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 Magnetic Properties of Perovskite-Related Os and Ir Oxides
（ペロブスカイト関連オスミウムおよびイリジウム酸化物の高圧合成と結晶構造と磁気的性質）

Over the past quarter century, oxides and compound containing 5d transition metal ions, e.g. Ir and Os, have attracted considerable attention with solid-state physicists because of various unconventional physical phenomena. Due to the competition between localization and itinerancy of d electron, there are a lot of interesting and unusual properties with different crystal structures reported, such as metal-insulator transitions, topological phases, and frustrated magnetism. In this study, we used a high-pressure method to synthesize the 5d oxides and researched their crystal structures and magnetic properties.

5d Solid-state oxides $K_{0.84}OsO_3$ ($Os^{5.16+}$; $5d^{2.84}$) and $Bi_{2.93}Os_3O_{11}$ ($Os^{4.40+}$; $5d^{3.60}$) were synthesized under high-pressure and high-temperature conditions (6 GPa and 1500—1700 ° C). Their crystal structures were determined by synchrotron x-ray diffraction and their 5d electronic properties and tunnel-like structure motifs were investigated. A $KSbO_3$-type structure with a space group of $Im\overline{3}$ and $Pn\overline{3}$ was determined for $K_{0.84}OsO_3$ and $Bi_{2.93}Os_3O_{11}$, respectively. The magnetic and electronic transport properties of the polycrystalline compounds were compared with those obtained theoretically. It was revealed that the 5d tunnel-like structures are paramagnetic with metallic charge conduction at temperatures above 2 K. This was similar to what was observed for structurally relevant 5d oxides, including $Bi_3Re_3O_{11}$ ($Re^{4.33+}$; $5d^{2.66}$) and $Ba_2Ir_3O_9$ ($Ir^{4.66+}$; $5d^{4.33}$). The absence of long-range magnetic order seems to be common among 5d $KSbO_3$-like oxides, regardless of the number of 5d electrons (between 2.6 and 4.3 per 5d atom).

Double-perovskite oxides Ca_2MgOsO_6 and Sr_2MgOsO_6 have been synthesized under high-pressure and high-temperature conditions (6 GPa and 1500 ° C). Their crystal structures and magnetic properties were studied by a synchrotron X-ray diffraction experiment and by magnetic susceptibility, specific heat, isothermal magnetization, and electrical resistivity measurements. Ca_2MgOsO_6 and Sr_2MgOsO_6 crystallized in monoclinic ($P2_1/n$) and tetragonal ($I4/m$) double-perovskite structures, respectively; the degree of order of the Os and Mg arrangement was 96% or higher. Although Ca_2MgOsO_6 and Sr_2MgOsO_6 are isoelectric, a magnetic glass transition was observed for Ca_2MgOsO_6 at 19 K while Sr_2MgOsO_6 showed an antiferromagnetic transition at 110 K. The antiferromagnetic-transition temperature is the highest in the family. A first-principles density functional approach revealed that Ca_2MgOsO_6 and Sr_2MgOsO_6 are likely to be antiferromagnetic Mott insulators, in which the band gaps open, with Coulomb correlations of $\sim$1.8 − 3.0 eV. These compounds offer a better opportunity for the clarification of the basis of 5d magnetic sublattices, with regard to the possible use of perovskite related oxides in multifunctional devices.

Double perovskite containing Ir^{6+}/Ir^{5+} with formula Ca_2NiIrO_6 is synthesized using a high-pressure synthesis technique. Its electronic state is studied through magnetic susceptibility, heat capacity and electrical resistivity measurement. It is found that Ca_2NiIrO_6 crystallizes in space group $P2_1/n$ with lattice parameters $a = 7.6456(2)$ Å, $b = 5.5343(1)$ Å, $c = 9.3287(4)$ Å, $\beta = 144.870(5)$ ° . The magnetic susceptibility measurement indicates that Ca_2NiIrO_6 orders in a canted antiferromagnetic state at about 72 K. Ca_2NiIrO_6 exhibits semiconductor like behavior. Double perovskites containing Ir^{6+} are rarely reported. In particular, we observe the extraordinary large coercivity at 10 K, compared with other canted antiferromagnetic iridium oxides.