. Strong magnetic interactions between the localized Fe moments give rise to ferrimagnetic ordering below Néel temperatures (T_N) ~ 250 K.[3–7] From the magnetic study of single-crystalline $\mathrm{LuFe_2O_4}$, the direction of the Fe spins is parallel to the crystallographic *c* axis.[6] The ordering is accompanied by the development of a superlattice cell because of the frustrated antiferromagnetic interactions on a triangular lattice.

The system also involves a charge interaction between Fe^{2+} and Fe^{3+}. Because of the average Fe valence of 2.5+, the Fe^{2+} and Fe^{3+} ions can be regarded as an excess and a deficiency of half an electron, respectively.[8–15] Thus the interaction between Fe^{2+} and Fe^{3+} is accompanied by a frustration on the triangular plane, as is the case of the magnetic interaction. This frustration manifests itself as a charge-ordered state at ~330 K, in which the unit cell has the same $\sqrt{3}\times\sqrt{3}$ structure as that in the ferrimagnetic state.[15] We recently found that the ferroelectricity is ascribable to the ferroelectric regions generated by a polar arrangement of the ordered Fe-3*d* charges because the centers of Fe^{2+} and Fe^{3+} do not coincide.[15] Therefore $R\mathrm{Fe_2O_4}$ belongs to an entirely novel class of ferroelectric materials. Such ferroelectricity is quite a contrast to ordinary ferroelectrics, in which the displacement of cation and anion pairs plays an essential role.[16]

This system exhibits a few other characteristic properties. The electric polarization was found to change at around the magnetic transition temperature of 250 K, suggesting that $R\mathrm{Fe_2O_4}$ is regarded as a kind of multiferroic system.[15] Most recently, a giant magnetodielectric response at room temperature was reported for $\mathrm{LuFe_2O_4}$.[17] This result suggests the presence of multiferroicity at low temperatures in $R\mathrm{Fe_2O_4}$. It is noteworthy from the viewpoint of practical applications that the small activation energy required for switching the direction of each polar region (activation energy Q ~ 0.29 eV) offers a possibility for the fabrication of some devices, such as fatigue-free capacitors.[15] The absence of lead (Pb) is also suitable for application, as the development of lead-free ferroelectrics is desired from an ecological standpoint.[18]

It is known that the crystallographic iron site in $R\mathrm{Fe_2O_4}$ can accommodate several other transition-metal ions, such as Mn^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+}.[19–26] The chemical formula of this system is expressed as $R\mathrm{Fe}M\mathrm{O_4}$, in which the M ion is randomly substituted at the crystallographic Fe site. The formal valence of the Fe ion in this system is 3+, while that of the M ion is 2+. As the substitution of M^{2+} plausibly brings about changes in the physical parameters, such as a charge transfer and a magnetic moment at the Fe/M site, their physical properties are expected to differ from those of

RFe$_2$O$_4$, in which the properties are governed mainly by the interactions between the Fe^{2+} and Fe^{3+} ions. However, the properties of RFeMO$_4$ have been reported only for a few combinations of R and M.

Single-crystalline YFeMnO$_4$ was found to show magnetic ordering at ~60 K.[21] LuFeCoO$_4$ exhibited the presence of a magnetic transition with a cusp at ~70 K, for which the anisotropic effects of the Co^{2+} ion were discussed.[22] The system containing the nonmagnetic ion (Mg^{2+}), LuFeMgO$_4$, was reported to have a characteristic magnetic fluctuation. The behavior was interpreted in terms of thermal fluctuations and freezing of short-range magnetically ordered regions.[23] From a neutron-scattering experiment combined with a Monte Carlo simulation, local cationic ordering of Fe^{3+} and Mg^{2+} was observed in this material.[24] The ordering is accompanied by a short coherence length (about 10 atomic lengths) with the $\sqrt{3}\times\sqrt{3}$ structure, which is likely the origin of the magnetic fluctuation.[24] It is interesting that a similar ionic short-range ordering of Fe^{3+} and Cu^{2+} was also observed for the Cu-substituted system LuFeCuO$_4$ in our recent electron-microscopic measurement.[25] As the ordering may resemble the charge-ordered state of Fe^{2+} and Fe^{3+} in RFe$_2$O$_4$ (Ref. 15), a formation of polar regions would also be realized in these substituted oxides. Therefore RFeMO$_4$ may provide characteristic dielectric properties.

The dielectric properties of RFeMO$_4$ have been studied for the Cu-substituted TmFeCuO$_4$.[26] It was found that this oxide has considerably different dielectric properties from the parent material TmFe$_2$O$_4$; i.e., TmFeCuO$_4$ exhibits fairly smaller dielectric constants (~200) than those of TmFe$_2$O$_4$ ($\gtrsim$3000–5000). It is also characteristic that magnetic ordering is not observed for TmFeCuO$_4$, whereas a ferrimagnetic transition occurs at $T_N\sim 250$ K for TmFe$_2$O$_4$.[26] These results were explained in connection with the charge transfer between the transition-metal ions.[26]

In this work, we have carried out a more systematic investigation of the magnetic and dielectric properties of RFe$_2$O$_4$ and its substituted materials for R=Yb and Lu, since only Cu could be substituted for Fe in TmFe$_2$O$_4$.[26] For the parent materials YbFe$_2$O$_4$ and LuFe$_2$O$_4$, the formation of the RFeMO$_4$ phase was observed for M=Co as well as M=Cu, as noted later. The properties were also studied for RGaCuO$_4$, in which all the Fe ions are replaced by magnetic Cu^{2+} and nonmagnetic Ga^{3+}. Both RFeCuO$_4$ and RGaCuO$_4$ were reported to form the $R\bar{3}m$ structure only for the limited rare earths of R=Tm, Yb, and Lu.[19,20] However, their detailed physical properties, especially the dielectric properties, have not been reported so far. All these Fe-site-substituted oxides can be synthesized in a solid-state reaction in air, which requires only a simple apparatus compared to that for RFe$_2$O$_4$ prepared in a reduced atmosphere.[7] Therefore the investigations of their properties would be also interesting from the viewpoint of applications. The obtained experimental results are discussed in comparison with those of RFe$_2$O$_4$ oxides.

II. EXPERIMENTAL PROCEDURES

Polycrystalline samples were prepared by the solid-state reaction according to the methods described in Ref. 2, 7, 19, and 20. The RFe$_2$O$_4$ phase was prepared by a solid-state reaction in a flow of a mixed CO-CO$_2$ gas at around 1200 °C.[7] The other materials were prepared in air between 1000 and 1380 °C.[19,20] Powder x-ray diffraction measurements using Cu $K\alpha$ radiation showed the formation of RFe$_2$O$_4$, RFeMO$_4$, and RGaCuO$_4$. Each experimental pattern was fitted by the Rietveld analysis using the program RIETAN-2000.[27]

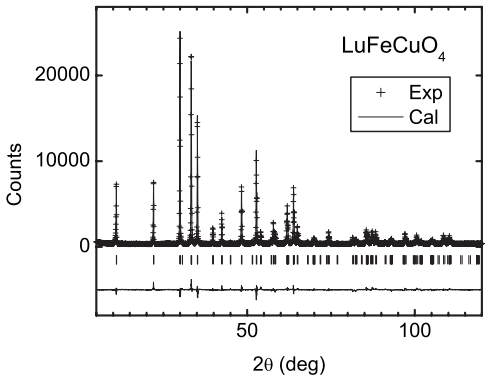

FIG. 1. XRD patterns of LuFeCuO$_4$ ($R\bar{3}m$, R_{WP}=7.33%). The cross markers, upper solid line, and the lower solid lines stand for the experimental data (Exp), the calculated pattern (Cal), and the difference between the experimental and calculated patterns, respectively. The vertical markers show the calculated Bragg angles.

The magnetization measurements were carried out in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) between 5 and 300 K. The magnetization-temperature curves were measured in both field-cooled (FC) and zero-field-cooled (ZFC) modes with an applied magnetic field of 1000 Oe. The FC measurements were performed while cooling the sample with the applied magnetic field. On the other hand, the ZFC magnetization was measured while heating the sample with the field after zero-field cooling to 5 K. In addition to field-cooled (FC) and zero-field-cooled (ZFC) magnetization, thermoremanent magnetization (TRM) was also measured to determine the transition temperature, as follows. The sample was cooled in the applied field of 1000 Oe down to 5 K, at which the field was reduced to zero. The remanent magnetization was then measured while heating the sample. Isothermal magnetization was also measured at 5 K while sweeping the magnetic field within ±50 000 Oe. The ac magnetic susceptibility was measured in the same apparatus with the amplitude of the ac field of 4 Oe. The frequency of the ac field was changed between 1 and 1000 Hz.

The dielectric measurements were performed below room temperature using an impedance analyzer (HP-4284A) equipped with a He refrigerator. The amplitude of the ac electric field was ~0.1–10 V/cm. The frequency of the field was swept between 20 Hz and 1 MHz. Other details of the experimental procedures have been noted elsewhere.[7–9,11,26]

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Figure 1 demonstrates the XRD patterns of one of the

TABLE I. Lattice parameters for all the oxides studied in this work.

Material	a (Å)	c (Å)	V (Å)^3
$YbFe_2O_4$	3.4572(1)	25.1165(7)	259.978(15)
$YbFeCoO_4$	3.4302(1)	25.1805(7)	256.593(16)
$YbFeCuO_4$	3.4853(1)	24.0695(5)	253.207(10)
$YbGaCuO_4$	3.4585(2)	24.1855(9)	250.543(19)
$LuFe_2O_4$	3.4389(1)	25.2567(8)	258.662(17)
$LuFeCoO_4$	3.4172(1)	25.2831(6)	255.680(13)
$LuFeCuO_4$	3.4695(1)	24.1594(5)	251.851(11)
$LuGaCuO_4$	3.4423(1)	24.2846(6)	249.200(13)

materials, $LuFeCuO_4$. The experimental patterns were found to consist only of the reaction products and could be fitted to the rhombohedral structure of $R\bar{3}m$ assuming a random occupation of the Fe and Cu ions at the same crystallographic site. The lattice lengths are shown in Table I, in which the results of all the other oxides are also listed. The fractional coordinates of each atom are essentially the same as those of the isostructural oxide $ErFeMnO_4$.[28] All parameters were verified to be quite similar to those in previous studies,[1,2,19,20] i.e., with replacing Yb with Lu, the a-length and the cell volume decreases, while the c-length is slightly elongated. Although the reason for the behavior of the c-length is unclear,[19,20] the decrease in both the a-length and the cell volume is explained in terms of the lanthanide contraction.

It was found that the variation of the cell volume with the change in the Fe-site ions is qualitatively in accord with the average ionic radii calculated from the effective radii of Fe^{3+}, Co^{2+}, Cu^{2+}, and Ga^{3+} for the coordination number of 5,[29] assuming that the radius of Fe^{2+} is the average of the effective ionic radii for the coronation numbers of 4 and 6 in the high-spin state.[29] Using the assumed Fe^{2+} radius of 0.71 Å, the average ionic radii of $M_1{}^{3+}$ and $M_2{}^{2+}$ in $RM_1{}^{3+}M_2{}^{2+}O_4$ ($M_1{}^{3+}M_2{}^{2+}$=$Fe^{3+}Fe^{2+}$, $Fe^{3+}Co^{2+}$, $Fe^{3+}Cu^{2+}$, and $Ga^{3+}Cu^{2+}$) are estimated to be 0.645, 0.625, 0.615, and 0.6 Å, respectively. $RFeCoO_4$ has the shortest a-length and the longest c-length among the $RM_1M_2O_4$ oxides when M_1M_2 is changed. The reason for this characteristic phenomenon should be clarified in the future.

We have attempted to prepare some other isostructural oxides, such as $RFeZnO_4$ and $RGaCoO_4$, which were reported to be prepared by firing in air.[19,20] However, it was found that the samples were not in a single phase; a few impurity peaks were observed in the XRD patterns. Attempts are still in progress to find a method to obtain single-phase samples of these oxides.

B. Magnetic properties

Table II shows a summary of the magnetic properties of RFe_2O_4, $RFeMO_4$, and $RGaCuO_4$ (R=Yb and Lu, M=Co and Cu). The values of the magnetic transition temperature (T_N) and the dielectric constant (ϵ) are plotted in Fig. 2 to show the variation of the characteristic physical properties with changing of the Fe-site ions. The label of $\langle r \rangle$ in the abscissa represents the average ionic radius of $M_1{}^{3+}$ and $M_2{}^{2+}$. The results of the dielectric properties will be discussed in the next section. From the magnetic measurements, it was found that the substitution at the Fe site in RFe_2O_4 leads to a systematic change of the magnetic properties. The properties are discussed in connection with several possible factors.

1. Magnetization data of RFe_2O_4 (R=Yb and Lu)

Figure 3 shows the temperature dependences of the field-cooled (FC) and zero-field-cooled (ZFC) magnetization for $YbFe_2O_4$ and $LuFe_2O_4$. The overall features of the present

TABLE II. Representative parameters obtained from magnetic and dielectric measurements in the present systems. T_N: magnetic transition temperature (K). θ: Weiss temperature (K). P_{eff}: effective paramagnetic moment per formula unit (μ_B). ϵ (RT): dielectric constant with the applied ac electric field of 30 Hz at room temperature. For RFe_2O_4, the values are shown for those at 250 K because of the fluctuation of the experimental data between 260 and 300 K. α: fitting parameter in the Debye model. Q: activation energy (eV) calculated from tan δ. HT: high-temperature peak, LT: low-temperature peak. ρ: ac resistivity (Ω cm) at around room temperature obtained from the imaginary part of the dielectric response for the ac field with ~30–1000 Hz and ~0.1–10 V/cm. See the text for details.

Material	T_N (K)	θ (K)	P_{eff} (μ_B)	ϵ (30 Hz, RT)	α	Q (eV)	ρ (Ω cm)
$YbFe_2O_4$	256			12000 (250 K)	0.08	0.29	$\sim 2\times10^2$–1×10^3
$YbFeCoO_4$	85	−215	8.4	2600	0.35	0.38 (HT) 0.35 (LT)	$\sim 2\times10^6$–5×10^6
$YbFeCuO_4$	45	−250	6.8	80	0.35		$\sim 1\times10^8$–5×10^8
$YbGaCuO_4$		−90	4.9	11	0.38		$\gtrsim 10^8$–10^9
$LuFe_2O_4$	250			20000 (250 K)	0.08	0.31	$\sim 4\times10^2$–5×10^3
$LuFeCoO_4$	90	−550	6.9	2400	0.30	0.37 (HT) 0.36 (LT)	$\sim 2\times10^6$–1×10^7
$LuFeCuO_4$	47	−1300	7.0	120	0.29		$\sim 1\times10^8$–5×10^8
$LuGaCuO_4$		−50	1.7	8	0.38		$\gtrsim 10^8$–10^9

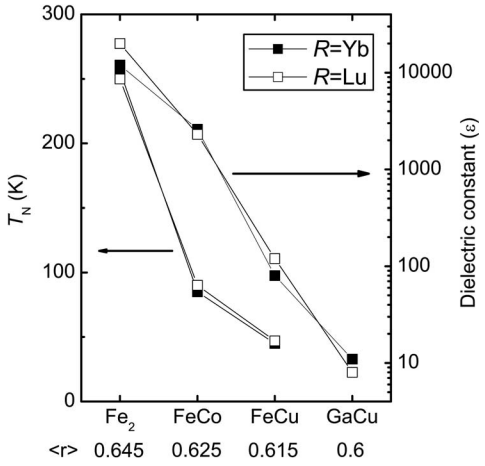

FIG. 2. Magnetic transition temperature (T_N) and dielectric constant (ϵ) extracted from Table II. In the abscissa, the combinations of M_1 and M_2 in $RM_1M_2O_4$ are shown (R=Yb and Lu). The average ionic radius of M_1^{3+} and M_2^{2+} in $RM_1^{3+}M_2^{2+}O_4$ ($M_1^{3+}M_2^{2+}$ =$Fe^{3+}Fe^{2+}$, $Fe^{3+}Co^{2+}$, $Fe^{3+}Cu^{2+}$, and $Ga^{3+}Cu^{2+}$) estimated in Sec. III A is denoted as $\langle r\rangle$ (Å).

data are essentially identical to those in Ref. 4–6. The upturn of magnetization at around 250 K indicates the appearance of the ferrimagnetic order of the Fe spins. By observing the thermoremanent magnetization (TRM), the Néel temperatures (T_N) were estimated to be almost the same value, about 256 and 250 K, for Yb and Lu, respectively (Table II). The T_N values are comparable to those of nearly stoichiometric $YbFe_2O_4$ and $LuFe_2O_4$ samples in the previous work.[4,6] Nearly stoichiometric $ErFe_2O_4$ was also found to show T_N of ~250 K.[5] In our recent study of $TmFe_2O_4$, a similar T_N value of ~250 K was also obtained.[7] As no systematic study of the variation of T_N with changing R in RFe_2O_4 has been reported, detailed investigations should be conducted for all R elements between Ho and Lu. From thermogravimetric measurements (Rigaku TAS200), oxygen contents of about δ=3.98(2) in RFe_2O_δ were obtained for both materials. Thus the present samples are almost stoichiometic.

The present data provide a few other characteristic features. For $YbFe_2O_4$ containing the magnetic rare-earth ion of Yb^{3+} ($4f^{13}$, 4.5μ_B, Ref. 30), there exists a small hump of the FC magnetization at ~130 K and a decrease in the magnetization below ~30 K. $LuFe_2O_4$ with the nonmagnetic Lu^{3+} ion ($4f^{14}$) exhibits a similar broad maximum of the magnetization at ~180–200 K in all the FC, ZFC, and TRM data. These results show that the hump at ~130 K for $YbFe_2O_4$ is due to either a modulation of the magnetic structure or a coherent spin fluctuation in the Fe sublattice. A possible change of the magnetic structures below T_N is also implied from the magnetization data of YFe_2O_4 and $TmFe_2O_4$.[3,7] The previous magnetization study of $YbFe_2O_4$ showed a very weak magnetic interaction between the Yb and Fe moments down to ~10 K.[4] However, the decrease in magnetization below ~30 K is likely attributable to antiferromagnetic coupling between Yb and Fe sublattices because no such decrease was observed for $LuFe_2O_4$.

Inverse magnetization data of these systems showed a hyperbolic profile and non-Curie-Weiss behavior up to 400 K,

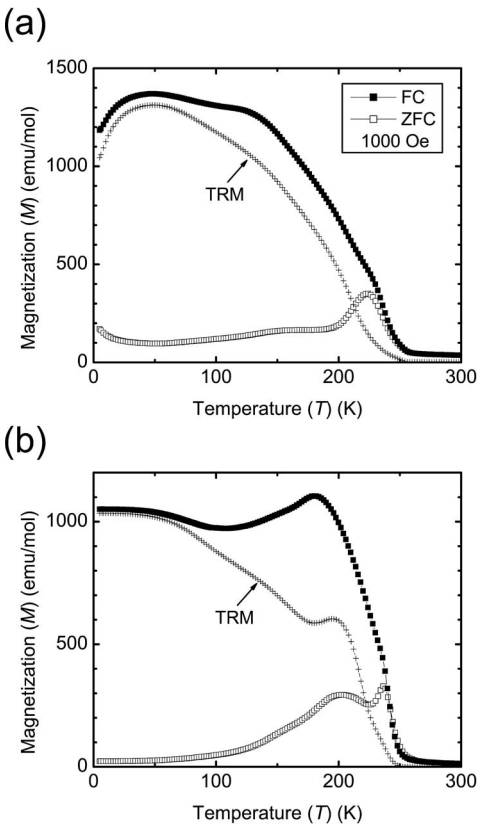

FIG. 3. Magnetization (M) plotted against the temperature (T) for (a) $YbFe_2O_4$ and (b) $LuFe_2O_4$, measured with the applied magnetic field of 1000 Oe. FC and ZFC stand for field-cooled and zero-field-cooled magnetization, respectively. The thermoremanent magnetization is labeled as TRM.

as found for YFe_2O_4 (Ref. 31), likely due to either the formation of short-range magnetically ordered regions or a tendency toward magnetic ordering at high temperatures. Such a profile has often been observed for ferrimagnetic materials.[32] From the Curie-Weiss fit above ~400 K for YFe_2O_4 (T_N ~250 K), the Curie temperature (θ) of this oxide was found to be ~−400 K.[31] The existence of spin-only moments of Fe^{3+} ($3d^5$; S=5/2; 5.92μ_B) and Fe^{2+} ($3d^6$; S=2; 4.90μ_B) was also observed from the same analysis.[31]

2. Magnetization data of substituted systems

The Co- and Cu-substituted systems show a drastic lowering of the transition temperature. Figure 4(a) shows the FC and ZFC magnetization as well as TRM for $YbFeCoO_4$. With decreasing the measurement temperature, both the FC and ZFC magnetization provides a Curie-Weiss-like increase. Compared to the behavior of $LuFeCoO_4$ in Fig. 4(b), this increase is due to a paramagnetic response of Yb^{3+}. It is characteristic that a slight inflection of magnetization occurs at ~80 K, below which a deviation of the FC and ZFC curves is observed. These phenomena indicate the appearance of magnetic ordering. Judging from the TRM data, the transition temperature is 85 K (Table II). The inverse magnetization above ~200 K in the inset provided an effective paramagnetic moment (P_{eff}) of 8.4μ_B/formula unit and a

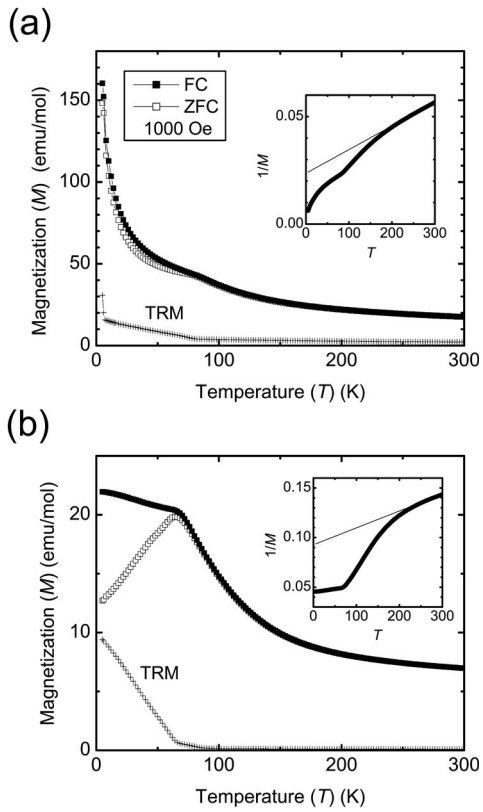

FIG. 4. Magnetization (M) plotted against the temperature (T) for (a) $YbFeCoO_4$ and (b) $LuFeCoO_4$. The insets show the inverse magnetization data ($1/M$; thick solid line) and the Curie-Weiss fit (thin solid line).

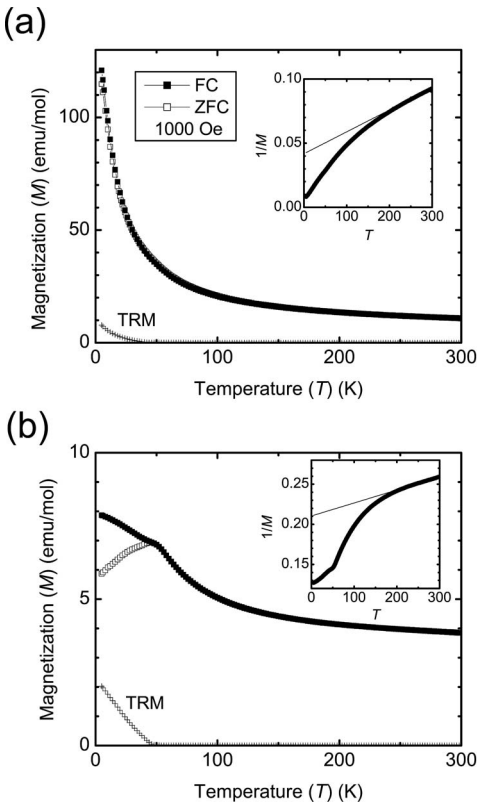

FIG. 5. Magnetization (M) plotted against the temperature (T) for (a) $YbFeCuO_4$ and (b) $LuFeCuO_4$. The insets show the inverse magnetization data ($1/M$; thick solid line) and the Curie-Weiss fit (thin solid line).

Weiss temperature (θ) of −215 K. The former value is almost the same as that calculated by the use of the magnetic moments of Yb^{3+} ($4f^{13}$; $4.5\mu_B$) and spin-only Fe^{3+} ($3d^5$; $S=5/2$; $5.92\mu_B$) and Co^{2+} ($3d^7$; $S=3/2$; $3.87\mu_B$) ions. The negative Weiss temperature indicates the existence of antiferromagnetic couplings between the localized moments below 85 K, similarly to a few other isostructural oxides.[21–23] Because of the negative Weiss temperature, the transition temperature is tentatively denoted as T_N hereafter.

The data of $LuFeCoO_4$ in Fig. 4(b) closely resemble those in a previous study on a single crystal.[22] The peak temperature in the ZFC curve of around 75 K is close to that in this reference. From the TRM data, T_N is estimated to be 90 K (Table II). This T_N is slightly higher than that of $YbFeCoO_4$. From the Curie-Weiss fit, the θ value was found to be −550 K. The P_{eff} value of $6.9\mu_B$ is almost the same as that based on the spin-only Fe^{3+} and Co^{2+} moments.

The appearance of TRM at low temperatures in both $YbFeCoO_4$ and $LuFeCoO_4$ indicates the existence of either a weak-ferromagnetic or a ferromagnetic-ordered moment. This is consistent with the proposed ferrimagnetic spin alignment in $LuFeCoO_4$, the origin of which was discussed in connection with several factors, such as an anisotropic effect of Co^{2+}.[22] Three different spin components were found: one spin has a parallel direction to the c axis, and the other two spins orient with 120° to the c axis.[22] Similar ordering is also expected for $YbFeCoO_4$.

The Cu-substituted materials exhibit a further lowering of the transition temperature to ~45 K.[25] Figure 5(a) shows that the temperature dependence of the FC and ZFC magnetization of $YbFeCuO_4$ has a Curie-Weiss-like profile, such as $YbFeCoO_4$. Although a deviation between the FC and ZFC curves is unclear, the appearance of TRM below ~45 K shows that the transition temperature T_N is ~45 K (Table II), which suggests the existence of ferrimagnetism below this temperature, as in the case of $LuFeCoO_4$.[22] These results provide a considerable contrast with those of the isostructural $TmFeCuO_4$ showing the absence of magnetic ordering.[26] The inverse magnetization above ~200 K in the inset provides P_{eff} of $6.8\mu_B$/formula unit and θ of −250 K. The former value is close to that calculated from the magnetic moments of Yb^{3+} ($4f^{13}$; $4.5\mu_B$) and spin-only Fe^{3+} ($3d^5$; $S=5/2$; $5.92\mu_B$) and Cu^{2+} ($3d^9$; $S=1/2$; $1.73\mu_B$) ions. The data of $LuFeCuO_4$ in Fig. 5(b) show a magnetization peak similar to that of $LuFeCoO_4$. The T_N value is 47 K (Ref. 25) from the TRM data. The Weiss temperature exhibited a quite large absolute value of $|\theta|=1300$ K. As the absolute value of this temperature is much higher than that of the highest measurement temperature of the apparatus (400 K), experiments at higher temperatures should be conducted in the future.

The magnetic ordering was not clearly detected for $RGaCuO_4$. Figures 6(a) and 6(b) show the Curie-Weiss-like behavior of the magnetization for $YbGaCuO_4$ and $LuGaCuO_4$, respectively. The deviation of the Curie-Weiss

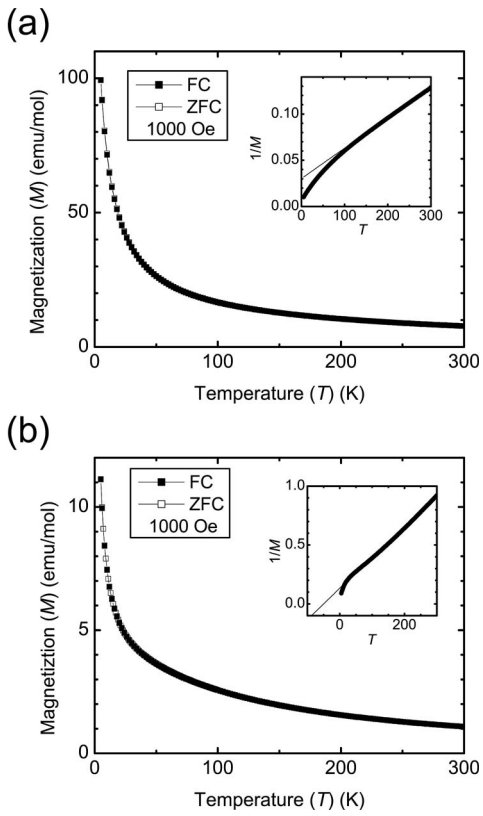

FIG. 6. Magnetization (M) plotted against the temperature (T) for (a) $YbGaCuO_4$ and (b) $LuGaCuO_4$. The insets show the inverse magnetization data ($1/M$; thick solid line) and the Curie-Weiss fit (thin solid line).

law at low temperatures (inset) may indicate a tendency toward magnetic ordering. The lack of a magnetic transition was confirmed by the absence of TRM as well as the lack of deviation between the FC and ZFC curves. The Curie-Weiss fit for R=Lu could be achieved assuming the existence of only Cu^{2+}(S=1/2, 1.73μ_B); this is consistent with the nonmagnetic state of Ga^{3+}. The Weiss temperatures were found to show negative values (Table II).

The existence of magnetic ordering for $R\mathrm{Fe_2O_4}$, $R\mathrm{FeCoO_4}$, and $R\mathrm{FeCuO_4}$ was observed in isothermal magnetization measurements as well. Figure 7 shows the result at

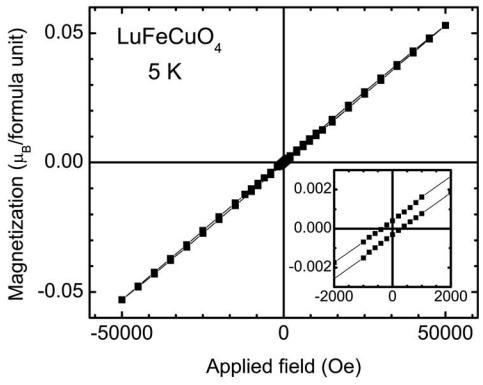

FIG. 7. Isothermal magnetization at 5 K for $LuFeCuO_4$. The inset shows the data in the low-applied-field region.

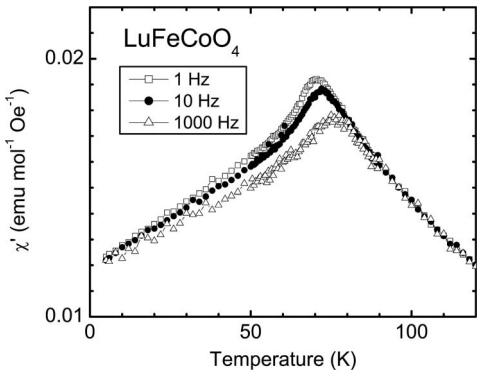

FIG. 8. Real part of the ac susceptibility for $LuFeCoO_4$ with ac frequencies of 1, 10, and 1000 Hz.

5 K for $LuFeCuO_4$. The small hysteresis loop and the lack of saturated magnetization are in accord with the existence of either weak ferromagnetism or ferrimagnetism noted earlier.

3. ac magnetic susceptibility

Figure 8 shows the real part of the ac magnetic susceptibility for $LuFeCoO_4$. A peak at ~80 K corresponds to the magnetic ordering noted earlier. This peak monotonically shifts to higher temperatures with increasing the frequency of the ac magnetic field. The shift width defined as $(\Delta T/T)/\Delta \log f$ was calculated to be ~0.01 (ΔT is the peak shift; T the peak temperature; and $\Delta \log f$ the difference of the logarithm of frequency), which is a typical value reported for short-range ordered substances, such as spin glasses.[33] The shift width was found to be less than 0.001 for $YbFe_2O_4$ and $LuFe_2O_4$. It is known that the ac susceptibility peak exhibits no temperature shift in a long-range ordered system, while the shift becomes apparent for short-range ordering.[33] Thus this result indicates that the magnetic ordering becomes short-ranged and leads to distributed sizes of magnetically ordered small regions with the substitution at the Fe site.

For $LuFe_2O_4$, the magnetic state below T_N was discussed in terms of an assembly of the ferrimagnetic clusters whose average size is ~100 Å.[6] A successive freezing process of these regions explains the cooling-field dependence of the temperature variation of TRM.[6] In our previous study on this oxide, ac magnetic susceptibility measurements under the dc magnetic field offered the activation energy required for changing the directions of magnetization of the clusters.[34] A broad peak was observed at ~130 K for the imaginary part of the susceptibility and shifted toward higher temperatures with increasing the ac frequency.[34] The Arrhenius-type fitting was carried out for this peak shift. This fitting indicated that the activation energy was ~0.3 eV.[34] In this study, we confirmed almost the same activation energy of ~0.28 eV. It is interesting that this value is very close to that calculated for the dielectric response shown later, suggesting a potential multiferroic coupling.[15] We have attempted the same measurement for $R\mathrm{FeCoO_4}$ and $R\mathrm{FeCuO_4}$. However, the corresponding susceptibility peaks were not clearly observed at low temperatures because their susceptibilities were too small (~10^{-5} emu mol^{-1} Oe^{-1}).

4. Characteristic features and interpretation of experimental results

From these experimental data, some characteristic magnetic phenomena have been obtained for $R\mathrm{Fe_2O_4}$, $R\mathrm{Fe}M\mathrm{O_4}$, and $R\mathrm{GaCuO_4}$ (R=Yb and Lu, M=Co and Cu). The most characteristic feature is that T_N is lowered in the order of $R\mathrm{Fe_2O_4}$ ($T_N \sim 250$ K), $R\mathrm{FeCoO_4}$ ($T_N \sim 85$ K), $R\mathrm{FeCuO_4}$ ($T_N \sim 45$ K), and $R\mathrm{GaCuO_4}$ (no ordering), as shown in Table II. The deviation of the transition temperature from the absolute θ value (Table II), which is most evident for $\mathrm{LuFeCuO_4}$, may be explained in terms of the magnetic frustration on a triangular lattice.

The change of the transition temperature by the substitution at the Fe site is qualitatively understood in terms of the spin value of M^{2+} ions. As is well-known, a magnetic transition temperature is simply understood by both an exchange interaction and a localized spin moment.[35] For the present materials, the spin-only moments of Fe^{2+}, Co^{2+}, Cu^{2+}, and Ga^{3+} are 4.90, 3.87, 1.73, and $0\mu_B$, respectively. These values are in qualitative agreement with the change of T_N. The lack of magnetic ordering in $R\mathrm{GaCuO_4}$ is attributed to the smallest spin value given by the combination of Cu^{2+} and Ga^{3+}.

The change of T_N also implies a decrease in the magnetic interaction by the Fe-site substitution. The average ionic radius of ${M_1}^{3+}$ ${M_2}^{2+}$ in $R{M_1}^{3+}{M_2}^{2+}\mathrm{O_4}$ (${M_1}^{3+}{M_2}^{2+}=\mathrm{Fe^{3+}Fe^{2+}}$, $\mathrm{Fe^{3+}Co^{2+}}$, $\mathrm{Fe^{3+}Cu^{2+}}$, and $\mathrm{Ga^{3+}Cu^{2+}}$) was assumed to be decreased in the order of $R\mathrm{Fe_2O_4}$, $R\mathrm{FeCoO_4}$, $R\mathrm{FeCuO_4}$, and $R\mathrm{GaCuO_4}$ (Sec. III A and Fig. 2). This change leads to a decrease in the average distance between the Fe-site ions. Considering that an exchange interaction (J) in a simple model is given by $J \sim t^2/U$ (t is the electron transfer and U the Coulomb repulsion),[35] the magnetic interaction plausibly becomes stronger with shortening the distance between the magnetic ions, since the electron transfer is promoted by the shortening. Thus the experimental tendency is not understood in this context. A possible decrease in the electron transfer was suggested in our previous work;[26], it is plausible that the replacement of Fe with M in $R\mathrm{Fe_2O_4}$ (M = Co and Cu) reduces strong Fe-Fe magnetic interactions owing to a reduction of the electron transfer arising from a difference in the energies of the $3d$ orbitals between Fe and M. This suppression, consistently with the magnetic data, will be experimentally estimated from the dielectric response in the next section.

The reduction of the magnetic interaction is explained by the temperature shift of the ac magnetic susceptibility peak (Fig. 8), since the formation of short-range magnetically ordered regions plausibly originates from a magnetic dilution in which a magnetic network is suppressed.[23] It is noteworthy that the same temperature shift was observed in an isostructural magnetic system, $\mathrm{LuFeMgO_4}$ (Ref. 23), in which the dilution of the magnetic interactions between the Fe ions causes the distribution of the size of each magnetic region. The possible distribution and the shrinkage of the region size will also be discussed from the observation of the dielectric response in the next section, in which a correlation between the dielectric and magnetic properties is suggested.

The T_N value of $\mathrm{YbFe_2O_4}$ (256 K) is slightly higher than that of $\mathrm{LuFe_2O_4}$ (250 K). On the other hand, for $R\mathrm{FeCoO_4}$ and $R\mathrm{FeCuO_4}$, T_N for R=Lu is slightly higher than that for R=Yb. Namely, T_N=85 K for $\mathrm{YbFeCoO_4}$, 90 K for $\mathrm{LuFeCoO_4}$, 45 K for $\mathrm{YbFeCuO_4}$, and 47 K for $\mathrm{LuFeCuO_4}$. In each system, the replacement of Yb with Lu leads to a decrease in the a-length and an increase in the c-length (Table I). Therefore the magnetic interaction inside the a-b plane is enhanced, while the interaction between the adjacent a-b planes is weakened. Although the transition temperature is governed by this compensation effect, quantitative discussions cannot be given at the present stage. Thus further investigations are currently being carried out. From our recent study for R=Tm, the lack of magnetic ordering in $\mathrm{TmFeCuO_4}$ suggests a possible weakening of magnetic interactions inside the a-b plane, originating from the elongation of the a-length.[26]

We also comment on the characteristic properties of $\mathrm{LuFeCuO_4}$; this oxide shows a quite large absolute value of the Weiss temperature ($|\theta|$=1300 K) and a larger paramagnetic moment ($\sim$110%) than that calculated using the spin-only values of Fe^{3+} and Cu^{2+}. This behavior implies the formation of small magnetic regions at high temperatures, considering that short-range microregions containing the local ordering of Fe^{3+} and Cu^{2+} were observed at room temperature for $\mathrm{LuFeCuO_4}$.[25] This ordering seems to be very similar to that in $\mathrm{LuMgFeO_4}$ noted in the Introduction.[24] As is discussed later, the formation of such regions may play a considerable role in the dielectric properties.

C. Dielectric properties

In this section, the dielectric properties are shown for $R\mathrm{Fe_2O_4}$, $\mathrm{RFe}M\mathrm{O_4}$, and $R\mathrm{GaCuO_4}$. The dielectric properties of these compounds, except for $R\mathrm{Fe_2O_4}$, had never been reported before.[7–15] A summary of the results obtained from the data analysis is shown in Table II [ϵ (30 Hz, RT), α, Q, ρ] and Fig. 2. As this table provides essentially the same properties between the Yb and Lu series, the experimental data will be demonstrated mainly for the nonmagnetic R^{3+} ion of Lu^{3+}. The data show a change of the dielectric properties caused by a replacement of the transition-metal ions and suggest a possible origin of this behavior.

1. Dielectric response of $R\mathrm{Fe_2O_4}$ (R=Yb and Lu)

Figure 9(a) shows the dielectric constant (ϵ) plotted against the temperature for $\mathrm{LuFe_2O_4}$. The dielectric constants of $\sim$20 000–30 000 at around room temperature are larger than those in our previous paper,[15] although both $\mathrm{LuFe_2O_4}$ samples are assumed to have nearly the same oxygen content. The large dielectric constant is the common feature of the $R\mathrm{Fe_2O_4}$ family. The other oxides ($\mathrm{TmFe_2O_4}$ and $\mathrm{ErFe_2O_4}$) were found to exhibit ϵ values larger than $\sim$5000.[7–9] The present figure also indicates that ϵ monotonically decreases with increasing the frequency of the ac electric field. This behavior is known as a dielectric dispersion and will be discussed later together with the results of the other oxides. Figure 9(b) confirms that $\mathrm{YbFe_2O_4}$ also shows large ϵ values ($\sim$10 000–20 000) as well as dielectric dispersion.

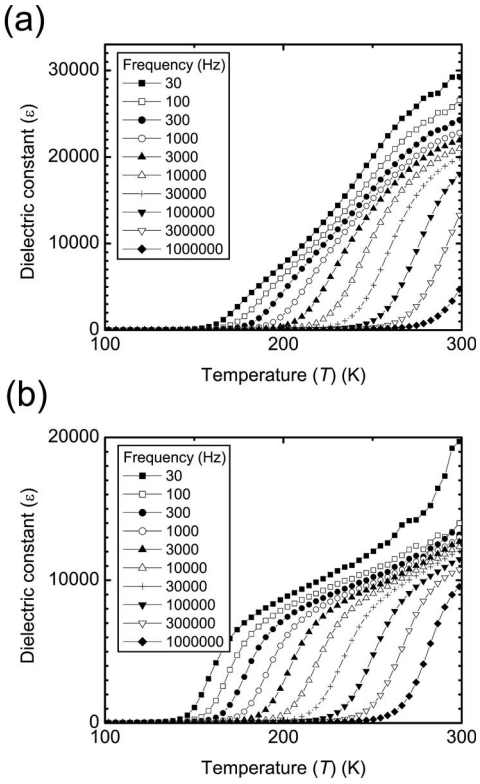

FIG. 9. Dielectric constant (ϵ) plotted against the temperature (T) for (a) $LuFe_2O_4$ and (b) $YbFe_2O_4$. The frequencies of the ac electric field are also shown.

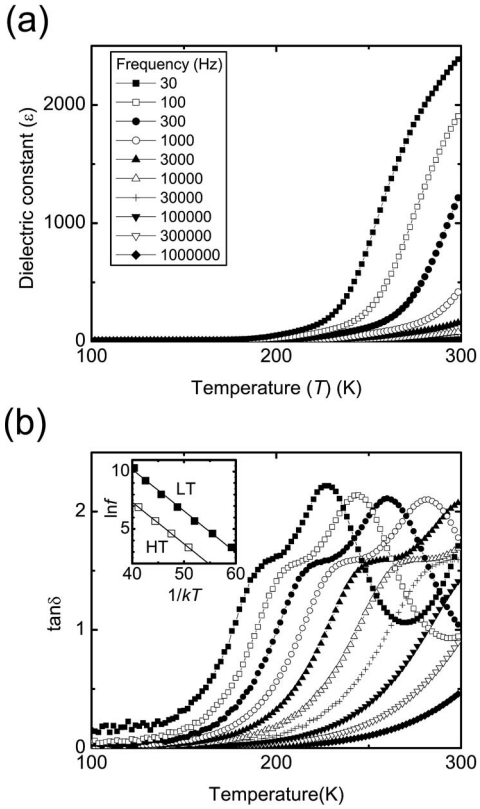

FIG. 10. (a) Dielectric constant and (b) tan δ component plotted against the temperature (T) for $LuFeCoO_4$. The inset shows the Arrhenius fitting of tan δ. The ordinate scale stands for the logarithm of the frequency. The abscissa (kT) is expressed in terms of eV (k: Boltzmann constant and T: temperature). The data of the high- and low-temperature peaks are labeled as HT and LT, respectively.

The loss part (tan δ) of the dielectric response indicated that a peak of tan δ monotonically shifted to higher temperatures with increasing the frequency of the ac field.[7–9,15] Following these references, the Arrhenius-type fitting was carried out for the peak temperature. The formula is expressed as

$$f = f_0 \exp\left(-\frac{Q}{kT}\right). \quad (1)$$

Here, f and f_0 stand for the ac frequency and the preexponential factor, respectively. Q, k, and T mean the activation energy, the Boltzmann constant, and the temperature, respectively. The obtained Q was ~0.30 eV for both $YbFe_2O_4$ and $LuFe_2O_4$, as shown in Table II. This is the value commonly found for RFe_2O_4 materials ($Q \sim 0.28$ eV).[7–9,15] The Q value stands for the energy required for switching the direction of each polar region.[8,15,36] As noted in the Introduction, the present Q of ~0.30 eV is smaller than those of ordinary ferroelectric materials. For example, thin films of ferroelectric $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) were reported to give Q values of ~0.9 eV.[37] The result also indicates that the dielectric response in this material is determined by an electron fluctuation on the Fe ions.[15] The value Q of ~0.30 eV is close to the activation energy obtained from the imaginary part of the ac magnetic susceptibility, as noted earlier.[34] This correspondence implies the coupling between dielectric and magnetic properties.[15]

2. Dielectric response of substituted systems

Dielectric measurements have been also carried out for all of the substituted oxides. Figure 10(a) qualitatively shows the existence of either electric dipoles or polar regions in $LuFeCoO_4$. The dielectric constants are found to be smaller than those of RFe_2O_4 but reach ~1000–2000 at around room temperature with ac frequencies lower than ~1000 Hz. The tan δ component is plotted in Fig. 10(b). For each ac frequency, the data show two peaks with an interval of ~30 K. This behavior suggests the existence of two different electron-transfer routes, which were reported recently, as in the case of La_2NiRuO_6.[38] For each of the peaks, the Arrhenius fitting was carried out in the inset. The analysis led to the activation energies Q of ~0.37 and ~0.36 eV for the high and low temperature peaks, respectively (Table II), both of which are comparably close to those for RFe_2O_4. Thus the switching of the directions of polar regions is probably associated with an electron transfer of the 3d electrons in this system.

Figure 11(a) shows dielectric constants smaller than ~200 for $RFeCuO_4$. Much smaller values of the dielectric constants of ~10 have been observed for $RGaCuO_4$, as is shown in Fig. 11(b). For both $RFeCuO_4$ and $RGaCuO_4$, the tan δ

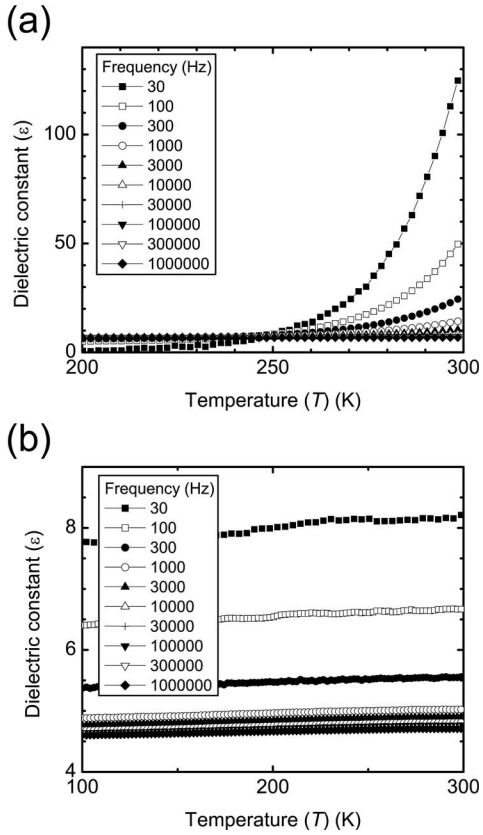

FIG. 11. Dielectric constant (ϵ) plotted against the temperature (T) for (a) $LuFeCuO_4$ and (b) $LuGaCuO_4$.

component exhibited no apparent peak below 300 K, suggesting that the Q values are larger than those of RFe_2O_4 and $RFeCoO_4$.[26]

From the measurements of the dielectric constant, all the systems exhibited different dielectric dispersions. The dispersion at a specific temperature was found to obey the so-called Debye model,[8]

$$\epsilon = \frac{\epsilon_1}{1 + (i\tau\omega)^{1-\alpha}} + \epsilon_2. \quad (2)$$

Here, τ and ω stand for a center of distribution time and an angular frequency ($\omega = 2\pi f$), respectively. The fitting parameter of α is a measure of the distribution width of the fluctuating time of each polar region.[8] An example of the fitting for the dielectric constant is shown for $LuFeCoO_4$, $LuFeCuO_4$, and $LuGaCuO_4$ in Fig. 12. The data of $LuFe_2O_4$ are also plotted in the figure. The calculated parameter of α was ~0.1 for RFe_2O_4, which is almost the same value of $ErFe_2O_4$.[8] The result means that the distribution width of the fluctuating time is quite narrow. The distribution becomes considerably wider for the other systems, i.e., their α values were ~0.30–0.40. All the values calculated are listed in Table II.

3. Interpretation of experimental results

These results of the dielectric response provide some features of the present systems. The parent oxides RFe_2O_4 exhibit quite large dielectric constants of ~10 000–30 000 at around room temperature. This is qualitatively due to the charge-ordering-induced ferroelectricity.[15] Another characteristic feature is that, although the existence of polar regions was found in each of the oxides studied, the dielectric constants below 300 K are smaller in $RFeCoO_4$, $RFeCuO_4$, and $RGaCuO_4$. The ferroelectric state in RFe_2O_4 is realized by the formation of polar regions consisting of Fe^{2+} and Fe^{3+}, in which the electron transfer between the Fe ions plays a central role for the response toward an ac electric field.[15] Thus the present phenomenon means that the substitution at the Fe site suppresses the coherence of such polar charge-ordered regions.

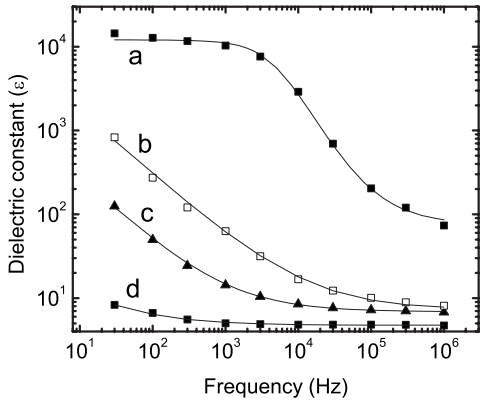

FIG. 12. Dielectric dispersion of (a) $LuFe_2O_4$, (b) $LuFeCoO_4$, (c) $LuFeCuO_4$, and (d) $LuGaCuO_4$. The markers and the solid lines stand for the experimental data and the fitting lines, respectively. The temperature for each material was chosen to show the dielectric dispersion most clearly in the frequency range between 30 Hz and 1 MHz. The α values are 0.08, 0.30, 0.29, and 0.38 for $LuFe_2O_4$ (230 K), $LuFeCoO_4$ (250 K), $LuFeCuO_4$ (300 K), and $LuGaCuO_4$ (300 K), respectively. See the text for details.

The dielectric constants also exhibit a qualitative tendency with the substitution at the Fe site. Namely, the ϵ values monotonically decrease in the order of RFe_2O_4, $RFeCoO_4$, $RFeCuO_4$, and $RGaCuO_4$ (Fig. 2). This tendency implies a relationship between the dielectric and magnetic properties; the change of ϵ coincides with the magnetic moments of the transition-metal ions in RFe_2O_4, $RFeMO_4$, and $RGaCuO_4$, judging from the spin-only magnetic moments of Fe^{2+}, Co^{2+}, Cu^{2+}, and Ga^{3+} noted earlier. An analogous relationship was reported for the ruthenium double perovskites La_2MRuO_6(M=Mg, Co, Ni, and Zn).[38] It was found that, while large dielectric constants of ~5000 at around room temperature were observed only for the magnetic M^{2+} ions of Co^{2+} and Ni^{2+}, the values became smaller down to ~200 for the nonmagnetic M^{2+} ions of Mg^{2+} and Zn^{2+}.[38]

Another correspondence is addressed by the change of the magnetic transition temperature (T_N, Table II, Fig. 2) because this temperature monotonically decreases in the order of RFe_2O_4 (T_N~250 K), $RFeCoO_4$ (T_N~85 K), $RFeCuO_4$ (T_N~45 K), and $RGaCuO_4$ (no ordering). Since the transition temperature is governed by the exchange interaction as well as the localized spin moment,[35] the tendency of the change of ϵ may be related to the exchange coupling, which

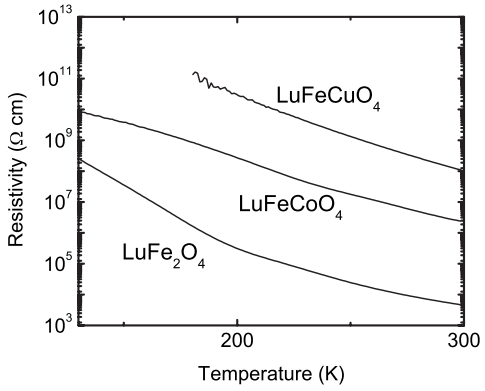

FIG. 13. Temperature dependence of the ac resistivity for $LuFe_2O_4$, $LuFeCoO_4$, and $LuFeCuO_4$. The activation energies of $LuFe_2O_4$, $LuFeCoO_4$, and $LuFeCuO_4$ at around room temperature are ~0.23, ~0.26, and ~0.28 eV, respectively.

seems to be relevant to our scenario of the ferroelectricity in RFe_2O_4.[15] As commented in Sec. III B, the exchange interaction (J) in a simple theoretical model is given by $J \sim t^2/U$, in which t and U stand for the electron transfer and Coulomb repulsion, respectively.[35]

It is inferred that the electron transfer is more suppressed with increasing the atomic number of the M^{2+} ion for M =Fe, Co, and Cu in $RFeMO_4$, as the difference of the energies of the 3*d* orbitals between M^{2+} and Fe^{3+} is plausibly enhanced. The electron transfer likely becomes the smallest in $RGaCuO_4$, since the transfer of the 3*d* electrons is most suppressed by the filled 3*d* orbitals of the nonmagnetic Ga^{3+} ion. The suppression of the transfer was experimentally estimated from the ac resistivity extracted from the loss term of the ac dielectric response.[26,39] The resistivity and the activation energy at around room temperature for the ac field with ~30–1000 Hz and ~0.1–10 V/cm were $\sim 10^2$–10^3 Ω cm and ~0.23–0.26 eV for RFe_2O_4 ($T_N \sim 250$ K), $\sim 10^6$–10^7 Ω cm and ~0.26–0.29 eV for $RFeCoO_4$ ($T_N \sim 85$ K), and $\sim 10^8$ Ω cm and ~0.28–0.33 eV for $RFeCuO_4$ ($T_N \sim 45$ K). The results of RFe_2O_4 are comparably close to that of the dc resistivity of isostructural YFe_2O_4.[31,40] The data for the Lu-system are demonstrated in Fig. 13. The values of $RGaCuO_4$ could not be determined accurately because of very high resistivity. The resistivity of this system was estimated to be higher than $\sim 10^8$–10^9 Ω cm at around room temperature, which possibly indicates that the electron transfer is most suppressed in this system. This result is qualitatively consistent with the absence of a tan δ peak in $RFeCuO_4$ and $RGaCuO_4$, since the energy loss due to the electrical resistivity is smaller in $RFeCuO_4$ and $RGaCuO_4$ than in RFe_2O_4 and $RFeCoO_4$. The change of the average ionic radii (Sec. III A and Fig. 2) shows that the electron transfer may be enhanced in the order of RFe_2O_4, $RFeCoO_4$, $RFeCuO_4$, and $RGaCuO_4$ since this change leads to a decrease in the average distance between the Fe-site ions, as noted in Sec. III B. However, the present result strongly suggests that this effect is not dominant in the change of the resistivity.

The suppressed charge transfer by the substitution is consistent with the analysis based on the Debye-type model (Table II). From the α values of all the materials, the distribution of the fluctuation time of polar regions is wider in $RFeCoO_4$, $RFeCuO_4$, and $RGaCuO_4$ than in RFe_2O_4.[8] This fact means the breaking of a coherent motion of polar regions against the applied electric field in the substituted systems, consistent with their smaller dielectric constants than those of RFe_2O_4. The change of α by the substitution at the Fe site is understandable from the magnetic properties of the Mg-substituted $LuFeMgO_4$,[23] in which the dilution of the magnetic interactions causes the distribution of the sizes of magnetically ordered regions, as shown for $RFeMO_4$ (Fig. 8). This magnetic-dilution model of $LuFeMgO_4$ can be applied to the change of the charge interactions in the present systems. Thus the dielectric response of $RFeCoO_4$, $RFeCuO_4$, and $RGaCuO_4$ may possess similar properties, in which the formation of a charge-transfer network between the transition-metal ions is prevented by the substitution at the Fe site.

From these discussions, the tendency of the variation of ϵ by the substitution is interpreted as follows. The ferroelectricity in RFe_2O_4 is rooted in the polar regions consisting of the Fe^{2+} and Fe^{3+} ions.[15] The origin of such regions is the frustrated charge interaction.[15] In the $RM_1{}^{3+}M_2{}^{2+}O_4$ oxides studied in this work (M_1=Fe or Ga, M_2=Co or Cu), the replacement of $M_1{}^{3+}$ and $M_2{}^{2+}$ at the Fe site in RFe_2O_4 may realize short-range ionic ordering, as was observed from the electron microscope measurements at room temperature.[25] This ordering forms short-range polar regions because the ionic ordering of $M_1{}^{3+}$ and $M_2{}^{2+}$ is accompanied by the same $\sqrt{3} \times \sqrt{3}$ structure as that in the charge-ordered state of Fe^{3+} and Fe^{2+} in RFe_2O_4.[15] At the same time, the Fe-site substitution causes the geometrical restriction on the electron-transfer route between the Fe ions.

It should be noted that dielectric dispersion is observed only if the polar regions change their directions in accordance with the applied ac electric field. Namely, the dielectric response is suppressed in the absence of motion of the polar regions; the dielectric constant is small in such a substance. In RFe_2O_4, the domain-boundary motion is attained by the charge interaction between Fe^{2+} and Fe^{3+}.[15] In other words, the directions of the polar regions are flipped by the electron exchange between Fe^{2+} and Fe^{3+}. As noted earlier, the electron transfer decreases in the order of RFe_2O_4, $RFeCoO_4$, $RFeCuO_4$, and $RGaCuO_4$. This tendency means that the rotation of the polar regions by the ac electric field becomes harder in this order, owing to the suppression of the electron transfer. As a result, the dielectric constant shows the tendency: $\epsilon(RFe_2O_4) > \epsilon(RFeCoO_4) > \epsilon(RFeCuO_4) > \epsilon(RGaCuO_4)$. This discussion coincides with the larger Q values of $RFeCoO_4$ than those of RFe_2O_4 as well as the absence of a tan δ peak in $RFeCuO_4$ and $RGaCuO_4$ below room temperature (Table II).

In the case of $RCoFeO_4$, its dielectric constants of ~1000–2000 indicate that the substitution effects of Co are not so large because of the weak suppression of the electron transfer. However, the presence of two kinds of electron-transfer routes (Fig. 10, Q values in Table II) shows that the dilution effect begins to appear.[23] Namely, the dilution of the electron transfer creates two or more electron-transfer routes and results in the appearance of two different polar regions showing the dielectric response.

Finally, we will discuss the Q values obtained from the tan δ component, $Q \sim 0.30$ eV, for $R\mathrm{Fe_2O_4}$ and ~ 0.37 eV for $R\mathrm{FeCoO_4}$. These values of Q are smaller than those of the usual ferroelectric or dielectric materials, a fact indicating that polar domains are easily rotated by the weak coupling between polarization switching and lattice distortion.[15] The absence of a peak of tan δ for $R\mathrm{FeCuO_4}$ and $R\mathrm{GaCuO_4}$ below 300 K implies that the Q values are larger than that of $R\mathrm{Fe_2O_4}$ and $R\mathrm{FeCoO_4}$. Together with the other results (Table II), the present results show that $R\mathrm{FeCoO_4}$ as well as $R\mathrm{Fe_2O_4}$ may offer a possible application for fatigue-free devices (Ref. 15) because of their comparably large dielectric constant, small Q values, and simple preparation method, i.e., solid-state reaction in air.

IV. SUMMARY

The magnetic and dielectric properties have been investigated for the isostructural oxides of $R\mathrm{Fe_2O_4}$, $R\mathrm{Fe}M\mathrm{O_4}$, and $R\mathrm{GaCuO_4}$ (R=Yb and Lu, M=Co and Cu). The magnetization measurements for $R\mathrm{Fe_2O_4}$ showed ferrimagnetic ordering at $\sim$250 K. This system also exhibited large dielectric constants of $\sim 10\,000-30\,000$ at around room temperature, which was attributable to the charge-ordering-induced ferroelectricity, as was proposed in our recent paper. The magnetic transition temperatures were lowered down to $\sim 45-90$ K for $R\mathrm{Fe}M\mathrm{O_4}$. Magnetic ordering was not found for $R\mathrm{GaCuO_4}$. ac magnetic susceptibility measurements indicated that magnetic ordering becomes short-ranged by the substitution at the Fe site. The overall characteristic behavior of the magnetic properties was explained in terms of the change of the spin value as well as the dilution of the magnetic interactions. Although the ac dielectric measurements showed the existence of polar regions in each material, the dielectric constants below 300 K became smaller in the order of $R\mathrm{Fe_2O_4}$, $R\mathrm{FeCoO_4}$, $R\mathrm{FeCuO_4}$, and $R\mathrm{GaCuO_4}$. From the analysis of the dielectric dispersion, the distribution of the fluctuation time of polar regions was wider in $R\mathrm{FeCoO_4}$, $R\mathrm{FeCuO_4}$, and $R\mathrm{GaCuO_4}$ than in $R\mathrm{Fe_2O_4}$; the coherent motion of polar regions was suppressed in the substituted systems. By comparison to the results from the magnetic measurements, the dielectric properties were discussed in connection with the charge transfer between the transition-metal 3d orbitals, consistent with the proposed mechanism of the ferroelectricity in $R\mathrm{Fe_2O_4}$.

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