Collapsing processes of charge ordered structure in charge- and spin- frustrated ferrite YbFe$_2$O$_4$

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Abstract. In order to clarify the stability of charge ordered structure (CO) in charge- and spin-frustrated ferrite YbFe$_2$O$_4$, we have investigated changes of the CO structure by partial substitution of Mn$^{2+}$ for Fe$^{2+}$ in YbFe$_2$O$_4$ by a transmission electron microscope (TEM), in combination with conventional dielectric measurement. It is revealed that subtle substitution of Mn$^{2+}$ for Fe$^{2+}$ in YbFe$_2$O$_4$ destroyed drastically the CO structure with the wave vector of $q=<1/3 1/3 1/2>$ and, instead, induced polar clustering structure characterized by honeycomb-shaped diffuse scatterings in the reciprocal space. The formation of polar clustering structure should be responsible for the characteristic dielectric dispersion.

1. Introduction

Mixed-valence ferrite RFe$_2$O$_4$ (R=Y, Yb, and Lu) is one of the multiferroic materials which is well-known for the presence of charge ordering (CO) of Fe$^{2+}$ and Fe$^{3+}$ ions on geometrically frustrated triangular lattices [1-4]. RFe$_2$O$_4$ has the rhombohedral crystal structure (space group: $Rar{3}m$) characterized by the alternative stacking of triangular-lattice Fe-O bilayers and R-O layers along the [001] direction, and exhibits strong two-dimensionality (Fig. 1) [5]. The spin- and charge-ordering on Fe bilayers with the geometrically frustrated triangular lattice is expected to result in intriguing physical phenomena and structural changes in this system [6-9]. For example, charge imbalance within bilayers in the CO state of LuFe$_2$O$_4$ is suggested to be responsible for ferroelectricity below the two dimensional (2D) three-fold CO transition temperature at about 350 K [4,9]. This CO-driven ferroelectricity can be a new mechanism for ferroelectricity from the degree of freedom of spins and charges. The evolution of three-fold CO from 2D to three dimensional (3D) in the geometrically frustrated lattice leads to a structural phase transition with a development of double periodicity along the [001] direction in LuFe$_2$O$_4$ and YFe$_2$O$_4$ [10].

On the other hand, stability of the 3D CO by partial substitution of other transition-metal elements such as Co, Mn and Cu for Fe in RFe$_2$O$_4$ have been examined so far. These compounds show the glass-like magnetic transition and the transition temperatures are much lower than the ferrimagnetic transition temperatures in RFe$_2$O$_4$ [11-13]. LuFeMgO$_4$ with the nonmagnetic ion (Mg$^{2+}$) shows a magnetic transition around 30K and shows a characteristic magnetic fluctuation [12]. Neutron diffraction experiments and Monte Carlo simulation revealed the presence of the short-ranged spin
correlation [12]. It was suggested that a magnetic fluctuation in the LuFeMgO$_4$ has close relation with thermal fluctuation and freezing of the short-ranged magnetically ordered regions (magnetic clusters).

In this work, we have investigated changes of 3D CO structure by partial substitution of Mn$^{2+}$ for Fe$^{2+}$ in YbFe$_2$O$_4$ by a transmission electron microscopy (TEM). The 3D CO structure in YbFe$_2$O$_4$ is drastically destroyed by partial substitution of Mn$^{2+}$ for Fe$^{2+}$. It was found that there exist characteristic honeycomb-shaped diffuse scatterings in the reciprocal space, which were caused by the presence of the polar clustering structure.

2. Experimental procedure

We prepared single crystals of YbFe$_{2-x}$Mn$_x$O$_4$ with 0$\leq$x$\leq$1 by a conventional solid-state reaction from the mixture of Yb$_2$O$_3$, Fe$_2$O$_3$ and MnO and followed by the floating zone technique in reduction atmosphere under careful control of CO$_2$/CO gas ratio. Note that oxygen partial pressure in the reduction atmosphere, which is significant to synthesize the YbFe$_2$O$_4$ phase, can be controlled by changing the CO$_2$/CO mixture ratio in the chemical equilibrium state. Crystallographic information was obtained from powder x-ray diffraction at RT. The thin specimens for TEM observation were prepared by crushing methods, in order to avoid induction of oxygen deficiencies. The TEM observation was carried out with conventional JEM-2010 TEM equipped with a double-tilted holder. Note that the diffraction spots are indexed in a consistent manner among the electron diffraction patterns using the hexagonal notation with the space group of $\overline{R}3m$.

3. Results and discussion

Figure 1: Crystal structure in the rhombohedral structure of $\overline{R}3m$.

Figure 2: Powder x-ray diffraction profiles obtained in YbFe$_{2-x}$Mn$_x$O$_4$ with 0$<$x$<$1 at 298 K.
We successfully synthesized single crystals of YbFe$_{2-x}$Mn$_x$O$_4$ with $0 \leq x \leq 1$. Crystal structures at 298 K were examined by powder x-ray diffraction experiment. Figure 2 shows powder x-ray diffraction profiles of YbFe$_{2-x}$Mn$_x$O$_4$ with $0 < x < 1$ and all the diffraction peaks can be indexed based on the hexagonal structure with the space group of $R\bar{3}m$ without any impurity phases. The lattice parameters are determined to be $a_0=0.344$ nm and $c_0=2.52$ nm in YbFe$_2$O$_4$. Figure 3 displays changes of lattice parameters as a function of Mn concentration ($x$) in YbFe$_{2-x}$Mn$_x$O$_4$ with $0 < x < 1$. The lattice parameter ($c_0$) along the $c$ axis increases monotonically as the Mn concentration ($x$) increases and, on the other hand, the lattice parameter ($a_0$) in the in-plane remains to be almost constant. From this result, it is expected that the interaction between the Fe bilayers should become weak and the 3D CO structure should change into the 2D CO character as the Mn concentration ($x$) increases in YbFe$_{2-x}$Mn$_x$O$_4$.

Thus, we have investigated changes of the 3D CO structure by partial substitution of Mn for Fe in YbFe$_2$O$_4$ by obtaining various ED patterns. Figure 4 shows a series of selected-area ED patterns at 298 K in YbFe$_{2-x}$Mn$_x$O$_4$. Superlattice diffraction spots at the 1/31/3 3/2 positions can be seen, as indicated by an arrow in Fig. 4(a). This implies that, as has been reported previously in LuFe$_2$O$_4$, the 3D CO structure characterized by the modulated structure with the modulation vector of $\mathbf{q}=<1/3, 1/3, 1/2>$ is formed in YbFe$_2$O$_4$. When Mn ion is partially substituted for Fe ion in YbFe$_2$O$_4$, diffuse streaks elongating along the [001] direction appear, in addition to the superlattice spots at the 1/3 1/3 3/2 positions in the $x=0.05$ sample. The appearance of the diffuse streaks indicated the change from the 3D CO structure to the two dimensional (2D) CO structure. That is, in the $x=0.05$ sample, the coexisting state between the 3D and 2D CO structures is formed spatially. As the Mn concentration ($x$) increases in YbFe$_{2-x}$Mn$_x$O$_4$, the superlattice reflection spots at the 1/31/3 3/2 positions disappear and zig-zag shaped diffuse streak along the [001] direction appear, as indicated by arrows in Figs. 4(c) and 4(d). These experimental results imply that the interaction between the Fe bilayers becomes weak and short-ranged local structure with the 2D character is formed in Mn-doped YbFe$_2$O$_4$. It is suggested that partial substitution of Mn for Fe in YbFe$_2$O$_4$ destroyed the 3D CO structure drastically.

To clarify the spatial distribution of the diffuse scatterings in the reciprocal space, ED patterns with various zone-axis directions were examined in YbFeMnO$_4$ at 298 K and found that the shape of the diffuse scattering is honeycomb-shaped. Fig. 5(a) shows the ED pattern exhibiting the honeycomb-shaped diffuse scattering in YbFeMnO$_4$. Schematic representation of honeycomb-shaped diffuse scattering in YbFeMnO$_4$ was displayed in Fig. 5(b). These characteristic faint diffuse scatterings often have been observed in some binary alloys with the face-centered cubic structure such as Ni-Mo alloys [14,15]. In case of binary alloys, it was explained that characteristic diffuse scattering originates from the short-ranged ordered structure, which comprise the polyhedral clusters of atoms. It is speculated...
that the honeycomb-shaped diffuse scatterings found in Mn-doped YbFe$_2$O$_4$ should stem from the short-range ordered structure consisting of Fe$^{3+}$ and Mn$^{2+}$ ions in the triangular lattice. The detailed analysis of the honeycomb-shaped diffuse scatterings will be reported elsewhere [16].

Figure 4; Changes of ED patterns taken along the [1-10] zone-axis as a function of the Mn concentration (x) in YbFe$_{2-x}$Mn$_x$O$_4$. (a) x=0.0 (b) 0.05 (c) 0.1 (d) 0.2.

Figure 5; (a) ED pattern tilted to the [-111] direction slightly from the [1-10] zone-axis ED pattern (Fig. 4(d)) in YbFe$_{2-x}$Mn$_x$O$_4$ with x=0.2. (b) Schematic representation of honeycomb-shaped diffuse scattering.

In addition, we have examined dielectric properties in YbFe$_{2-x}$Mn$_x$O$_4$ with x~0.1. Figure 6 shows (a) the dielectric constant ($\varepsilon'$) and (b) dielectric loss (tan\(\delta\)) plotted in the temperature range between 25 K and 300 K. As shown in Fig. 6(a), $\varepsilon'$ has a broad peaks in the temperature range between 150 K and 300 K and monotonically decreases with increasing the frequency of the ac electric field. This behaviour is known as a dielectric dispersion and can be observed in the RFe$_2$O$_4$ compounds [11]. According to our previous work in LuFeCoO$_4$, it is suggested that the dielectric dispersion originates from the presence of the polar clustering structure, which should give rise to the characteristic honeycomb-shaped diffuse scatterings in Fig. 5(b) [17]. The characteristic dielectric dispersion found in Mn-doped YbFe$_2$O$_4$ should originate of the polar clustering structure, which gives rise to the honeycomb-shaped diffuse scatterings in the reciprocal space.
4. Summary

We have investigated collapsing processes of the 3D CO structure by partial substitution of Mn$^{2+}$ for Fe$^{2+}$ in YbFe$_2$O$_4$ by TEM experiment and conventional dielectric measurement. It is revealed that the 3D CO structure was collapsed by partial substitution of Mn$^{2+}$ for Fe$^{2+}$ in YbFe$_2$O$_4$. Electron diffraction experiments revealed that there appear honeycomb-type diffuse streaks in Mn-doped YbFe$_2$O$_4$. It is considered that short-range ordered structure consisting of Fe$^{3+}$ and Mn$^{2+}$ ions in the triangular lattice is formed, which gives rise to the honeycomb-type diffuse scatterings. The present results suggested that the polar clustering structure should play important roles in dielectric properties in Mn-doped YbFe$_2$O$_4$.

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