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Short review of high-pressure crystal growth and magnetic and electrical properties of solid-state osmium oxides

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ABSTRACT

High-pressure crystal growth and synthesis of selected solid-state osmium oxides, many of which are perovskite-related types, are briefly reviewed, and their magnetic and electrical properties are introduced. Crystals of the osmium oxides, including $NaOsO_3$, $LiOsO_3$, and Na_2OsO_4, were successfully grown under high-pressure and high-temperature conditions at 6 GPa in the presence of an appropriate amount of flux in a belt-type apparatus. The unexpected discovery of a magnetic metal–insulator transition in $NaOsO_3$, a ferroelectric-like transition in $LiOsO_3$, and high-temperature ferrimagnetism driven by a local structural distortion in Ca_2FeOsO_6 may represent unique features of the osmium oxides. The high-pressure and high-temperature synthesis and crystal growth has played a central role in the development of solid-state osmium oxides and the elucidation of their magnetic and electronic properties toward possible use in multifunctional devices.

1. Introduction

The synthesis of materials under high-pressure conditions has been studied for more than half a century, and the successful development of high-pressure instruments has accelerated the studies of artificial diamonds and related hard materials [1]. At pressures ranging over several GPa, the crystal growth of hard materials has been successful with or without the presence of appropriate chemical catalysts [2]. An important instrument used in a series of studies of hard materials is a belt-type apparatus, which usually consists of a top, bottom, and flat-belt cylinder core anvils (for example, see Fig. 1) [3]. The apparatus has also been employed for the synthesis of layered copper oxides since the discovery of high critical temperature (T_c) superconductivity in 1986 [4]. Despite this, high-T_c superconductors have a highly anisotropic crystal structure that tends toward being two-dimensional, unlike that of diamond, and the high-pressure and high-temperature (HPHT) synthetic method has been remarkably effective to expand the range of chemical compositions of the superconductors beyond the limits set by the regular solid-state method. Indeed, expanded chemical compositions occasionally provided opportunities to improve the superconducting properties; for example, the majority of superconductors with a T_c of 100 K or higher were synthesized by the high-pressure method [5,6]. Besides, the method was beneficial not only for the studies of hard materials and high-T_c superconductors, but also for the development of materials with correlated electrons and a pioneering study of these materials by the HPHT method was carried out by Sleight and his colleagues in the 1960s and 1970s [7–12].

Our institute (NIMS) has operated a series of belt-type high-pressure apparatus, many of which were principally designed in-house by staff scientists, to satisfy the demands of the scientific studies of materials since the establishment of the predecessor of NIMS in 1966. We have applied a belt-type high-pressure apparatus (Fig. 1) for the high-pressure crystal growth of transition metal oxides, and to study the properties of materials with strong electronic correlations for possible applications. A partial list of osmium oxides, which were compositionally or structurally new when synthesized in NIMS or cooperating institutes, is presented in Table 1. Solid-state materials containing a 5d element have attracted increasing attention in recent years owing to their potential significance in advanced applications especially in the fields of spintronics and topological technologies [13–18]. In general, 5d atoms exhibit significant radially extended valence orbitals and large spin–orbit couplings, which distinguish their electromagnetic behavior from that of 3d materials. The unexpected discovery of a Slater-like transition in the perovskite oxide $NaOsO_3$ [19–24], and a ferroelectric-like transition in the metallic oxide $LiOsO_3$ [25–30] may represent unique features of the 5d oxides. Recently, we successfully prepared the 5d compound Ca_2FeOsO_6, which shows a ferrimagnetic (FIM) transition above room

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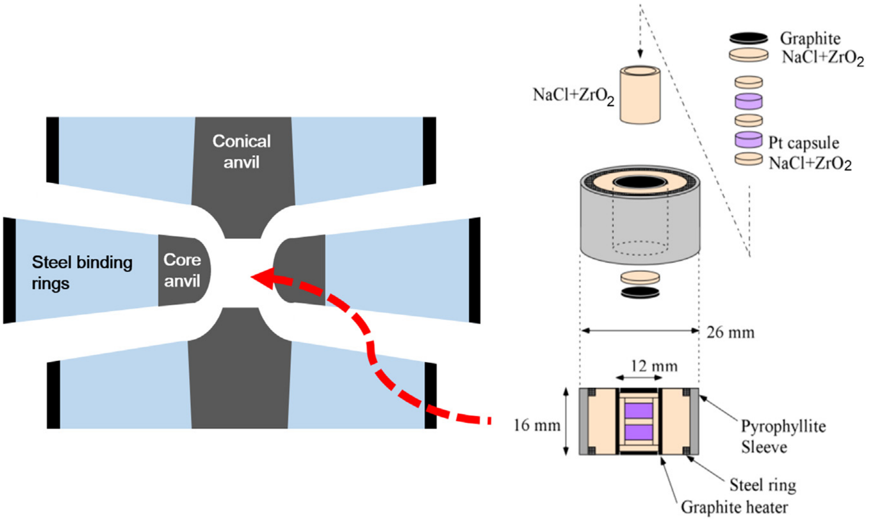

Fig. 1. Assembled views of a belt-type high-pressure apparatus and sample cell, which have been used in this study. The view does not correctly represent relative sizes and shapes of the apparatus (anvils are somewhat exaggerated).

temperature [31–33].

In this paper, we report a brief outline of the HPHT synthesis and crystal growth of selected osmium oxides roughly in the chronological order in which the studies were conducted at NIMS.

2. Experiments

Typically, we attempted the possible synthesis of a polycrystalline form of the target compound by carrying out a solid-state reaction under HPHT conditions in the belt-type apparatus (Fig. 1). This was performed by sealing a mixture of high-purity starting materials in a Pt (or Au or Ta) capsule in an Ar-filled glove box. Then, the capsule was statically and isotropically compressed to a pressure of several GPa (typically 6 GPa) in the belt-type high-pressure apparatus, followed by heating at a temperature of 2000 °C or below for a few hours (typically 1 h). The pressure was maintained during heating. Subsequently, the capsule was quenched to ambient temperature within a minute by cutting off the electric power supply; then, the pressure was gradually released over a few hours. The possibility of growing a crystal under HPHT conditions was tested by adding an amount of flux to the starting mixture, and by optimizing the heating temperature and time under high pressure. We expected a small temperature gradient in the capsule to partially facilitate crystal growth under HPHT conditions in the presence of an appropriate amount of flux.

A polycrystalline pellet obtained in this way was usually dense. A small piece was cut from the pellet and finely ground, and then, it was washed in water to remove possible chemical residues. The fine powder was thoroughly dried and then subjected to X-ray diffraction (XRD) in an X-ray diffractometer with Cu Kα radiation for qualitative evaluation. If necessary, the powder was further studied by synchrotron X-ray diffraction (SXRD) at ambient temperature in a beam line facility such as the NIMS contract beam line (BL15XU) at SPring-8, Japan. In the BL15XU, SXRD data were collected using a large Debye–Scherrer-type diffractometer [41] and the "MYTHEN" one-dimensional semiconductor X-ray detector [42] in an incident photon-energy range of 2.2–36 keV. The

Table 1
List of selected osmium oxides, which were compositionally or structurally new when synthesized at NIMS or cooperating institutes by various methods including the HPHT method.

Compounds	Formal valence of Os	Lattice-type	Space group	Lattice constants[a] (Å or °)	Single crystals	Flux	Note and Ref.
$BaOsO_3$	+4.0	Cubic perovskite	*Pm-3m*	$a=4.02573(1)$	No		HPHT at 17 GPa, [34]
OsO_2	+4.0	High-pressure PdF_2	*Pa-3*	$a=4.89561(1)$	No		HPHT at 17 GPa, [35]
$NaOsO_3$	+5.0	$GdFeO_3$	*Pnma*	$a=5.38420(1)$ $b=7.58038(1)$ $c=5.32817(1)$	Yes	NaCl	HPHT at 6 GPa, [24]
$LiOsO_3$	+5.0	$LiNbO_3$	*R-3c* (> 140 K) *R3c* (< 140 K)	$a=5.06379(5)$ $c=13.2110(2)$	Yes	LiCl	HPHT at 6 GPa, [30]
Ca_3LiOsO_6	+5.0	K_4CdCl_6	*R-3c*	$a=9.2738(2)$ $c=10.7801(4)$	Yes	LiCl, KCl	Grown in an evacuated quartz tube, [36]
Ca_2FeOsO_6	+5.0	Double perovskite	$P2_1/n$	$a=5.3931(6)$ $b=5.5084(3)$ $c=7.6791(3)$ $\beta=90.021(5)$	No		HPHT at 6 GPa, [33]
$Na_{1.4}Os_2O_6$-H_2O	+5.3	Pyrochlore	*Fd-3m*	$a=10.16851(1)$	No		Ion-exchanged from KOs_2O_6, [37]
Na_2OsO_4	+6.0	Ca_2IrO_4	*P-62m*	$a=9.6133(3)$ $c=3.1567(3)$	Yes	NaCl	HPHT at 6 GPa, [38]
Ba_2CuOsO_6	+6.0	Double perovskite	*I*4/m	$a=5.5679(2)$ $c=8.5118(4)$	No		HPHT at 6 GPa, [39]
$YbOs_2Al_{10}$		$YbFe_2Al_{10}$	*Cmcm*	$a=9.1005(4)$ $b=10.1855(4)$ $c=9.1118(5)$	Yes	Al, self-flux	Grown in an evacuated quartz tube, [40]
$LuOs_2Al_{10}$		$YbFe_2Al_{10}$	*Cmcm*	$a=9.0947(4)$ $b=10.1608(5)$ $c=9.1007(4)$	Yes	Al, self-flux	Grown in an evacuated quartz tube, [40]

[a] The parameters were measured at either 300 K or room temperature.