## Magnetocapacitance effect and related microstrucuture in Ti-doped YMnO<sub>3</sub>

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We have investigated microstructures giving rise to magnetocapacitance effect in Ti-doped YMnO<sub>3</sub> (YMn<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub>) by both electron diffraction and real-space imaging techniques. Diffuse scattering elongating along the [110] direction due to the instability of the Mn trimerization were found in the x=0.175 compound, which exhibits the enhanced magnetocapacitance effect. With increasing Ti concentration, the centrosymmetric (paraelectric)  $R\bar{3}c$  phase grows up at the expense of the ferroelectric  $P6_3cm$  phase around x=0.20 and the  $R\bar{3}c$  phase is dominant above x=0.30. Our present results indicate that the Mn trimers with the short-range correlation inside the ferroelectric nanodomains with the 10–20 nm size should be responsible for the enhancement of the magnetocapacitance and, on the other hand, the appearance of the  $R\bar{3}c$  phase suppressed the magnetocapacitance effect.

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Recently magnetic ferroelectrics have attracted renewed interest because of their potential in novel magnetoelectric and magneto-optical devices.<sup>1–3</sup> In magnetic ferroelectrics, magnetism and ferroelectricity are involved with local spins and off-center structural distortion, respectively. These two seemingly unrelated phenomena can coexist in magnetic ferroelectrics.<sup>4–6</sup> In addition, recently the mutual control of magnetization and electric polarization can be realized in hexagonal manganites such as TbMnO<sub>3</sub> and HoMnO<sub>3</sub>.<sup>7–9</sup>

Hexagonal manganites  $RMnO_3$  (R=Sc, Y, In, Ho-Lu) are interesting compounds showing a wide variety of physical properties due to unusual combination of electric and magnetic interaction. RMnO<sub>3</sub> with large ionic size show a perovskite-type structure with the orthorhombic distortion (space group Pnma). When  $R^{3+}$  cations are displaced by  $A^{2+}$ ones (A = Ca, Sr, Ba), these compounds exhibit some unusual electric and magnetic properties such as colossal magnetoresistive effect (CMR).  $^{10-12}$  On the other hand, RMnO<sub>3</sub> with smaller ionic size than Tb<sup>3+</sup>, the crystal structure changes from the perovskite-type structure to the hexagonal one. In YMnO<sub>3</sub> with the hexagonal structure, a ferroelectric phase appears at high temperature around 900 K and the antiferromagnetic transition takes place around  $T_N \sim 70$  K. As a result, the low-temperature phase is characterized as a coexistence of the ferroelectric ordering with the magnetic ordering.<sup>13–17</sup> The materials with the coexistence of ferroelectric and magnetic orderings are referred as "multiferroics."18

Here we will pay attention to the YMnO<sub>3</sub> compound with the hexagonal structure. YMnO<sub>3</sub> exhibits several magnetic/ electric phase transitions on cooling from the hightemperature phase with the  $P6_3/mmc$  crystal structure, as mentioned above.<sup>19,20</sup> Recently, anomalies in the dielectric constant in YMnO<sub>3</sub> near the Neel temperature were found and the coupling in YMnO<sub>3</sub> between the ferroelectric and magnetic orderings was clearly demonstrated.<sup>17</sup> In addition, Aikawa *et al.*, investigated the effect of the Ti substitution on the electric and magnetic properties in YMnO<sub>3</sub>.<sup>21</sup> It is found that the magnetocapacitance effect takes place in  $YMn_{1-r}Ti_rO_3$ , which were obtained by partial substitution of Ti of Mn, and is enhanced around x=0.175<sup>21</sup> As further increasing the Ti concentration (x) above x=0.175, the magnetocapacitance effect is suppressed and vanished around x=0.30. In addition, electron diffraction and x-ray diffraction experiments revealed the presence of the structural phase transition from the ferroelectric  $P6_3cm$  phase to the rhombohedral one around x=0.175 at room temperature.<sup>21</sup> Note that the crystal symmetry of the new rhombohedral phase is not determined exactly and is now controversial.<sup>22</sup> These experimental findings suggested that the magnetocapacitance in  $YMn_{1-r}Ti_rO_3$  should be related to the structural phase transition from the ferroelectric  $P6_3cm$  to the rhombohedral phases around x=0.175.

To clarify the appearance of the magnetocapacitance induced by partial substitution of the Ti ion for the Mn one, we investigated carefully changes in microstructures related to both the ferroelectric properties and structural phase transition in YMn<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> by both electron diffraction and realspace imaging methods. The stable ferroelectric phase in YMnO<sub>3</sub> characterized by the large ferroelectric domains with the six antiphase domains changes into the ferroelectric microdomains with the size of 10–20 nm in the x=0.175 compound. Furthermore, diffuse streak due to local lattice fluctuation related to the structural instability of the Mn trimers were found in the x=0.175 compound. On the other hand, by further substituting Ti for Mn, new centrosymmetric phase with the  $R\overline{3}c$  symmetry grows up inside the ferroelectric  $P6_3cm$  phase and the two different phases coexist above x = 0.20. The interrelation between local structural fluctuation and enhanced magnetocapacitance found in Ti-doped YMnO<sub>3</sub> will be discussed briefly.

Polycrystalline samples of  $YMn_{1-x}Ti_xO_3$  with x=0.0, 0.175, 0.20, 0.30, and 0.40 were prepared by a conventional solid state reaction. The transmission electron microscopy (TEM) observation was carried out by using the JEM-2010 TEM. Changes in the microstructures by the Ti substitution were investigated by obtaining both various electron diffraction (ED) patterns and real-space images. Furthermore we examined temperature variation of both ED patterns and microstructures in the temperature window between 298 and 5 K. The physical properties in  $YMn_{1-x}Ti_xO_3$  used in the present study have been reported in Ref. 21. Here we briefly explain the magnetic-field dependence of dielectric constants at 5 K in Ti-substituted YMnO<sub>3</sub>, which is characterized as the so-called magnetocapacitance.<sup>21</sup> In YMnO<sub>3</sub>, no anomaly in the magnetic-field dependence of dielectric constant was detected. With increasing the Ti concentration, it is found that the dielectric constant is changing by applying the magnetic field up to 5 T. With increasing the Ti concentration, the magnitude of the magnetocapacitance increases and reached at the maximum value around x=0.175. With further increasing the Ti concentration, the magnitude of the magnetocapacitance decreases and the magnetocapacitance vanishes around x=0.30. According to the recent study by Aikawa et al.,<sup>21</sup> it is suggested that the appearance of the magnetocapacitance should be related to the structural phase transition from the ferroelectric  $P6_3cm$  structure to the rhombohedral one. Thus, in order to clarify the relation between the magnetocapacitance and the structural phase transition from the ferroelectric  $P6_3cm$  to the rhombohedral phases, we thoroughly investigated both the crystal structures and the microstructure related to the ferroelectric P6<sub>3</sub>cm and rhombohedral phases in  $YMn_{1-x}Ti_xO_3$  by obtaining both various ED patterns and real space images.

Figure 1 displays ED patterns at room temperature in  $YMn_{1-x}Ti_xO_3$  with (a) x=0.0, (b) 0.175, (c) 0.20, and (d) 0.40, respectively. As reported previously, the crystal structure of YMnO<sub>3</sub> in the ferroelectric phase is characterized as the regular arrangement of Mn trimers on the triangular lattice in the *ab* plane and has a space group of  $P6_3cm$ .<sup>17,21,22</sup> In the ED pattern obtained from YMnO<sub>3</sub>, the 1/3 1/3 0-type spots can be seen clearly, as indicated by an arrow in Fig. 1(a). Note that indexes in the ED patterns are based on the high-temperature paraelectric phase (space group;  $P6_3/mmc$ ) to emphasize the appearance of the superlattice structure induced by structural phase transition. From the ED pattern in Fig. 1(a), we confirmed that the crystal structure in  $YMnO_3$ is characterized as the  $P6_3cm$  space group. Thus, we examined change of the crystal structure by partial substitution of Ti at the Mn site by obtaining various ED patterns. It is found that characteristic diffuse scattering with weak intensities elongated along the [001] direction by substituting Ti for Mn around x=0.175 and above x=0.20 new phase with the space group of  $R\bar{3}c$  appears.<sup>23</sup> Figure 1(b) shows an ED pattern obtained in the x=0.175 compound at room tempera-



FIG. 1. Electron diffraction patterns at room temperature for (a) x=0.0, (b) 0.175, (c) 0.20, and (d) 0.40, respectively.

ture. As indicated by an arrow in Fig. 1(b), diffuse scattering with weak intensities elongating both the [001] direction can be seen. This type of the diffuse scattering appear just around x=0.175. As the Ti concentration increases furthermore, it is revealed that new reflection spots appear at the 1/3 1/3 1/3-type positions above x=0.20, as shown in Figs. 1(c) and 1(d), respectively. From careful analysis of the ED pattern in Fig. 1(c), it is understood that the two different phases of the ferroelectric  $P6_3cm$  and the  $R\overline{3}c$  phases coexist at room temperature in the YMn<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compounds above x=0.20.<sup>21</sup> In

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FIG. 2. Real-space images in (a) x=0.0, (b) 0.175, (c) 0.20, and (d) 0.40, respectively.

addition, as shown in Fig. 1(d), the  $R\overline{3}c$  phase is dominant in the x=0.40 compound.

We investigated the microstructures giving rise to the characteristic diffuse scattering in x=0.175 and the coexisted state of the two different phases in x > 0.20. Figure 2 shows microstructures obtained at room temperature in  $YMn_{1-x}Ti_xO_3$  for (a) x=0.0, (b) 0.175, (c) 0.20, and (d) 0.40, respectively. In the ferroelectric phase of YMnO<sub>3</sub>, large ferroelectric domains can be seen, as shown in Fig. 2(a).<sup>17</sup> On the other hand, as shown in Fig. 2(b), it is found that in the x=0.175 compound ferroelectric nanodomains with the 10-20 nm size exist stably at room temperature. That is, the ferroelectric large domains in YMnO<sub>3</sub> change drastically into the ferroelectric nanodomains with the size of 10-20 nm in x=0.175. As the Ti concentration (x) increases, new phase with the  $R\overline{3}c$  symmetry grows up at the expense of the ferroelectric  $P6_3cm$  phase. As shown in Fig. 2(c), the R3c phase coexists with the ferroelectric  $P6_3cm$  phase with the several nanometer size. As the Ti concentration increases furthermore, the  $R\overline{3}c$  phase is dominant, as understood in Fig. 2(d). We should confirm the coexistence of the two distinct crystal structures with the space groups of  $P6_3cm$  and R3c in the  $YMn_{1-x}Ti_xO_3$  above x=0.20. Figure 3 displays the real-space images showing the coexistence of the  $P6_3cm$  and R3cphases with the nanometer scale, which were taken by using the superlattice 1/3 1/3 1 and 2/3 2/3 2/3 spots, respectively. In the image [Fig. 3(a)] taken by using the superlattice 1/3 1/3 1 spot, which originated from the P6<sub>3</sub>cm structure, regions with the bright and dark contrast can be seen clearly with the 30-40 nm size. The regions with the bright contrast can be regarded as the domains with the  $P6_3cm$  structure. On the other hand, as shown in Fig. 3(b), which was taken by using the 2/3 2/3 2/3 superlattice spot, characteristic bright and dark contrast can be seen with the 20-30 nm size. The regions with the bright contrast correspond to the domains with the R3c structure. These two images shown in Fig. 3 demonstrate clearly the fine mixture of the two distinct crystal structures with the space groups of  $P6_3cm$  and  $R\overline{3}c$  in the x = 0.20 compound.



FIG. 3. Real-space images showing the coexistence of the  $P6_3cm$  and  $R\overline{3}c$  structures. (a) Dark-field (DF) image taken by using the superlattice 1/3 1/3 1 spot charactering the  $P6_3cm$  crystal structure and (b) DF image taken by using the superlattice 2/3 2/3 2/3 spot characterizing the  $R\overline{3}c$  crystal structure.

We found the diffuse scattering elongating along both the [001] direction in the x=0.175 compound at room temperature, as shown in Fig. 1(b). On the other hand, it is demonstrated clearly from the dielectric measurement under the magnetic field that the magnetocapacitance effect appears in the x=0.175 compound.<sup>21</sup> It is important to elucidate the relationship between the magnetocapacitance effect and diffuse scattering along the [001] direction. Thus, in order to clarify structural change related to the magnetocapacitance in the x=0.175 compound, we carefully examined temperature variation of ED patterns with the  $[1\overline{10}]$  incidence in the wide temperature window between 298 and 5 K. Figure 4 shows changes of the ED patterns in the x=0.175 compound. Figure 4(a) displays the ED pattern showing the presence of the diffuse scattering elongating along the [001] direction at 5 K. On warming from 5 K, it is found that new diffuse scattering elongating along the [110] direction appears around 40 K, which corresponds to the structural anomaly in the *ab* plane, as displayed in Fig. 4(b) at 44 K. This suggested that local structural fluctuation in the *ab* plane, which should be related to the structural instability of the Mn trimers induced by the Ti substitution, is enhanced at low temperature in the x=0.175 compound. On further warming to room temperature, the intensity of the diffuse scattering along the [110] direc $YMn_{1-x}Ti_{x}O_{3}$  (x=0.175)



FIG. 4. Change of the electron diffraction patterns with the  $[1\overline{10}]$  incidence in the x=0.175 compound, which were taken at (a) T=5 K, (b) 44 K, and (c) 209 K, respectively. The arrow in (a) indicates the diffuse scattering elongating the [001] direction and, on the other hand, the arrow in (b) indicates the diffuse scattering along the [110] direction.

tion becomes weak and, on the other hand, diffuse scattering along the [001] direction still remains intact, as shown in Fig. 4(c) at 209 K. This indicates that diffuse scattering along the [001] direction should be related to the static stacking faults of the Mn trimers along the [001] direction in the  $P6_3cm$  crystal structure. On the other hand, diffuse scattering along the [110] direction shows significantly temperature variation on warming from 5 K. This indicates the presence of dynamical fluctuation of the Mn trimers inside the ferroelectric nanodomains with the 10–20 nm size, which should be responsible for the enhancement of the magnetocapacitance effect in the x=0.175 compound. We also examined temperature variation of the ferroelectric nanodomains found





FIG. 5. Ferroelectric nanodomains taken at (a) T=5 K and (b) 298 K in the x=0.175 compound, respectively. The arrows indicate the same area in the observed sample.

in x=0.175 at room temperature. As understood by comparing between Figs. 5(a) and 5(b), it was found that the size of the ferroelectric nanodomains remains unchanged around 5 K and can be estimated to be about 10–20 nm. That is, the ferroelectric nanodomains exist stably in the wide temperature range between 298 and 5 K. There exists no relation between the ferroelectric nanodomains with the 10–20 nm size and the diffuse scattering along the [110] direction.

We demonstrated clearly the relationship between the enhanced magnetocapacitance and local lattice fluctuation related to the Mn trimerization inside the ferroelectric nanodomains with the 10-20 nm size. Here we discuss a possible origin for the enhanced magnetocapacitance in the x=0.175 compound on the basis of the present experimental results. As reported in the previous paper,<sup>17</sup> three Mn<sup>3+</sup> ions in the triangular lattice displaced toward each other and  $Mn^{3+}$  trimerization formed in the ferroelectric  $P6_3cm$  phase of YMnO<sub>3</sub>. This Mn<sup>3+</sup> trimerization induces Y displacement giving rise to the ferroelectric polarization along the [001] direction.<sup>24</sup> On the other hand, spins on the three Mn<sup>3+</sup> ions in the triangular lattice order antiferromagneticaly below the Néel temperature of  $T_N \sim 70$  K. When the Ti ions were substituted for the Mn ions, the tendency to form the Mn<sup>3+</sup> trimerization decreases and long-range AFM ordering at low temperature disappeared around x=0.2<sup>21</sup> Recently it is suggested that short-range AFM coupling inside the Mn trimers in the *ab* plane still exists for the x > 0.2 compound. On the other hand, in the x=0.2 compound, new centrosymmetric (paraelectric)  $R\overline{3}c$  phase appears and coexists with the ferroelectric P63cm phase as the nanodomains with the size of 10-20 nm. Spins on the Mn sites did not order completely at low temperature and remains fluctuated below the Neel temperature. The fluctuated state of the spins on the three Mn sites is sensitive to the application of the magnetic field. As a result, the Mn displacement forming the Mn trimerization becomes much larger by the application of the magnetic field and the magnetic-field-induced dielectric response (the magnetocapacitance effect) was enhanced.

In summary, the microstructures related to the magneto-

capacitance in YMn<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> were investigated by the ED and real-space imaging methods. It was found that local lattice fluctuation related to the formation of the Mn trimers in the two-dimensional triangle lattice is induced by the substitution of Ti for Mn in YMnO<sub>3</sub> and simultaneously local spin fluctuation on the Mn sites still remains intact at low temperature below  $T_N$ . These spin and lattice fluctuations related to the Mn trimerization play a crucial role in the enhanced magnetocapacitance around the x=0.175 compound.

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