Dilution effect on microstructures with respect to magnetic and dielectric properties in charge-ordered ferroelectric LuFe$_2$O$_4$

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We investigated magnetic/dielectric properties and related microstructures in LuFeCuO$_4$, which was obtained by substituting Cu^{2+} for Fe^{2+} in LuFe$_2$O$_4$. It was found that LuFeCuO$_4$ shows a characteristic low-frequency dielectric dispersion around 300K. We analyzed it using the Debye model and found that LuFeCuO$_4$ is a dielectric compound with an orientational polarization. Electron diffraction experiments revealed that there exists characteristic zigzag-shaped diffuse scattering in LuFeCuO$_4$. In addition, we found the presence of nano-sized domains, which consist of a short-range ordering of Fe^{3+} and Cu^{2+} on the triangular lattice. The present results suggest that the short-range ordering gives rise to some anomalous dielectric properties in LuFeCuO$_4$.

Key words: charge ordering, iron oxide, triangular lattice system, transmission electron microscopy

1. INTRODUCTION

Ferroelectric materials are used widely as the electric device, because of their ferroelectricity, piezoelectricity, pyroelectricity and electro-optical effect. Ferroelectric materials such as BaTiO$_3$ have a spontaneous polarization arising from a coherent arrangement of electric dipoles due to the relative displacement of cations and anions [1,2]. On the other hand, recent works revealed that a ferroelectric polarization in the charge-frustrated system, LuFe$_2$O$_4$, originates from the charge ordering, which is characterized by a regular arrangement of Fe^{2+} and Fe^{3+} ions on the triangular lattice [3].

LuFe$_2$O$_4$ belongs to the charge-frustrated systems RFe$_2$O$_4$ (R=Ho-Lu, Y) and has a rhombohedral structure with the space group of $R\bar{3}m$ [4]. In these compounds, triangular lattice planes of irons are stacked along the [001] direction and the Fe-O plane is called W-layer, as shown in Fig.1. Because the average valence of Fe ions is +2.5 in LuFe$_2$O$_4$, Fe^{3+} and Fe^{2+} ions coexist on the triangular lattice in the W-layer. This coexisting state of Fe^{3+} and Fe^{2+} should lead to the spin/charge frustration on the triangular lattice. Recent electron diffraction and neutron diffraction experiments revealed that the relaxation of the charge frustration results in the formation of a charge ordering (CO) on the triangular lattice below 500K. Note that the CO structure is characterized by the regular arrangement of Fe^{3+} and Fe^{2+} ions [5,6]. In addition, it has been reported that the emergence of the spontaneous polarization (P$_s$) is strongly correlated to the formation of the CO structure and the magnitude of P$_s$ increases discontinuously at the ferrimagnetic transition temperature of about 250K [1]. This suggests that LuFe$_2$O$_4$ has some interaction between ferroelectric and magnetic orderings.

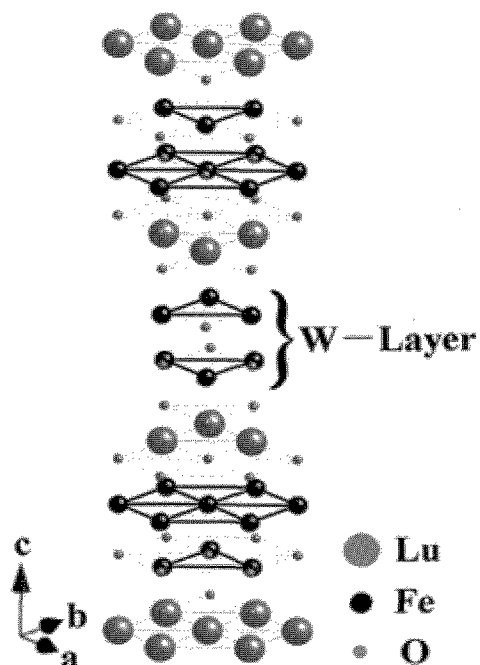Figure 1, Crystal structure of LuFe$_2$O$_4$

According to a previous work on $RFeMO_4$ (M ; Mg^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}) [7], these compounds show some characteristic magnetic transitions and the transition temperatures are much lower than the ferrimagnetic transition temperature of $LuFe_2O_4$ [8-10]. For instance, $YFeMnO_4$ shows a magnetic transition at around 70K [8]. $LuFeCoO_4$ exhibits a magnetic transition with a cusp at 75K due to the anisotropic effects of the Co^{2+} ion [9]. $LuFeMgO_4$ with the nonmagnetic ion (Mg^{2+}) shows a characteristic magnetic fluctuation [11]. Neutron diffraction experiments and Monte Carlo simulation revealed the presence of a local cationic ordering of Cu^{2+} and Fe^{3+} in $LuFeMgO_4$ with a short-range coherent length (about 10 atomic length). It was discussed that the magnetic fluctuation in $LuFeMgO_4$ has a close relation with thermal fluctuations and freezing of the short-range magnetically ordered regions (magnetic clusters) [12]. Furthermore, it was reported that $YbFeMnO_4$ has a static magnetic short-range ordered structure with a two-dimensional character, which was characterized by a magnetic superlattice structure with the wave vector q=[1/3 1/3 *l*] [13]. In this work, in order to clarify the short-range ordered (SRO) structure in $RFeMO_4$, we will pay attention to the $LuFeCuO_4$ compound and carefully investigated microstructures related to the magnetic/dielectric properties mainly by means of the transmission electron microscopy (TEM).

2. EXPERIMENTAL METHOD

$LuFeCuO_4$ polycrystalline samples were prepared by a conventional solid-state reaction method. Samples for the TEM observation were prepared by Ar^+-ion milling method. The TEM observation was carried out with JEM-2010 TEM in a wide temperature window between 100K and 700K. The complex dielectric constant was measured by LCR-meter (hp-4284A) in the temperature range between 293K and 600K.

3. RESULTS AND DISCUSSION

In Fig. 2, we displayed typical electron diffraction (ED) patterns of $LuFeCuO_4$ at room temperature. Note that we indexed the diffraction spots in Fig. 2 as a hexagonal unit cell notation. As shown by arrows (A) and (B) in Figs. 2(a) and 2(b), respectively, spotty diffuse scatterings with weak intensity can be seen around the $(1/3-\delta\ 1/3-\delta\ 0)$-type ($\delta$=0.06) positions. On the other hand, as shown by an arrow (C) in Fig. 2(c), zigzag-shaped diffuse streaks with intensity maxima can be seen around the (1/3 1/3 *l*) positions. Thus, we examined the configuration of these diffuse scatterings in the reciprocal space by obtaining various ED patterns at room temperature and determined the distribution of the diffraction spots and diffuse scatterings in the reciprocal lattice of $LuFeCuO_4$, as shown Fig. 3(a). As clearly evident in Fig. 3(b), there appear spotty diffuse scatterings around the $(1/3-\delta\ 1/3-\delta\ l)$ positions, where the magnitude of the deviation (δ) from the (1/3 1/3 0)-type positions is estimated to be about 0.06. On the other hand, there exist diffuse streaks with weak intensity elongating along the approximately [11$\underline{12}$]

direction. From a careful analysis of the diffuse scatterings, it can be considered that a SRO structure with the modulation vector q=[1/3-δ 1/3-δ 0] (δ=0.06) is formed in $LuFeCuO_4$.

Then, in order to clarify what gives rise to these characteristic diffuse scatterings, we tried to obtain high-resolution (HR) lattice images at room temperature. From the analysis of the HR lattice images, it is revealed
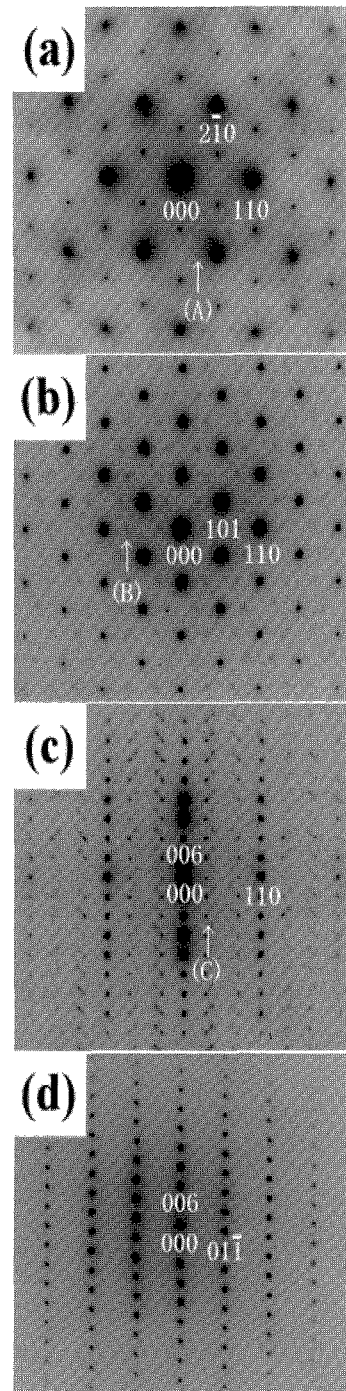
Fig. 2. Electron diffraction patterns of $LuFeCuO_4$ taken along the (a) [001], (b) [$\bar{1}$11] , (c) [1$\bar{1}$0] and (d) [$\bar{1}$00] zone-axis directions at room temperature, respectively.

that there exists a characteristic short-range ordering of Fe^{3+} and Cu^{2+} ions on the triangular lattice. The details have been reported in Ref. [14]. In addition, in order to elucidate the spatial distribution of the SRO structure in the real space, we obtained a dark-field (DF) image using a spotty diffuse scattering at ($1/3$-δ $1/3$-δ 0) (δ=0.06) position. As understood in Fig.4, a bright dot-shaped contrast with the size of 5-10nm can be seen. This suggests that there exist nano-sized domains with the 5-10nm size, which originates from the short-range ordering of the Fe^{3+} and Cu^{2+} ions. From these results, the substitution of Cu^{2+} for Fe^{2+} suppresses the long-ranged CO structure and forms the nano-sized domains with the 5-10nm size. It should be noted that the presence of the nano-scaled domains in $LuFeCuO_4$ is
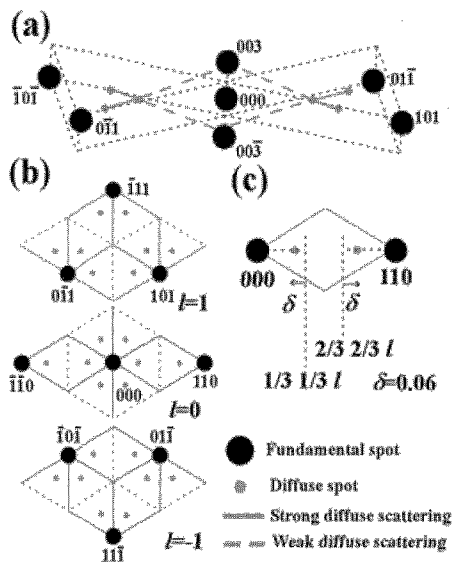

Fig. 3. Schematic representation of the reciprocal lattice. (a) Reciprocal lattice, (b) Cross-section diagram and (c) Arrangement of diffuse spot, respectively.
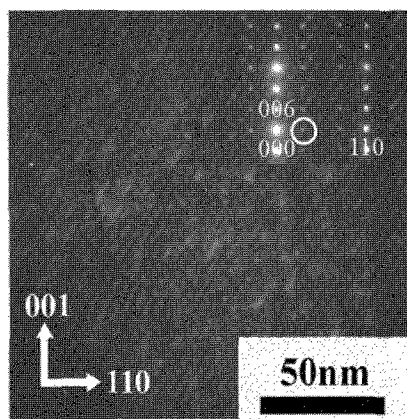

Fig. 4. Dark-field image obtained by using the spotty diffuse scattering indicated by the white circle in the ED pattern at room temperature. (inset) Electron diffraction pattern with the [1 1̄ 0] incidence.
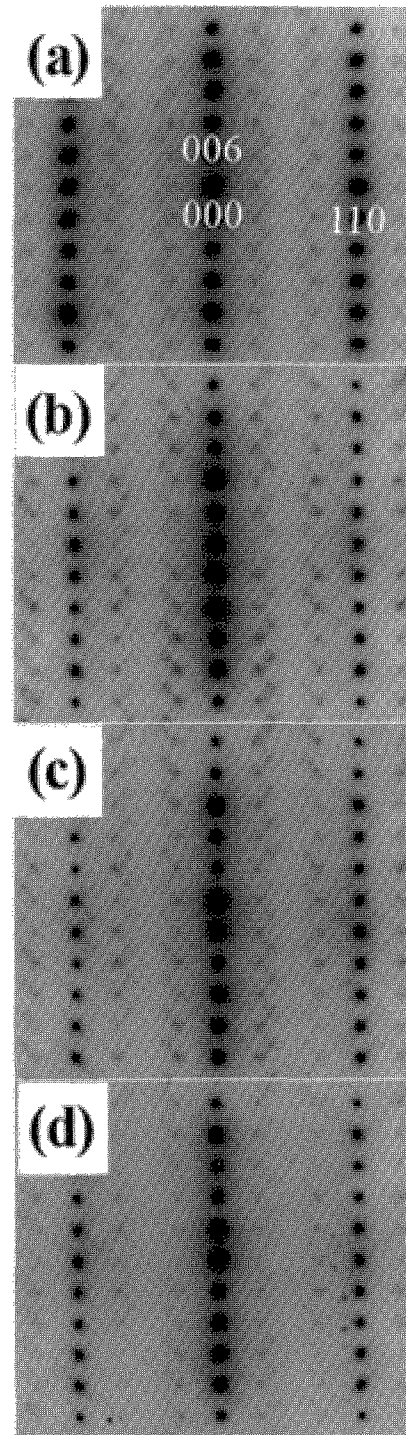

Fig. 5. Temperature dependence of electron diffraction patterns with the [1 1̄ 0] incidence obtained at (a) 100K, (b) 298K, (c) 408K and (d) 641K, respectively.

similar to that of the magnetic clusters in $LuFeMgO_4$ [12]. In addition, the temperature dependence of the magnetization in $LuFeCuO_4$ exhibits a similar behavior to that in $LuFeMgO_4$ [10]. The nano-sized domains originating from the short-range ordering of Fe^{3+} and Cu^{2+} ions on the triangular lattice should be strongly related to the magnetic clusters. On the other hand, it is found that $LuFeCuO_4$ shows a characteristic low-

frequency dielectric dispersion around 300K. We analyzed it using the Debye model and found that $LuFeCuO_4$ is a dielectric compound with an orientational polarization [15].This suggests that the ordering of Fe^{3+} and Cu^{2+} ions on the triangular lattice gives rise to an electric dipole in each of the nano-sized domains. In addition, in order to elucidate temperature change of the nano-sized domains on warming, we examined the temperature variation of the ED patterns in $LuFeCuO_4$. Figure 5 shows the temperature variation of the ED pattern with the $[1\bar{1}0]$ zone axis. Though intensities of both the spotty diffuse scatterings and the diffuse streaks become weak as the temperature is increased, zigzag-shaped diffuse scattering with intensity maxima can be still seen around 641K. This suggests that the nano-sized domains in $LuFeCuO_4$ are static. The static nano-sized domains in $LuFeCuO_4$ are similar to the static magnetic clusters in $YbFeMnO_4$ [12]. The present results suggest that the nano-sized domains in $LuFeCuO_4$ have a close relation to the characteristic magnetic/dielectric properties. The nano-sized domains are characterized as the static clusters with both the short-range correlation and the orientational polarization.

4. CONCLUSION

In summary, we investigated diluting effects on the microstructures with respect to the magnetic/dielectric properties mainly by substituting Fe^{2+} for Cu^{2+} ions in $LuFe_2O_4$. The substitution suppresses the formation of a long-ranged CO structure in $LuFe_2O_4$ and forms static nano-sized domains, which originates from a short-range ordering of Fe^{3+} and Cu^{2+} ions. In addition, it is suggested that this short-range ordered structure of Fe^{3+} and Cu^{2+} ions causes the electric and magnetic dipoles of the nano-sized domains and gives rise to some anomalous dielectric properties in $LuFeCuO_4$.

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