March 2016

String-like ferroelectric domain structure in a hexagonal $Lu_{0.5}Sc_{0.5}FeO_3$ single crystal

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KEY WORDS:, frustration system, multiferroics, ferroelectric domain, toroidal moment, hexagonal rare-earth ferrite

I. Introduction

Hexagonal manganites RMnO$_3$ (R=Y, In, Ho-Lu) attracted a huge attention due to their fascinating properties of high temperature ferroelectricity and magnetic frustration structure [1]. Fig.1 shows the crystal structure of hexagonal RMnO$_3$. RO layer and FeO_2 layer are alternately stacking along c-axis. Mn^{3+} ion is surrounded by three in-plane and two apical O^{2-} ions. The tilt of trigonal bipyramids of MnO_5 results in breaking of space inversion symmetry and spontaneous polarization along c axis. At lower temeprature, hexagonal RMnO$_3$ shows magnetic order of Mn^{3+} ions. Especially in YMnO$_3$, clump of ferroelectric and antiferromagnetic domain wall is reported [1]. This report suggests that magnetic domain can manipulate by electric field.However, most of hexagonal RMnO$_3$ exhibits antiferromagnetic order [2], so manipulation of spontaneous magnetization by electric field is impossible.Ferroelectricity and ferromagnetism in hexagonal rare earth ferrites RFeO$_3$ thin film (Y, In, Ho-Lu) [3], which is isostructural to hexagonal RMnO$_3$, were reported [3].But in order to observe the ferroelectric and ferromagnetic domain structure, bulk single crystal of hexagonal RFeO$_3$ is necessary. Recently, synthesis and ferromagnetism of hexagonal $Lu_{0.5}Sc_{0.5}FeO_3$ (LSFO) polycrystalline was reported [4].

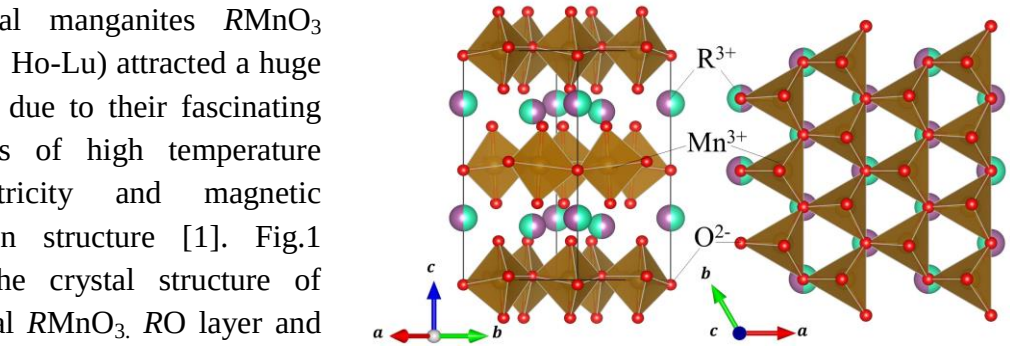

Fig.1: Crystal structure of hexagonal RMnO$_3$ at room temperature. Space group is P6$_3$cm.

The purpose of this thesis is to observe each ferroic domain structure and uncover the origin of magnetic order in hexagonal rare earth ferrites and mangaties.

II. Experiment

High purity Lu_2O_3, Sc_2O_3 and Fe_2O_3 was stoichiometrically mixed to synthesize LSFO polycrystalline. Prepared powder was heated at 1200°C for 24 hours in air with several intermediate grindings. Flux method, floating zone method and chemical vapor transfer method (CVT) were carried out in order to obtain a bulk single crystal of LSFO, By PbO-PbO_2-PbF_2-B_2O_3 flux method, a hexagonal reddish brown crystal has been obtained. By single crystal X-ray diffraction pattern, it was found that the lattice parameter is

consistent with the polycrystalline of LSFO reported by Masuno [4]. The sample obtained by floating zone method is not crystallographic mono-domain. There is not LSFO phase in the sample obtained by CVT method using Cl^2 as a transport agent. So the following experiments were carried out against samples obtained from the flux method.

The physical properties of LSFO single crystals grown in several condtions were investigated. Using piezoresponse force microscopy (PFM), imaging of the ferroelectric domain structure of LSFO was performed at room temperature. Pyroelectricity measurement was performed using superconducting quantum interference device (SQUID, PPMS, Quantum Design) electrometer at RIKEN, Wako. Polarization of samples was measured under fields ranging from -7 T to 7 T at 2, 24, 50, 75, 100, 125, 150, 175 and 190 K. Electric field dependence of polarization was measured at 2 K under voltage ranging from -300 V to 300 V. Magnetization measurement was carried out using superconducting quantum interference device (SQUID, MPMS, Quantum Design) magnetometer at ISSP. Magnetization of sample was measured over the temperature range of 10-300 K under 100-1000 Oe and magnetic moment were measured under fields ranging from -7 T to 7 T at 2, 150, 160 and 180 K.

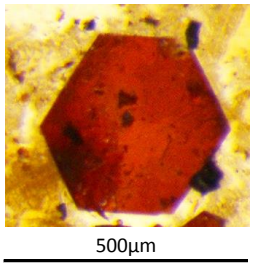

Fig.2: Crystal obtained by PbO-PbO_2-PbF_2-B_2O_3 flux method. The thickness is thinner than 10 μm.

Optical measurement was carried out. Absorption rate was measured over the wavelength range of 700-1100 nm at 3, 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 K.

III. Result and Discussion

Fig.3 shows the phase imaging of pizoresponse signal. The color contrast corresponds to ferroelectric domain. String-like domain structure was observed in LSFO grown over 1200°C. This domain structure is consistent with that of hexagonal $ErMnO_3$ at around ferroelectric transition temperature [5]. However, LSFO grown at 1200°C seems to be ferroelectric mono-domain. This result implies that the ferroelectric transition occurs between 1200°C to 1250°C in LSFO. Fig. 4 shows electric field dependence of polarization in multi-domain LSFO at 2 K. because a hysteresis loop was observed when voltage was induced over

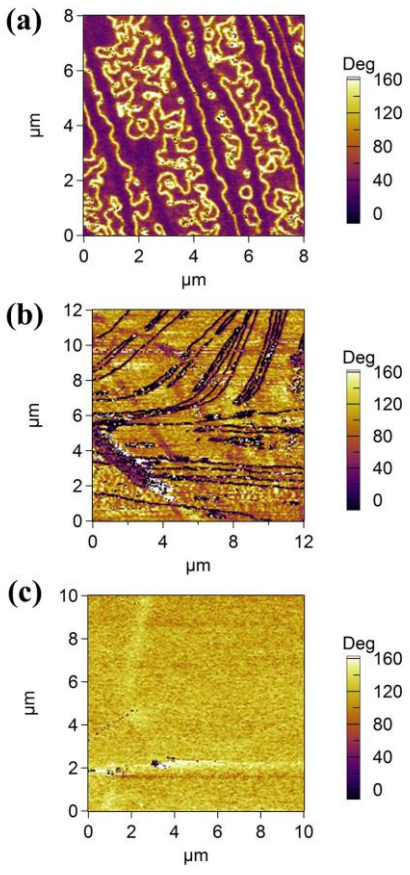

Fig.3: Phase of piezoresponse signal of LSFO. Color contrast corresponds to ferroelectric domain. (a)LSFO grown at 1250°C (b) LSFO grown below 1250°C (c) LSFO grown at 1200°C

300 V. This results exhibits that spontaneous polarization in multi-domain LSFO is switchable by electric field.

Fig.5 shows spectra of LSFO at each temperature. The large absorption peak over 1.9 eV is thought as charge transfer transition from Fe^{3+} to O^{2-}. The wide absorption around 1.23 eV is thought as *d-d* transition in Fe^{3+}.

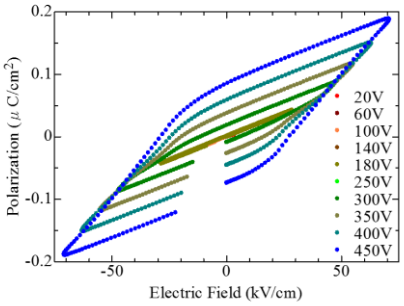

Fig. 4 : Hysteresis loop of polarization of LSFO at 2 K.

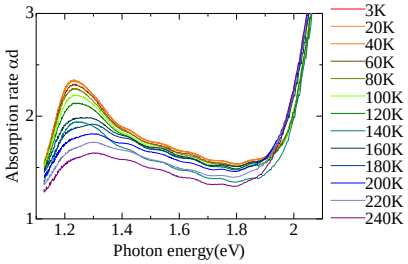

Fig.5: Spectra of LSFO at each temperature.

IV. Summary

We succeeded in single crystal growth of hexagonal LSFO and observation of the ferroelectric domain structure. The ferroelectric domain structure is similar to that of hexagonal manganites, but no singular point was observed in LSFO. Furthermore, the ferroelectric domain can switch by electric field. If ferroelectric and ferromagnetic domain clump exists in LSFO, manipulation of magnetization by electric field may be possible.

Unfortunatel, magnetoelectric effect and Faraday rotation were not detected from these samples. That is because the size of samples to small and thin. So we try to prepare a larger LSFO crystal by improving the synthesis condition of floating zone method and CVT method.

V. Reference

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【Presentation】

1. 第 71 回　日本物理学会春季年会「マルチフェロイック物質六方晶 Lu0.5Sc0.5FeO3 の単結晶育成と強誘電ドメイン観測」。