



Title	High-Pressure Synthesis, Crystal Structures and Physical Properties of Perovskites in R <sub>2</sub> O <sub>3</sub> -Mn <sub>2</sub> O <sub>3</sub> Systems (R = Rare Earth Elements) [an abstract of dissertation and a summary of dissertation review]
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学位論文内容の要旨

博士の専攻分野の名称

博士 (理学)

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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 layers 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.  $RMn_3O_6$  crystallizes in space group  $Pm\bar{m}n$  with  $a = 7.2479(2)$  Å,  $b = 7.4525(3)$  Å, and  $c = 7.8022(2)$  Å for  $DyMn_3O_6$  (at 213 K), being structurally related to  $CaFeTi_2O_6$ . It appeared that they are non-stoichiometric and can be described as  $R_{1-\delta}Mn_3O_{6-1.5\delta}$  with  $\delta = -0.071$  to  $-0.059$  for  $R = Gd$ ,  $\delta = 0$  for  $Dy$ ,  $\delta = 0.05-0.1$  for  $Ho$  and  $Y$ , and

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

Chapter 4 introduces a quadruple perovskite  $\text{CeCuMn}_6\text{O}_{12}$  synthesized under high-pressure and high-temperature conditions at 6 GPa and about 1670 K.  $\text{CeCuMn}_6\text{O}_{12}$  crystallizes in space group  $Im-3$  above 297 K and  $R-3$  below the temperature with the 1:3 ( $\text{Mn}^{4+}:\text{Mn}^{3+}$ ) charge and orbital orders. Unusually compressed  $\text{Mn}^{3+}\text{O}_6$  octahedra found in  $\text{CeCuMn}_6\text{O}_{12}$  closely resembles what was found for the  $-Q_3$  Jahn-Teller distortion mode in  $\text{CaMn}_7\text{O}_{12}$ . 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.  $\text{CeCuMn}_6\text{O}_{12}$  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  $\text{RMnO}_3$  ( $R = \text{Er} - \text{Lu}$ ), which were self-doped with Mn to form  $(\text{R}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  compositions. The series was synthesized by a high-pressure and high-temperature method at 6 GPa and about 1670 K from  $\text{R}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$ . The average oxidation state of Mn is +3 in  $(\text{R}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$ . 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  $\text{Mn}^{2+}$  was confirmed by hard X-ray photoelectron spectroscopy measurements. Crystal structures were studied by synchrotron X-ray powder diffraction.  $(\text{R}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  crystallizes in space group  $Pnma$  with  $a = 5.50348(2)$  Å,  $b = 7.37564(1)$  Å, and  $c = 5.18686(1)$  Å for  $(\text{Lu}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  at 293 K, and they are isostructural with the parent  $\text{RMnO}_3$  manganites. By comparing with  $\text{RMnO}_3$ ,  $(\text{R}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  exhibits enhanced Néel temperatures of about  $T_{N1} = 106\text{-}110$  K and canted antiferromagnetic properties. Compounds with  $R = \text{Er}$  and Tm show additional magnetic transitions at about  $T_{N2} = 10\text{-}15$  K.  $(\text{Tm}_{0.667}\text{Mn}_{0.333})\text{MnO}_3$  exhibits a magnetization reversal effect with the compensation temperature of 15 K.

Chapter 6 provides the general conclusion and future prospects.