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Oxygen-vacancy effect on structural, magnetic, and ferroelectric properties in multiferroic YMnO₃ single crystals

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We have investigated the structural, magnetic, and ferroelectric properties of magnetically frustrated multiferroic YMnO₃ single crystals. The ferroelectric domain structures of YMnO₃ samples were studied by piezoresponse force microscopy. Instead of domain vortex structure in stoichiometric crystals, YMnO₃₋ₓ shows a random domain configuration. This random domain configuration is controlled by oxygen vacancies, which are induced by Y defects. The defects, including structural, nonstoichiometric, and topological defects, are expected to possess distinct electronic properties at multiferroic DWs, which, in turn, enhances magnetoelectric coupling in multiferroics.

YMnO₃, which is crystallized in the hexagonal structure, is a well-known multiferroic compound. It exhibits antiferromagnetic order at room temperature, high Curie temperature (~74 K), and antiferromagnetic Neel temperature (~914 K). Recent studies have shown that the oxygen vacancies in YMnO₃ are critical for the multiferroicity of this compound. The oxygen vacancies can be induced by Y defects, which can lead to new magnetoelectric phenomena through multiferroic DWs. In this paper, we report on the oxygen vacancy-induced multiferroicity through modifying DWs in oxygen-deficient YMnO₃ single crystals.

EXPERIMENTAL

YMnO₃ single crystals were grown by the floating zone method (Crystal System Inc.). Two kinds of crystals were grown in air (PO₂ = 0.1 MPa) and Ar (PAr = 0.4 MPa) atmospheres, which were denoted as the “air-grown” (air-grown YMnO₃) and “Ar-grown” (Ar-grown YMnO₃₋ₓ) samples, respectively. The crystal structure of samples was examined by powder x-ray diffraction (XRD; GBC MMA). The crystal was ground into powder in order to do XRD refinement. XRD refinement calculation was performed by the Rietica software package (version 1.7.7). Platelet crystals with area of 1 mm² in the ab-plane and thickness of 50 μm along the c-axis were prepared for piezoresponse force microscopy (PFM, Asylum Research MFP-3 D) observations. Pt/Ir coated Si cantilevers (tip radius ~28 nm) with force constant of 2.8 N/m were used. The magnetic measurements were carried out using a 14 T physical properties measurement system (PPMS, Quantum Design).

RESULTS AND DISCUSSION

Figure 1(a) shows the XRD pattern and refinement calculation results for YMnO₃ and YMnO₃₋ₓ crystals. The diffraction peaks can be indexed well with a hexagonal structure by Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 25-1079. Rietveld refinement results show that YMnO₃₋ₓ has a unit cell with lattice parameters a = b = 6.137(9) Å and c = 11.411(2) Å, which are very close to those of YMnO₃ [a = b = 6.138(4) Å and c = 11.407(3) Å].
The deficiency of oxygen is estimated to be 3% in Ar-grown YMnO3-δ crystal, based on the refinement result. The oxygen deficiency might possibly lead to Mn ions exhibiting multiple valences in order to maintain the charge balance. As has been reported for other multiferroic compounds,8 the valences of transition metals can significantly influence magnetic properties and electric properties. XPS measurements were carried out at room temperature in order to determine the valences of Mn ions in YMnO3-δ crystal, as shown in Fig. 2. The binding energy peaks of Y, Mn, and O have been indexed in the spectra. The XPS spectrum of the Mn 2p region of the sample and the fitting result are shown in the inset. Two main peaks at 653.701 and 642.156 eV correspond to Mn 2p1/2 and 2p3/2, respectively, which indicates that manganese ions present a valence of +3 in YMnO3-δ crystal. The XRD and XPS results confirm that there is no secondary phase formation in the oxygen deficient crystal sample.

Figure 3 shows out-of-plane PFM images of the ab surface of YMnO3 single crystals. A typical wedge-shaped ferroelectric domain structure has been observed in stoichiometric YMnO3 crystal, as shown in Fig. 3(a). Six different domain phases assigned as ±x, ±β, and ±γ with downward P1 (bright area) and three upward P1 (dark area) polarizations join at a clamping point. The domain size is 0.5–2.0 μm. Figure 3(b) shows a PFM image of the ab surface of Ar-grown YMnO3-δ crystal. Interestingly, the domain structures of the Ar-grown YMnO3-δ crystal are notably distinct from that of the air-grown sample. The domain sizes in the Ar-grown YMnO3-δ are in the range of 2.0–8.0 μm, which is four times larger than was observed for the air-grown samples. Instead of domain vortices as in the stoichiometric sample, the domain structure exhibits random shapes in YMnO3-δ, with one or more straight DW. At high concentration, oxygen vacancies tend to be ordered as pinning centers at DWs, forming vacancy chains and planes in ferroelectrics15,16 such as SrTiO3.17 In our sample, the concentration of oxygen vacancy reaches as high as ~3%. It is proposed that the straight DWs are induced by ordered oxygen vacancies in our YMnO3-δ.

Figure 4 shows the field-cooling magnetization (M) as a function of temperature (T) for YMnO3 and YMnO3-δ crystals measured in the temperature range from 5 to 300 K in a magnetic field of 1000 Oe. Compared to the YMnO3 crystal, the oxygen deficient YMnO3-δ sample shows lower magnetization from 5 to 300 K. The magnetic transitions were observed at T1 = 73 K and T2 = 78 K for YMnO3 and YMnO3-δ, respectively. In stoichiometric YMnO3, Mn-O-Mn is ordered antiferromagnetically through empty Mn3+ 3d orbitals and O2− 2p orbitals. However, the ordered oxygen vacancies at multiferroic DWs in YMnO3-δ lead to a local structural distortion, which will result in weak Mn-O-Mn ordering at DWs. As a result, the ordering temperature of YMnO3-δ is slightly higher than for the stoichiometric crystal. In order to further confirm the magnetic properties of YMnO3-δ crystal, the magnetization as a function of magnetic field (H) was measured in a magnetic field of 5 T at 10 and 300 K, as shown in the Fig. 4 inset. The linear M-H loops of YMnO3-δ indicate that the sample exhibits antiferromagnetic behavior at both low and room temperature.
CONCLUSION

In summary, the structural, ferroelectric, and magnetic interaction between oxygen vacancies and domain structures has been investigated in oxygen deficient YMnO$_{3-\delta}$ crystal. The valence of Mn ions remains +3, even with the high oxygen vacancy concentration (~3%) present in the sample. The ordered oxygen vacancies were verified to induce quasi-straight DWs in YMnO$_{3-\delta}$ with spontaneous polarization. The Néel temperature and magnetization of the YMnO$_{3-\delta}$ crystal were found to be lower than those of the stoichiometric YMnO$_3$, which is possibly attributable to the location of structural distortion at DWs induced by oxygen vacancies.

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