学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

High-Pressure Synthesis, Crystal Structures and Physical Properties of Perovskites in R_2O_3-Mn_2O_3 Systems (R = Rare Earth Elements)

（R_2O_3－Mn_2O_3 系ペロブスカイトの高圧合成と結晶構造と物性）

Perovskite-type manganese oxide has attracted enormous attention for decades because of its useful interplay between spin, charge, and orbital degrees of freedom. It led to discovery of colossal magnetoresistance, spin-driven multiferroics, and other interesting physical properties. In this study, I investigated the perovskite-type manganese oxide in chemical systems between R_2O_3 (R = rare earth elements) and Mn_2O_3. Novel compositions were discovered by applying a high-pressure and high-temperature synthesis method, and those crystal structures and fundamental physical properties were clarified.

Chapter 1 introduces the general background, and chapter 2 explains the principal technologies used in this study. Chapters 3 to 5 consist of the main outcomes and the conclusion is drawn in chapter 6.

Chapter 3 describes unusual five-fold cation/charge ordering in high-pressure-synthesized RMnO$_3$ perovskites of R = Gd-Tm and Y (at 6 GPa and 1673 K). The R^{3+}, Mn^{2+}, and Mn^{3+} cations are ordered at the perovskite A site in two separate chains consisting of R^{3+} and alternating Mn^{2+} (in tetrahedral coordination) and Mn^{3+} (in square-planar coordination). Mixed-valent Mn^{3+}/Mn^{4+} cations are ordered in layeres at the perovskite B site; the ordering can be described as $[R^{3+}Mn^{2+}_{0.5}Mn^{3+}_{0.5}]_A[Mn^{3+}Mn^{3.5+}]_BO_6$. The triple cation ordering observed at the A site is very rare, and the layered double B-site ordering is also scarcely seen. RMn$_3$O$_6$ crystallizes in space group *Pmmn* with a = 7.2479(2) Å, b = 7.4525(3) Å, and c = 7.8022(2) Å for DyMn$_3$O$_6$ (at 213 K), being structurally related to CaFeTi$_2$O$_6$. It appeared that they are non-stoichiometric and can be described as $R_{1-\delta}Mn_3O_{6-1.5\delta}$ with δ = - 0.071 to - 0.059 for R = Gd, δ = 0 for Dy, δ = 0.05-0.1 for Ho and Y, and

δ = 0.12 for Er and Tm. All of them show complex magnetic behaviors with several transitions, and the magnetic properties are highly sensitive to the δ values.

Chapter 4 introduces a quadruple perovskite $CeCuMn_6O_{12}$ synthesized under high-pressure and high-temperature conditions at 6 GPa and about 1670 K. $CeCuMn_6O_{12}$ crystallizes in space group *Im*-3 above 297 K and *R*-3 below the temperature with the 1: 3 (Mn^{4+}: Mn^{3+}) charge and orbital orders. Unusually compressed $Mn^{3+}O_6$ octahedra found in $CeCuMn_6O_{12}$ closely resembles what was found for the -Q_3 Jahn-Teller distortion mode in $CaMn_7O_{12}$. Below approximately 90 K, structural instability results in a phase separation and appearance of competing phases; and below 70 K, two *R*-3 phases coexist. $CeCuMn_6O_{12}$ exhibits a ferrimagnetic-like transition below T_c of 140 K, and it is semiconducting with the magnetoresistance reaching - 40 % (at 140 K and 70 kOe).

Chapter 5 reports orthorhombic rare-earth trivalent manganites $RMnO_3$ (*R* = Er – Lu), which were self-doped with Mn to form $(R_{0.667}Mn_{0.333})MnO_3$ compositions. The series was synthesized by a high-pressure and high-temperature method at 6 GPa and about 1670 K from R_2O_3 and Mn_2O_3. The average oxidation state of Mn is +3 in $(R_{0.667}Mn_{0.333})MnO_3$. However, Mn enters the A-site in the oxidation state of +2 creating the average oxidation state of +3.333 at the B site. The presence of Mn^{2+} was confirmed by hard X-ray photoelectron spectroscopy measurements. Crystal structures were studied by synchrotron X-ray powder diffraction. $(R_{0.667}Mn_{0.333})MnO_3$ crystallizes in space group *Pnma* with *a* = 5.50348(2) Å, *b* = 7.37564(1) Å, and *c* = 5.18686(1) Å for $(Lu_{0.667}Mn_{0.333})MnO_3$ at 293 K, and they are isostructural with the parent $RMnO_3$ manganites. By comparing with $RMnO_3$, $(R_{0.667}Mn_{0.333})MnO_3$ exhibits enhanced Néel temperatures of about T_{N1} = 106-110 K and canted antiferromagnetic properties. Compounds with *R* = Er and Tm show additional magnetic transitions at about T_{N2} = 10-15 K. $(Tm_{0.667}Mn_{0.333})MnO_3$ exhibits a magnetization reversal effect with the compensation temperature of 15 K.

Chapter 6 provides the general conclusion and future prospects.