

Change in crystal structure and physical properties of the Multiferroics YMnO₃ single crystals by Strong gravitational field

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Abstract. Many researchers have studied the multiferroicity of the hexagonal RMnO₃ (R: rare-earth element) for both applications and fundamental studies. To investigate the relationship between the structure and physical properties of materials, some people apply the chemical pressure effect. The procedure of chemical pressure effect involves substituting rare-earth elements for ones which have a different ionic radius. Mashimo et al. have developed a high-temperature ultracentrifuge apparatus that can generate extended duration strong gravitational field in excess of 10⁶ G under a wide range of temperatures (up to 500°C). Strong gravitational fields directly act on each atom as a different body force. This can cause the change in crystal structure. Thus, we subjected YMnO₃ single crystal to strong gravity experiments (0.78×10⁶ G, 400°C, 2 h) and investigated the resulting changes in the crystal structure and physical properties of the gravity sample. The single crystal four-circle X-ray diffraction measurements revealed the change in the nearest neighboring Mn-Mn and M-O bond distances. The temperature dependence of magnetic susceptibility by SQUID showed the change in the magnetic anisotropy of gravity sample.

1. Introduction

RMnO₃ (R is rare earth) crystallizes in a hexagonal structure (Space group: $P6_3cm$) when the ionic radius of R is small (R = Ho-Lu, Y, and Sc). These compounds have been investigated due to showing the typical multiferroic effects [1,2]. In this hexagonal structure, each Mn³⁺ ions with $S = 2$ is surrounded by three in-plane and two apical oxide ions, and thus subject to a trigonal crystal field. These MnO₅ trigonal bipyramids are two-dimensionally connected with each other on their corners on ab -plane and each MnO₅ layers are separated by RO₇ layers [3]. Mn³⁺ ions forms two-dimensional triangular lattice in ab -plane with stacking along c -axis. This two-dimensional triangular lattice with an antiferromagnetic interaction is a good canonical example of a geometrical frustrated system. Actually, frustration parameter f which is defined as the ratio of $|\theta_{CW}|$ to T_N is very large (~ 10) compared with other triangular lattice compounds. The magnetic properties of RMnO₃ single crystals also have been studied [4, 5, 6]. Hexagonal RMnO₃ single crystals have a magnetic anisotropy, which causes the difference of susceptibility of parallel and perpendicular to c -axis. The susceptibility parallel to c -axis $\chi_c(T)$ shows the cusp of susceptibility curve at Néel temperature ($T_N \sim 70$ K); on the other hand, the susceptibility perpendicular to c -axis $\chi_{ab}(T)$ shows no cusp at Néel temperature. Curie-Weiss temperature θ_{CW} calculated from inverse susceptibility $1/\chi_{ab}(T)$ is about -700 K. The study of structural change for YMnO₃ has been investigated for fundamental understanding of physical properties. According to high-pressure study in temperature range 10-295 K, Kozlenko, et al., revealed



that the triangular lattice of Mn ions at high-pressure enhances the effects of geometrical magnetic frustration [7]. By study of high-temperature and -pressure for YMnO_3 , Waintal, et al., found orthorhombic YMnO_3 , which is perovskite-type structure [8]. Park, et al. investigated the relationship between the structure and physical properties used by the chemical pressure effect on $\text{Y}_{1-x}\text{Lu}_x\text{MnO}_3$ [9]. Both Y^{3+} and Lu^{3+} ions are nonmagnetic elements therefore there is no magnetic contribution and no disturbing the Mn magnetic moments.

Mashimo et al. have developed a high-temperature ultracentrifuge apparatus that can generate extended duration strong gravitational field in excess of 10^6 G under a wide range of temperatures (up to 500°C) [10]. Gravity is a field state variable, whereas pressure and temperature are thermodynamic state variables. Thus, gravitational fields directly act on the respective atoms by body force in alloys and compounds, while pressure or temperature influence atoms isotopically. Under a strong gravitational field ($\sim 10^6$ G), heavy atoms are displaced in the gravitational direction, while light atoms are shifted towards the opposite direction by the different body forces relative to their respective atomic weight in the crystal compound [11, 12]. Under a strong gravitational field, unique structural changes can be generated in compounds by the one-dimensional displacement of atoms caused by different body forces. Thus, the applying strong gravitational field is a clean way of exploring the relationship between the structure and physical properties.

In this work, we performed strong-gravity experiments on YMnO_3 single crystals to examine the changes in crystal structure and physical properties.

2. Experimental Procedure

YMnO_3 single crystal was grown by floating-zone method using the desktop-type single crystal growth equipment (Canon Machinery, Japan) at a feeding speed of 5 mm/h in air. A stoichiometric mixture of Y_2O_3 (99.99%) and Mn_3O_4 (99.9%) powder was ground and clacined three times at 1000°C in air for 12 h with an intermittent grinding procedure. Then resulting powder was cold-pressed under 400 kg cm^{-2} and sintered in air at 1400°C for 48 h. The direction of obtained crystal was confirmed by observation of a Laue X-ray backscattering photograph (TRY SE TRY-YGR) obtained using a W target and radiation at 35kV-15mA. We cut to the plate sample with $2 \times 1 \times 1\text{ mm}^3$ whose plane ($2 \times 1\text{ mm}^2$) is parallel to (0001) plane. The sample was set on a Si_3N_4 plate in a stainless steel SUS304 capsule, as shown in Fig 1. A strong-gravitational field was applied along the c -axis of the crystal where the maximum distance from the rotor axis was about 35.5 mm. The rotor was radiatively heated to 400°C by a follow carbon cylinder, which in turn was heated by a high-frequency heating system.

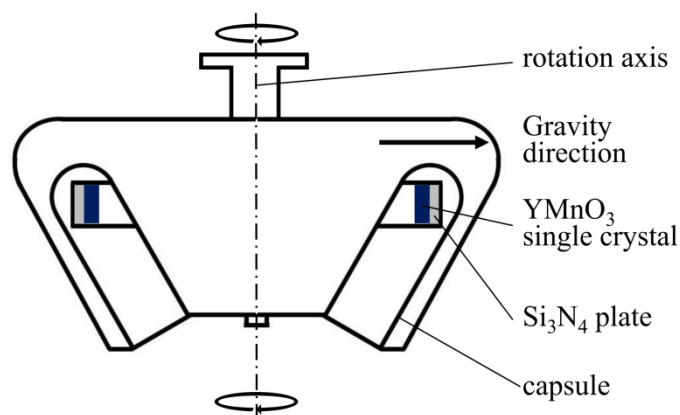


Figure 1. the schematic illustration of the rotor assembly. The sample was fixed on a Si_3N_4 plate. A gravitational field was applied along the

c-axis of the crystal where the maximum distance from the rotor axis was about 35.5 mm.

The duration of each experiment was 2 h. At the end of the experiment, the sample was quenched down to room temperature, and then strong gravitational field was removed. The rotor was radiatively heated to 400°C by a follow carbon cylinder, which in turn was heated by a high-frequency heating system. The duration of each experiment was 2 h. At the end of the experiment, the sample was quenched down to room temperature, and then strong gravitational field was removed.

The magnetic properties were measured using a superconducting quantum interference devise magnetometer (Magnetic Property Measurement System MPMS-XL, Quantum Design) under magnetic field of 0.1 T and temperature range between 5 and 300 K.

Single crystal X-ray diffraction measurements for initial and gravity samples were performed with Rigaku AFC-7R automated four-circle diffractometer. The radiation source Mo $K\alpha$ ($\lambda = 0.7102$ Å) is near the absorption K edge of Y atom (~ 0.7277 Å) therefore YMnO_3 compounds have a large linear absorption coefficient $\mu = 28.118 \text{ mm}^{-1}$. To carry out the accurate structure refinement, we should compute the absorption coefficient $\mu \cdot r$, where r is the radius of sample shaped into a sphere. Structure refinements were carried out by minimizing the function using Shelx97 program (Sheldrick, 1997).

3. Results and Discussion

We examined the crystal structures of initial and gravity samples at room temperature. The least-squares calculation for initial and gravity samples was converged at R_1 ($I > 2.0\sigma(I)$) 2.28, and 2.53%, respectively. The obtained crystal structure for initial sample is in agreement with previous reported [13]. The selected bond distances are summarized in Table 1. In all hexagonal RMnO_3 compounds, the two apical bond distances (Mn-O1 and Mn-O2) are shorter than the three equatorial bond distances (Mn-O3 and Mn-O4). The difference in apical bond distances for gravity sample increased. According to previous high-pressure study, the difference in apical bond distances increases with increasing pressure [8]. By analogy with this, the increase in difference in apical bond distances was caused by compressed uniaxially. The Mn-O bond distance in *ab*-plane splits the inequivalent bond distances Mn-O3 and Mn-O4. There are two ways of the direction of Mn trimerization, namely around O3 site and O4 site. The Mn-O bond distances in *ab*-plane of initial and gravity sample has a significant difference. It means that Mn trimerization changed after strong -gravity experiment.

Table 1. Results of least-squares calculation lattice parameters, and selected bond distances for initial and gravity samples.

	initial	gravity
<i>R1 and S values</i>		
R_1 ($I > 2.0\sigma(I)$)	2.28	2.53
S	1.018	1.015
<i>lattice parameter</i>		
a (Å)	6.1352(4)	6.1421(4)
c (Å)	11.4137(8)	11.4160(10)
<i>MnO₅ bipyramid</i>		
Mn-O1 (Å)	1.869(6)	1.886(14)
Mn-O2 (Å)	1.865(5)	1.854(11)
Mn-O3 (Å)	2.0631(15)	2.053(4)
Mn-O4 (Å) [$\times 2$]	2.0542(9)	2.0636(16)

mean Mn-O (Å) 1.9811(16) 1.9840(37)

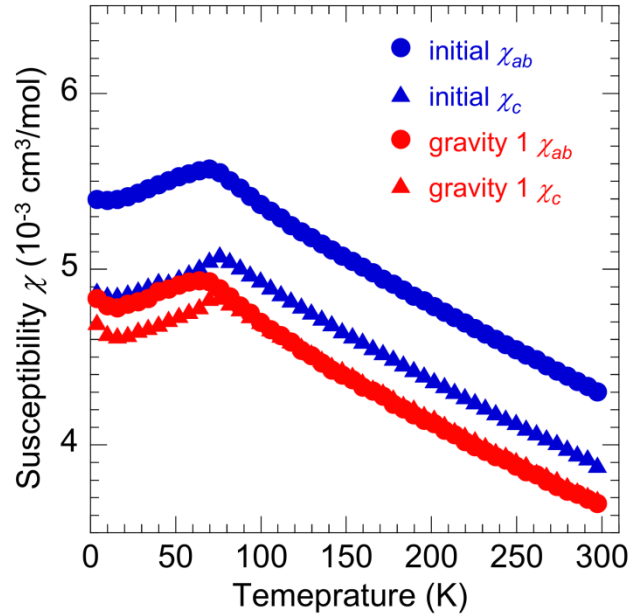


Figure 2. Temperature dependence of magnetic susceptibility of initial and gravity samples. The closed circle in blue and red represent the susceptibility with magnetic field perpendicular to c -axis (χ_{ab}) for initial and gravity samples, respectively. The closed triangle in blue and red represent the susceptibility with magnetic field parallel to c -axis (χ_c) for initial and gravity samples, respectively.

Figure 3 shows temperature dependence of magnetic susceptibility of initial and gravity samples. In YMnO_3 , the susceptibility of $\chi_c(T)$ and $\chi_{ab}(T)$ are parallel to and perpendicular to c -axis, respectively. The susceptibility of initial sample is consistent with previous reports, which state that $\chi_{ab}(T)$ is larger than $\chi_c(T)$ in whole temperature range [5, 6]. However, the susceptibility after gravity experiment is different from the one of initial and previous reports. The $\chi_c(T)$ and $\chi_{ab}(T)$ of gravity sample is close to each other. In other word, the anisotropy of $\chi(T)$ for gravity sample is suppressed. We should note that the anomaly at T_N still remain in gravity samples. The Curie-Weiss temperature θ_{CW} is derived from the inverse susceptibility $1/\chi$. The obtained θ_{CW} of initial and gravity samples were -708 and -602 K, respectively. The frustration parameter f of initial and gravity samples were 9.3 and 8.2 , respectively. To estimate the value of nearest neighboring interaction J , we use the theoretical Curie-Weiss temperature using a high-temperature expansion of spin susceptibility. The obtained J of initial and gravity samples were 2.5 and 2.2 meV, respectively, which is consistent with the theoretical calculation of recently reported [9].

Now, we consider that the correlation with Mn-O bond length in ab -plane and Curie-Weiss temperature θ_{CW} . Above mentioned before, The Mn-O bond distance in ab -plane splits the inequivalent bond distances Mn-O3 and Mn-O4. This leads to two different magnetic exchange interactions between the neighboring Mn^{3+} ions in ab -plane [14] and to relieve a geometric frustration in the system. We note that observed Néel temperature T_N are ~ 72 K for initial and gravity samples. Therefore the ratio of Mn-O3 and Mn-O4 bond distances in room temperature range is the major factor controlling the Curie-Weiss temperature $|\theta_{CW}|$ and frustration parameter f . Mn trimers of initial connect to each other organically over ab -plane, which means the strong two-dimensional character.

On the other hand, each Mn trimers of gravity sample are isolated. We assume that it leads to change in the susceptibility $\chi_c(T)$ and $\chi_{ab}(T)$ and Curie-Weiss temperature $|\theta_{CW}|$ for gravity sample.

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