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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 Perovskite-Related
5d Transition Metal Oxides
(ペロブスカイト型 5d 遷移金属酸化物の高圧合成、結晶構造と物性)

Perovskite-related materials have gained significant popularity in recent years due to their unconventional and outstanding physical and chemical properties, including ferroelectricity, multiferroicity, magnetoresistance, and exchange bias effects. Notably, materials related to perovskites that incorporate 5d elements have emerged as a leading and potentially applicable research area in inorganic and solid-state chemistry. This is attributed to the competition between local and itinerant d electrons, which can yield a range of beneficial characteristics, including frustrated magnetism, metal-insulator transitions, high- T_c superconductivity, and more. In this study, I successfully synthesized several 5d perovskite-related compounds using the high-pressure high-temperature method and subsequently investigated their crystal structures, as well as their magnetic and electrical transport properties.

Chapter 1 provides an overview of the research background, encompassing the fundamental crystal structure, mechanisms related to magnetism, material conductivity models referenced in this work, and the historical significance of high-pressure technology in materials science.

Chapter 2 predominantly outlines the experimental details and characteristic techniques employed in this study.

Chapter 3 presents the investigation of two double perovskite oxides, $\text{Cd}_2\text{FeReO}_6$ and $\text{Cd}_2\text{FeOsO}_6$, obtained under high-temperature and high-pressure conditions, with a space group of $P2_1/n$. Structure and composition determinations were confirmed by synchrotron powder X-ray diffraction and electron probe microanalysis. Magnetic and electronic property measurements revealed that $\text{Cd}_2\text{FeReO}_6$ exhibits ferrimagnetic order well above room temperature at 460 K, with a soft ferrimagnetic feature. Additionally, a tunneling-type magnetoresistance as large as 37% was discovered in $\text{Cd}_2\text{FeReO}_6$, while first-principles calculations indicated its half-metallic state. In $\text{Cd}_2\text{FeOsO}_6$, significant exchange bias (EB) effects were detected under remarkably small cooling fields, revealing a unique mechanism and providing valuable guidance for the advancement of materials exhibiting significant EB effects. Both materials behave as semiconductors, in accordance with a three-dimensional variable-range hopping transport model. These results not only provide a new platform for enhancing advanced EB-effect materials but also demonstrate that A-site Cd-occupied double perovskites constitute a promising class of oxides for exploring new materials with practical significance, particularly in the realm of soft and hard magnets or in the field of spintronics.

Chapter 4 primarily focuses on the KSbO_3 -type Fe-doped $\text{Bi}_3\text{Re}_3\text{O}_{11}$ and $\text{Bi}_3\text{Os}_3\text{O}_{11}$ compounds, synthesized under high-pressure and high-temperature conditions. Doping with Fe up to 29 atomic% was achieved under these conditions. The crystal structures and chemical compositions of $\text{Bi}_3\text{Os}_{2.45}\text{Fe}_{0.55}\text{O}_{11}$ and $\text{Bi}_3\text{Re}_{2.13}\text{Fe}_{0.87}\text{O}_{11}$ were determined through synchrotron powder X-ray diffraction and electron probe microanalysis. Both crystal structures were elucidated using a KSbO_3 -type model with the space group $Pn\bar{3}$. Measurements of magnetic and electronic transport properties revealed that $\text{Bi}_3\text{Os}_{2.45}\text{Fe}_{0.55}\text{O}_{11}$ exhibited a ferrimagnetic transition at the highest magnetic ordering temperature of 490 K in the KSbO_3 -type structure,

while $\text{Bi}_3\text{Re}_{2.13}\text{Fe}_{0.87}\text{O}_{11}$ displayed a spin-glass behavior below 22 K. The magnetoresistance at 5 K and 90 kOe was nearly zero for $\text{Bi}_3\text{Os}_{2.45}\text{Fe}_{0.55}\text{O}_{11}$, but -10% for $\text{Bi}_3\text{Re}_{2.13}\text{Fe}_{0.87}\text{O}_{11}$. These findings suggest that KSbO_3 -type 5d oxides, which have thus far exhibited only weak temperature-dependent paramagnetism, represent a class of compounds that can be transformed into spintronic materials through doping with 3d elements, thereby paving the way for the development of new KSbO_3 -type materials with both theoretical and practical significance.

Chapter 5 introduces ABO_3 -type perovskite oxides $\text{MnV}_{0.5}\text{Nb}_{0.5}\text{O}_3$ and $\text{MnV}_{0.5}\text{Ta}_{0.5}\text{O}_3$, prepared under high-pressure and high-temperature conditions. Structure analysis using synchrotron XRD patterns revealed that both crystallize in a GdFeO_3 -type structure with the space group $Pnma$. Magnetic measurements confirmed that $\text{MnV}_{0.5}\text{Nb}_{0.5}\text{O}_3$ and $\text{MnV}_{0.5}\text{Ta}_{0.5}\text{O}_3$ order ferrimagnetically at 17 and 18 K, respectively. Both phases are semiconductors, with activation energies of 0.13 eV and 0.31 eV.

Chapter 6 presents the overall conclusions and future prospects based on this body of work.