

希土類酸化物RMnO3における元素置換効果と化学圧 力効果

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	キーワード (Ja):
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	作成者: バオ, ジンファ
	メールアドレス:
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Thesis for a Degree of Doctor of Engineering

Effects of Element Substitution and Chemical Pressure on Rare-Earth Oxide RMnO₃

(希土類酸化物 RMnO3 における元素置換効果と化学圧力効果)

BAO JIANHUA



Division of Engineering Course of Advanced Production Systems Engineering Muroran Institute of Technology

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Abstract

The ABO₃ type perovskite RMnO₃ (R: rare-earth element) has investigated extensively as the multiferroic materials which possess two or more types of orders simultaneously. In this thesis, we investigated the effect of element substitution and chemical pressure in orthorhombic GdMnO₃ (space group *Pnma*) and hexagonal TmMnO₃ (*P6₃cm*).

The X-ray diffraction measurement results of GdMnO₃ shows A-type antiferromagnetism is below T_N , but it is known that Mn spins are not perfectly antiparallel, but exist with a slight tilt. This is called cant magnetism or weak ferromagnetism. The crystal structure of GdMn_{1-x}Co_xO₃ is orthorhombic for $0 \le x \le 1.0$. For x=0.3, 0.5, and 0.7, at the ordering temperature $T_{\rm C}$, the field-cooled (FC) magnetization MFC rapidly increase which results from cating of the Mn and Co moments with decreasing temperature. Especially, M_{FC} for x = 0.3 showed maximum values at 40K, decreased rapidly with decreasing temperature and showed a negative magnetization blow 20K. On the other hand, the heavy rare earth oxide TmMnO₃ is that an antiferromagnetic transition temperature $T_{\rm N}$ is 41K, and ferroelectric transition temperature $T_{\rm C}$ is 86K. It is known that the crystal structure of RMnO₃ having this structure changes to the orthorhombic (Pnma) by performing high-pressure synthesis, but even in TmMn_{1-x}Co_xO₃ with substitution by Co the structure changes from hexagonal to an orthorhombic, and we can obtain an orthorhombic single phase (space group *Pnma*) at $0.5 \le x$. *M*_{FC} of TmMn_{1-x}Co_xO₃ was increase in ferromagnetically at about 60K with decreasing temperature, and also showed negative magnetization in 0.7 $\le x$. but *M*_{FC} for *x*=0.8 no longer showed a ferromagnetic increase with decreasing temperature. The increase in ferromagnetic magnetization with decreasing temperature at *T*_C can be understood as a result of the mixed-valence state due to Co substitution. the negative magnetization observed in both samples. So-called the spin reversal, can be explained by the antiferromagnetic coupling of the Gd or Tm spin to the Mn and Co moments.

We investigated $Gd_{1-y}R_yMn_{1-x}Co_xO_3$ and $Tm_{1-y}R_yMn_{0.5}Co_{0.5}O_3$ also (R: nonmagnetic rare-earth element) with substitution by nonmagnetic rare- earth elements La, Y, Lu. We can expect the chemical pressure effect due to the unit-cell volume (V) change by substituting Tm or Gd with nonmagnetic rare-earth elements. From $Tm_{1-y}(Y, Y)$ Lu)_yMn_{0.5}Co_{0.5}O₃ observation we can obtained some remarkable structural details: owing to the ion radii, V of Tm1-yLuyMn0.5C00.5O3 and Tm1-yYyMn0.5C00.5O3 decreases and increases with increasing y, respectively; the parameter (a-c)/a, which is characterizes the orthorhombic distortion, continuously increases on Lu doping and decreases on Y-doping due to the substitution of Tm ions. Substitution of Tm with Y or Lu in orthorhombic Tm_{1-y}(Lu, Y)_yMn_{1-x}Co_xO₃induces a systematic unit-cell volume change. This is the chemical pressure effect. From the magnetization measurement, we conclude that an increase of $M_{\rm FC}$ and the unit-cell volume is responsible for the increase in transition temperature $T_{\rm C}$. We also studied the effects of chemical pressure with Gd₁- $_{y}R_{y}$ Mn_{1-x}Co_xO₃ y = 0.1, 0.3, and 0.5. The substitution of Gd with La, Y, or Lu in orthorhombic Gd_{1-y} R_{y} Mn_{1-x}Co_xO₃ induced a systematic change in the unit-cell volume. Our results reveal that increasing or decreasing the average ionic radius of the rare-earth element in the compound affects the magnetic ordering temperature T_{c} . The reduction in the proportion of Gd owing to substitution by nonmagnetic elements weakens the spin reversal effect.

論文内容の要旨

ABO3型ペロブスカイト RMnO3 (R:希土類元素)は同時に複数の秩序状態を 持つマルチフェロイック物質として広く研究されている。本論文では、直方晶 GdMnO3 (空間群 Pnma)と六方晶 TmMnO3 (P63cm)について、元素置換効果 と化学圧力効果を調べた。

GdMnO3のX線回折測定結果は、TN以下でAタイプの反強磁性であること を示しているが、Mn スピンは完全には反平行でなく、わずかにチルトしてい ることが知られている。これはキャント磁性あるいは弱強磁性と呼ばれている。 この系の Mn を Co で置換した GdMn1-xCoxO3の結晶構造は、0≤x≤1 で直方晶系 である。x=0.3,0.5,0.7 では、転移温度 T_cにおいて磁場中冷却(FC)磁化 M_{FC} は、 温度低下とともに Mn と Co モーメントのキャントの結果として急激に増加す る。特に、x=0.3の MFC は約 40K で最大値を示し、温度の低下とともに急激に 減少し、20K以下では負の磁化を示した。他方、重希土類酸化物 TmMnO3は、 反強磁性転移温度 TNが 41K, 強誘電転移温度 Tc が 86K である。この構造を持 つ RMnO3 の結晶構造は、高圧合成により直方晶に変化することが知られてい るが、Coで置換したTmMn1-xCoxO3においてもその構造はxに依存して六方晶 から直方晶系へ変化し、0.5≤xでは、錯体重合法により直方晶単相(Pnma)を 得た。TmMn_{1-x}Co_xO₃の M_{FC}は、温度の減少とともに、約 60K で強磁性的に増 加し、0.6≤x≤0.7 でも負の磁化を示す。しかし、x=0.8 の M_{FC} はもはや温度低下 とともに強磁性的な増加を示さない。これらの温度低下に伴う T. での強磁性 的な磁化の増大は、Co 置換による混合原子価状態の結果として理解できる。

また負の磁化、すなわちスピン反転は、Mn と Co モーメントに対する Gd ある いは Tm スピンの反強磁性的カップリングによって説明できる。

我々はまた、GdやTm を非磁性希土類元素La、Y、Luで置換したGd₁,RyMn₁xCoxO3 と Tm_{1-y} R_y Mn_{1-x}CoxO3 の物性についても調べた。Gd³⁺、Tm³⁺、La³⁺、Y³⁺、 Lu³⁺のイオン半径の違いから、我々は、Tm または Gd を非磁性希土類元素で 置換することによる単位格子体積(I)の変化による圧力効果を期待できる。 Tm1-v(Y,Lu)vMn0.5Co0.5O3の調査から、いくつかの顕著な構造の詳細が得られた。 Tm1-yLuyMn0.5Co0.5O3 と Tm1-yYyMn0.5Co0.5O3 の V は、それぞれ y の増加ととも に減少と増加した。直方晶歪みを特徴づけるパラメータ(a-c)/aは、Tmイオン を置換するために、Lu ドープでは連続的に増加し、Y ドープでは減少する。 直方晶 Tm1-y(Y,Lu)yMn0.5Co0.5O3 における Tm の Y または Lu による置換は、系 統的な単位格子体積の変化を誘起する。これは化学圧力効果である。磁化測定 から、我々は MFC と単位胞体積の増加が転移温度 Tc における増加に寄与する と結論する。直方晶 Gd1-vRvMn0.7Co0.3O3(R=非磁性希土類元素)の v=0.1,0.3,0.5 についても、化学圧力効果の研究を行った。Gd1-yRyMn1-xCoxO3における Gdの La, Y, Lu 置換は、単位胞体積の系統的な変化を誘起する。我々の結果は、化合 物の希土類元素の平均イオン半径の増加あるいは減少が、磁気転移温度 Tc に 影響することを示す。非磁性元素による置換で生じた Gd の割合の減少は、ス ピン反転効果を弱める。

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Chapter I Introduction

1.1 Multiferroic Materials

Ferroelectric / piezoelectric materials are a class of dielectric functional materials, occupying an important position in the fields of sensing, driving, and information storage, forming disciplines such as "ferroelectric physics". Magnetic materials are still extensively used and dominate, especially, as information storage, the development of magnetic storage technology produced a new subject "spintronics", etc. in general, the ferroelectric / piezoelectric material is electrically insulating, and magnetic material is electrically conductive, and thus are not usually two types of material compatible, they belong to two different independent fields. Multiferroic materials combine two or more different (ferroelectric / piezoelectric, and ferromagnetic) characteristics into one, ordered coexistence, and more importantly, new effects are generated due to the mutual coupling of multiple order parameters. For example, ferroelectric / piezoelectric and magnetic coupling generate magnetoelectric effects, which is polarization by the external magnetic field, or regulates magnetic in external electric field.

In dielectric materials, the order of electric dipoles produces and the polarization P can be controlled by the electric field E, and the spontaneous polarization in ferroelectricity occurs in zero electric field E_0 . On the other hand, the magnetization M, which is produced by the order of spin can be controlled by the magnetic field H, ferromagnetic has a spontaneous magnetization in zero applied field H_0 . However, in

multiferroic, have not only PE and MH characteristics, but also a magnetic-electric cross-regulation effect, that is, the magnetization M can be regulated by the magnetic field H or the electric field E as Fig .1 shows.



Fig. 1.1 Schematic diagram of the magnetoelectric effect of multiferroic

Multiferroic (magnetoelectric) material is a new type of multifunctional material, it is basically literally understood, both having multiple "ferrous" is multiferroic. But now the magnetoelectric multiferroic has widened this range, as long as it is magnetic (not only ferromagnetic) and polarized (not necessarily ferroelectric), it can be called multiferroic, which can be used not only in the application field of a single ferrous material, but also in the fields of new type magnetic-electric sensor devices, spin electronic devices, new information storage devices, etc. On the other hand, the physical connotation of multiferroic-electrical coupling involves multiple categories of condensed matter physics such as electric charge, spin, orbit, and lattice; therefore, it has become a new international frontier research area. From the perspective of the discipline, multiferroic materials organically combine the two major types of materials which ferroelectric and magnetic that have traditionally lacked intrinsic links with the fields of electronics with information and energy^{1,2)}.

1.2 History and Development

Wilhelm Conrad Röntgen discovered in 1888 that a dielectric became magnetized when moving in a uniform electric field³). His study was motivated by the following reasoning: when the polarized in the external electric field dielectric sheet moves in the direction perpendicular to the field line, the motion of negative and positive charges, separated through the induced polarization, then becomes equivalent to two electrical currents moving into opposite directions on either side of the sheet. Those currents generate a magnetic field, so the dielectric was magnetized. The experimental setup to prove the magnetoelectric effect did involve a fast-rotating dielectric disc between two horizontal capacitor plates. In 1894, Curie pointed out through symmetry analysis that the intrinsic magnetoelectric coupling effect may exist in some crystals⁴). In the same communication, Röntgen also conjectured that the inverse effect should exist, namely the change of the polarization of a moving dielectric induced by an external magnetic field, which was indeed experimentally shown by Wilson in 1905⁵). In 1961, American scientists first reported that the intrinsic magnetoelectric effect was observed at low and medium temperatures of Cr₂O₃, predicted by Dzyaloshinskii^[6] on symmetry grounds, was experimentally verified through the demonstration that an electric field did induce a magnetization^[7–9] as well as the reverse effect, the magnetic field induce dielectrically polarization^[10] is making early. The study of magnetoelectric effect reached a small climax in the 1970s, and low-temperature magnetoelectric effects were observed in some borate, phosphate, and manganate crystals. At the same time, the concept and materials of composite magnetoelectricity also appeared for the first time. However, due to lack of practical application drive, low temperature conditions, and complicated coupling mechanisms, all related studies subsequently entered a trough " low ebb " of nearly 30 years. Until the beginning of the 21st century, research on multiferroic materials began^[11].

The following briefly summarizes the development status and trends of singlephase and composite multiferroic materials and related components.

In the past ten years, with the advancement of material preparation technology, characterization methods and theoretical calculations, and the urgent demand for new information functional devices in the modern information society, the research on multiferroic materials and related devices has experienced unprecedented rapid development. International well-known journals such as "Nature" and "Science" have successively reported the rich physical connotations and novel experimental phenomena in multiferroic materials, which has caused great attention to multiferroicity in the world. The research results published in the form of papers have grown exponentially. Since 2005, at the American Materials Research Society (MRS) of materials conference "multiferroic research. the annual has listed and

magnetoelectricity" as one of the conference's chapters, attracting Many researchers have participated and paid attention. At the end of 2007, Science "Areas To Watch" has listed multiferroic materials as one of the seven leading research areas worthy of attention in the future (European Large Hadron Collider, MicroRNA, artificial microorganisms, paleogenomics, multiferroicity, human microbiome, neural circuits of the brain). Currently, the United States, Japan, Germany, France, China and other countries have invested a lot of resources to carry out research on multiferroic materials.

The research scope of multiferroic materials mainly includes: 1) Electrical / magnetic functional materials science (ferroelectric materials, magnetic materials, multiferroic materials); 2) solid state physics (strongly correlated condensed matter systems, Spin-orbit-charge-lattice interaction); 3) spintronics (spintronics, magnetoelectronics, multiferroic electronics); 4) physics and technology of electronic devices.

In 2000, the American scientist Hill¹²⁾ theoretically discussed the conditions required for the coexistence of ferroelectricity and ferromagnetism in oxides. At the same time, the development of thin-film preparation technology and advanced characterization methods (Such as simultaneous observation of electric and magnetic domains) has promoted the experimental research of single-phase multiferroic materials. In recent years, there have been many review and articles summarizing and discussing the research of single-phase multiferroic materials^{1–2,12–17)}. Among this, in 2009 Liu¹⁴⁾ research of Nanjing University, China, summarized the research progress in this field

in a comprehensively and in detail, and the first review article published by the group in Advanced Physics. Similarly, in 2018, we reported in detail the physical properties of perovskite manganese oxide $TmMn_{1-x}Co_xO_3^{15}$ in the Journal of the Physical Society of Japan, and analyzed the effect of Co substitution on $TmMnO_3$, and summarized many constructive conclusions.

1.3 Classification

From the perspective of material composition, multiferroic materials can be divided into two types: single-phase compounds and composite materials. In the two types of materials, the magnetoelectric effect has different origins.

1.3.1 Single-Phase Multiferroic

For single-phase multiferroic compounds, the mechanism of coexistence of ferroelectricity and magnetic properties can be attributed to paramagnetic ion doping, structural anisotropy, asymmetric lone pair of electrons, geometric and electrostatic force-driven ferroelectricity, and microscopic magnetoelectricity effects have been found in more than ten different system compounds, including bismuth ferrite (BiFeO₃) and rare earth manganese oxides, which have been widely studied. Although single-phase multiferroic compounds have intrinsic magnetoelectric effects, however, the Curie temperature (T_c) or Neel temperature (T_N) of most materials is very low, and it is

difficult to achieve a strong magnetoelectric coupling effect at room temperature. BiFeO3 is currently the only single-phase multiferroic magnetoelectric material with a temperature above room temperature over the past few years. Curie temperature and Neel temperature materials have been widely studied. However, BiFeO3 is G-type antiferromagnetic or weakly ferromagnetic, and its magnetoelectric coupling effect is weak, which limits this kind of multiferroicity to a certain extent practical application of compounds. The intrinsic magnetoelectric effect of single-phase multiferroic compounds is still in the fields of materials and physics in recent years due to its rich physical connotation and its application prospects in fields such as spin electronics and polymorphic storage. Cause the research boom has sought to find single-phase multiferroic compounds with strong magnetoelectric coupling effects at room temperature, and exploring their physical mechanisms has become an important direction in the field of multiferroic research.

In recent years, the research status and development trends of the new single-phase multiferroic system can be summarized into the following aspects.

1. Synthesis and magnetoelectric coupling mechanism and application of singlephase multiferroic materials. It is mainly to explore the new material system including ferroelectric, ferromagnetic and significant magnetoelectric coupling of type I and II multiferroic materials: type I Multiferroic materials are mainly classified as perovskite oxides (such as BiFeO₃, etc.), and also contain some fluorides and sulfides, usually with higher ferroelectric Curie temperature and polarization strength, and higher magnetic Curie temperature. type II multiferroic materials is mainly classified into spin-frustrated oxide systems. The advantage is that the ferroelectricity is derived from the specific spin configuration and spin-orbit and spin-lattice coupling associated with the spin. Therefore, it has an intrinsic and significant magnetoelectric crossregulation effect. However, the nature of spin failure determines that its magnetic moment is small, and the ferroelectric Curie temperature is low and the polarization is small.

2. Research on new effects of related electrons in multiferroic materials. Multiferroic materials belong to a typical strongly correlated electronic system. Exploring and mining related new effects in multiferroic materials originating from related electronic physics is also an important content of multiferroic research. First of all, the multiferroic material combines the characteristics of ferroelectric and ferromagnetic materials, and its energy gap is between the wide band gap (2.5 ~ 5.0 eV) of a typical ferroelectric and the narrow band gap (~ 1.0 eV) of a spin system. It shows a huge response to external stimuli. Typical effects include magneto-resistance, electroresistance, and resistive effect. These effects are important results related to the physical connotation of electrons. Second, the complex band structure of multiferroic materials makes them more sensitive to photons. The excitation has a strong response. Since the band gap of the multi-iron system is closer to

the energy of visible and infrared photons, the energy band can be adjusted by spin and polarization, and in turn, the spin and polarization order parameters can also be controlled by photon excitation, so it is of great value for the development of new optoelectronic functional materials. Again, the interface between multiferroic materials and semiconductor materials is also worthy of attention.

- 3. In the research and development of multiferroic new materials, in addition to large-scale experimental exploration, multi-scale simulation calculations and first-principles calculations have played an indispensable role, providing a multiferroic new material electronic structure design and synthesis favorable analysis guidance tools: (1) Theoretical calculations provide a reasonable explanation for the experimental phenomenon of multiferroic new materials. (2) Theoretical calculations provide reference data for experimental research. For example, first-principles calculations calculate the dual origin of HoMn₂O₅ iron polarization, and simulate the microscopic mechanism of polarization generated in TbMnO₃. (3) The cross-scale phase field calculation provides a theoretical basis for the design of new multiferroic heterojunction devices.
- 4. From the perspective of scientific interest, more and more research in the future will focus on several aspects such as the detection of new materials, new structures, and novel quantum effects at the nanoscale in electronic

correlation systems. On the other hand, for the application of future electronic devices, how to face the challenges of high density, low energy consumption, high read and write speed is the core issue at present. With the birth of higher material preparation equipment, people have started to pay more attention to the high-quality crystal preparation under extreme conditions (ultra-highpressure single crystal growth, etc.), and atomic-level growth control of thinfilm materials (laser molecular beam epitaxy, etc.). Only in this way can we provide a good model system for studying the mutual coupling of charges, orbits, lattices and other degrees of freedom that may occur in related systems, especially multiferroic materials, and then explore the derivation at smallscale domain walls and heterojunction interfaces singular physical characteristics. Moreover, more advanced testing methods have enriched the researches on multiferroic systems. Especially in the past few decades, the insitu growth measurement of materials under specific conditions by advanced experimental methods applied to strongly correlated electronic systems in the field of condensed matter may become one of the future development trends of scientific research. For example, angle-resolved photoelectron spectroscopy, synchrotron radiation X-ray, etc. combined with laser molecular beam epitaxy or molecular beam epitaxy. In addition to the exploration of fundamental scientific issues, micro-nano processing technology will also become a necessary means for the research of multiferroic materials based on

ABO₃. At present, many research teams have started to focus on the application of micro-processing technology on the basis of fully obtaining high-quality crystals and material structures.

1.3.2 Composite Multiferroic

Composite multiferroic materials are completely different. The ferroelectric and ferromagnetic phases that make up a magnetoelectric composite do not have a magnetoelectric effect, but the coupling between the two makes the ferroelectricferromagnetic coexistence system at room temperature. In a classic composite multiferroic materials, the magnetoelectric effect is the "product" of the magnetostrictive effect (or piezomagnetic effect) in magnetic phase and the piezoelectric effect (or inverse piezoelectric effect) in ferroelectric phase, indicating that the mechanical and electrical coupling between the two phases in the composite multiferroic material is achieved by mechanical strain / stress transfer. When the composite multiferroics is placed in a magnetic field, the magnetic phase produces strain due to the magnetostrictive effect, and the strain is transferred to the pressure. In the electrical phase, the piezoelectric effect produces polarization. This is the positive magnetoelectric effect, and its size is generally expressed by the magnetoelectric coefficient α (or magnetoelectric voltage coefficient α_E), which is generally expressed in V/cmOe. For composite multiferroic, the properties of the constituent phase materials themselves, the microstructure formed after the composite, and the interface coupling coefficient are important factors. By adjusting the phase composition and microstructure, the magnetoelectric effect can be achieved optimization and for magnetoelectric composite design provides flexibility.

1.4 ABO₃ Type Multiferroic

The most studied and generally used of multiferroic is ABO₃ perovskite structure oxide. Among this structure, the ferroelectricity mostly comes from the B-site ion located at the center of the oxygen octahedra, below the Curie temperature, it deviates from the center of the oxygen octahedron, which reduces the symmetry of the crystal structure and separates the positive and negative charge centers to an electric dipole moment. ABO3 perovskite-structured ferroelectrics usually require no electrons in the d-orbital of the B-site ion showing d^0 state. If there are zero electrons in the d-orbit, the local magnetic moment will not be formed, and all kind of magnetic ordered structure (including ferromagnetic, ferrimagnetic, and antiferromagnetic) can't be generated. In most cases, once the d-orbit of the B-site ion is partially occupied by electrons, its tendency to deviate from the center of symmetry will eliminated. It can be seen that, the conventional ferroelectricity and magnetic orderly generation mechanism at the atomic scale are mutually exclusive, most of them magnetic perovskite is a centersymmetric cubic or orthorhombic structure, and the ferroelectric structure of the perovskite structure must be non-centrally symmetric. If there is a single-phase material

that allows ferroelectricity and ferromagnetism to coexist, then it must have a condition that can satisfy both the symmetry of the ferroelectric crystal structure and the ferromagnetic electronic shell structure.

At present, through first-principles calculations and fine experimental observations, many single-phase multiferroic systems have been continuously proposed. For example, the perovskite compounds, chemical formulas like ABO3 or A₂B'B''O₆, Such as BiFeO3, BiMnO3, PbFe_{1/2}Nb_{1/2}O3; RMn₂O₅ (R = Y, Tb, Dy, Ho) in orthogonal structure; M₃B₇O₁₃X (M=Cr, Mn, Fe, Co, Cu, Ni, X = Cl, Br); BaMF₄ compounds (M = Mg, Mn, Fe, Co, Ni, Z), and rare earth manganese oxides, such as hexagonal RMnO₃ (R = Sc, Y, In, Ho, Er, Tm, Yb, Lu), etc.

Among these multiferroic compounds, the mechanisms by which ferroelectricity and ferromagnetic coexist may be:

- Paramagnetic ion doping. Paramagnetic ion is used to partially replace the transition metal ions of the outer electron arrangement such as inert gas, which may produce "traditional" ferroelectricity and magnetic properties. For example, in solid solution PbFe1/2Nb1/2O3 and [PbFe2/3W1/3O3]1x[PbMg1/2W1/2O3]x multiferrocity observed.
- Structural anisotropy. Using the factors leading to structural anisotropy, electrostatic double potential wells can be realized in paramagnetic ions. For example, the diagonal apex of the octahedron is occupied by different ions. M₃B₇O₁₃X-type arborite is this mechanism.

- 3) Asymmetric lone pair of electrons. The ferroelectricity of the compound BiRO₃ (R = Fe, Mn, Cr) is derived from the hybridization of the s lone pair of electrons and the empty p-orbital to form a localized electron cloud, which leads to structural distortion and triggers ferroelectric. On the other hand, Bsite magnetic ions contribute to the magnetism.
- Ferroelectricity driven by geometry and electrostatic force. Ferroelectricity is generated by geometric and electrostatic force drive in hexagonal manganite.
- 5) Micro-magnetoelectric interactions. Orbital order, geometric magnetic suppression, Jahn-Teller deformation, super-exchange and double-exchange can produce significant electrical, magnetic, and stress-modulated micromagnetoelectric effects, such as in TbMnO₃ and TbMn₂O₅ multiferrocity.
- 6) Frustrated magnet system. In the experiment, researchers have observed the coexistence of ferroelectricity and ferromagnetism at low temperatures in various compounds. For example, in the YMnO₃ single crystal, the German Fiebig team¹⁸⁾ used the second harmonic method to observe for the first time the domain structure formed by the interaction of the domain walls of the antiferromagnetic and ferroelectric domain, which is determined by the product of the magnetic and electrical sequence parameters, thus revealing the mechanism of magnetoelectric coupling. Induced by strong magnetic field at a low temperature, the DyMnO₃ single crystal produce a dielectric

constant change up to 500%, which is called the "colossal magneticdielectric effect". TbMn₂O₅ single crystal is also observed at low temperature the magnetic field regulates the dielectric and ferroelectric properties, under the action of the magnetic field, the direction of the polarization changes 180°, and this kind of reversal can be repeated many times. This phenomenon originates from the magnetic-induced phase transition, which is most likely to be magnetically induced by Tb magnetism. Based on the manganese oxide phase diagram, the Guoquan Zhang team¹⁹⁾ of Nanjing University predicted that there may be huge ferroelectricity in the system with strong antiferromagnetic interaction and weak Jahn-Teller distortion mode, on the basis of which a new CaMn₇O₁₂ with excellent performance was synthesized Multiferroic system.

1.5 RMnO₃

In the many of study with single-phase multiferroic materials, the rare-earth manganese oxide RMnO₃ (R^{3+} is a rare-earth ion) is a most classics multiferroic with a wide range of physical properties. It is typical example of the compound represented by the composition formula of ABO₃, RMnO₃ has a different crystal structure depending on the ionic radius of the rare earth element R (= Sc, Y, La to Lu). In the synthesis under normal pressure, the hexagonal structure (space group: *P63cm*, Fig.1.1

left side) for R = Sc, Y, Ho ~ Lu with relatively small ionic radius, the ferroelectric phase transition temperature (Curie temperature) of the hexagonal RMnO3 is about 590-1000K²⁰, and the orthorhombic perovskite structure (space group: *Pnma*, Fig.1.1 right side) for $R = La \sim Dy$ with relatively large ionic radius for R^{3+} (R = La-Dy) with a larger ionic radius. If R^{3+} is partially replaced by A^{2+} (A = Ca, Sr, Ba) cations, the substance exhibits a giant magnetoresistance effect. It is known that the crystal structure becomes cubic when RMnO₃ having this hexagonal structure is synthesized under high pressure, and it has both ferroelectricity and antiferromagnetism, and the antiferromagnetic phase transition temperature (Neel temperature) is about 70K-130K²²). The simple perovskite structure (space group: Pm-3m, Fig. 1.2), which is an ideal perovskite structure, has Asite ion located at the corner of the cube, B-site ions are located at the body center, and oxygen ions are located at the face center of the cube. Six oxygen ions around the Bsite ion form a BO₆ octahedron, and are connected three-dimensionally by sharing the vertices of the octahedron. It is thought that A-site ions are also located in gaps in this MnO₆ octahedral network. In an actual RMnO₃ crystal, R ions do not have a sufficient ionic radius to fill the octahedral gap, so that the octahedron is inclined and the crystal structure often takes a perovskite-type rectangular structure deviated from cubic (as Fig.1.2 shows).



Fig. 1. 1 Rare earth crystal structure model of the manganese oxide RMnO₃.



Fig. 1. 2 Cubic perovskite structure of ABO₃.

1.5.1 TmMnO₃

The crystal structure of the heavy rare earth oxide TmMnO₃ is hexagonal space group (*P63cm*), antiferromagnetic transition temperature T_N is 41K^{23,24}), and ferroelectric transition temperature T_C is 86K. It is known that the crystal structure of RMnO₃ having this structure changes to the orthorhombic (*Pnma*) by performing high-pressure synthesis.

High-pressure synthesis is mainly used to synthesize substances composed of nonmetallic elements. The advantage of performing at high-pressure synthesis is that the synthesis can be carried out under temperature conditions that cannot be achieved under normal conditions. This is because the melting point of the substance increases when pressure is applied. When determining the structure and state of a substance, pressure is as important as temperature. Generally, a gas becomes a liquid when pressure is applied, and becomes solid at higher pressure. With pressure increases, the solid changes its crystal structure to a dense crystal structure, so the physical properties change a lot, just like the pressure turns the insulator into a metal. The experimental results show that h-TmMnO₃ undergoes a phase transition from a hexagonal to an orthorhombic structure at about 10.2 GPa²⁴⁾. The evolution of bond angles and bond distances between Mn and O atoms under high pressure has been imply that the magnetic-ordering temperature will be enhanced with increasing pressure, which will affect magnetoelectric coupling.



Fig.1.3 Powder X-ray diffraction pattern of TmMnO₃

From the magnetization measurement results (Fig 1.4 a), the overall magnetization appears to be paramagnetic. However, separation of ZFC and FC was confirmed at $T_N \sim 82$ K. This is thought to be due to the antiferromagnetic transition with Mn ions, which is in good agreement with the reported value^{23,24)}. In the magnetization measurement, the applied magnetic field was measured at both H = 250 Oe and 25 Oe, but it was difficult to determine the temperature of the separation with the applied magnetic field of 250 Oe. This is cause by the applied magnetic field is strength, the moment is directed, so that the antiferromagnetic transition becomes difficult to observed.



Fig. 1.4 Temperature dependence of magnetization (a) and specific heat (b) of TmMnO₃•: ZFC (zero magnetic field cooling magnetization) ■: FC (magnetic field cooling magnetization). Applied magnetic field is zero when measuring specific heat

In the results of specific heat measurement (Fig 1.4 b), the vertical axis is represented by C/T (specific heat C and temperature T). At $T_N \sim 82K$, the peak was observed of specific heat is considered to be due to antiferromagnetic transition, this value corresponds to the separation of ZFC magnetization and FC magnetization due to the antiferromagnetic transition observed at about 9.4K, which was considered to be due to the Tm³⁺ Schottky anomaly.

1.5.2 GdMnO₃

The X-ray diffraction measurement results of GdMnO₃ (space group: *Pnma*) obtained in the past studies are shown in Fig. 1.5, and the temperature dependence of the magnetization is shown in Fig. 1.6. Separation of M_{ZFC} and M_{FC} is observed at $T_N \sim$ 30 K. This is thought to be due to the antiferromagnetic transition of Mn spins. GdMnO₃ shows A-type antiferromagnetism is below T_N , but it is known that Mn spins are not perfectly antiparallel, but exist with a slight tilt. This is called cant (anti) ferromagnetism or weak ferromagnetism. Spins below the transition temperature are aligned in a slightly inclined state and exhibit an increase in ferromagnetic magnetization. There are various causes of this spin gradient, and the Dzyaloshinsky-Moriya interaction (DM interaction) is considered to be one of the reasons. The DM interaction is not given by the scalar product ($S_1 \cdot S_2$) between two spin vectors that express super-exchange interaction, but it has the form of a vector product ($S_1 \times S_2$). This interaction was phenomenologically guided by the introduction of symmetry of

the crystal and the symmetry operation of spin (time) inversion by Dzyaloshinsky, and clarified by Moriya from a microscopic point of view through the reflection of the crystal symmetry and magnetic coupling. The Hamiltonian of DM interaction is expressed by the following equation:

$$H_{\rm DM} = \boldsymbol{D}_{12} \cdot (\boldsymbol{S}_1 \times \boldsymbol{S}_2)$$

 D_{12} is a DM vector and S_1 and S_2 are spin operators.

Here, we classically consider the energy stable state of two Heisenberg spin S_1 , S_2 systems with DM interaction $D_{12} \cdot (S_1 \times S_2)$ in addition to the usual Heisenberg type interaction- $J S_1 \cdot S_2$. Since we think classically, we think of S_1 and S_2 as vectors of length 1 (classical Heisenberg spin). If the angle between S_1 and S_2 is θ , the energy is - $J \cos \theta$ - $D \sin \theta$. (D is the magnitude of DM interaction) If this is minimized with respect to θ ,

$$\tan \theta = \frac{D}{J}$$

The energy becomes stable at an angle θ that satisfies. In other words, when there is DM interaction, the directions of adjacent spins incline to each other. The position of the spin across the crystal in the presence of the DM interaction depends on how the D vector exists in the crystal.

If the D vector has the same orientation, the position of the spiral spin is stable. When the directions of the D vector are alternating, a spin structure of a type in which inclined pairs of spins repeat periodically is stable. In the latter case, the antiferromagnetic component is added when the sign of the exchange interaction J is ferromagnetic (J > 0), in the antiferromagnetic (J < 0) case, a ferromagnetic component is added.



Fig.1.5 X-ray diffraction pattern of GdMnO3



Fig.1.6 Temperature dependence of magnetization of GdMnO₃

1.6 Purpose

Replacing the Mn and (or) R site with another transition metal element in the rareearth manganese oxide RMnO₃, shows that mixed valence perovskite composed of ions of multiple valences (such as Mn⁴⁺, Mn³⁺, Co²⁺, and Co³⁺ Enables composition). This causes a change in the Mn⁴⁺ / Mn³⁺ ratio and a new interaction between Mn and Co, and the material exhibits various physical properties. Thus, the influence of substitution of R or Mn sites in RMnO₃ is very important in physical properties, but may also affect geometric parameters such as lattice volume, average ionic radius of R site, Mn-O-Mn bond angle and tolerance factor. Research on replaced of the R site with another element is known to be a system that replaces rare earth elements such as La_{1-x}Sr_xMnO₃ with divalent alkaline earth metal elements, but simultaneously with changes in structural parameters such as lattice volume. Substituting Mn with Co element also causes a change in the valence of Mn ions, which affects the magnetic properties as described above. In order to more clearly examine the effects of changes in structural parameters such as lattice volume and bond angle on the properties of rare-earth manganese oxides, the structure analyses and magnetic measurements were performed in $Tm_{1-y}Y_yMn_{1-y}$ _xCo_xO₃. On the other hand, the Gd of Gd_{0.7}Co_{0.3}O₃ is replaced with La, Y, and Lu, which are trivalent, stable and nonmagnetic rare earth elements. The purpose of this study is to investigate the magnetism of the ABO₃-type perovskites systems. In addition, we clarify the effect of chemical pressure on magnetism in the mixed-valence system.

Chapter II

Experiment

2.1 Preparation methods

2.1.1 Solid State Reaction Method

The solid-state reaction method is one of the classical sample preparation methods and is mainly two or more substances (particles) generate new matter through the chemical reactions. The microscopic process should be: reactant molecules or ions contact plus chemical reaction to generate new material (break and formation of bonds). In solution reactions, the reaction molecules or ions can be directly contacted. In the solid phase reaction, the reactants are generally mixed in the form of a powder, and the particle size of the powder is mostly on the order of micrometers, and the contact of the reactants is insufficient. Particles such as oxides and carbonates of the elements contained in the target substance are mixed well in an appropriate ratio using a ball mill or mortar, and then calcined at a high temperature to reduce the contact between the particles of the base material. The diffusion of the ions occurs, and the particles come into contact with each other through the reactant layer to obtain the target substance. In fact, the solid reaction is the diffusion of reactants in the crystal lattice through the particle contact surface. The diffusion rate is usually the determining factor of the speed and degree of the solid phase reaction.

Taking the preparation of $Tm_{1-y}Y_yMn_{0.3}Co_{0.7}O_3$ as an example, in the solid phase reaction method, the base material was weighed so that the total amount of the target sample was 5 g. Powders of Tm_2O_3 , Y_2O_3 , Mn_2O_3 and Co_3O_4 were used as the base
material. The purity is 99.9% for Tm₂O₃, Mn₂O₃ and Co₃O₄ and Y₂O₃ for99.99%. In order to accurately weigh the sample and dried in an oven at 200°C. for about 24 hours, and then each base material was weighed so as to obtain a target sample. The weighed value was determined from the following formula:

$$(1-y) \operatorname{Tm}_2O_3 + y \operatorname{Y}_2O_3 + \frac{3}{10} \operatorname{Mn}_2O_3 + \frac{14}{30} \operatorname{Co}_3O_4 + \infty O_2 \to 2 \operatorname{Tm}_{1-y} \operatorname{Y}_y \operatorname{Mn}_{0.3} \operatorname{Co}_{0.7}O_3$$

The weighed sample was thoroughly mixed in an agate mortar for 1 hour to make it uniform. After applying a pressure of about 500 kg / cm² to form pellets, it was calcined twice on an alumina boat. The calcination condition is that the temperature is heated from room temperature to 1150° C within 8 hours and then maintained for 24 hours, then naturally cooled to room temperature within 8 hours. Normally, we calcined in powder state, but in the sample containing Co, the contact surface between the firing boat and the sample became blue due to the collapse of the sample caused by the body release and the distribution of the oxygen atmosphere throughout the sample, which indicates that Co₃O₄ as one of the basic materials may have escaped. Therefore, in order to minimize the contact surface between the alumina boat and the sample, it is mainly compressed and solidified to increase the sintered density, and granulated before calcination, and calcined in a granular form.

 Co_3O_4 is a black solid and is a mixed valence compound containing Co^{2+} and Co^{3+} . The substance can be stable at temperatures up to 600 to 700°C, but when it exceeds 950°C, it will decompose with oxygen and stabilize to CoO with Co^{2+} , the specific reaction formula is as follows:

$$2Co_3O_4 \rightarrow 6CoO + O_2 \quad (950^{\circ} \text{ C})$$

35

CoO is a black or gray powder, also known as colorant or cobalt blue. As a result, it can be considered that as the amount of Co_3O_4 substitution increases, the amount of CoO remaining in the alumina boat increases.

The electric furnace we use is a silicon electric furnace, it is composed of a digital program temperature control system, a single-phase power feedback thyristor regulator and a rotary vacuum pump that control the output voltage to be constant. In order to prevent the lack of oxygen in the synthetic sample, calcination is carried out in an atmosphere filled with oxygen. in order to replace Mn with Co, must be create a pure environment, at first, put the sample in an electric furnace and then wash it with oxygen 3 times or more.

2.1.2 Complex Polymerization Method

The solid-state reaction is a method in which an oxide or a carbonate is physically mixed as a starting material and sintered at a high temperature. Since calcination at a high temperature is required, sintering proceeds and fine particles of the composite oxide cannot be obtained (As described in 2.1.1). In addition, since the composition is biased due to the non-uniform particle size of the starting material, it is necessary to repeat milling, mixing and firing, and this is a synthesis method that is extremely disadvantageous in terms of energy. In the early stage of the research, samples were prepared by the above method, but it was confirmed that Co₃O₄ of the base material escaped due to high-temperature sintering, and that Tm₂O₃ was mixed in the low Y concentration range ($0 \le y \le 0.5$). There were problems such as being done.

Therefore, our laboratory focused on the complex polymerization method, which is a new sample preparation method.

As one of the prescriptions for maintaining the uniformity of the composition, a method of synthesizing a metal complex precursor having the same metal composition as the composite oxide and developing the target composite oxide by heat treatment has been developed. In general, in the complex polymerization method, a metal nitrate is dissolved in an aqueous solution containing a hydroxycarboxylic acid such as citric acid, tartar or malic acid, and the solution is heated to synthesize a gelled metal carboxylic acid complex. The gel is dried and calcined to form an oxide.

In the complex polymerization method, a base material was weighed so that a total of 2.5 g of a target sample was prepared. Tm(NO₃)₃·4H₂O, Y(NO₃)₃·6H₂O, Mn(NO₃)₂·6H₂O, and Co(NO₃)₂·6H₂O were used as base materials. Since Mn(NO₃)₂·6H₂O is a gel at room temperature, it was weighed after making it liquid with hot water. Further, it is difficult to weigh the liquid according to the weighed value, and the liquid was actually weighed more than the weighed value. Based on the weighed value of Mn (NO₃)₂·6H₂O, the weighing calculation of another base material was performed again, and each base material was put into a beaker containing pure water and dissolved. Thereafter, citric acid was added and the mixture was stirred for 1 hour. Citric acid has a role of complexing a plurality of metal species and gelling the solution. After stirring, the temperature of the solution was set to 70°C. Using a hot plate, and the solution was further stirred for 1 hour.

Thereafter, ethylene glycol was added. Ethylene glycol serves as a polymerization accelerator by esterifying a plurality of complexed metal species into a polyester. Since the solution containing the metal nitrate thus obtained contains a large amount of water, the water was evaporated at 90 to 130°C for several days. Since this is a complex synthesis in the presence of a large amount of water, hydrolysis may proceed rapidly and precipitation of a hydroxide may occur before a metal complex is obtained. When such a phenomenon occurs, uniformity of the composition cannot be maintained. Therefore, in the process of evaporating the water, the temperature was adjusted in detail. After the gel precursor was obtained, it was heated at 300 to 400°C. until it became a powder in order to remove organic substances contained in the sample. The obtained powder was put in an alumina boat and calcined using an electric furnace. The firing conditions are as follows: the temperature is raised from room temperature to 900°C. in an air atmosphere over 6.5 hours, the temperature is maintained for 7 hours, and the furnace is cooled down to room temperature over 6.5 hours. In the second main firing, firing was performed under the same firing conditions as above in an oxygen atmosphere after forming into pellets.

2.2 Experimental Method

2.2.1 X-ray fold measurement and structural analysis

In this study, the X-ray diffractometer (Mini Flex) manufactured by Rigaku Co.,

Ltd. was used for simple measurement such as investigation of X-diffraction pattern and measurement with an accuracy higher than that required for analysis.

Since the shape of the sample could be solid after firing, it was pulverized sufficiently in a mortar and finely powdered for measurement. The powdered sample was placed in a concave portion of a glass sample holder, and another glass plate was used to fill the concave and convex portions uniformly so that the sample surface and the reference surface were aligned.

Measurement conditions is using Cu target, tube voltage 30 kV, tube current 10 mA, operation mode: continuous, scan range: $10^{\circ} - 80^{\circ}$, step width 0.02, scan speed 1.0 deg / min.

If the diffraction intensity pattern of the sample with good crystallinity is measured by an ideal device, it should be observed as a very sharp peak-shaped pattern. However, in the actually-observed powder diffraction data, each diffraction peak has a finite width, mainly due to the influence of "blur" due to the apparatus. Diffraction peaks may spread due to imperfections (finite size, strain) of crystals in the sample due to the influence of scattered light, fluorescence, stray light, electrical noise, etc., a finite intensity (background) usually appears at diffraction angles other than the peak position. In the Rietveld method, a peak shape model function (profile function) is placed at the calculated peak position, and the total diffraction intensity figure is calculated as the sum with the background model function. The least squares method is used for the optimization calculation in the Rietveld method. How to fit individual peaks (fitting), in order of (1) peak intensity, (2) peak position, (3) peak width, (4) peak shape (distortion), (5) peak shape sharpness A strong influence appears. Among these, (1) parameters related to strength (type of atom, site occupancy g at atomic position and x, y, z coordinates of atom, atomic displacement parameter B) and scale factor (factor that multiplies the whole intensity figure by a constant), There are selective orientation parameters depending on the orientation of the diffraction plane, and (2) the peak position is affected by the lattice constants (a, b, c, α , β , γ) and the peak shift parameter. The values of (3), (4), and (5) are assumed to be represented by an appropriate model function that depends on the diffraction angle and the diffraction plane orientation, and the parameters that characterize this model function are optimized. In this study, the program RIETAN-FP and X'pert High Score was used for Rietveld analysis.

2.2.2 Magnetization Measurement

For the magnetization measurement, a magnetic property measuring device MPMS manufactured by Quantum Design Co., Ltd. installed in the lab was used. This device is a high-sensitivity magnetometer equipped with a superconducting quantum interference device (SQUID) and is a measuring device that can detect minute changes in magnetic flux of a substance. It is used to investigate the magnetic properties of various organic and inorganic compounds. This device can measure the magnetic field dependence and temperature dependence of the magnetization. Due to its extremely high sensitivity, it is possible to measure not only ferromagnetic materials but also paramagnetic materials and diamagnetic materials. It can also be applied to samples with a small total magnetization, such as magnetic thin films and nano-magnetic particles. After setting the sample in the device, temperature control and data acquisition can be controlled by a computer, and the measurement sequence can be set up on a personal computer.

A part of the measurement sample was cut out from the fired pellet-shaped sample and shaped with a cutter or sandpaper (# 1,000, 2,000). For measurement, set the sample in a straw with a length of 200 mm and an inner diameter of 5 mm. Upon shaping the sample, the shape was made into a spheroid. In general, when the larger the cross-sectional area perpendicular to the direction of the magnetic field and the thinner the magnetization direction, the larger demagnetizing field. The sample was shaped into a wire-shaped spheroid to reduce the influence of such a demagnetizing field. After shaping, the sample was weighed and fixed inside by using cellophane tape so that the position of the sample was about 7 cm from the end of the straw. The air bubbles created between the cellophane tape and straws were pierced with sharp tweezers or thumbtacks. Chapter III

Experimental Results and Discussion

$3.1 \text{ TmMn}_{1-x}\text{Co}_x\text{O}_3$

As part of this research, we prepared $\text{Tm}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($0.0 \le x \le 1.0$) in which Mn of TmMnO₃ was replaced by Co and investigated its structure and magnetism. We were compare the solid-state reaction and complex polymerization to find which better method for sample preparation, and the sample was evaluated by X-ray diffraction and magnetization measurement by MPMS.

3.1.1 Structure Analysis

Figure 3.1 shows X-ray diffraction (XRD) patterns for TmMn_{1-x}Co_xO₃ prepared by CP (complex polymerization method), with the XRD pattern for Tm₂O₃ included as a reference (pink line). TmMnO₃ (*x*=0), which was prepared by the SSR (solid-state reaction method) was hexagonal. These XRD patterns were refined by Rietveld, and we obtained the lattice parameters *a*, *b*, *c* and the unit cell volume *V* in Fig. 3.2, along with the mass fraction of the hexagonal and orthorhombic phases shown in the inset, all as a function of *x*. The inset in Fig. 3.2 shows the mass fraction of the components of the SSR samples. Hexagonal and orthorhombic phases coexist for $0 \le x \le 0.5$ in samples prepared by either the SSR or CP. For $0.5 \le x \le 0.9$, the CP samples are almost single-phase orthorhombic, while the SSR samples contain a small amount of Tm₂O₃. The amount of this impurity increases with increasing *x*. This indicates that the CP method is superior to the SSR for the synthesis of samples with $0.5 \le x \le 0.9$. The space group for the hexagonal phase is *P6scm*, and the orthorhombic phase is a distorted perovskite with the space group

Pnma. The lattice parameters a_h , c_h , and V_h in the hexagonal phase are almost constant except for x=0.4. It is thought that the discrepancies for x=0.4 are caused by errors due to the small mass fraction of the hexagonal phase. The lattice parameters a_0 , b_0 , c_0 , and V_0 for the orthorhombic phase decrease with increasing x for $0.5 \le x \le 0.9$. This is presumably related to the ionic radii in TmMn_{1-x}Co_xO₃. Peña et al. suggested that for ErMe_xMn_{1-x}O₃, the general formula is of the type RE³⁺Mn^{4+1-x}Co^{2+1-x}Co³⁺_{2x-1}O²⁻³ (RE=rare earth element), when the substitution at the manganese site exceeds 50%.²³⁾ If we assume this valence state formula for TmMn_{1-x}Co_xO₃, then the average ionic radius of the 3d transition metal ions in TmMn_{1-x}Co_xO₃ decreases. This would qualitatively account for the decrease in the lattice parameters and the unit cell volume.



Fig. 3.1 X-ray diffraction patterns for various TmMn_{1-x}Co_xO₃ samples.

The XRD pattern for Tm₂O₃, which is considered an impurity.



Fig. 3.2 Lattice parameters and unit cell volume as a function of *x*. Open symbols are obtained from Ref. 24. The inset plots mass fraction vs. *x*. All these values, except for those for *x*=0, were obtained from samples prepared by complex polymerization.

3.1.2 Magnetic properties

Figures 3.3 and 3.4 plot, respectively, the temperature dependence of the field-cooled (M_{FC}) and zero-field-cooled (M_{ZFC}) magnetization for the $0 \le x \le 0.4$ SSR samples²⁶⁾ and the $0.5 \le x \le 0.9$ CP samples in a magnetic field of 250 Oe. The insets of Figs. 3.3 and 3.4 respectively show the mass fraction of the SSR samples and the temperature dependence of $\chi_{FC}^{-1} = H/M_{FC}$ for the CP samples above 20 K. M_{FC} increases ferromagnetically below 60 K with decreasing temperature for $0.1 \le x \le 0.7$, and M_{FC} increases in going from x=0.1 to 0.5 and decreases from x=0.5 to 0.9. With increasing x, the mass fraction of the orthorhombic phase increases, as do M_{FC} and M_{ZFC} . A discrepancy is observed between

 $M_{\rm FC}$ and $M_{\rm ZFC}$ below about 160 K for $0.1 \le x \le 0.3$, where the hexagonal and orthorhombic phases coexist, and $M_{\rm FC}$ and $M_{\rm ZFC}$ exhibit a different temperature dependence below about 60 K. The $M_{\rm FC}$ and $M_{\rm ZFC}$ for $x \ge 0.5$, where the main phase is orthorhombic, are different below about 60 K. The appearance of the orthorhombic phase induces a rapid increase in magnetization below 60 K. For x=0.8 and 0.9, there is no ferromagnetic increase, but a separation between $M_{\rm FC}$ and $M_{\rm ZFC}$ can be seen below about 60 K. We will discuss the temperature dependence of $M_{\rm FC}$ for the orthorhombic phase at low temperatures in more detail below.



Fig. 3.3 Temperature dependence of field-cooled (FC, filled symbols) and zero-fieldcooled (ZFC, open symbols) magnetization for TmMn_{1-x}Co_xO₃ for $0.0 \le x \le 0.4$, prepared by solid-state reaction. The inset plots mass fraction vs. *x* for samples prepared by solid-

state reaction.



Fig. 3.4 Temperature dependence of FC (filled symbols) and ZFC (open symbols)

magnetization for TmMn_{1-x}Co_xO₃ for $0.5 \le x \le 0.9$.



Fig. 3.5 Effective paramagnetic moment P_{eff} and Weiss temperature Θ as a function of x for TmMn_{1-x}Co_xO₃. Filled (open) symbols are the experimental (calculated) P_{eff} data for the two-spin states of Co³⁺.

The inverse susceptibility of TmMn_{1-x}Co_xO₃ ($0.5 \le x \le 0.9$) above 130 K, shown in the inset of Fig. 3.4, can be fitted as a linear function of temperature, that is, by the Curie-Weiss law:

$$\chi_{\rm FC} = \frac{M_{\rm FC}}{H} = \frac{C}{T - \Theta} \tag{1}$$

where C is the Curie constant, Θ is the Weiss temperature, and H is the external magnetic field. C is related to the effective paramagnetic magnetic moment, P_{eff} , via

$$P_{\rm eff}^{2} = \frac{3Ck_{\rm B}}{N\mu_{\rm B}^{2}}$$
 (2)

where N is the magnetic atom (Tm, Mn, Co) number per gram, μ_B is the Bohr magneton, and $k_{\rm B}$ is the Boltzmann constant. The values of $P_{\rm eff}$ and Θ , obtained from $M_{\rm FC}$, are plotted in Fig. 3.5 as a function of x. It can be seen that Θ , which is about 15 K for x=0.5, decreases with increasing x, and is negative for $x \ge 0.8$. It is found that ferromagnetic and antiferromagnetic interactions predominate for $x \le 0.7$ and x > 0.7, respectively. P_{eff} also decreases with increasing x. Ghiasi et al. investigated the valence states of Mn and Co in LaMn_{1-x}Co_xO₃ nanoperovskites by X-ray absorption spectroscopy.²⁷⁾ They obtained the results that LaMn0.75C00.25O3 contained Mn³⁺, Mn⁴⁺, and Co²⁺, while LaMn0.25C00.75O3 contained Mn⁴⁺, Co²⁺, and Co³⁺, and LaMn_{0.5}Co_{0.5}O₃ contained Mn³⁺, Mn⁴⁺, Co²⁺, and Co^{3+} . In order to facilitate the discussion, we will again assume the following valence state formula for REMn_{1-x}Co_xO₃ for $x \ge 0.5$: RE³⁺Mn⁴⁺_{1-x}Co²⁺_{1-x}Co³⁺_{2x-1}O²⁻₃. Among these ions, Co^{2+} and Co^{3+} can have S=3/2 (high spin, HS) or S=1/2 (low spin, LS), and S=2 (HS) or S=0 (LS) states, respectively. Assuming that the theoretical paramagnetic moments of Tm³⁺, Mn⁴⁺, and Co²⁺ are 7.57 μ B, 3.87 μ B, and 3.87 μ B (HS), respectively, at x = 0.5, a P_{eff} equal to 6.01 µ_B per atom is obtained for these magnetic atoms from

Equation:

$$P_{\rm eff} = \sqrt{\frac{\sum p_i^2}{2}} \tag{3}$$

The 2 in the dominator of Equation above is corresponds to the number of magnetic atoms in the formula TmMn_{1-x}Co_xO₃. This calculated P_{eff} is close to the experimental value. It is concluded from the P_{eff} value for x=0.5 that Co²⁺ must be HS. In Fig. 3.5, the x dependence of P_{eff} is also shown for Co³⁺(HS) and Co³⁺(LS). If the electronic state of Co³⁺ for x>0.5 is HS, P_{eff} increases with x. This contradicts the experimental results in Fig. 3.5. The values of P_{eff} agree qualitatively with calculations in which Co²⁺ and Co³⁺ were assumed to be in the HS and LS states, respectively.

For $0.5 \le x \le 0.7$, both M_{FC} and M_{ZFC} increase ferromagnetically at $T_C \approx 58$ K with decreasing *T*. Since the ferromagnetic interaction is predominant for $0.5 \le x \le 0.7$, this increase in magnetization is thought to be due to the canted magnetic transition of the Mn and Co ions, as reported for other rare-earth manganese oxides. The maximum values of M_{FC} are observed between 25 and 35 K. M_{FC} decreases with decreasing *T* and shows negative values below $T_{comp} \approx 13$ K for x=0.7. No ferromagnetic increase of magnetization is seen for x=0.8 and 0.9, though a small peak can be seen at about 44 K in M_{ZFC} for x=0.8. The discrepancy between M_{FC} and M_{ZFC} for x=0.8 and 0.9 is thought to be due to antiferromagnetic ordering or competition between ferromagnetic and antiferromagnetic interactions.



Fig. 3.6 Temperature dependence of $M_{\rm FC}$ for x = 0.5 to 0.7.

Another characteristic of the temperature dependence of M_{FC} below ~30 K for $0.5 \le x \le 0.7$ is the rapid decrease with decreasing *T*. A similar decrease in M_{FC} is seen in other rare-earth manganese oxides.^{24, 28-31} Such a rapid decrease in M_{FC} points to spin reversal phenomena related to rare-earth ions. The *M*-*H* curves for TmMn_{0.5}Co_{0.5}O₃ prepared by the solid-state reaction method showed a large high-field magnetic susceptibility even below 20 K, which suggests that Tm³⁺ (*J*=6) is paramagnetic even at low temperatures. According to Cooke et al.,²⁹ the temperature dependence of M_{FC} can be fitted using the equation

$$M_{\rm FC} = M_{\rm Mn,Co} + \frac{C_{\rm Tm}(H+H_{\rm int})}{T-\Theta_{\rm W}} \qquad (4)$$

where $M_{Mn,Co}$ and H_{int} are the saturated moment and the internal field at the Tm sites due to the canted Mn-Co moment, respectively. C_{Tm} is the Curie constant for paramagnetic Tm³⁺ ions, Θ_W is the Weiss temperature, and *H* is the applied field, which is 250 Oe. The solid lines in Fig. 3.6 show that the temperature dependence of the magnetization below ~25 K can be well approximated using Eq. (4); the fitting parameters are listed in Table. 3.1.

Co concentration <i>x</i>	$M_{\rm Mn,Co}$ / emu g ⁻¹	Hint / kOe	$\Theta_{\rm W}$ / K
0.5	7.8	-4.0	-11
0.6	4.0	-3.0	-14
0.7	1.8	-2.1	-13

Table. 3.1 Fitting parameters for $M_{\rm FC}$ for x = 0.5, 0.6, and 0.7.

This successful model, which is based on a ferromagnetically ordered Mn-Co sublattice and a paramagnetic Tm sublattice, suggests that the negative internal field induced by the Mn-Co sublattice affects the Tm sublattice. It is thought that at low temperatures (below ~25 K), the Tm³⁺ spin is oriented in the direction opposite to *H* by H_{int} . Such spin inversion due to 3*d* transition metal elements and rare-earth elements seems to be common in perovskite-type oxides with the structure ABO₃, although the crystallographic reasons why H_{int} acts antiferromagnetically on the rare-earth element A are not clear.

3.1.3 Conclusion

In comparison with the plots of mass fraction vs. x (the insets of Figs. 3.2 and 3.3), the CP method was clearly demonstrated to be more suitable than the SSR method for

 $0.5 < x \le 0.9$. Thus, we achieved the substitution of Mn through CP, and obtained almost a single orthorhombic phase for $0.5 \le x \le 0.9$ in TmMn_{1-x}Co_xO₃.

At $T > T_C \approx 58$ K, TmMn_{1-x}Co_xO₃, in which the Tm³⁺, Mn⁴⁺, Co²⁺, and Co³⁺ ions are paramagnetic, is also paramagnetic. From the data on the unit cell volume and the effective moment, it is concluded that Co²⁺ has a high spin state (*S*=3/2) and that Co³⁺ in TmMn_{1-x}Co_xO₃ remains a low-spin-state ion (*S*=0). At $T = T_C$, a canted magnetic transition occurs as a result of the interaction between Mn and Co, and the magnetization increases ferromagnetically with decreasing *T*. Below the temperature at which *M*_{FC} is maximized, the interaction between Mn and Co ions induces a negative internal field *H*_{int} at the Tm sites. *H*_{int} reorients the Tm³⁺ spin in the direction opposite to the external field *H*. The total magnetization at low temperatures is explained on the basis of a twosublattice model.

$3.2 \text{ Tm}_{1-y} Y_y Mn_{0.2} Co_{0.8} O_3$

In the previous chapter, we have prepared TmMn_{1-x}Co_xO₃ and investigated the physical properties. at $0.5 \le x \le 0.7$, an increase in ferromagnetic magnetization was observed, but no increase in ferromagnetic magnetization after x = 0.8, Therefore, in this section, we focused on TmMn_{0.2}Co_{0.8}O₃, the Tm site was substitution with nonmagnetic Y, and study the influence of the change in the lattice volume by substitution of Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃ (0≤y≤0.9).

3.2.1 Structure analysis

The Fig. 3.4 (a) and (b) is the X-ray diffraction pattern of the $Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O_3$ ($0.0 \le y \le 0.9$) series of samples prepared by the Complex Polymerization (CP) Method.



Fig. 3.4 X-ray diffraction patterns of $Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O_3$ (a) $0.0 \le y \le 0.5$

and (b) 0.5≤*y*≤0.9

Through the X-ray diffraction pattern, we can determine that all samples are orthorhombic (space group: *Pnma*) single-phase structure, and all peak positions slowly move to higher angles as the substitution element increases, and the lattice constant impact of substitution.

Tables 3.2 ~ 3.3 are obtained by Rietveld refinement of the diffraction data of the obtained samples, *a*, *b*, and *c* are the lattice constants / Å in each axis direction, *V* is the lattice volume / Å³, x, y, z are the fractional coordinates of each atom, B is the isotropic atom displacement parameter, *S* is the adaptability index (goodness of fit index) = R_{wp} / R_e (R_{wp} : *R*-weighted mode, reliability factor of the weighted mode, R_e : R expected, R_{wp} in the best-fit state considering statistical error, and the analysis has almost no change from beginning to end). Fig. 3.5 to Fig. 3.6 show the Y concentration dependence of the lattice constant and lattice volume of $Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O_3$ ($0.0 \le y \le 0.9$) obtained from Rietveld analysis.

In all analyses, the S value is around 1.0 to 2.0, it is considered a reliable analysis result.



Fig. 3.5 Dependence of lattice constant of Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃ (0.0≤y≤0.9) on Y

concentration.

Y	0.0	0.05	0.1	0.2	0.3
V	207.8967	207.8304	207.4046	208.0710	208.1925
а	5.48082	5.47927	5.47403	5.47961	5.47942
b	7.37633	7.37571	7.37138	7.37885	7.38069
С	5.14235	5.14260	5.13999	5.14604	5.14794
<i>B</i> (Tm)	0.6	0.682	0.575	0.185	0.313
B(Y)		0.682	0.575	0.185	0.313
B(Mn)	0.6	0.492	0.350	0.372	0.372
B(Co)	0.6	0.492	0.350	0.372	0.372
<i>B</i> (O1)	0.764	0.764	0.974	0.151	0.369
<i>B</i> (O2)	0.764	0.764	0.974	0.151	0.369
S	2.1491	1.8690	1.9840	1.7534	1.5673

Table. 3.2 Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃ ($0.0 \le y \le 0.3$)

у	0.4	0.5 0.7		0.9	
V	208.7452	208.7148 209.1476		209.7917	
а	5.48228	5.48134	5.48134 5.48091		
b	7.38819	7.38733	7.39451	7.40285	
С	5.15368	5.15441 5.16048		5.16764	
<i>B</i> (Tm)	0.356	0.258	0.147	0.282	
<i>B</i> (Y)	0.356	0.258	0.147	0.282	
B(Mn)	0.372	0.372 0.372		0.101	
B(Co)	0.372	0.372 0.372		0.101	
<i>B</i> (O1)	1.328	0.164	0.164	0.164	
<i>B</i> (O2)	0.611	0.164	0.164	0.164	
S	2.1991	1.1633	1.3390	1.1637	

Table. 3.3 Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃ (0.4 $\leq y \leq 0.9$)



Fig. 3.6 Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃ (0.0≤y≤0.9) dependence of lattice volume on Y

concentration

The lattice constant tended to increase slightly with increasing Y concentration. The lattice volume tended to increase linearly with the substitution of Y, confirming the negative pressure effect.

3.2.2 Magnetic measurement

The non-substitution of $\text{Tm}\text{Mn}_{0.2}\text{Co}_{0.8}\text{O}_3$ (*y*=0.0), where almost no ferromagnetic magnetization increase with temperature decrease.



Fig. 3.7 Temperature dependence of magnetization of $Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O_3$ ($0.0 \le y \le 0.1$) (cooling magnetization in magnetic field)

At y = 0.05, there was a small ups and downs behavior near 40 K, but no ferromagnetic magnetization peak was shown. It is considered that the value of the internal magnetization of the sample increased by substituting Y, but it was not so large

as to cancel the external magnetic field of 250 Oe and reverse the magnetization.

At y = 0.1, an increase in ferromagnetic magnetization was confirmed around 40K. It is considered that the interaction between Mn and Co changed due to the negative chemical pressure effect observed in the volume expansion, it induced magnetism increased with Y substitution. In addition, after the maximum value around 40K, the magnetization was inverted to negative, and negative magnetization was observed at low temperature.



Fig. 3.8 Temperature dependence of magnetization of Tm_{0.9}Y_{0.1}Mn_{0.2}Co_{0.8}O₃.

In Fig. 3.8, the behavior of magnetization differs between ZFC magnetization and FC magnetization at low temperatures. It is considered that the magnetization is reduced because the Tm moment is inverted by creating details of this phenomenon will be described later.

At $0.2 \le y \le 0.9$, the peak of ferromagnetic magnetization increase at y = 0.1 tended to increase with the increase of Y substitution. The increase in magnetization at $T_{\rm C} \sim 60$ K is due to cant magnetism.



Fig. 3.9 Temperature dependence of magnetization of $Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O_3$ (0.2 \leq y \leq 0.9) (cooling magnetization in magnetic field)

Fig. 3.9 show that the Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃ ($0.2 \le Y \le 0.9$) at the lowest temperature has a negative value is observed within the range of $0.1 \le y \le 0.7$. This is considered that because the Tm moment of the negative orientation becomes so large that the magnetization is cancelled due to the transition metal elements (Mn, Co). The minimum value of magnetization is y = 0.3. By substitution of Y, the internal magnetic field caused by the transition metals (Mn, Co) increases, and the total number of Tm moments decreases due to the substitution of the nonmagnetic element Y. Fig. 3.10 shows the fitting diagram of $Tm_{0.9}Y_{0.1}Mn_{0.2}Co_{0.8}O_3$. The fitting showed good agreement below about 35K. The results of this fitting are summarized in Table 3.4.



Fig. 3.10 Temperature dependence of magnetization of Tm_{0.9}Y_{0.1}Mn_{0.2}Co_{0.8}O₃.

Table. 3.4 Change of $M_{\rm Me}$ (Magnetization by cant magnetism), $H_{\rm int}$ (Internal magnetic field), Θ

Y concentration	$M_{\rm Me} \ ({ m emu} \ / \ { m g})$	H _{int} (Oe)	$\Theta(\mathbf{K})$	
<i>y</i> = 0.1	0.83553	-1039.4	-14.431	
<i>y</i> = 0.3	1.4188	-2637	-12.901	
<i>y</i> = 0.5	1.6132	-2687.7	-12.248	
<i>y</i> = 0.7	1.5038	-1878.1	-10.399	
<i>y</i> = 0.9	1.6044	-1188.5	-10.785	

(Weiss temperature) by fitting result

By substituting Y from the fitting results, M_{Me} shows a generally upward trend, and

 H_{int} tended to increase until y = 0.5 and decrease thereafter. It is thought that the decrease in magnetization at low temperature is due to the negatively oriented Tm moment, it is considered that the total number of Tm moments was reduced in this sample by substituting the non-magnetic element Y. The minimum value of magnetization at y=0.3at the lowest temperature seems to be due to two relations between the magnitude of the internal magnetic field and the total number of Tm moments.



Fig.3.11 Temperature dependence of inverse susceptibility Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃

(0.0≤y≤0.9).

In general, Θ has a positive value in the case of a ferromagnetic substance, and has a negative value in many substances in an antiferromagnetic substance. Also, in the case of paramagnetism where the interaction of magnetic atoms is very small, it shows paramagnetism at sufficiently low temperature, and χ changes according to the Curie law with $\Theta = 0$. Above about 70-90K. It is considered that the canted magnetic order developed from around this temperature to the low temperature. The Weiss temperature Θ and the Curie constant *C* were obtained from the above measurement results. Furthermore, the effective magnetic moment P_{eff} was calculated from the formula (2).

Table. 3.5 Weiss temperature Θ and effective magnetic moment P_{eff}

Y concentration y	Weiss temperature Θ	effective magnetic moment $P_{\rm eff}$
0.0	-3.488	7.856
0.05	-2.572	7.5773
0.1	0.381	7.1639
0.3	1.612	6.5883
0.5	7.414	5.8123
0.7	15.927	4.7361
0.9	32.124	3.5133

of $Tm_{1-\nu}Y_{\nu}Mn_{0.2}Co_{0.8}O_{3}$

The Weiss temperature Θ increased and the effective magnetic moment P_{eff} decreased with increasing y. The Weiss temperature at y = 0.0, 0.05, have negative value, become no increase in ferromagnetic magnetization, and after y = 0.1, which showed an increase in ferromagnetic magnetization, and showed a positive value. It increased with the increase of y. From this, it is considered that the ferromagnetic component is strengthened by substituting Y.

3.2.3 Conclusion

The structure of $Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O_3$ shows perovskite type orthorhombic single phase (*Pnma*) is same like TmMn_{0.2}Co_{0.8}O_3 prepared by complex polymerization. Based on Fig. 3.4, the XRD pattern tendency for each peak to shift to a higher angle side with Y substitution and the lattice volume increased with the amount of Y substitution.

As increase in magnetization due to cant magnetism was observed at $T_{\rm C} \sim 58$ K after y = 0.1, and the value of magnetization increased with Y substitution. The magnetization value at the lowest temperature has a minimum value at y = 0.3, and a negative value at y = 0.2 to 0.7. When the external magnetic field was set to 50 Oe, the increase of the magnetization due to the cant magnetism was observed in the sample with y = 0.05. Tm_{1-y}Y_yMn_{0.2}Co_{0.8}O₃ ($0.0 \le y \le 0.9$) exhibits paramagnetism according to the Curie-Weiss law above about 80K. The Θ increases with Y substitution and becomes positive after y = 0.1. The $P_{\rm eff}$ decreases with Y substitution, it is calculated using J or S of Tm³⁺, Mn⁴⁺, Co²⁺ (HS), Co³⁺ (LS) (Tm³⁺ is the total angular momentum J), and Mn⁴⁺, Co²⁺ (HS), Co³⁺ (LS) is the spin angular momentum S. It is agreed with the calculated value when using S.

$3.3 \text{ GdMn}_{1-x}\text{Co}_x\text{O}_3$

As part of this research, we prepared $GdMn_{1-x}Co_xO_3$ ($0.0 \le x \le 1.0$) in which Mn of $GdMnO_3$ was replaced by Co and investigated its structure and magnetism. The SSR (solid-state reaction method) was used for sample preparation, and the sample was evaluated by X-ray diffraction measurement and magnetization measurement by MPMS.

3.3.1 Structure Analysis

The X-ray diffraction measurement results of $GdMn_{1-x}Co_xO_3$ ($0.0 \le x \le 1.0$) are shown

in Fig. 3.12. All samples could be indexed by the orthorhombic structure (space group: Pnma), and the crystal system did not change by Co substitution. No impurities were observed and a single-phase sample was obtained in all products. Fig. 3.13 shows the dependence of the lattice constant and volume of $GdMn_{1-x}Co_xO_3$ on the Co concentration. The *a*-axis length decreases significantly with the increase of Co substitution. The *b*-axis length increases from $x = 0 \sim 0.1$, but then decreases with increasing Co substitution, and the *c*-axis length is almost constant but have a slightly decrease. It can be seen that the Co substitution causes the reducing lattice distortion induce by a, b, and c-axis lengths to approach each other. The lattice volume decreases almost linearly with the increase of Co substitution, reflecting the remarkable decrease of the *a*-axis length, but the lattice volume at $0.5 < x \le 1.0$ is decrease more obvious than that at $0 \le x \le 0.5$. It is considered that this is due to the change in valence of Mn ions due to Co substitution and the difference in ionic radius between Mn with Co ions. Table. 3.6 shows the ionic radii of Mn and Co ions in each valence and spin state assuming 6-coordination²³⁾. In addition, as reported in the Bsite substitution system of other rare earth manganese oxides²⁵⁾, the valence of ions in GdMn_{1-x}Co_xO₃ was determined.

range	valence of ions (In the expected state)				
0≤ <i>x</i> ≤0.5	Gd^{3+} Mn^{3+}_{1-2x} Mn^{4+}_{x} Co^{2+}_{x} O^{2-}_{3}				
0.5≤ <i>x</i> ≤1.0	Gd^{3+} Mn^{4+}_{1-x} Co^{2+}_{1-x} Co^{3+}_{2x-1} O^{2-}_{3}				

In this model, Mn^{3+} is replaced by Co^{2+} at $0 \le x \le 0.5$, and in addition, Mn^{3+} changes to Mn^{4+} to maintain electrical equilibrium, and at x=0.5, only Mn^{4+} and Co^{2+} are present. When $0.5 \le x \le 1.0$, the composition Co^{3+} replaces Mn^{4+} and Co^{2+} at the same time. The

average ionic radii of Mn and Co ions in each composition in this model are shown in Table. 3.6. Above composition formula, the average ionic radii decrease with Co substitution, especially when $0.5 < x \le 1.0$.



Fig. 3.12 X-ray diffraction pattern of GdMn_{1-x}Co_xO₃



Fig. 3.13 Dependence of lattice constant and lattice volume of GdMn_{1-x}Co_xO₃ on Co

concentration

Table. 3.6 Ion radius of Mn and Co ions

	Mn ³⁺ (HS)	Mn ⁴⁺	Co ²⁺ (HS)	Co ³⁺ (HS)	Co ³⁺ (LS)
Ion radii [Å]	0.645	0.53	0.745	0.61	0.545

Table. 3.7 Average ionic radii of Mn and Co ions in GdMn_{1-x}Co_xO₃ (Co³⁺ assumes LS)

x	0.0	0.1	0.3	0.5	0.7	0.9	1.0
Average ion radii	0.6450	0.6435	0.6405	0.6375	0.6005	0.5635	0.5450
of Mn, Co	010.00	010 155	0.0105	0.0370	0.0002	0.0000	0.0 100



Fig. 3.14 Definition of Mn-O-Mn bond angle of GdMn_{1-x}Co_xO₃ and dependence on Co

concentration

The Mn-O2-Mn bond angle in the *ac* plane does not change significantly and is almost constant, but the Mn-O1-Mn bond angle in the b-axis direction tends to increase

with Co substitution. This increase may be due to the decrease in the average ionic radius of the B-site element due to Co substitution of Mn as shown in Table. 3.7. The decrease in the average ionic radius of the A-site element supporting the MnO₆ octahedra causes the decrease of the Mn-O-Mn bond angle as described above, whereas the decrease of the average ionic radius of the B-site element decreases the inclination of the MnO₆ octahedra. It may decrease and increase the Mn-O-Mn bond angle.

3.3.2 Magnetic Properties

Fig. 3.15 shows the temperature dependence of FC magnetization of GdMn_{1-x}Co_xO₃ $(0.0 \le x \le 1.0)$. At x=0.0 and 0.1, no increase in ferromagnetic magnetization was observed, and antiferromagnetic interaction was dominant. At x = 0.3, ferromagnetic magnetization increases to the peak at about 67 K or less. This increase in the ferromagnetic magnetization is considered due to the cant magnetic transition in GdMnO₃, and it is assuming that increase in the ferromagnetic magnetization is caused by the increase in the cant magnetism due to Co substitution. At lower temperatures, the magnetization sharply decreases and shows negative magnetization below about 20K. It is thought that this decrease in magnetization is due to antiferromagnetic coupling between the Gd moment that contributes as paramagnetism and the canceled Mn and Co moments. At x = 0.5, the increase in ferromagnetic magnetization is largest in this system, and after reaching a peak at about 50 K, the magnetization decreases same like at x = 0.3, but no negative magnetization is shown. When Co is further replaced, at x = 1.0 the increase in ferromagnetic magnetization is suppressed and becomes almost non-observable. Figure.

3.16 shows the magnetic transition temperature analysis from the magnetization temperature dependence of $GdMn_{1-x}Co_xO_3$, the Weiss temperature Θ estimated from the paramagnetic susceptibility according to the Curie-Weiss law, and the Co concentration dependence of the effective magnetic moment $P_{\text{eff.}}$ In addition, x = 0.0, 0.1 is the temperature $T_{\rm N}$ at which ZFC magnetization and FC magnetization are separated, and x = 0.3 to 0.9 is the temperature $T_{\rm C}$ corresponding to the inflection point of FC magnetization. x = 1.0 present almost no increase in ferromagnetic magnetization, by fowling Curie-Weiss temperature dependence, and it is not observed separation between ZFC magnetization and FC magnetization. The magnetic transition temperature and Weiss temperature Θ increase from x = 0.0 to 0.5, reach a maximum at x = 0.5, and decrease with further substitution of Co. Therefore, the Co concentration dependences of the magnetic transition temperature and Weiss temperature suggest that Co substitution gradually enhancement of the ferromagnetic interaction up to x = 0.5, and that weakens the ferromagnetic interaction in substitution above x = 0.5.



Fig. 3.15 Temperature dependence of FC of GdMn_{1-x}Co_xO₃ (0.0≤x≤1.0)



Fig. 3.16 Dependence of transition temperatures T_N , T_C , Weiss temperature Θ , effective magnetic moment P_{eff} on Co concentration x in GdMn_{1-x}Co_xO₃ ($0.0 \le x \le 1.0$)

The measured value of the effective magnetic moment P_{eff} is compared with the total orbital angular momentum J and the spin angular momentum S. It has good agreement with the result of $P_{cal} = g \left[(J (J + 1)) \right]^{1/2}$ and P_{exp} , when the total angular momentum J is used for the effective magnetic moment of trivalent lanthanide group ions. However, the effective magnetic moments in the ions of 3d transition metal elements do not match in the calculation using J, and they do well when using the spin angular momentum S. From this, it seems that there is no orbital moment, and the orbital angular momentum is frozen. Therefore, Gd³⁺ is the total angular momentum J, and Mn³⁺, Mn⁴⁺, Co²⁺, and Co³⁺ are spin angular momentum S was calculated value P_{cal} assumed composition as using following formula. Three kinds of spin states of Co³⁺, high spin state HS, intermediate spin state IS, and low spin state LS were calculated. Table 3.8 shows the effective magnetic moment calculated using Table 3.8 and the following formula and the measured value.

0≤*x*≤0.5

$$p_{cal} = \sqrt{(p_{Gd})^2 + (1 - 2x) \times (p_{Mn^{3+}})^2 + x \times (p_{Mn^{4+}})^2 + x \times (p_{Co^{2+}})^2}$$

 $0.5 \le x \le 1.0$

$$p_{cal} = \sqrt{(p_{Gd})^2 + (1-x) \times (p_{Mn^{4+}})^2 + (1-x) \times (p_{Co^{2+}})^2 + (2x-1) \times (p_{Co^{3+}})^2}$$
	Spin state	g	J / S	p Gd, Mn, Co
Gd ³⁺		2	7/2	7.94
Mn ³⁺	HS	2	2	4.90
Mn ⁴⁺		2	3/2	3.87
C0 ²⁺	HS	2	3/2	3.87
C0 ³⁺	HS	2	2	4.90
	IS	2	1	2.83
	LS	2	0	0

Table. 3.8 Effective magnetic moment in each spin state of constituent ions



Fig. 3.17 Comparison of actual measured value of effective magnetic moment P_{eff} and calculated value considering the spin state of Co^{3+}

From Fig. 3.17, the actual measured value of the effective magnetic moment P_{eff} agrees best with when the calculated value Co^{3+} is assumed to be LS. Therefore, Co^{3+} , assumed to be contained in the sample when the Co substitution amount *x* is 0.6 or more, we consider that LS having no magnetism. In addition, the decrease in magnetization and the decrease in transition temperature on the high Co concentration side where *x* = 0.6 or

more, in the temperature dependence of magnetization can also be explained by the existence of this low-spin Co^{3+} . It can be seen that the measured value is lower than the calculated value at an almost constant rate. Although the reason for this is unknown, the composition ($0 \le x \le 0.5$) of the sample for each Co substitution amount is assumed in this study, so even when $0 \le x \le 0.5$, a small amount of Co^{3+} is present, or when the sample is calcined. There is a possibility that the compositional deviation due to the escape of Co etc. is the cause of the low value of the effective magnetic moment.

3.3.3 Conclusion

The substitution of Mn with other transition metal elements Co, causes a transformation of Mn³⁺ into Mn⁴⁺. We have reconfirmed and studied about the structural and magnetic properties of GdMn_{1-x}Co_xO₃. For x = 0.3, 0.5, and 0.7, at the ordering temperature $T_{\rm C}$ the $M_{\rm FC}$ showed a rapidly increase which results from canting of the Mn and Co moments. Especially, for x = 0.3, the maximum values of $M_{\rm FC}$ was observed and $M_{\rm FC}$ decreased rapidly with decreasing temperature and showed a negative magnetization below $T_{\rm comp} \sim 20$ K, which is so-called a spin reversal phenomenon.

$3.4 \, Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$

In this work, we report the physical properties of $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$ (R: La, Y, or Lu, $y = 0.1 \sim 0.5$) to study the chemical pressure effect of the magnetic properties caused

by non- magnetic rare- earth element substitutions. All samples were prepared by solid state reaction method at ambient pressure.

3.4.1 Structure analysis

Figures 3.18 (a) -3.18 (c) show the XRD patterns of Gd_{1-y}R_yMn_{0.7}Co_{0.3}O₃ samples with substitution by the nonmagnetic elements La, Y, and Lu, respectively. These samples are hereafter referred to as the La, Y, and Lu series, respectively. There were no impurity phases detected, and the patterns indicated that all samples had a single phase with a perovskite-type orthorhombic structure (space group: Pnma). The lattice parameters a, b, band c and the unit-cell volume V are shown in Table. 3.9. In the La series, b and c increase markedly after the substitution, indicating that the unit-cell volume V greatly increases, and the increase is about 3% when y increases from 0.0 to 0.5. On the other hand, b and c decrease in the Y and Lu series, and V decreases by about 1.3% in the Y series and by about 2.5% in the Lu series. These changes are considered to be due to the differences in the ionic radii of La, Y, and Lu from that of Gd. Figures 3.19(a) and 3.19(b) show a, $b(b/\sqrt{2})$, and c, and V, respectively, as functions of the average ion radius $\langle r_A \rangle = (1-y)$ $r_{\rm Gd} + yr_{\rm R}$ (La³⁺= 1.216 Å, Gd³⁺= 1.107 Å, Lu³⁺= 1.032 Å, and Y³⁺= 1.075 Å). The parameters a, $b(b/\sqrt{2})$, and c change as functions of $\langle r_A \rangle$ and appear to become closer to each other with increasing $\langle r_A \rangle$. This indicates that Gd_{1-y}R_yMn_{0.7}Co_{0.3}O₃ approaches the cubic perovskite structure with increasing $\langle r_A \rangle$. On the other hand, it seems that V is linearly related to $< r_A >$ and is independent of the substituted ion. This volume change represents the effect of chemical pressure.



Fig. 3.18 XRD patterns of $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$ sample with y=0.1, 0.3, and 0.5 with substitution with the non- magnetic elements La, Y, and Lu. (a), (b), and (c) correspond

to R=La, Y, and Lu, respectively.



Fig. 3.19 Average ion radius $\langle r_A \rangle$ dependence of (a) lattice parameters *a*, $b/\sqrt{2}$, and *c*,

and (b) unit-cell volume V.

Table. 3.9 Lattice parameters for the solid solutions $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$ (R= La, Y, and Lu) for *y*=0.1, 0.3, and 0.5. The upper, waddle, and lower values of each parameter to

y(La) y(Y) y(Lu)	0.0	0.1	0.3	0.5
а	5.6425	5.6301	5.6018	5.5724
		5.6429	5.6419	5.6411
		5.6411	5.6329	5.6263
b	7.5434	7.5775	7.6401	7.6991
		7.5346	7.5175	7.5000
		7.5311	7.5018	7.4757
с	5.3100	5.3331	5.3785	5.4243
		5.3028	5.2889	5.2750
		5.2969	5.2670	5.2414
V	226.01	227.52	230.19	232.72
		225.46	224.32	223.17
		225.03	222.56	220.46

the La, Y, and Lu series, respectively.

3.4.2 Magnetic properties

Figure 3.20 shows the temperature dependence of M_{FC} . It shows a rapid increase in M_{FC} at T_C with decreasing temperature, which results from the canting of the Mn and Co moments. T_C increases rapidly with increasing concentration y for the La series, decreases with increasing y for the Y series, and decreases rapidly with increasing y for the Lu series. These changes in T_C correspond to the increase and decrease in the unit-cell volume V, as shown in Fig. 3.21, where both V and T_C increase almost linearly as $\langle r_A \rangle$ increases. Their linear dependence with the same slope suggests that there is a correlation between V and T_C .

The inverse magnetic susceptibility $\chi_{FC}^{-1} = H/M_{FC}$, shown in Figs. 3.22(a), (b) and (c)

for the La, Y, and Lu series, respectively, can be fitted above 200K using the Curie-Weiss law (Eq. (1)).

In Fig. 3.23, we plot P_{eff} as a function of the Co concentration y. Assuming that the electronic states of the ions in the samples are Gd³⁺ [S=7/2], Mn⁴⁺ [S=3/2], Mn³⁺ [S=2, high spin (HS)], and Co²⁺ [S=3/2, HS], and there is no change in the valence on substituting for Gd, the effective number of Bohr magnetons P_{cal} is estimated as:

$$\boldsymbol{P_{\text{cal}}} = \sqrt{(1-y)P_{\text{Gd}^{3+}}^2 + 0.3P_{\text{Mn}^{4+}}^2 + 0.4P_{\text{Mn}^{3+}}^2 + 0.3P_{\text{Co}^{2+}}^2}$$

where $P_{Gd^{3+}}$, $P_{Mn^{4+}}$, $P_{Mn^{3+}}$, and $P_{Co^{2+}}$ are 7.94, 3.87, 4.90, and 3.87, respectively. P_{eff} and P_{cal} are indicated by colored symbols and the broken line in Fig. 3.23, respectively. P_{eff} almost corresponds to P_{cal} despite the elemental substitution. We considered that the substitution of Gd by nonmagnetic elements in this system changes the strength of the interaction between Mn and Co without changing the valences of Mn and Co.

To explain the decrease in $M_{\rm FC}$ below 40 K, the so-called spin reversal phenomenon, we adopt the two-sublattice model used in studies of other rare-earth oxides. In this model, the temperature dependence of $M_{\rm FC}$ can be fitted using the following Eq. (4)

The fitting parameters are listed in Table 3.10. The fitting results for y=0.0 and the La series are shown by solid lines in Fig. 3.20 We assume that the decrease in magnetization is caused by the interaction of the two magnetic sublattices, "Gd" and "Mn and Co", and that the Gd moment is paramagnetic. It is clear that the negative internal field induced by the Mn and Co sublattice affects the Gd sublattice, because at low temperatures the Gd³⁺ spin is oriented in the direction opposite to H_{ext} by H_{int} . With increasing concentration of the *R* element, $M_{\text{Mn, Co}}$ increases in the La series, decreases

in the Y and Lu series, and markedly decreases in the Lu series. H_{int} tends to decrease with increasing concentration of the *R* element in all series.



Fig. 3.20 Temperature dependence of $M_{\rm FC}$ for Gd_{1-y} R_y Mn_{0.7}Co_{0.3}O₃. The broken line shows

 $T_{\rm C}$ for y=0.0. The solid lines for the La series are fits using Eq. (4).



Fig. 3.21 V and T_C as functions of $< r_A >$. The boundary denotes the ion radius of Gd³⁺.



Fig. 3.22 Inverse magnetic susceptibility $\chi_{FC}^{-1} = H/M_{FC}$ for (a) La series, (b) Y series, and

(c) Lu series.

The changes in $M_{Mn,Co}$ indicate that the interaction between Mn and Co is enhanced by increasing V and suppressed by decreasing V. From Table 3.10, we can deduce that the increase in H_{int} is caused by enhancement of the interaction between Mn and Co owing to the increase in the maximum value of magnetization in the La series, also that the suppression of spin reversal is caused by the reduction in the Gd concentration owing to the substitution by non-magnetic elements.





$_{y}R_{y}Mn_{0.7}Co_{0.3}O_{3}$ (*R*=La, Y, Lu)

Samples R concentration y	$M_{Mn, Co}$ /emug ⁻¹	H _{int} /kOe	Θ/K
La series 0.5	17	-1.2	-9.4
0.3 0.1	8.3 6.3	-5.4 -5.6	-19 -12
GdMn _{0.7} Co _{0.3} O ₃ 0.0	6.1	-7.4	-16
Y series 0.1	5.0	-5.9	-14
0.3 0.5	3.8 3.4	-3.9 -4.0	-9.9 -15
Lu series 0.1	4.3	-6.0	-15
0.3 0.5	2.1 0.38	-3.6 -0.7	-22 -36

Table. 3.10 Fitting parameters for Gd_{1-y}R_yMn_{0.7}Co_{0.3}O₃.

3.4.3 Conclusion

The unit-cell volume V for $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$ (R= non-magnetic rare-earth element) shows an increase or decrease with function of the average ion radius $\langle r_A \rangle$, which is dependent of substitutions of R. Both V and T_c parameters are linear with $\langle r_A \rangle$.

The interaction between Mn and Co is enhanced by increasing V and suppressed by decreasing V, and the enhancement of the interaction increases the maximum value of the magnetization. The substitution of Gd with non-magnetic rare-earth element changes the unit-cell volume V, an increase of V raises the transition temperature $T_{\rm C}$, and a decreases of V lowers $T_{\rm C}$ in Gd_{1-y}R _yMn_{0.7}Co_{0.3}O₃ system. It is considered that these chemical pressure effects and the spin reversal phenomena occur simultaneously and produce the temperature dependence of $M_{\rm FC}$. The R of Gd_{1-y}Y_yMn_{0.7}Co_{0.3}O₃ is not largely different from that of GdMn_{0.7}Co_{0.3}O₃, it is showing that the contribution of non-magnetic substitutions Y does not significantly reduce electrical resistance.

3.5 TmMn_{1-x}Fe_xO₃

In this section, we mainly made another experimental, attempt to replace the Mn element with the initial perovskite manganese oxide TmMnO₃ sample of TmMn_{1-x}Co_xO₃, therefore, we did not conduct an in-depth investigation. We tried to replace Mn with Fe, and analysis the structure and magnetic properties of TmMn_{1-x}Fe_xO₃ (x=0.1, 0.5).

3.5.1 Structure Analysis

The sample was prepare by SSR, and mainly presents the hexagonal crystal structure, space group is *P63cm*. As Fig. 3.24 shows the content of *x* increases as heterozygosity increases, the Heterozygous phase was TmFeO₃ and Tm₂O₃, space group is *Pbnm*. With the increase of sintering times, the strength of Tm₂O₃ hetero phase peak weaken to disappears, but the intensity of TmFeO₃ hetero peak has no obvious change. When the sintering temperature up to the 1400K, as Fig. 3.25 shows, the sample mainly presents the Hexagonal crystal structure, space group is *P63cm*. As the content of *x* increases, the heterozygosity increases. Compared with the Fig. 3.24, the increase in sintering temperature does not significantly change the structure of the sample. It is suggested that another method (such as CP) used for prepare the sample.



Fig. 3.24 X-ray diffraction patterns of various samples for TmMn_{1-x}Fe_xO₃. sintering

temperature at 1150 K.



Fig. 3.25 X-ray diffraction patterns of various samples for TmMn_{1-x}Fe_xO₃. sintering

temperature at 1400 K.

3.5.2 Magnetic properties

Figures 3.26 and 3.27 plot, respectively, the temperature dependence of the fieldcooled (M_{FC}) and zero-field-cooled (M_{ZFC}) magnetization for the x=0.1 and 0.5 SSR samples. The insets of Figs. 3.26 and 3.27 respectively show the $\chi_{FC}^{-1} = H/M_{FC}$ for the SSR samples above 180 K or 350K. No increase in ferromagnetic magnetization in x =0.1. At x = 0.5, there was an anomalous behavior near 175 K, but also no ferromagnetic magnetization peak was shown. It is considered that the MPMS machine is abnormal or the value of the internal magnetization of the sample increased by substituting Fe, but it was not so large as to cancel the external magnetic field of 250 Oe and reverse the magnetization. The inverse magnetic susceptibility $\chi_{FC}^{-1}=H/M_{FC}$ for the Fe substitutions, respectively, can be fitted in the Curie-Weiss law.



Fig. 3.26 Temperature dependence of FC and ZFC magnetization of TmMn0.9Fe0.1O3.



Fig. 3.27 Temperature dependence of FC and ZFC magnetization of TmMn_{0.5}Fe_{0.5}O₃.

Chapter IV

Summarizes

In Chapter 3, we discussed four important groups of substitutions compounds in the RMnO₃ series of samples. They are TmMn_{1-x}Co_xO₃ with Co replacing Mn, and Tm_{1yYyMn_{0.2}Co_{0.8}O₃ with further transition metals to substitute in Tm, and GdMn_{1-x}Co_xO₃ with elements replacing Mn and Gd_{1-y}R_yMn_{0.7}Co_{0.3}O₃ with elements replacing Ga.}

First of all, we mainly focus on the impact of the preparation method on the final molded samples. Comparing two methods, the complex polymerization method preparation is clearly better than solid phase reaction method. We using complex polymerization method performed the substitution of Mn with Co, and Co content $x \ge 0.5$, the structure will change to orthorhombic single phase in TmMn_{1-x}Co_xO₃ and all Y concentration y in Tm_{1-y}Y_yMn_{0.3}Co_{0.7}O₃. And this effect is not only limited to the structure and sample purity, but also has a profound impact on the magnetic properties. At $T > T_C \approx 58$ K of TmMn_{1-x}Co_xO₃, and $T > T_C \approx 60$ K of Tm_{1-y}Y_yMn_{0.3}Co_{0.7}O₃. in which the Tm³⁺, Mn⁴⁺, Co²⁺, and Co³⁺ ions are paramagnetic, corresponds Curie-Weiss law, Co^{2+} is considered to be high spin state (S=3/2); the Co^{3+} in TmMn_{1-x}Co_xO₃ remains low spin state (S=0), on the other hand, Co^{3+} in $Tm_{1-\nu}Y_{\nu}Mn_{0.3}Co_{0.7}O_3$ seem to change from low spin state to high spin state (S=2). At $T = T_c$, the canted magnetic transition due to the interaction among Mn^{3+} , Mn^{4+} and Co^{2+} occurs, and the magnetization increase ferromagnetically. The M_{max} (which means the maximum value of the magnetization) of all Tm compound, shows interaction between Mn and Co ion induces a negative internal field H_{int} at Tm site, Tm³⁺ is oriented toward the opposite direction of external field H by H_{int} .

Secondly, we discussed the relationship between chemical pressure effects and

compounds, the characters of this part are GdMn1-xCoxO3 and Gd1-yRyMn0.7Co0.3O3. We first specifically analyzed physical properties of GdMn_{1-x}Co_xO₃ series compounds, and found that the substitution of Mn with other transition metal elements Co, causes a transformation of Mn^{3+} into Mn^{4+} . For x = 0.3, 0.5, and 0.7, at the ordering temperature $T_{\rm C}$ the $M_{\rm FC}$ showed a rapidly increase which results from canting of the Mn and Co moments. Especially, for x = 0.3, the maximum values of M_{FC} was observed and M_{FC} decreased rapidly with decreasing temperature and showed a negative magnetization below $T_{\rm comp} \sim 20$ K, which is so-called a spin reversal phenomenon. So that, we have a huge curiosity about the sample with x = 0.3, analysis of unit-cell volume V for Gd₁- $_{y}R_{y}Mn_{0.7}Co_{0.3}O_{3}$ (R= non-magnetic rare-earth element) shows an increase or decrease with function of the average ion radius $\langle r_A \rangle$ (average ion radius $\langle r_A \rangle = (1-y) r_{Gd} + yr_R$), which is dependent of substitutions of R. Both V and $T_{\rm C}$ parameters are linear with $\langle r_{\rm A} \rangle$. The interaction between Mn and Co is enhanced by increasing V and suppressed by decreasing V, and the enhancement of the interaction increases the maximum value of the magnetization. Meantime, the substitution of Gd with non-magnetic rare-earth element changes the unit-cell volume V, an increase of V raises the transition temperature $T_{\rm C}$, and a decreases of V lowers $T_{\rm C}$ in Gd_{1-v}R _vMn_{0.7}Co_{0.3}O₃ system. It is considered that these chemical pressure effects and the spin reversal phenomena occur simultaneously and produce the temperature dependence of $M_{\rm FC}$.

In conclusion, the R of $Gd_{1-y}R_yMn_{0.7}Co_{0.3}O_3$ is not largely different from that of $GdMn_{0.7}Co_{0.3}O_3$, it is showing that the contribution of non-magnetic substitutions Y does not significantly reduce electrical resistance. Substitution of the R with the non-

magnetic elements R = La, Y, Lu for $R(Mn, Co)O_3(R = Gd, Tm)$ lead to the increase or decrease of *V*, it seems that the changes in *V* are related to the ion radius of the rareearth as we called the chemical pressure effect.

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Publications

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Effect of Co Doping on the Structure and Magnetic Properties of TmMn_{1-x}Co_xO₃. Journal of the Physical Society of Japan. Vol.87, 124704 (2018.11).

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Effects of Chemical Pressure on Rare-Earth Oxide GdMn_{0.7}Co_{0.3}O₃ with Nonmagnetic Element Substitution.

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