Doping effect on charge ordered structure in $RFe_2O_4$ ($R=$Lu and Yb)

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Abstract. Doping effects on the charge ordered (CO) structure in $RFe_2O_4$ ($R=$Lu, Yb) were investigated by an energy-filtered transmission electron microscope (EF-TEM), in combination with conventional magnetic measurement. The replacement of Cu$^{2+}$ and Co$^{2+}$ for Fe$^{2+}$ in $RFe_2O_4$ ($R=$Lu, Yb) destroyed drastically the CO structure. In LuFeCuO$_4$, the CO structure with $q=1/3$ 1/3 1/2 disappear and short-ranged domains consisting of cationic ordering of Fe$^{3+}$ and Cu$^{2+}$ ions are formed, which gives rise to characteristic zigzag-shaped diffuse streaks with diffuse spots at the h/3−δ h/3−δ 0-type positions (h: integer, δ=0.06) in reciprocal space. In addition, the magnetic measurement revealed that LuFeCuO$_4$ exhibits a magnetic transition around 50K, which is much lower than the Neel temperature of 250K in LuFe$_2$O$_4$. In YbFeCoO$_4$, clusters consisting of Fe$^{3+}$ and Co$^{2+}$ in the triangular lattice are formed and give rise to honeycomb-shaped diffuse streaks.

Introduction

Recently magnetic ferroelectric materials have attracted renewed interest because of their potential in novel magnetoelectric and magneto-optical devices [1]. In these materials, magnetism and ferroelectricity are involved with local spins and off-center structural distortion, respectively. These two seemingly unrelated phenomena can coexist in these materials. In addition, mutual control of magnetization and electric polarization can be realized in some orthorhombic manganites such as TbMnO$_3$ [2]. On the other hand, the coexisting state of the magnetic and electric orderings was found in insulating ferrimagnetic compounds such as $RFe_2O_4$ ($R=$Ho-Lu, Y) with the two-dimensional triangular lattice and with the strong geometrical frustration [3].

$RFe_2O_4$ ($R=$Ho-Lu,Y) crystallized a rhombohedral structure with the space group of $\bar{R}3m$ [4]. In these compounds, the hexagonal double-layers of Fe ions are sandwiched by thick layered blocks composed of rare-earth and oxygen ions. Because the average valence of Fe ions in $RFe_2O_4$ is Fe$^{2.5+}$, Fe$^{2+}$ and Fe$^{3+}$ ions sit on the same crystallographic site on the triangular lattice with equal density. This coexistence of Fe$^{2+}$ and Fe$^{3+}$ on the triangular lattice should lead to a spin/charge frustration. Some peculiar properties such as the anomalous dielectric behaviour were found in LuFe$_2$O$_4$. According to the previous work [5-8], it is revealed that the relaxation of the charge frustration results in the formation of the charge
ordering (CO) on the triangular lattice below 350 K, which is characterized as the unique arrangement of Fe\(^{2+}\) and Fe\(^{3+}\) ions. In addition, Ikeda et al. found that the appearance of this CO structure in LuFe\(_2\)O\(_4\) gives rise to the spontaneous polarization and suggested that the emergence of the electric polarization is mainly due to the spatial distribution of the Fe\(^{2+}\) and Fe\(^{3+}\) ions in the CO structure [9].

In this work we investigated changes of the CO structure by replacing Cu\(^{2+}\) and Co\(^{2+}\) for Fe\(^{2+}\) in \(R\)Fe\(_2\)O\(_4\) (\(R\)=Lu and Yb) by means of the energy-filtered transmission electron microscopy (TEM), combining with the conventional magnetic measurement.

**Experimental**

Polycrystalline samples of LuFeCuO\(_4\) (YbFeCoO\(_4\)) were prepared by a conventional solid-state reaction from the mixture of Lu\(_2\)O\(_3\) (Yb\(_2\)O\(_3\)), Fe\(_2\)O\(_3\) and CuO (CoO). Since there involved no Fe\(^{2+}\) ion in LuFeCuO\(_4\) and YbFeCoO\(_4\), it is not considered that oxygen deficiencies have any key influence on physical properties and local lattice structures [10]. Thin foils for the TEM studies were prepared by conventional Ar\(^{-}\)-ion milling method. The TEM observation was carried out with conventional JEM-2010 and LEO-922D TEM equipped with an in-column type energy filter.

![SAED patterns](images)
Results and discussion

We investigated doping effect on the three-dimensional CO structure in YbFe$_2$O$_4$ and LuFe$_2$O$_4$. YbFe$_2$O$_4$ and LuFe$_2$O$_4$ have the three-dimensional CO structure at 110 K and 298 K, respectively [5-9]. Figure 1 shows the selected-area electron diffraction (SAED) patterns taken along the [1-10] zone-axis directions in (a) YbFe$_2$O$_4$ and (b) YbFeCoO$_4$ at 110 K. Note that all the diffraction spots are indexed on the basis of the $R\bar{3}m$ rhombohedral structure. As shown in Fig. 1(a), superlattice reflection spots at the 1/3 1/3 1/2-type positions can be seen, in addition to the fundamental reflection spots due to the $R\bar{3}m$ rhombohedral structure. The presence of the superlattice spots implies that the three-dimensional CO structure is formed in YbFe$_2$O$_4$ at 110 K. Thus, we investigated change of the three-dimensional CO structure by the replacement of Co$^{2+}$ for Fe$^{2+}$. Figure 1(b) is a SAED pattern in YbFeCoO$_4$ at 110K. Superlattice spots at the 1/3 1/3 1/2-type positions disappear and, on the other hand, honeycomb-type diffuse streaks can be seen. The shape of the honeycomb-type diffuse streaks is schematically shown in Fig. 1(c). Note that the shape of the honeycomb-type diffuse streaks found in YbFeCoO$_4$ is similar with that found in LuFeCoO$_4$ [11]. This appearance of the honeycomb-type diffuse streaks suggests that clusters consisting of Fe$^{3+}$ and Co$^{2+}$ are formed on the triangular lattice. The details of the analysis of the diffuse streaks will be reported elsewhere [12].

Figure 2 displays the SAED patterns taken along the [1-10] zone-axis directions in (a) LuFe$_2$O$_4$ and (b) LuFeCuO$_4$ at 298 K. As shown in Fig. 2(a), superlattice reflection spots at the 1/3 1/3 1/2-type positions can be seen, in addition to the fundamental reflection spots due to the $R\bar{3}m$ rhombohedral structure. The presence of the superlattice spots implies that the three-dimensional CO structure is formed in LuFe$_2$O$_4$ at 298 K. Figure 2(b) is a SAED pattern in LuFeCuO$_4$ at 298 K. As shown by an arrow A in Fig. 2(b), diffuse spots with the intensity maxima at the 1/3-δ 1/3-δ 0-type positions (δ=0.06) can be seen, in addition to the fundamental reflection spots due to the $R\bar{3}m$ rhombohedral structure. On the other hand, as shown by an arrow B in Fig. 2(b), there appear zigzag-shaped diffuse streaks with intensity maxima at the h/3-δ h/3-δ 0-type positions. The characteristic zigzag-shaped diffuse streaks with intensity maxima originated from the formation of the cationic ordered structure consisting of Fe$^{3+}$ and Cu$^{2+}$ ions on the triangular lattice [13]. Note that the zigzag-shaped diffuse streaks are caused by lattice distortion associated with the cationic ordered structure. These experimental results indicate that the CO structure in RFe$_2$O$_4$ is destabilized by the replacement of Co$^{2+}$ (Cu$^{2+}$) for Fe$^{2+}$ and changes into the cationic ordered structure consisting of Fe$^{3+}$ and Co$^{2+}$ (Cu$^{2+}$) in the triangular lattice. The details of local lattice structures induced by the replacement of Cu$^{2+}$ for Fe$^{2+}$ in LuFe$_2$O$_4$ have not been clarified thus far.

Figure 3. Dark-field image of LuFeCuO$_4$ taken using one of the diffuse spots by energy-filtered TEM.

Figure 4. Magnetization plotted against the temperature for LuFeCuO$_4$.
In order to clarify domain structures caused by the cationic ordering of Fe$^{3+}$ and Cu$^{2+}$ in LuFeCuO$_4$, a dark-field image was taken by using one of the (h/3-δ h/3-δ 0)-type diffuse spots by energy-filtered TEM. Figure 3 is a typical dark-field image obtained using one of the diffuse spots by energy-filtered TEM. The dark-field image in Fig. 3 reveals the presence of tiny nanometer-sized speckles, which are referred to the cationic ordered domains consisting of Fe$^{3+}$ and Cu$^{2+}$ ions. We estimated correctly the shape and the size of domain structures in LuFeCuO$_4$ using the dark-field image of Fig. 3 and found that the shape of the tiny speckles is nearly isotropic and the size is approximately in the range from 5 to 10 nm. On the other hand, we tried to take real-space images giving rise to the honeycomb-type diffuse streaks in Fig. 1(b) by energy-filtered TEM. Unfortunately, we did not succeed in observing the domain structures giving rise to the honeycomb-type diffuse streaks in YbFeCoO$_4$ in the present work.

Magnetic properties in LuFeCuO$_4$ were examined between 298 K and 5 K. As shown in Fig. 4, LuFeCuO$_4$ exhibits a magnetic transition around 50K, which is much lower than the Neel temperature of 250K in LuFe$_2$O$_4$. On the other hand, magnetic transition is found around 80 K in YbFeCoO$_4$ [14].

Summary

Doping effect on the CO structure in dielectric materials LuFe$_2$O$_4$ and YbFe$_2$O$_4$ were examined by the energy-filtered TEM, in combination with the conventional magnetic measurements. It is revealed that the CO structures were destabilized by the replacement of Cu$^{2+}$ and Co$^{2+}$ for Fe$^{2+}$ in RFe$_2$O$_4$ (R=Lu and Yb). The electron diffraction experiments revealed that there exist characteristic zigzag-shaped diffuse streaks with diffuse spots at the 1/3-δ 1/3-δ 0-type positions in LuFeCuO$_4$. Moreover, dark-field images by energy-filtered TEM revealed that the size of the domains can be estimated to be approximately in the range from 5 to 10 nm. In contrast, honeycomb-like diffuse streaks were found in YbFeCoO$_4$. From the fact that there are no diffuse spots exhibiting the existence of the ordered structures, it is considered that the clusters consisting of Fe$^{3+}$ and Co$^{2+}$ ions in the triangular lattice are formed. The present results suggested that the nanometer-sized domains and the clusters should play important roles in magnetic properties in LuFeCuO$_4$ and YbFeCoO$_4$.

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