学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Isovalent and Aliovalent Doping Effects on the Structural and Magnetic Properties of A-Site Columnar-Ordered Quadruple Perovskites Synthesized under High Pressure
（高圧合成された A サイト柱状秩序型四重ペロブスカイトの構造および磁気特性に対する等価および非等価ドーピングの影響）

Perovskite materials have been the focus of intensive research for decades due to their rich and diverse physical properties. They exhibit unique thermoelectric, electrochemical, catalytic, and magnetic behaviors, stemming from the complex interplay among spin, charge, and orbital degrees of freedom. The perovskite structure, typically represented by the general formula ABO_3, is one of the most versatile frameworks in solid-state chemistry, giving rise to numerous structural variants. Among the various classes of perovskites, the A-site columnar-ordered $A_2A'A''B_4O_{12}$ quadruple perovskites have garnered particular interest owing to their remarkable structural and magnetic characteristics. This thesis focuses on the design, synthesis, and investigation of new members of this family, employing rare-earth oxides and transition metals. The crystal structures and magnetic properties of the synthesized compounds are examined in detail.

Chapter 1 provides an overview of the fundamental background on perovskite materials, including their structural and magnetic properties, with particular emphasis on the characteristics of A-site columnar-ordered quadruple perovskites. This lays the foundation for the subsequent discussion.

Chapter 2 describes the experimental procedures employed in this study, including the synthesis methods and various characterization techniques, such as synchrotron X-ray powder diffraction and magnetic measurements. Chapters 3 to 5 present three distinct series of perovskites, highlighting the structure–property relationships within the $A_2A'A''B_4O_{12}$ family. Chapter 6 concludes the thesis by summarizing the key findings and proposing directions for future research.

Chapter 3 investigates the solid solution $Nd_2MnMn(Mn_{4-x}Sb_x)O_{12}$, which belongs to the A-site columnar-ordered quadruple perovskite subfamily. These compounds were synthesized by adjusting the Sb^{5+} content ($0.2 \leq x \leq 2.0$) and characterized using synchrotron X-ray powder diffraction. Aliovalent Sb^{5+} substitution enabled a continuous modulation of the Mn oxidation states. The study identified two distinct cation-ordering regimes within the B-site sublattice: for $0.8 \leq x \leq 1.0$, the structure is B-site disordered with space group $P4_2/nmc$ (No. 137), whereas for $1.6 \leq x \leq 2.0$, a rock-salt-type B-site ordering appears with space group $P4_2/n$ (No. 86). Magnetic measurements revealed complex behavior featuring two ferromagnetic transitions. The transition temperature T_C varies with x, reflecting the intricate correlation between cation ordering and magnetic properties.

Chapter 4 investigates the negative magnetization effect (NME) observed in $Ce_2MnM(Mn_2Sb_2)O_{12}$ (M = Mn, Zn), A-site columnar-ordered quadruple perovskites derived from the previous series and incorporating the highest Sb content. These compounds exhibited pronounced NME under low-field field-cooled magnetic measurements. Their room-temperature crystal structures were examined using synchrotron X-ray powder diffraction. Both compounds crystallize in space group $P4_2/n$, featuring full rock-salt ordering of Mn

and Sb at the B sites. Bond-valence sum analysis suggests that Ce is in the trivalent state. Magnetic measurements revealed a single magnetic transition in both compounds, with compensation points varying depending on the M-site ion. The robust, intrinsic NME is likely attributable to their ferrimagnetic structure.

Chapter 5 focuses on a new series of A-site columnar-ordered quadruple perovskites, $R_2MnZn(MnZnSb_2)O_{12}$ (R = La, Pr, Nd, and Sm), derived from the previous series, and examines the effects of different rare-earth cations and non-magnetic Zn^{2+} doping on their structural and magnetic properties. The crystal structure of the R = Nd sample (space group $P4_2/n$) was analyzed using synchrotron X-ray powder diffraction data. Zn^{2+} cations were found to occupy both the octahedral B site (alongside Mn^{2+}) and the tetrahedral A″ site, although minor antisite disorder of Mn^{2+} and Zn^{2+} between the square-planar A′ and octahedral B sites was also observed. The second B site is fully occupied by Sb^{5+}. Magnetic measurements revealed that rare-earth elements have a significant impact on the magnetic transitions. The presence of rare-earth cations enhanced the ferrimagnetic transition temperatures, indicating their role in strengthening exchange interactions among magnetic cations.

Chapter 6 summarizes the key findings of this study and outlines directions for future research. The results demonstrate that the structure and magnetic properties of $A_2A'A''B_4O_{12}$ quadruple perovskites can be finely tuned by manipulating cation distributions and incorporating rare-earth elements. These insights open new avenues for exploring functional applications of these materials. Future work may focus on synthesizing additional compounds and evaluating their potential across a range of advanced material systems.

Keywords: Quadruple perovskites, A-site columnar-ordered, High-pressure, Ferrimagnet, Crystal structures