学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

High-Pressure Synthesis, Crystal Structure and Physical Properties of Layered Manganese and Zinc Oxyhalides

（マンガンおよび亜鉛の層状オキシハライドの高圧合成と結晶構造と物性）

Over the past decades, mixed-anion compounds including $A_2M(OX)_4$ (typically A: alkali earth or rare earth elements, M: transition metal, X: halogen) attract significant attention. $A_2M(OX)_4$ is a subgroup of A_2MO_4-based oxide, which usually crystalizes in the K_2NiF_4-type structure. The different anions of $A_2M(OX)_4$ seem to favor ordering, compared with those of the perovskite-type compounds. Owing to the specific characters of X, such as electronegativity, polarizability, ionic radius, and valence state, the anions order offers opportunities to further develop the quantum magnetic properties of $A_2M(OX)_4$. Indeed, intriguing properties were occasionally discovered by anions-mixing in an oxide host. In this study, a high-pressure technology was used to synthesize newly anion-ordered oxyhalides; and the crystal structures and magnetic properties were subsequently investigated.

In chapter 1, perovskite-type compounds, layered perovskite-type compounds, and their electronic properties are outlined. Additionally, magnetism and magnetic interactions which are frequently mentioned in this thesis are reviewed.

In chapter 2, general descriptions of experimental methods of materials preparation (including a high-pressure technique) and materials characterizations (including synchrotron X-ray diffraction, magnetic properties measurements, and UV-vis spectrum) used in this study are provided.

In chapter 3, an additional member of the layered oxyfluoride family, Sr_2MnO_3F, which was successfully synthesized by a high-pressure method (6 GPa and 1800 °C) is introduced. It crystallizes into a body-centered tetragonal structure (the space group: $I4/mmm$) with lattice parameters of a = 3.79009(1) Å and c = 13.28974(6) Å. The compound exhibits structure features that have never been reported for layered oxyhalides: coexistence of anion disorder between O and F at the apical site (of the K_2NiF_4-type structure) and the octahedral coordination. The MnO_2 planes are well separated by non-magnetic Sr(O/F) rock-salt layers, resulting in appearance of a low-dimensional magnetism. The antiferromagnetic behavior with an ordered state below 133 K is qualitatively different from the paramagnetic behaviors usually observed for the K_2NiF_4-type manganese oxyfluorides.

In chapter 4, a new layered perovskite zinc oxychloride $Sr_2ZnO_2Cl_2$ successfully synthesized by a high-pressure method is reported. In the structure, infinite layers of a ZnO_2 squares sheet, which is quite rare, has been found. The compound $Sr_2ZnO_2Cl_2$ has the lattice constants a = 4.06981(2) Å and c = 15.20076(8) Å and is isostructural with $Sr_2CuO_2Cl_2$. The band gap was measured by UV-vis spectroscopy to be 3.66 eV (an indirect gap). The observation was supported by the first principles calculation for the electronic state, in which the square planar ZnO_2 sheets play an essential role in forming the indirect gap between O 2p and Zn 4s bands dispersion.

In chapter 5, a manganese oxychloride $Sr_2MnO_2Cl_2$ synthesized by a high-pressure method (6 GPa and 1800 °C) is introduced. It crystallizes into a body-centered tetragonal structure (space group: $I4/mmm$) with lattice constants of a = 4.09239(6) Å and c = 14.9380(2) Å. The sample quality was much improved than that in a previous study. The magnetic susceptibility measurements revealed the divalency of manganese with the high-spin state configuration ($3d^5$; S = 5/2). A typical low dimensional behavior of antiferromagnetic correlations was observed with a broad magnetic susceptibility maximum at 42 K. Neutron diffraction revealed development of a short range magnetic order below a temperature of ~80 K and absence of long-range magnetic order down to 2 K. Such the magnetic behaviors are remarkably different from what were reported for the K_2NiF_4-type compounds, and suggested that the $Sr_2MnO_2Cl_2$ may be a possible ideal 2D antiferromagnet.

In chapter 6, an overall conclusion and prospect are stated. This study focused on synthesis of oxyhalide materials with the K_2NiF_4-type structure as well as discovery of notable magnetic properties; and this study was eventually successful to demonstrate the high flexibility of $A_2M(OX)_4$ toward further developments of scientific and engineering properties for such as spintronics, memory devices, and magnetic sensors applications. The newly added members to the class of $A_2M(OX)_4$ certainly deserve advanced studies.