Structural Study of a Hollandite-Type K_xIrO_2

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The new ternary oxide K_xIrO_2 ($x \approx 0.25$) was prepared by heating stoichiometric proportions of K_2CO_3 and pure, chlorine-free IrO_2 at 1000°C for 1 hr. The monoclinic cell of the phase corresponds to the following parameters: $a = 10.0206(4)$ Å, $b = 3.15268(9)$ Å, $c = 10.0535(4)$ Å, and $\beta = 90.113(3)°$. The Rietveld atomic structure refinement made in the $I2/m$ space group yielded a reliability factor of $R_{wp} = 17.0$ and $\chi^2 = 1.19$. The structure corresponds to a slight distortion of the well-known hollandite-type structure, with a mean Ir–O distance of 2.03 Å, a value intermediary between that found for Ir(III) and Ir(IV), in agreement with partially reduced iridium in K_xIrO_2. © 1995 Academic Press, Inc.

INTRODUCTION

In a previous paper (1) we reported the preparation of a pure rutile-type IrO_2 compound whereas "commercial IrO_2" has been shown to be either an iridium oxychloride ($Ir^{III}_{0.14} Ir^{IV}_{0.86}O_{1.86}Cl_{0.14}$) or a mixture of pure IrO_2 with another oxychloride phase. The occurrence of the oxychloride phase in the commercial product was attributed to the industrial synthesis process where IrO_2 is prepared by the oxidation of $IrCl_3$ by oxygen. The process is apparently unable to eliminate chlorine from the sample, due to the affinity of iridium toward this element. Recently, we patented a new method of synthesis of pure iridium oxide through a soft chemistry process (2).

Using this pure rutile-type IrO_2 as starting material, the synthesis of a pure hollandite-type K_xIrO_2 was attempted with the aim of removing the potassium ions from the structure and of testing the electrochromic characteristics of the product versus proton or lithium intercalation. This article thus presents the successful synthesis and structural determination of a K_xIrO_2 compound with a hollandite structure.

EXPERIMENTAL

1. Synthesis

Several attempts were made to prepare a hollandite-type K_xIrO_2 phase using commercial IrO_2 and K_2CO_3 as

starting materials. By heating these two phases, with a K/Ir ratio of 0.25, we were able to obtain a pure phase. Only when the reaction was performed using potassium carbonate and chlorine-free IrO_2 powder (2) was a pure hollandite-type phase obtained.

The well-crystallized hollandite-type K_xIrO_2 material was thus prepared by the reaction of pure ground rutile-like IrO_2 and K_2CO_3 powders in the above ratio in a platinum crucible. The powders were heated using a torch to initiate the reaction. At this stage, the X-ray powder diffraction diagrams showed peaks which could be assigned to the new oxide. The material was then placed in a furnace at 1000°C for 1 h. Analysis of the potassium content of the obtained compound gave the formulation $K_{0.21}IrO_2$. Rietveld structure refinement led to the somewhat different composition $K_{0.25}IrO_2$, but the refinement of the light potassium atom in front of the very heavy iridium atom makes accurate alkali metal determination difficult. As a precaution, the general formulation K_xIrO_2 will be used throughout the text.

The phase macroscopic aspect observed through scanning electron microscopy (SEM) showed a fibrous aspect, as seen in Figs. 1 and 2, with a very good homogeneity. Most of the very thin fibers of the phase had thickness of about 0.2 μm, whereas their lengths span from 5–10 μm to more than 100 μm.

2. X-Ray Diffraction

Powder diffraction diagrams were recorded in a Debye–Scherrer geometry on an INEL CPS 120 position sensitive detector with a 2θ range of 0–120° (CuKα1 radiation and $Na_2Ca_3Al_2F_{14}$ as standard (3)). This geometry was used in spite of strong adsorption because of the scarcity of Ir and the small amount of phase available. However, a previous study of other adsorbing compounds (4), has shown that this procedure can work if a thin capillary and/or a dispersion of the phase is used.

After being ground and sieved to 10 μm, the powder was glued around a 0.1-mm Lindemann capillary in order to minimize the strong iridium adsorption. Due to the small amount of material around the capillary, the acquisition time was about 12 hr at 40 kV and 25 mA.
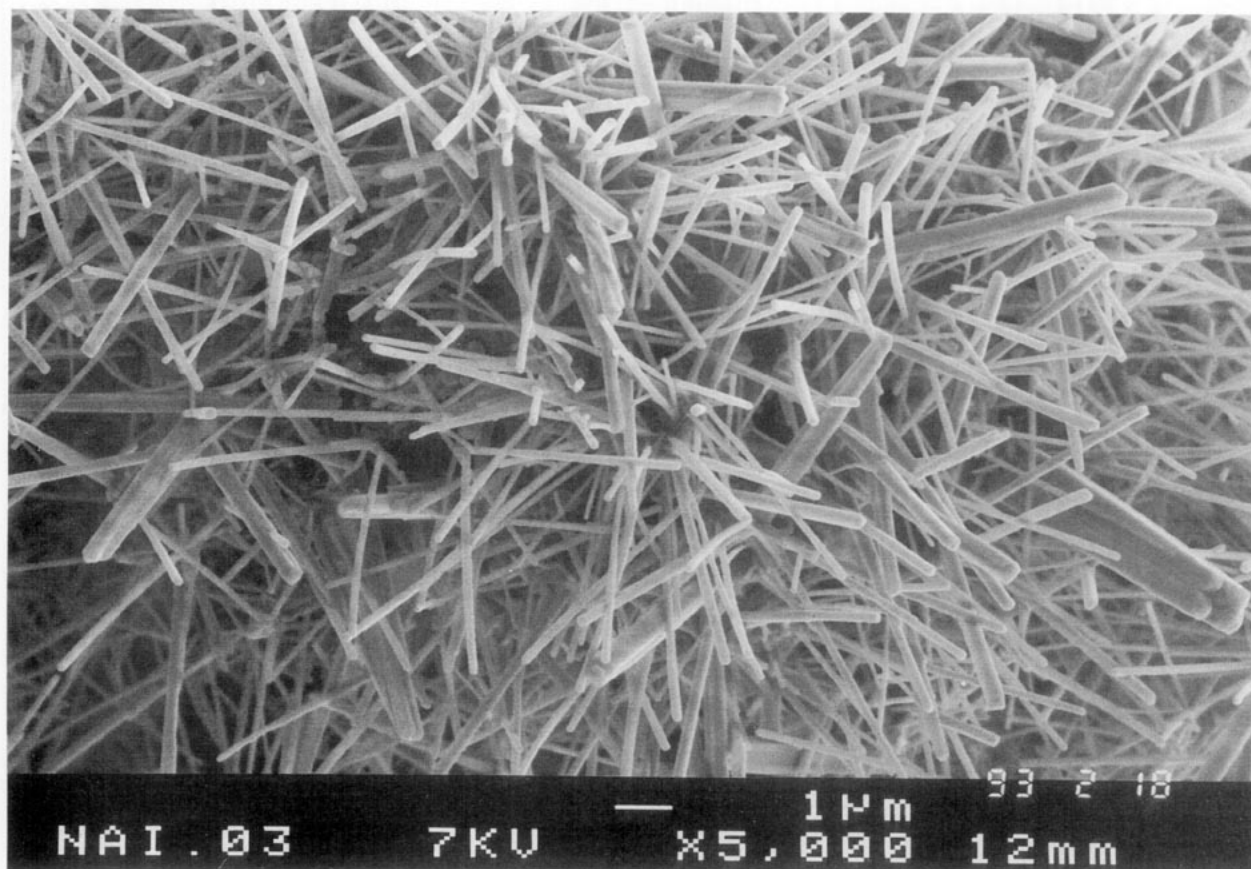
FIG. 1. SEM photograph of K_xIrO_2 (scale given at the bottom of the photograph), showing the fibrous aspect of the compound. The crystallite dimensions range from approximately 5–10 μm to more than 100 μm.

Intereticular distances were determined by the PRO-LIX program (4) (pattern decomposition program and profile refinement code). Using these distances as input for the U-FIT program (4) allowed the refinement of cell parameters, based on a mean-squares algorithm. The structural determination was carried out from a Rietveld refinement code (Fullprof) (5), using a preliminary step of full pattern matching calculations.

REFINEMENT RESULTS

1. Profile Refinement

The compound powder X-ray diffraction diagrams showed well-defined reflection peaks, indicative of a good crystallization state (Fig. 3) with mean widths at half-maximum ranging from 0.14° to 0.24° in 2θ. Since the space group generally encountered for the hollandite-type phase is $I4/m$, the least-squares parameters refinement was carried out from a pattern decomposition diagram (Prolix (3)) in the I-centered tetragonal symmetry. However, in that case eight reflections remained unaccounted

for. The following cell parameters were obtained: $a = b = 10.03(2)$ Å and $c = 3.152(6)$ Å, with rather high estimated standard deviations (e.s.d.'s).

Some hollandite phases present a small distortion that lowers the symmetry from tetragonal to monoclinic. This distortion corresponds to the transformation of the fourfold axis into a twofold axis. The symmetry then becomes $I2/m$, with an angle b close to or nonsignificantly different from 90° (7–10). The refinement of the parameters using the Fullprof program (5) in this symmetry proved much better, yielding the following parameters: $a = 10.0206(4)$ Å, $b = 3.15268(9)$ Å, $c = 10.0535(4)$ Å, and $\beta = 90.113(3)°$. The β angle did shift significantly from 90°; all the reflections were indexed, except for two weak lines, one of which ($I/I_0 = 2$, the more intense line) corresponds to the $I/I_0 = 100$ line of iridium metal. Table 1 shows indexed reflections for the first half of the X-ray diffraction diagram.

A subsequent Rietveld refinement (see below) yielded parameters identical, within error, to those shown above. The results gave small differences between observed and calculated data (Fig. 3). Also, to evaluate the influence of
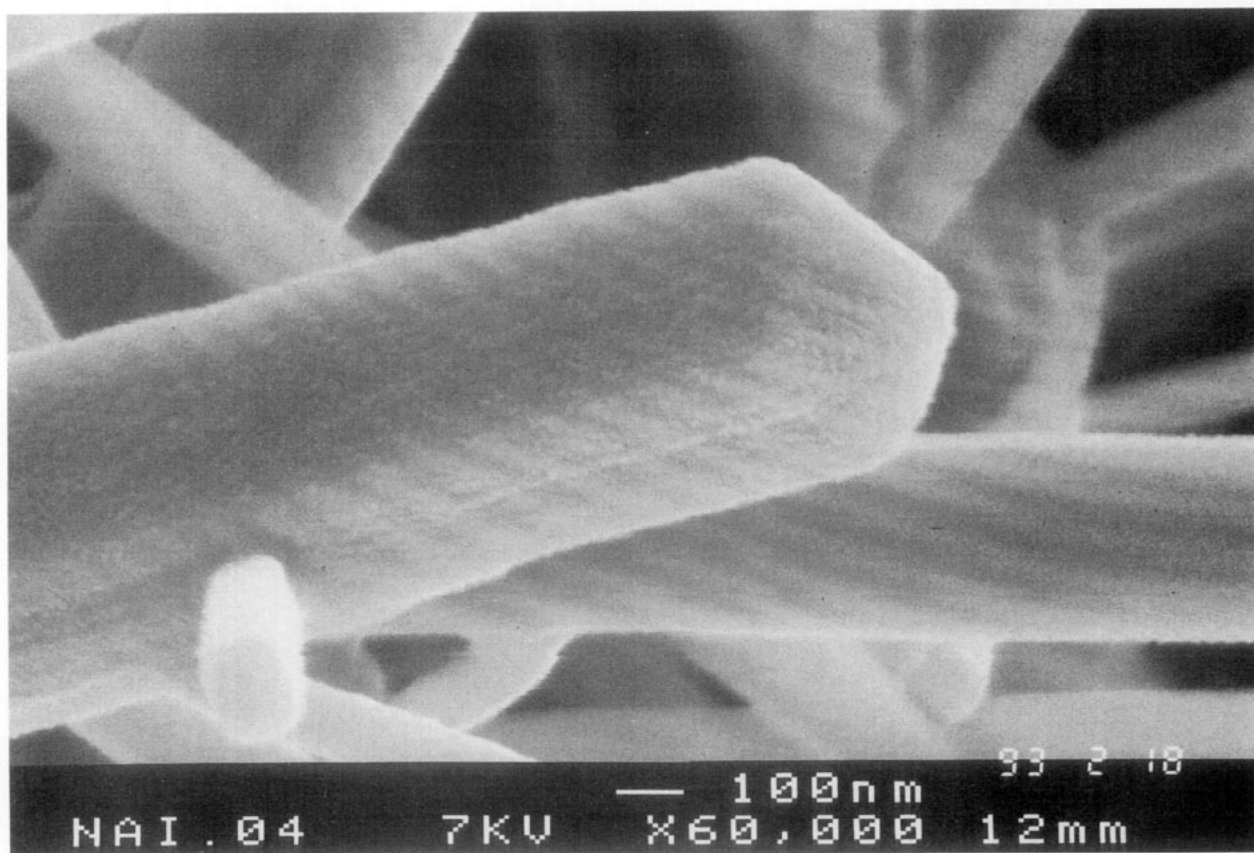
FIG. 2. SEM photograph of K_xIrO_2 (scale given at the bottom of the photograph), showing the fibrous aspect of the compound. The crystallite dimensions range approximately from 5–10 μm to more than 100 μm.

potassium, calculations were carried out with and without this cation. Figure 4 shows the rather strong influence of potassium, particularly at low θ.

From all these calculations, there is clearly a meaningful difference of about 0.03 Å between the a and c parame-

FIG. 3. Rietveld refinement data of K_xIrO_2 from a diagram recorded on an INEL CPS 120 with a Debye–Scherrer geometry. Above, calculated ($\cdots$) and observed (—) lines, the difference function is reported at the bottom.

ters, indicative of at least an orthorhombic distortion for the K_xIrO_2 structure. The structure of hollandite-type usually shows a monoclinic distortion, because in fact $I2/m$ is a relevant subgroup of $I4/m$. The refinement of the new hollandite was thus carried out in the space group $I2/m$.

2. Structure Refinement

The structural refinement was performed with the Rietveld program. The procedure was carried out according to the following procedure:

(a) The atomic positions were chosen from those usually encountered in the hollandite structures and derived from the $I4/m$ symmetry (O and Ir in $4i$ and K in $2a$; see Table 2.

(b) The isotropic atomic displacement parameters (ADP) of the oxygen atoms were fixed at 0.8 Å^2, a value generally found for this type of material. This was done because of the very light diffraction weight of oxygen ($Z = 8$) as compared to that of iridium ($Z = 77$), and because of the difficulty in stabilizing the least-squares calculations when the oxygen ADP refinement was introduced. In addition, a soft constraint was applied to the Ir–O distance to maintain the bond length above 2 Å, within an estimated standard deviation of 0.05 Å.

TABLE 1

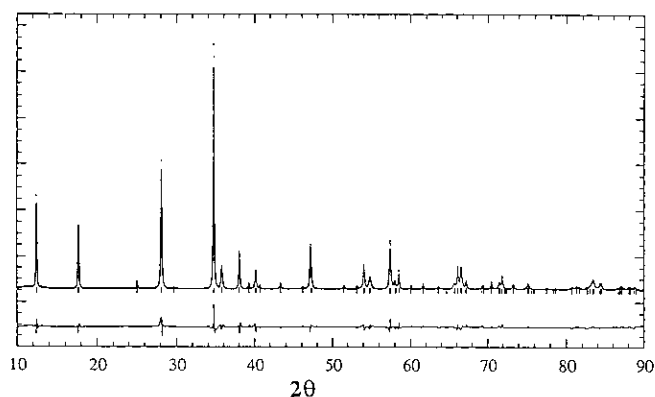X-Ray Powder Diagram of K_xIrO_2 Least-Squared Refined from Fullprof in the Monoclinic Symmetry
($a = 10.0206(4)$ Å, $b = 3.15268(9)$ Å, $c = 10.0535(4)$ Å, and $\beta = 90.113(3)°$)

h	k	l	d(Å)	I_{obs}	I_{calc}	h	k	l	d(Å)	I_{obs}	I_{calc}
1	0	−1	7.104	8	8	3	0	−5	1.72416	0	0
1	0	1	7.090	10	10	5	0	−3	1.72150	11	16
0	0	2	5.026	12	14	3	0	5	1.72116	4	6
2	0	0	5.010	14	16	5	0	3	1.71852	0	0
2	0	−2	3.5521	5	14	0	1	5	1.69526	33	27
2	0	2	3.5451	2	2	3	1	−4	1.69498	2	2
1	0	−3	3.1800	9	8	4	1	−3	1.69388	15	14
1	0	3	3.1762	73	67	3	1	4	1.69270	18	19
3	0	−1	3.1717	62	60	4	1	3	1.69160	1	1
3	0	1	3.1679	18	17	5	1	0	1.69132	9	9
0	1	1	3.0082	0	0	0	0	6	1.67558	50	47
1	1	0	3.0073	1	0	6	0	0	1.67010	61	54
1	1	−2	2.5814	80	80	2	1	−5	1.60664	26	28
1	1	2	2.5801	22	22	2	1	5	1.60502	49	50
2	1	−1	2.5797	24	24	5	1	−2	1.60382	44	42
2	1	1	2.5780	64	65	5	1	2	1.60221	49	47
0	0	4	2.5133	28	30	2	0	−6	1.59002	30	23
4	0	0	2.5051	31	31	2	0	6	1.58813	5	4
3	0	−3	2.36808	34	35	6	0	−2	1.58585	0	0
3	0	−3	2.36342	47	45	6	0	2	1.58398	14	14
0	1	3	2.29625	4	3	0	2	0	1.57634	98	104
3	1	0	2.29271	2	1	1	2	−1	1.53891	3	4
2	0	−4	2.24833	31	27	1	2	1	1.53877	4	5
2	0	4	2.24478	3	3	0	2	2	1.50412	6	7
4	0	−2	2.24391	2	2	2	2	0	1.50367	7	9
4	0	2	2.24038	18	16	1	1	−6	1.46409	6	8
1	1	1	2.21651	0	0	1	1	6	1.46335	1	2
2	1	−3	2.08853	2	2	6	1	−1	1.46053	1	1
3	1	−2	2.08705	0	0	6	1	1	1.45980	5	5
2	1	3	2.08639	2	3	2	2	−2	1.44084	2	3
3	1	2	2.08492	4	4	2	2	2	1.44037	1	1
1	0	−5	1.97215	1	1	1	0	−7	1.42208	6	4
1	0	5	1.97065	3	4	1	0	7	1.42129	41	28
5	0	−1	1.96619	5	7	5	0	−5	1.42085	2	1
5	0	1	1.96471	1	2	5	0	5	1.41805	2	2
1	1	−4	1.92910	23	24	7	0	−1	1.41761	20	15
1	1	4	1.92798	17	18	7	0	1	1.41683	0	0
4	1	−1	1.92561	33	34	1	2	−3	1.41234	5	5
4	1	1	1.92449	23	23	1	2	3	1.41201	43	41
2	0	0	1.91956	0	0	3	2	−1	1.41161	38	36
4	0	−4	1.77606	3	3	3	2	1	1.41128	11	11
4	0	4	1.77256	12	18	4	1	−5	1.40509	43	42

Note. Only two weak lines could not be assigned to the phase. One of them corresponds well to iridium metal.

(c) The occupation ratio of the potassium site was introduced at the elemental analytical value of 0.21 and refined along with the ADP, which was refined isotropically. The occupancy ratio then set up at around 1.0 and was subsequently fixed at this value, which corresponds to full occupancy of the $2a$ site.

(d) Both iridium site ADPs were refined anisotropically and constrained to be equal to each other.

The refinement was then conducted to a reliability factor of $R_{wp} = 17.0$ and $\chi^2 = 1.19$. Figure 3 depicts the observed and calculated diagrams and the difference function. The atomic refined positions and anisotropic factors of Ir are gathered in Table 2. Table 3 gives the main atomic distances and angles.

DISCUSSION OF THE STRUCTURE

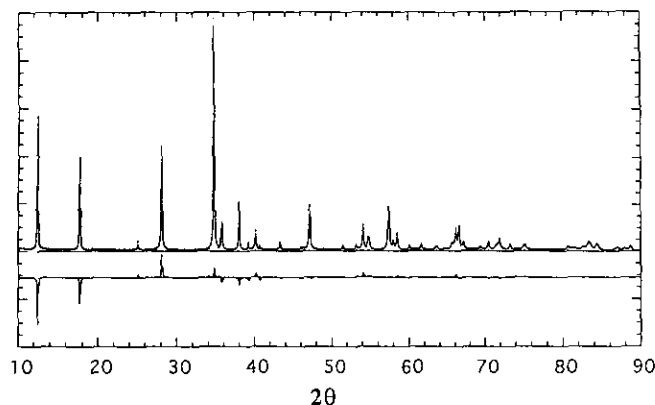Considering the true potassium composition of the hollandite-type phase, the discrepancy between the analyti-

FIG. 4. Simulated X-ray diffraction diagram of K_xIrO_2 with all atoms of the cell (—) and with potassium removed ($\cdots$). Note the rather strong influence of this atom at low θ, considering its relative weak contribution.

TABLE 3

Distances (Å)		Angles (°)	
Ir1–O3	1.99(3)	O1–Ir1–O1	88.4(9)
Ir1–O1	2.12(3)	O1–Ir1–O4	95.3(9)
Ir1–O1	2.08(2) × 2	O1–Ir1–O1	98.6(9)
Ir1–O4	2.07(2) × 2	O3–Ir1–O1	85.1(9)
Ir2–O4	1.80(3)	O3–Ir1–O4	80.9(8)
Ir2–O2	1.95(2) × 2	O4–Ir1–O4	99.2(9)
Ir2–O3	2.04(2) × 2	O2–Ir2–O2	78.7(9)
Ir2–O2	2.18(3)	O2–Ir2–O3	83.8(9)
		O3–Ir2–O3	100.08(9)
d_{mean}Ir1–O: 2.07(3) Å		O2–Ir2–O2	108(1)
d_{mean}Ir2–O: 1.99(3) Å		O4–Ir2–O2	98.7(9)
		O4–Ir2–O3	99.1(9)

Note. The mean Ir–O distances are calculated at $d_{Ir1-O} = 2.07$ Å and at $d_{Ir2-O} = 1.99$ Å for the two iridium sites, in agreement with reduced and unreduced cations.

cal and X-ray analysis data may be attributed to the occurrence of the iridium impurity that lowers the observed analytical K/Ir ratio of the sample. Considering the sizable influence of potassium to the diffraction diagram (see above), the occupancy ratio refinement may be considered fairly meaningful and the phase may be stoichiometric with the $K_{0.25}IrO_2$ composition.

From the crystal structure viewpoint, the structure is built up from IrO_6 octahedra sharing edges and corners to form a double chain along the b axis, as expected for a hollandite phase. The mean Ir–O distance is observed at $d = 2.03$ Å, between the distance calculated for Ir(III) ($d_{Ir-O} = 2.09$ Å) and that for Ir(IV) ($d_{Ir-O} = 1.99$ from (11)). It is of interest to note that one iridium atom (Ir1) presents an Ir–O mean distance of 2.07 Å, whereas the second one, (Ir2), shows the same distance at 1.99 Å. This is to be compared with the only Ir–O distance of

1.97 Å found in pure IrO_2 (1), corresponding to a unique oxydation state of IV. It is indeed tempting to attribute the first iridium site to the reduced iridium ion in K_xIrO_2 and the second site to the unreduced one, in agreement with the occurrence of a monoclinic distortion. However, the accuracy of the refinement data does not allow this conclusion to be made unambiguously. Also, since the reduced site does not correspond to a complete reduction of Ir(IV) into Ir(III), one may wonder whether a superstructure with an ordering cannot occur in the phase. The powder diffraction diagram of the phase does not allow one to answer this question, which could have confirmed the interpretation concerning the reduced site.

CONCLUSION

The newly synthesized K_xIrO_2 phase is of the hollandite type with a monoclinic distortion. It could only be pre-

TABLE 2
Atomic Parameters of the Rietveld Refinement for K_xIrO_2

Position	Atom	x	y	z	U_{eq} (Å^2 × 100)	Occupancy
4i	Ir1	0.3514(5)	0	0.1726(4)	0.58(5)	1
4i	Ir2	0.8311(5)	0	0.3621(4)	0.59(5)	1
4i	O1	0.141(3)	0	0.193(5)	1	1
4i	O2	0.782(3)	0	0.151(3)	1	1
4i	O3	0.549(3)	0	0.188(4)	1	1
4i	O4	0.857(4)	0	0.539(3)	1	1
2a	K	0	0	0	0.2(5)	1

Atom	U_{11} (Å^2 × 100)	U_{22} (Å^2 × 100)	U_{33} (Å^2 × 100)	U_{13} (Å^2 × 100)
Ir1	3.8(2)	1.9(1)	3.3(2)	−0.7(2)
Ir2	3.8(2)	1.9(1)	3.3(2)	−0.7(2)

Note. The potassium site was found to be fully occupied, corresponding to $x = 0.25$, whereas the analytical value yielded $x = 0.21$.

pared from pure IrO$_2$, not available on the market but obtainable through soft chemistry synthesis (patent pending (2)). The value of x was found in the vicinity of 0.25, with the analytical value being 0.21 and the Rietveld refined occupancy ratio yielding precisely 0.25. The two types of sites in the structure may agree with the model of unreduced and reduced iridium ions and may explain the monoclinic distortion of the phase.

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