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Precursor phenomenon on ferroelectric transition in multiferroic YMn_2O_5

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Abstract

Series of RMn_2O_5 (R = Sm-Lu, Bi, Y) are simultaneously ferroelectric and antiferromagnetic at low temperatures. The ferroelectric Curie temperature (T_{CE} = 25–40 K) is slightly lower than the antiferromagnetic Néel temperature (T_N = ∼45 K), implying that the ferroelectricity is induced with the antiferromagnetic long-range order in RMn_2O_5. Previously, we have investigated the thermal expansion anomaly in YMn_2O_5 at higher temperatures than T_N = 45 K, which would be the precursor phenomenon relating to the ferroelectric transition. This study tries to investigate a further detailed precursor phenomenon to make clear the origin of the ferroelectricity in YMn_2O_5. Particularly, we focus on the temperature factors of each cation in the temperature range from 50 K to 170 K. The single crystal X-ray diffraction of YMn_2O_5 was integrated at 298 K and 112 K by using a single crystal diffractometer with an imaging plate. The structural parameters were well refined as *Pbam* at both temperatures. In the refined result, it was found that the thermal ellipsoid became more anisotropic for the Mn or the Y ions with decreasing temperature from 298 K to 112 K. In addition, the long principal axis of the thermal ellipsoids rotated in the *a*–*b* plane with decrease of temperature. At 112 K, the long principal axis of Mn^{3+} thermal ellipsoid in *a*–*b* plane is almost parallel to the direction from the apex to the base of the pyramid square. The direction agrees with a possible ionic displacement speculated from the irreducible representation analysis.

Keywords: Mutiferroic; Ferroclectric properties; Magnetic properties; Single crystal X-ray diffraction; Thermal expansion

1. Introduction

Series of RMn_2O_5 (R = Sm-Lu, Bi, Y) are ferroelectric at low temperatures, where a spontaneous polarization appears along *b*-axis of orthorhombic structure (space group: *Pbam*).[1–3] The ferroelectric Curie temperature T_{CE} (25–40 K) is slightly lower than the Néel temperature (T_N = ∼45 K), where Mn^{3+} and Mn^{4+} ions are anti-ferromagnetically ordered. The origin of the ferroelectricity is strongly related to the magnetic long-range order in RMn_2O_5.[4–9] The magnetic structure of YMn_2O_5 is relatively simple compared to other RMn_2O_5 to make clear the origin of the ferroelectricity, because Y ion is non-magnetic. Previously, it has been found that anomalies in the second order-magnetoelectric effect and commensurate-incommensurate transition in magnetic propagation vector $\boldsymbol{q}$ at T_{CE} in YMn_2O_5.[7–9] The unusual phenomena suppose that the ferroelectric spontaneous polarization is accompanied with a variation of antiferromagnetic structure at T_{CE}. Based on the irreducible representation analysis and the results of the Mössbauer spectroscopy, we have proposed that the ferroelectric spontaneous polarization is caused by relaxation of the strong competitions between superexchange interactions of Mn–O–Mn with different paths.[4,6] However, the ionic displacement to support the speculation has been unclear, because the ionic displacement is too small to be detected within the experimental accuracy in the X-ray diffraction.

We have found another significant result that the thermal expansion coefficient of *b*-axis is negative in the temperature range from 50 K to 170 K, although the *a*- or the *c*-thermal expansion coefficient is positive.[4,10] The thermal expansion anomaly of *b*-axis is considerably related to appearance of ferroelectric spontaneous polarization along *b*-axis. In other word, the behavior of thermal expansion along *b*-axis would be precursor phenomenon for the ferroelectric transition characterized by the spontaneous polarization along *b*-axis. This study tries to investigate further detailed precursor phenomenon for the ferroelectricity in YMn_2O_5. In general, the thermal expansion results from temperature dependence on thermal vibration of each ion in crystals. With the point of view, we focus on the temperature factors and the interatomic distances in the temperature range from 50 K to 170 K. Based on the obtained results, we discuss a

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Table 1
Refined position coordinates of YMn_2O_5 at 298 K. S.G.: *Pbam* (orthorhombic). $a = 7.264(4)$ Å, $b = 8.476(5)$ Å, $c = 5.669(4)$ Å.

Atom	Site	*x*	*y*	*z*
Y	4*g*	0.1387(1)	0.1714(1)	0
Mn1	4*f*	0	0.5	0.2551(2)
Mn2	4*h*	0.4120(1)	0.3501(1)	0.5
O1	4*e*	0	0	0.2715 (9)
O2	4*g*	0.1627(7)	0.4445(6)	0
O3	4*h*	0.1512(7)	0.4315(6)	0.5
O4	8*i*	0.3951(5)	0.2063(4)	0.2435(6)

$R(F^2) = 2.87\%$. $wR(F^2) = 3.74\%$.

possible ionic displacement related to the ferroelectricity.

2. Experimental procedures

YMn_2O_5 single crystals were prepared by PbO–PbF_2 flux method.[11] Y_2O_3 (purity of 99.9%) and $MnCO_3$ (purity of 99.9%) were weighed according to the chemical formula of YMn_2O_5. The powders were mixed and then calcined in air at 1050 °C for 10 h. Then the powder was inserted in a Pt crucible with PbO, PbO_2 and PbF_2 flux. The crucible with the powders were fired in air at 1250 °C for 4 h, and then slowly cooled down to 800 °C by rate of 1.5 °C/h. In this preparation process, the euhedral prisms elongated along *c*-axis were obtained. The typical size of the grown crystals was approximately 1 mm × 1 mm × 3 mm. A grown crystal was ground into a sphere of 0.12 mm in diameter. Integrated intensity data of the grounded crystal was collected by using a single crystal diffractometer with imaging plate (Rigaku; R-AXIS RAPID), where Mo *K*α radiation was used as incident beam. The collected temperatures were at 298 K and 112 K (±1 K). The collected total reflections were over number of 3400, which are observed within $-9 \le h \le 9$, $-9 \le k \le 9$, $-6 \le l \le 6$. The structural parameters were refined by the full-matrix least-squares program *RADY*.[12]

3. Results

The refined structure parameters at 298 K and 112 K are tabulated in Tables 1 and 2, respectively. From the obtained structure parameters, the interatomic distances are calculated as tabulated in Tables 3 and 4. The temperature factors of the ions in YMn_2O_5 at 298 K and 112 K are tabulated in Tables 5 and 6 under the refinement of the structure.

Table 2
Refined position coordinates of YMn_2O_5 at 112 K. S.G.: *Pbam* (orthorhombic). $a = 7.244(4)$ Å, $b = 8.463(7)$ Å, $c = 5.657(4)$ Å.

Atom	Site	*x*	*y*	*z*
Y	4*g*	0.1383(1)	0.1716(1)	0
Mn1	4*f*	0	0.5	0.2550(2)
Mn2	4*h*	0.4121(2)	0.3504(1)	0.5
O1	4*e*	0	0	0.2717(10)
O2	4*g*	0.1628(8)	0.4441(7)	0
O3	4*h*	0.1505(8)	0.4309(7)	0.5
O4	8*i*	0.3953(5)	0.2062(5)	0.2433(7)

$R(F) = 3.04\%$. $wR(F^2) = 3.89\%$.

Table 3
Interatomic distances in YMn_2O_5 at 298 K in angstroms.

Mn1–O2(×2)	1.926(3)	R–O1(×2)	2.344(3)
Mn1–O3(×2)	1.863(3)	R–O2	2.321(5)
Mn1–O4(×2)	1.909(3)	R–O2	2.404(5)
⟨Mn1–O⟩	1.899(3)	R–O4(×2)	2.337(3)
		R–O4(×2)	2.472(3)
Mn2–O1(×2)	1.924(3)	⟨R–O⟩	2.379(4)
Mn2–O3	2.016(5)		
Mn2–O4(×2)	1.901(3)	Mn1–Mn1	2.777(2)
⟨Mn2–O⟩	1.933(2)	Mn1–Mn1	2.892(2)
		Mn2–Mn2	2.845(2)

The lattice parameters determined at 298 K in this study is comparable with that of the previous one within the experimental accuracy. It notes that the experimental accuracy for the previous study is much higher than the present study, since the Bond's method has been adopted to determine accurately the lattice parameters.[4]

The collected reflection data was well refined with space group of *Pbam*. No remarkable difference in atomic coordination was observed between 298 K and 112 K, indicating that no structural phase transition was observed in the temperature range from 298 K to 112 K as reported in other studies. From Tables 3 and 4, however, slight difference was found in the interatomic distances of Mn2–Mn2. The Mn2–Mn2 distances decreased with decreasing temperature.

Significant difference was found in anisotropic temperature factors. If we focus on the anisotropic thermal vibration of Mn^{4+} (Mn1), Mn^{3+} (Mn2) and Y ions, absolute value of the U_{12} became larger, while the U_{11} and the U_{22} became smaller with decreasing temperature from 298 K to 112 K. The crystal structure of YMn_2O_5 at 298 K and 112 K is illustrated in Figs. 1 and 2,[13] where the thermal ellipsoids obtained from the temperature factors are also shown. The thermal ellipsoid became more anisotropic for the Mn or the Y ions with decreasing temperature from 298 K to 112 K. In addition, a principal axis of the thermal ellipsoids rotated in the *a*–*b* plane with decreasing temperature.

The thermal ellipsoid of O1 or O2 also indicated same tendency, however, the experimental accuracy would not be enough to discuss the difference.

Table 4
Interatomic distances in YMn_2O_5 at 112 K in angstroms.

Mn1–O2(×2)	1.922(4)	R–O1(×2)	2.340(1)
Mn1–O3(×2)	1.858(4)	R–O2	2.313(6)
Mn1–O4(×2)	1.904(4)	R–O2	2.405(6)
⟨Mn1–O⟩	1.895(4)	R–O4(×2)	2.334(3)
		R–O4(×2)	2.462(4)
Mn2–O1(×2)	1.917(1)	⟨R–O⟩	2.374(4)
Mn2–O3	2.014(5)		
Mn2–O4(×2)	1.901(4)	Mn1–Mn1	2.772(2)
⟨Mn2–O⟩	1.930(3)	Mn1–Mn1	2.885(2)
		Mn2–Mn2	2.834(2)

Table 5
Refined temperature coordinates of YMn_2O_5 at 298 K.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}	U_{iso} (Å^2)
Y	0.0085(1)	0.0078(1)	0.0082(2)	−0.0002(1)	0	0	0.00823(2)
Mn1	0.0079(2)	0.0081(1)	0.0065(3)	0.0000(1)	0	0	0.00747(3)
Mn2	0.0091(2)	0.0079(1)	0.0074(3)	−0.0004(1)	0	0	0.00823(3)
O1	0.0108(8)	0.0093(6)	0.0083(15)	−0.0004(6)	0	0	0.00950(10)
O2	0.0103(9)	0.0084(6)	0.0062(14)	0.0007(6)	0	0	0.00823(10)
O3	0.0099(9)	0.0132(7)	0.0083(15)	0.0009(7)	0	0	0.0104(10)
O4	0.0123(6)	0.0073(5)	0.0091(10)	0.0012(4)	−0.0014(6)	−0.0001(7)	0.00963(9)

Table 6
Refined temperature coordinates of YMn_2O_5 at 112 K.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}	U_{iso} (Å^2)
Y	0.0064(2)	0.0061(1)	0.0064(2)	−0.0004(1)	0	0	0.00629(2)
Mn1	0.0045(2)	0.0045(2)	0.0049(3)	0.0004(1)	0	0	0.00463(2)
Mn2	0.0077(2)	0.0058(2)	0.0065(4)	−0.0006(1)	0	0	0.00667(2)
O1	0.0091(10)	0.0085(7)	0.0069(17)	0.0069(17)	0	0	0.00814(11)
O2	0.0105(11)	0.0062(7)	0.0080(18)	0.0014(7)	0	0	0.00824(12)
O3	0.0092(10)	0.0079(8)	0.0080(17)	0.0003(7)	0	0	0.00837(12)
O4	0.0084(7)	0.0069(5)	0.0083(12)	0.0069(5)	0.0002(5)	0.0001(7)	0.00789(8)

4. Discussion

As described above, the refined temperature factor indicates that anisotropy of thermal ellipsoid becomes larger with decreasing temperature. If we focus on the Mn^{3+} ion, the long principal axis in *a*–*b* plane of the Mn^{3+} thermal ellipsoid is almost parallel to the direction from the apex to the base of the pyramid square at 112 K, suggesting that the Mn^{3+} ions possibly displace along the direction below T_{CE}.

Previously, we have discussed a possible ionic displacement accompanying the ferroelectric spontaneous polarization along *b*-axis. The presence of the spontaneous polarization corresponds to disappearance of *a*-glide, where the space group goes down to $Pb2_1m$ or its subgroup from *Pbam*. The previous result of the Mössbauer spectroscopy implies that the displacement is related to splitting of Mn^{3+} site.[6] A possible Mn^{3+} displacement speculated from an irreducible representation Γ_{3u} of *Pbam* is indicated in Fig. 2.[4] The direction along the long principal axis of the Mn^{3+} thermal ellipsoid in the *a*–*b* plane at 112 K agrees the possible displacement. The possible displacement was also speculated by the ^{55}Mn nuclear magnetic resonance measurement.[14] Thus we propose that the behavior of the Mn^{3+} thermal ellipsoid in *a*–*b* plane is a precursor phenomenon for the ferroelectric transition in YMn_2O_5. It indicates an indirect evidence for a possible displacement of the Mn^{3+} ions.

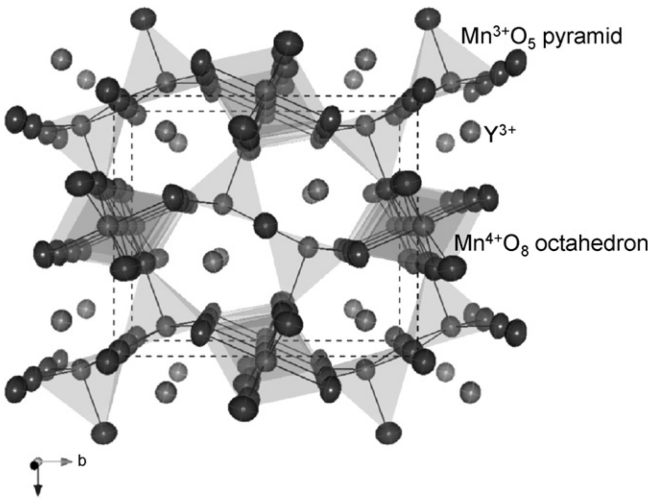

Fig. 1. Refined crystal structure of YMn_2O_5 at 298 K.

The competition resulting from the Mn–O–Mn superexchange interactions and the magnetic anisotropy in Mn^{3+} ions

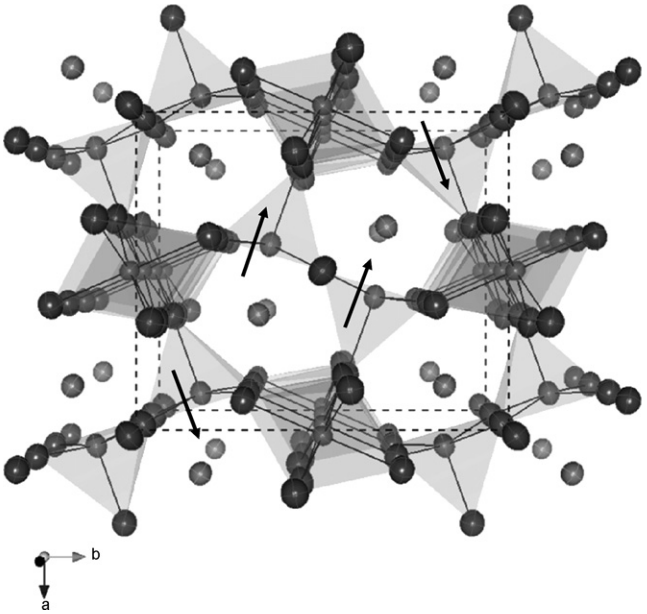

Fig. 2. Refined crystal structure of YMn_2O_5 at 112 K. The allows indicate a possible displacement of Mn^{3+} ion resulting in the ferroelectric polarization along *b*-axis.

can be relaxed by the displacement, as discussed in the previous studies.[4,6] As shown above, the Mn2–Mn2 distances at 112 K were smaller compared to the 298 K. The decrease of the Mn2–Mn2 distances makes the superexchange interaction larger. It is considerable that the behavior of the Mn^{3+} thermal ellipsoid depends on variation of the superexchange interactions.

The temperature factors also explain why the thermal expansion is negative in the temperature range from 50 K to 100 K. The thermal vibration along *b*-axis prevents the lattice of *b*-axis from shrinking. Further detailed temperature dependence of the principal direction should be investigated to make clear the relation between the thermal expansion and the anisotropic thermal vibration.

5. Conclusion

Single crystal X-ray diffraction was conducted to investigate the crystal structure parameters of YMn_2O_5 at 298 K and 112 K. The crystal structure was well refined as *Pbam* at the both temperatures. There was no remarkable difference in atoms coordination between 298 K and 112 K. On the other hand, a remarkable difference was found in temperature factors of the Mn or the Y ions. The thermal ellipsoids became more anisotropic for the Mn or the Y ions with decreasing temperature from 298 K to 112 K. In addition, the long principal axis of the thermal ellipsoids rotated in the *a*–*b* plane with decrease of temperature. At 112 K, the long principal axis of Mn^{3+} thermal ellipsoid in *a*–*b* plane is almost parallel to the direction from the apex to the base of the $Mn^{3+}O_5$ pyramid square. The direction corresponds to a possible displacement resulting in the ferroelectric spontaneous polarization along *b*-axis.

Acknowledgements

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