## Title
High-Pressure Synthesis, Crystal Structures, and Magnetic Properties of Perovskite-Related Os and Ir Oxides

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## Issue Date
2015-09-25

## Doc URL
http://hdl.handle.net/2115/59989

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## Type
theses (doctoral - abstract and summary of review)

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- Yuan_Yahua_abstract.pdf (論文内容の要旨)
High-Pressure Synthesis, Crystal Structures, and Magnetic Properties of Perovskite-Related Os and Ir Oxides

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 $\square$ 1700 $\square$ C). Their crystal structures were determined by synchrotron x-ray diffraction and their 5d electronic properties and tunnel-like structure motifs were investigated. A KSB$_3$O$_5$-type structure with a space group of $Im\bar{3}$ and $Pn\bar{3}$ 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 $Ba_2Ir_3O_9$ ($Ir^{4.66+}$; $5d^{1.33}$). 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 $\square$ 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 ($P21/n$) 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, $\beta = 144.870(5)$ $\square$. 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.