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Author(s)	袁, 亞華
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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miumおよびイリジウム酸化物の高圧合成と結晶構造と磁氣的性質)

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 $\text{K}_{0.84}\text{OsO}_3$ ($\text{Os}^{5.16+}$; $5d^{2.84}$) and $\text{Bi}_{2.93}\text{Os}_3\text{O}_{11}$ ($\text{Os}^{4.40+}$; $5d^{3.60}$) 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 $Im\bar{3}$ and $Pn\bar{3}$ was determined for $\text{K}_{0.84}\text{OsO}_3$ and $\text{Bi}_{2.93}\text{Os}_3\text{O}_{11}$, 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 $\text{Bi}_3\text{Re}_3\text{O}_{11}$ ($\text{Re}^{4.33+}$; $5d^{2.66}$) and $\text{Ba}_2\text{Ir}_3\text{O}_9$ ($\text{Ir}^{4.66+}$; $5d^{4.33}$). 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 $\text{Ca}_2\text{MgOsO}_6$ and $\text{Sr}_2\text{MgOsO}_6$ 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. $\text{Ca}_2\text{MgOsO}_6$ and $\text{Sr}_2\text{MgOsO}_6$ 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 $\text{Ca}_2\text{MgOsO}_6$ and $\text{Sr}_2\text{MgOsO}_6$ are isoelectric, a magnetic glass transition was observed for $\text{Ca}_2\text{MgOsO}_6$ at 19 K while $\text{Sr}_2\text{MgOsO}_6$ 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 $\text{Ca}_2\text{MgOsO}_6$ and $\text{Sr}_2\text{MgOsO}_6$ 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 $\text{Ir}^{6+}/\text{Ir}^{5+}$ with formula $\text{Ca}_2\text{NiIrO}_6$ 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 $\text{Ca}_2\text{NiIrO}_6$ 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 $\text{Ca}_2\text{NiIrO}_6$ orders in a canted antiferromagnetic state at about 72 K. $\text{Ca}_2\text{NiIrO}_6$ 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.