Solid-State Chemistry

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$Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$: Iridium(VI) Oxides Prepared under Ambient Pressure**

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The preparation of oxides containing transition metals in unusually high oxidation states has typically been an area reserved for high-pressure synthetic methods,[1–9] although other methods, such as the electrolytic oxidation of manganates to permanganate[10] or of Fe^{III} to Fe^{IV}[11] take place under ambient pressure. Specifically, under conditions of high pressure, that is, both mechanical pressure and oxygen pressure, it is possible to stabilize high oxidation states of transition metals in oxides, such as Ni^{3+}, Fe^{4+}, Mn^{5+}, Rh^{5+}, Ru^{6+}, and Ir^{6+}, by significantly increasing the covalency of the M–O bond. Oxides containing transition metals in such high oxidation states, such as $TlNiO_3$,[12] $LaCuO_3$,[13] $IrSr_2TbCu_2O_8$,[14] $Ln_4Cu_3MoO_{12}$ (Ln = La, Pr, Nd, and Sm)[15] $La_2CuO_{4+\delta}$,[16] $Hg_{0.8}V_{0.2}Ba_2Ca_{m-1}Cu_mO_{2m+2+\delta}$[17] often exhibit physical properties that are typical of covalent rather than of ionic compounds and are thus desired for investigations of their physical properties. More importantly, the ability to incorporate metals in high oxidation states with correspondingly smaller radii and potentially different coordination environment preferences can lead to the preparation of new structure types, as is the case for the title compounds.

A viable alternative to the high-pressure solid-state reaction for stabilizing high oxidation states is the use of hydroxide or hyperoxide melts, in which high oxygen activities can be achieved and, thus, transition metals in high oxidation states can be stabilized and incorporated into single crystals. In addition to being an excellent synthetic method for the discovery of new materials,[18–47] the highly oxidizing environment of a hydroxide flux enables the synthesis of many complex oxides containing elements in unusually high oxidation states, such as Ir^{5+} in Ln_2MIrO_6 (Ln = La, Pr, Nd, Sm, Eu; M = Li, Na),[18,31,33] $La_{2.5}K_{1.5}IrO_7$,[32] $La_9RbIr_4O_{24}$,[34] and Sr_3LiIrO_6;[19] $Ir^{5+/6+}$ in $Ba_3MIr_2O_9$ (M = Li, Na) and $Ba_{3.44}K_{1.56}Ir_2O_{10}$;[30] Rh^{5+} in Sr_3MRhO_6 (M = Li, Na);[39,40] $Ru^{5+/6+}$ in $Ba_7Li_3Ru_4O_{20}$[43] and $Ba_3MRu_2O_9$ (M = Li, Na);[45] $Os^{5+/6+}$ in $Ba_3MOs_2O_9$ (M = Li, Na);[42] Os^{7+} in Ba_2MOsO_6 (M = Li. Na);[46] Ni^{3+} in $MNiO_2$ (M = Li, Na);[48] Cu^{3+} in $Al_6Ba_{46}Cu_{24}O_{84}$;[47] Mn^{5+} in $Ba_4Mn_2NaO_9$,[49] and Fe^{4+} in $Ba_5Fe_5O_{14}$.[50]

Herein we report the ambient-pressure synthesis of the most-oxidized iridium oxides to date, two novel all-iridium(VI) containing oxides, $Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$, prepared as single crystals in a hydroxide flux, and found to form in a new structure type. This preparation of an iridium(VI) oxide without the use of traditional high-pressure techniques is unprecedented and the synthetic approach has the potential to enable the targeted synthesis of other novel oxides containing transition metals in unusually high oxidation states.

Prior to our work in molten hydroxides, the majority of known complex iridium oxides contained iridium in its most common oxidation state, +IV. In more recent years, however, polycrystalline powder techniques under flowing oxygen and crystal growth from high-temperature solutions have resulted in the preparation of a significant number of pentavalent and several mixed penta-/hexavalent iridates. Compounds composed entirely of hexavalent iridium cations are extremely rare and, until now, had only been prepared as polycrystalline powders using high-pressure synthetic methods, resulting in the discovery of the double perovskites, with the general formula A_2MIrO_6 (A = Ba, Sr, M = Ca, Sr, Mg, Zn).[3–7,51] Our investigations into the reactivity of the lanthanide elements and iridium metal in molten hydroxides at ambient pressure has resulted in the synthesis of single crystals of $Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$, the first all-Ir(VI) containing oxides to be prepared without the use of high-pressure techniques. Herein, we report their syntheses, crystal structures, and X-ray absorption near-edge structure (XANES) data.

Single crystals of $Ln_2K_2IrO_7$ (Ln = Nd, Sm) were grown from reactive potassium hydroxide flux reactions in covered silver crucibles.[52] The crystals were black and adopted a hexagonal morphology as shown in the scanning electron micrograph in Figure 1. The crystals are water sensitive and will degrade over time. The materials crystallize in the space group $R\bar{3}c$ with lattice parameters $a = 5.73260(10)$, $c = 38.0887(15)$ Å for $Nd_2K_2IrO_7$[53] and $a = 5.70310(10)$ A, $c = 37.8521(9)$ Å for $Sm_2K_2IrO_7$.[54] $Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$ are isostructural and represent a new structure type related to the $[A_nB_{n-1}O_{3n}][A'_2O]$ family of oxides,[55] exemplified by the Ir^{5+} oxide $La_{2.5}K_{1.5}IrO_7$.[32] The structure of $Ln_2K_2IrO_7$ (Ln = Nd, Sm) is shown in Figure 2a. The structure consists of an intricate slab-like network of isolated IrO_6 octahedra (Figure 2b), KO_{10} tetracapped trigonal prisms (Figure 2c), and LnO_{10} (Ln = Nd, Sm) irregular polyhedra (Figure 2d). The structure can be broken down into three repeating components: 1) a unit of eight isolated IrO_6 octahedra;

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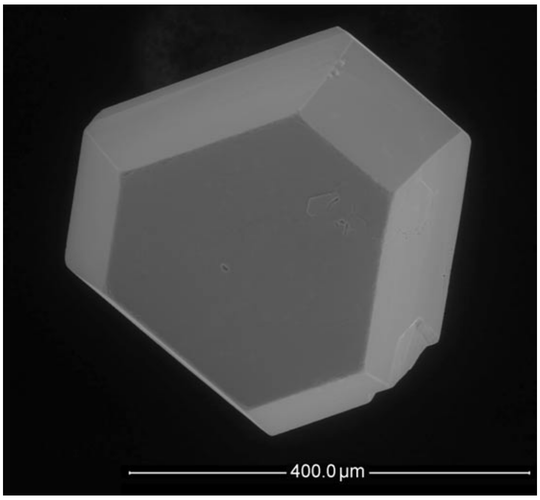

Figure 1. Scanning electron micrograph of a single crystal of $Nd_2K_2IrO_7$.

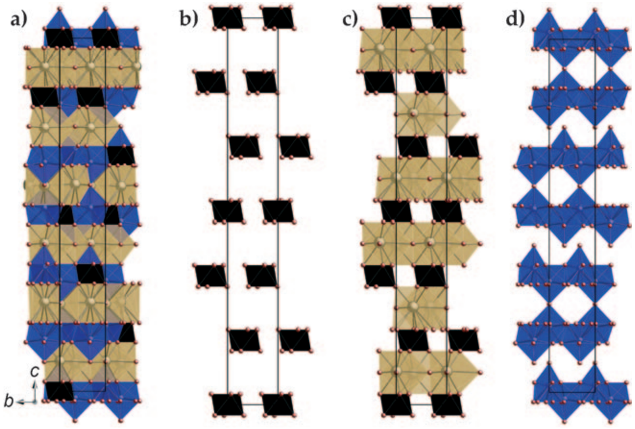

Figure 2. a) Structural representation of $Ln_2K_2IrO_7$ (Ln = Nd, Sm) viewed along the *c* axis. IrO_6 octahedra in black, KO_{10} polyhedra in beige, LnO_{10} polyhedra in blue, and oxygen atoms as red spheres. The structure's three components are shown to the right and consist of b) isolated IrO_6 octahedral units, c) IrO_6 octahedra shown with the slabs of KO_{10} polyhedra, d) LnO_{10} polyhedral slab-like units.

2) slabs of KO_{10} polyhedra; and 3) a slab-like double layer of LnO_{10} polyhedra. In each of the components, the threefold rotational axis is very evident. In addition, the center of inversion can be identified in the slabs of KO_{10} polyhedra (Figure 2c). The IrO_6 octahedra are separated from each other; along the *x* and *y* directions they share six edges with six of the LnO_{10} polyhedra and along the *z* direction they share two triangular faces with the KO_{10} polyhedra. The KO_{10} polyhedra within the slab-like units are face-shared to each other and further connected to the LnO_{10} polyhedra through the sharing of triangular faces. The KO_{10} units are isolated from each other along the *z* direction by the IrO_6 octahedra (Figure 2c). The LnO_{10} dual slab-like polyhedral units (Figure 2d) are connected to each other along the *x* and *y* directions through the sharing of triangular faces and along the *z* direction through the sharing of eight vertices, however, the three complete LnO_{10} units are isolated from each other by the slabs of KO_{10} polyhedra.

The oxidation state of iridium in $Ln_2K_2IrO_7$ (Ln = Nd, Sm) is well established by the single crystal X-ray diffraction data collected on high-quality crystals. The compounds crystallize in space group $R\bar{3}c$ and the asymmetric unit of the crystal consists of three metal atom positions (Ir1, Ln1, K1) and two oxygen atom positions (O1, O2). All site occupancy factors were refined and showed no significant deviation from unity (less than 1%). Thus, based on the sample stoichiometry, these two new oxides contain iridium in the +VI oxidation state.

Trends in bond lengths are often used to support oxidation states,[45] in particular when a series of isostructural compounds containing the metal center in different oxidation states is available. Demazeau performed such a study[3] using double perovskites. In our case, because $Ln_2K_2IrO_7$ has a new structure type, such data is not available. Reported Ir–O bond lengths are quite structure dependent and typical lengths are: Ir^{IV} 2.00–2.04 Å; Ir^{V} 1.97–1.99 Å; $Ir^{V/VI}$ 1.96 Å (average of 3 × 1.872 Å and 3 × 2.042 Å). The shortest bond for each oxidation state is found in perovskite structures that can readily accommodate diverse bond lengths. The Ir–O distances of 1.98 and 1.97 Å in $Ln_2K_2IrO_7$ (Ln = Nd, Sm) are comparatively long, and more in line with +5/+6 iridates (Ir–O 1.87–2.04). However, the $Ln_2K_2IrO_7$ structure is new and no other Ir(VI)–O bonds are available for comparison with this structure type.

To conclusively evaluate the oxidation states of the iridium, X-ray absorption spectroscopy (XANES) experiments were performed to complement the single-crystal X-ray diffraction data.[56] The Ir L_{III}-edge XANES spectrum of Ir^{6+} in $Nd_2K_2IrO_7$ was measured along with that of one iridium +4 and one iridium +5 oxide (see Supporting Information). A plot of the XANES data for Sr_3ZnIrO_6 (Ir^{4+}), Sr_3NaIrO_6 (Ir^{5+}), and $Nd_2K_2IrO_7$ (Ir^{6+}) is shown in Figure 3a. L_{III}-edge XANES are very sensitive to the oxidation state, the spin state and the crystal-field effect and can help us draw conclusions concerning the oxidation state of the iridium in $Nd_2K_2IrO_7$ by comparing the data to that of the reference samples, Sr_3ZnIrO_6 and Sr_3NaIrO_6. As the stabilization of iridium in the +VI oxidation state requires a very high degree of covalency in the Ir–O bonds, a large shift in the XANES spectrum between the already fairly covalent Ir^{4+} and Ir^{5+} reference samples is not expected. This situation was already established by prior XANES work on double perovskite iridates prepared at high pressure, which showed that there is a clear correlation between the average energy positions and the oxidation state of the iridium; a shift to higher energy of only approximately 1 eV was observed in going from Ir^{4+} to Ir^{5+} to Ir^{6+}.[57]

The data collected on Sr_3ZnIrO_6 (Ir^{4+}), Sr_3NaIrO_6 (Ir^{5+}), and $Nd_2K_2IrO_7$ (Ir^{6+}) are consistent with the literature data in that we observe a shift of just over 1 eV in going from Sr_3ZnIrO_6 (Ir^{4+}) to Sr_3NaIrO_6 (Ir^{5+}) to $Nd_2K_2IrO_7$ (Ir^{6+}). Figure 3b shows the change of the iridium oxidation state versus the energy of the transition measured by the XANES experiment. It can be clearly seen that peak position shifts to higher energies with an increase in the iridium oxidation state.

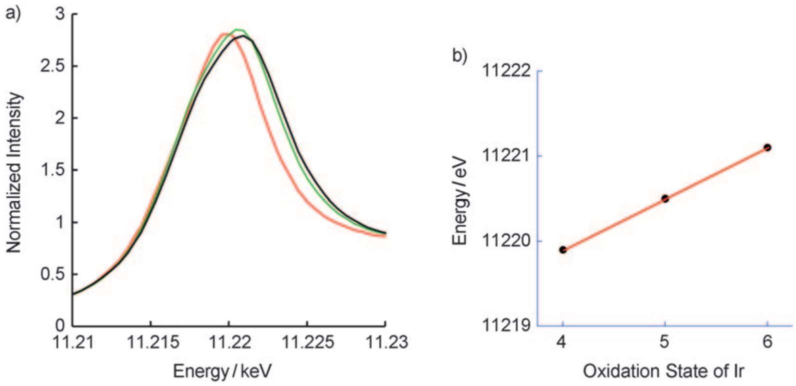

Figure 3. a) Normalized Ir L_{III}-edge XANES spectra for $Sr_3ZnIr^{IV}O_6$ (orange), $Sr_3NaIr^{V}O_6$ (green), and $Nd_2K_2Ir^{VI}O_7$ (black) with a slight shift in edge position indicating the oxidation state of iridium in $Nd_2K_2IrO_7$ is greater than +5. b) Plot of peak position versus iridium oxidation state. A virtually linear increase in the peak position with oxidation state is observed.

These data are consistent with what has been observed for Ir^{VI} oxides prepared by high pressure routes and nicely support the +VI oxidation state for iridium in these oxides.

In conclusion, the utilization of molten potassium hydroxide flux reactions has enabled the ambient-pressure synthesis of the most-oxidized iridium oxides to date, namely two novel all-Ir^{VI} containing oxides, $Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$. This synthetic approach has the potential of enabling the targeted synthesis of other novel oxides containing transition metals in unusually high oxidation states.

Experimental Section

See refs. [52–54,56]. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-419570 and -419571.

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[52] Single crystals of $Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$ were grown from a reactive potassium hydroxide flux. Nd_2O_3 (Alfa Aesar 99.9%, 1 mmol) or Sm_2O_3 (Alfa Aesar 99.9%, 1 mmol), Ir metal powder (Engelhard, 99.9%, 1 mmol), and KOH (Fisher ACS reagent, 20.0 g) were loaded into silver crucibles and covered with silver lids before being placed into a programmable box furnace. The crucibles were heated in air to 550 °C in one hour, held at that temperature for 24 h and then cooled to room temperature by shutting off the furnace. Single crystals were extracted from the flux matrix by dissolving the flux in methanol, aided by sonication, and isolated by vacuum filtration. The crystals appeared to be slightly moisture sensitive (most likely because of the unusually high oxidation state of iridium) and thus were stored in a vacuum desiccator to prevent surface degradation.

[53] Crystal data for $Nd_2K_2IrO_7$: $Z=6$, $M_r=670.88\ \mathrm{g\,mol^{-1}}$, crystal size $0.06\times0.03\times0.02\ \mathrm{mm^3}$, hexagonal space group $R\bar{3}c$, $a=5.73260(10)$, $c=38.0887(15)$ Å, $V=1084.00(5)$ Å^3, $\rho_{calcd}=6.166\ \mathrm{g\,cm^{-3}}$, $F(000)=1746$, $\lambda=0.71073$ Å, $T=294$ K, $\mu=33.668\ \mathrm{mm^{-1}}$, Bruker SMART Apex CCD area detector, 6869 reflections, 545 unique, ($R_{int}=0.0485$), structure solution using direct methods, refinement on $F2$ ($2\theta max=70.2°$), multiscan absorption correction, $R1(I>2\sigma(I))=0.0229$, $wR2=0.0448$, GoF = 1.054.

[54] Crystal data for $Sm_2K_2IrO_7$: $Z=6$, $M_r=683.10\ \mathrm{g\,mol^{-1}}$, crystal size $0.04\times0.03\times0.02\ \mathrm{mm^3}$, hexagonal space group $R\bar{3}c$, $a=5.70310(10)$, $c=37.8521(9)$ Å, $V=1066.21(4)$ Å^3, $\rho_{calcd}=6.383\ \mathrm{g\,cm^{-3}}$, $F(000)=1770$, $\lambda=0.71073$ Å, $T=294$ K, $\mu=36.143\ \mathrm{mm^{-1}}$, Bruker SMART Apex CCD area detector, 7392 reflections, 659 unique, ($R_{int}=0.0302$), structure solution using direct methods, refinement on F^2 ($2\theta_{max}=76.2°$), multiscan absorption correction, $R1(I>2\sigma(I))=0.0285$, $wR2=0.0545$, $GoF=1.142$.

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[56] XANES measurement: The Ir L_{III}-edge X-ray absorption spectroscopy (XAS) experiments were performed on Beam Line X19A of the National Synchrotron Light Source (NSLS). A pair of Si (111) crystals was used to monochromatize the radiation. Harmonic contamination was suppressed by detuning the monochromator to reduce the incident X-ray intensity by approximately 10%. Reference spectra were simultaneously collected for every measurement by using Ir metal foil to remove an energy-shift problem.

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