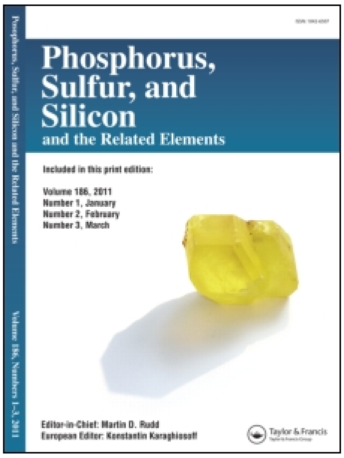

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A Low-Temperature Route for ReP_2O_7 Synthesis

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A low-temperature route for the synthesis of the Re(IV) diphosphate starting from ReO_4^- *is presented. The* ReP_2O_7 *polycrystals have been prepared in 63% yield by an interaction of* NH_4ReO_4 *with molten phosphoric acid at 673 K with subsequent cooling down to 298 K. The synthesized* ReP_2O_7 *was characterized by X-ray powder diffraction (XRPD) and DRIFT spectroscopy.*

Keywords Chemical synthesis; DRIFT spectroscopy; molten phosphoric acid; rhenium diphosphate; X-ray powder diffraction (XRPD)

INTRODUCTION

Diphosphates $M^{IV}P_2O_7$ and vanadates $M^{IV}V_2O_7$, (M^{IV} = Ti, Zr, Hf, Sn) had attracted much attention due to negative thermal expansion (NTE) registered for representatives of the series.[1] The anomalous thermal expansion of $M^{IV}P_2O_7$ is related to the flexibility of structural units of this framework built of vertex-sharing MO_6 octahedra and diphosphate groups.[2] The ability to accommodate tetravalent actinides[3–8] and the high stability of $M^{IV}P_2O_7$ make the diphosphates suitable host matrixes for the immobilization of radioactive cations from wastes. Similarities in chemical properties and structures of rhenium and technetium compounds cause interest in rhenium diphosphate.

Routes[9,10] for the preparation of the ReP_2O_7 reported in the literature include two stages: 1) reduction of ReO_4^- to ReO_2 (or Re^{+4}) by NH_2OH or N_2H_4[10]; 2) solid state reaction of ReO_2 with $(NH_4)_2HPO_4$[9]

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or thermal decomposition of $Re(HPO_4)_2$ precipitated from Re(IV) solutions[10].

In addition, solid solutions of ReP_2O_7–ZrP_2O_7 can be synthesized by high temperature sintering of ReO_2, Zr-containing precursors and $(NH_4)_2HPO_4$.[10] According to results of thermal analysis and proton induced X-ray emission (PIXE) studies,[10] the high-temperature treatment is accompanied by rhenium oxidation by air oxygen and by Re_2O_7 and P_4O_{10} effusion at $T = 903 - 1173$ K.

The present work is devoted to the elaboration of a convenient low-temperature route for the preparation of ReP_2O_7 from perrhenate solutions and to the examination of ReP_2O_7 by means of XRPD and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy.

EXPERIMENTAL

Synthesis

Rhenium(IV) diphosphate was synthesized from the appropriate amount of NH_4ReO_4 (prepared by the method reported by G. Brauer[11]), which was dissolved in 85% H_3PO_4 (Fluka) (Re:P ratio 1:2) at 673 K. The mixture was homogenized by mechanical stirring during 3–5 h. The obtained maroon solution containing reduction products of ammonium perrhenate was cooled to room temperature at a rate of ~2 K/h. The microcrystals of ReP_2O_7 were leached with hot distilled water and subsequently dried at 427 K in a Heraeus drying oven with subsequent annealing in vacuum at 773 K. The product was isolated as microcrystalline powder with a yield of 63%.

Analysis

The Re and P content was determined by energy dispersive X-ray analysis using analytical spectral lines (Re:Mα and P:Kα). The results are consistent with the stoichiometry ReP_2O_7 (Found: Re, 51.69; P, 17.19; Calcd.: Re, 51.70; P, 17.20%).

The resulting product was identified by X-ray diffraction, using a DRON-3 diffractometer (Ni-filtered CuKα radiation) with silicon powder applied as internal standard. The structural parameters and interatomic distances were obtained by Rietveld refinement of the diffraction pattern observed at 298 K in the angular range ($15^\circ < 2\theta < 120^\circ$). An 8 s counting time with step of 0.03° sample rotation was used for diffraction measurements. The refinement procedure was similar to the one reported.[12]

The DRIFT spectrum was recorded on a Nicolette 320X spectrometer in the region 400–4000 cm^{-1}. The spectral resolution was typically 4 cm^{-1}. The DRIFT spectrum was recorded from ReP_2O_7 powder pressed between parallel KBr plates.

RESULTS AND DISCUSSION

Advantages of the elaborated synthetic route are the high yield of ReP_2O_7 and the significantly lower temperature of synthesis, which enables to avoid the rhenium oxidation by air oxygen and the evaporation of the constituents. The XRPD pattern of the ReP_2O_7 prepared is represented in Figure 1. Indexing of the powder diffraction pattern led to cubic symmetry. A least-square refinement of the unit cell led to the data listed in Table I.

The lattice parameter of the ReP_2O_7 obtained (7.8790(7) Å) is smaller than those described for Zr[13] and for actinides,[3–7] and those reported earlier: 7.94 ± 0.02 Å[9] and 7.906 Å.[10] The space group P$a\,\bar{3}$ with $a \approx 8$ Å (Z = 4) is characteristic for high temperature $M^{IV}P_2O_7$ polymorphs while the low temperature phases exhibit $3a$ superstructure[13] or orthorhombic distortion,[14] while intermediate phases are incommensurate.[15] Very weak and diffuse peaks observed in the XRPD pattern are in agreement with the existence of the $3a$ superstructure first reported by E. Banks et al.[9] while no evident superstructure reflections were found for the ReP_2O_7 described by K. Popa et al.[10]

The crystal structures of $M^{IV}P_2O_7$ are rather complex at low and medium temperatures; exact structure determination is laborious and requires large amounts of precise XRPD data. Therefore, only preliminary refinement of average crystal structure omitting superstructural reflections has been performed at this stage of the ReP_2O_7 study. The XRPD data were refined in the Pa$\bar{3}$ space group with Z = 4, the initial position parameters of each atom in ReP_2O_7 were estimated to be equal to those reported for the cubic phase of MoP_2O_7.[16] The comparison of the observed and calculated XRPD plot intensities shows a good agreement with the proposed structure model (Figure 1). The results of the refinement procedure are listed in Table II. Selected interatomic distances and angles for ReP_2O_7: d(Re–O(2)) = 1.903(10) Å × 6, d(P—O(1)) = 1.432(6) Å, d(P—O(2)) = 1.426(12) Å × 3 with ∠O(2)–Re–O(2) = 89.7(4)°× 6 and 90.3(4)°× 6, ∠O(1)–P—O(1) = 115.1(3)°× 3, ∠O(1)–P—O(2) = 103.0(4)°× 3.

In the structures of cubic $M^{IV}P_2O_7$ with $a \approx 8$ Å the bridging oxygen atom of the diphosphate group is located on an inversion centre; therefore the P—O—P angle is equal to 180°, which is energetically

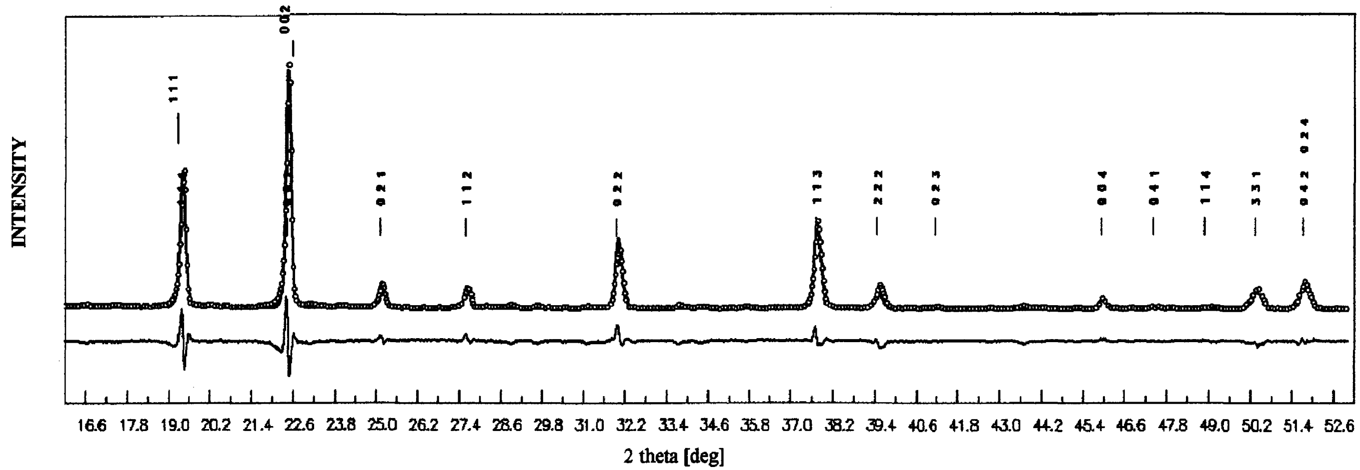

FIGURE 1 The part of Rietveld plot of the Cu Kα X-ray diffraction powder patterns for cubic ReP_2O_7.

TABLE I XRPD Data Obtained for ReP_2O_7. Cubic: a = 7.8790(7) Å. Rad. Ni-filtered CuKα

M*	2θ	I_{obs}	I_{calc}	h	k	1	M	2θ	I_{obs}	I_{calc}	h	k	1	M	2θ	I_{obs}	I_{calc}	h	k	1	M	2θ	I_{obs}	I_{calc}	h	k	1
1	19.50	643	644	1	1	1	1	69.51	1	0	3	3	4	1	90.75	1	1	0	2	7	1	108.60	11	0	1	8	2
1	22.55	1000	999	0	0	2	2	70.67	92	41	1	5	3	1	91.84	1	0	5	5	2	1	109.76	1	0	3	5	6
1	25.25	117	131	0	2	1	0	70.67	0	46	1	3	5	1	91.84	1	0	1	2	7	1	109.76	1	1	3	6	5
1	27.71	100	126	1	1	2	2	71.83	72	5	0	0	6	1	91.84	1	0	3	3	6	2	112.10	27	13	0	6	6
1	32.10	366	399	0	2	2	0	71.83	0	73	4	4	2	1	91.84	1	3	1	7	2	0	112.10	0	23	2	2	8
1	34.11	1	4	2	2	1	1	72.98	1	0	0	6	1	0	94.04	51	27	2	6	4	1	113.29	1	1	0	8	3
1	37.84	515	501	1	1	3	3	74.12	6	0	1	1	6	1	94.04	0	22	2	4	6	1	113.29	11	0	6	6	1
1	39.59	139	103	2	2	2	0	74.12	0	0	2	3	5	1	95.14	1	1	2	2	7	1	114.49	1	0	3	4	7
1	41.28	14	17	0	2	3	0	74.12	0	6	2	5	3	1	95.14	1	0	4	4	5	1	114.49	1	0	1	3	8
2	42.91	6	3	1	3	2	2	76.38	36	22	0	2	6	3	97.34	62	22	5	5	3	1	114.49	1	0	3	7	4
0	42.91	0	0	1	2	3	0	76.38	0	18	0	6	2	0	97.34	0	16	1	7	3	1	114.49	1	0	1	8	3
1	46.04	57	68	0	0	4	1	77.51	1	0	4	4	3	0	97.34	0	16	1	3	7	3	115.69	38	11	1	5	7
2	47.54	18	17	0	4	1	1	77.51	1	1	0	4	5	1	99.55	1	0	3	6	4	0	115.69	0	8	5	5	5
0	47.54	0	4	2	2	3	1	77.51	1	2	1	6	2	1	99.55	1	1	3	4	6	0	115.69	0	12	1	7	5
1	49.01	13	15	1	1	4	1	77.51	1	0	1	2	6	1	99.55	1	0	0	6	5	1	116.92	16	18	6	6	2
1	50.44	149	143	3	3	1	1	78.63	1	1	1	5	4	1	100.67	1	0	2	3	7	1	118.15	11	0	2	8	3
2	51.85	235	106	0	4	2	1	78.63	1	1	1	4	5	1	100.67	1	0	1	6	5	1	118.15	11	0	4	6	5
0	51.85	0	132	0	2	4	1	79.74	40	38	3	3	5	1	100.67	1	0	1	5	6	1	118.15	1	1	2	3	8
2	53.23	4	5	1	4	2	1	80.85	40	43	2	2	6	1	100.67	1	0	2	7	3	1	118.15	1	0	4	5	6
0	53.23	0	2	1	2	4	3	81.96	2	0	2	4	5	1	102.90	7	5	0	0	8	1	119.40	1	2	2	5	7
1	54.59	3	4	3	3	2	0	81.96	0	2	0	6	3	1	104.03	1	0	2	6	5	1	119.40	1	0	2	7	5
1	57.23	153	166	2	2	4	0	81.96	0	1	2	5	4	1	104.03	1	0	0	4	7	2	121.95	10	5	0	4	8
1	58.52	1	3	0	4	3	2	83.07	3	0	1	6	3	1	104.03	1	0	2	5	6	0	121.95	10	4	0	8	4
1	59.80	1	1	1	4	3	0	83.07	0	4	1	3	6	1	104.03	1	0	0	8	1	1	123.25	1	0	1	4	8
1	59.80	1	0	1	3	4	1	55.27	2	6	4	4	4	1	105.16	I	0	5	5	4	1	123.25	1	1	6	6	3
2	61.06	213	209	3	3	3	1	86.37	1	2	2	6	3	1	105.16	1	0	1	7	4	1	133.25	1	1	4	4	7
0	61.06	0	151	1	1	5	1	86.37	1	1	2	3	6	1	105.16	1	0	1	1	8	1	123.25	1	0	1	8	4
3	63.53	3	3	2	3	4	1	87.46	1	0	3	5	4	1	105.16	1	0	1	4	7	1	124.57	1	0	3	3	8
0	63.53	0	1	2	4	3	1	87.46	1	2	3	4	5	1	106.50	12	15	3	3	7	3	125.91	27	13	3	7	5
0	63.53	0	0	0	2	5	2	88.56	38	10	5	5	1	3	107.44	33	11	0	2	8	0	125.91	0	11	3	5	7
2	64.75	2	4	1	2	6	0	88.56	0	18	1	1	7	0	107.44	0	11	4	4	6	0	125.91	0	9	1	1	9
0	64.75	0	0	1	5	2	2	89.65	25	18	0	6	4	0	107.44	0	10	0	8	2	2	127.27	20	13	2	8	4
1	67.15	52	67	0	4	4	0	89.65	0	17	0	4	6	1	108.60	1	0	1	2	8	0	127.27	0	12	2	4	8
2	68.33	1	1	2	2	5	1	90.75	1	1	1	4	6	1	108.60	1	0	2	4	7	1	128.66	1	0	0	2	9
0	68.33	0	0	4	4	1	1	90.75	1	1	1	6	4	1	108.60	1	2	2	7	4	0						

M* is the multiplicity.

TABLE II Crystallographic Data for ReP_2O_7 (MoP_2O_7 Type Structure)

Space group	$Pa\bar{3}$
Lattice constant, a(Å)	7.8790(7)
Unit cell volume (Å^3)	489.114
Calculated density for $Z = 4$ ($g \cdot cm^{-3}$)	4.890
Independent reflections	139
Reliability factors R_{wp}, R_{0^*F}	0.0667, 0.0810
Specimen thickness (μm)	100.00
Linear absorption coefficient (cm^{-1})	532.40

Atomic parameters

Atom	Site	x/a	y/b	z/c	B(Å^2)
Re	4(a)	0.000(0)	0.000(0)	0.000(0)	2.00(5)
P(1)	8(c)	0.3951(8)	0.3951(8)	0.3951(8)	2.00(5)
O(1)	4(b)	0.5000(0)	0.5000(0)	0.5000(0)	4.20(1)
O(2)	24(d)	0.2278(11)	0.0628(26)	0.9498(26)	4.20(1)

unfavorable. The only exception is the structure of cubic UP_2O_7[17] ($a = 8.6311(2)$ Å), where the bridging oxygen atom is refined as located in a general position displaced from the inversion centre (with 1/6 occupancy). In the low temperature, phases with $3a$ superstructure 8/9 of the bridging oxygen atoms are displaced from the inversion center. The most recent refinement of the ZrP_2O_7 structure[14] led to the conclusion that this compound is orthorhombic at 298 K and does not contain linear diphosphate groups; average P—O—P angle is 146°.

The P—O distances in the structure of ReP_2O_7 are estimated to be rather regular, although usually for these diphosphates the P—O (bridging) distances are noticeably longer than P—O (terminal): 1.56–1.60 Å and 1.47–1.51 Å, respectively.[18] There are two ways to explain the shortening of the P—O (bridging) distances with increasing P—O—P angle: 1) a change of hybridization of the bridging oxygen atom and increase of π-bonding within the P—O (bridging) bond; and 2) deviation of the bridging oxygen atom from the average location at the inversion centre (dynamic or static).[1,2]

An alternative method for the estimation of the P—O—P angle is provided by the examination of the corresponding vibrational bands in the spectra.[19–21] The DRIFT spectrum of the ReP_2O_7 is shown in Figure 2. The bands observed in the range of 3800–2700 and 1700–1600 cm^{-1} have been attributed to the OH and H_2O vibrations. The bands located between 1250 and 400 cm^{-1} have been assigned to the

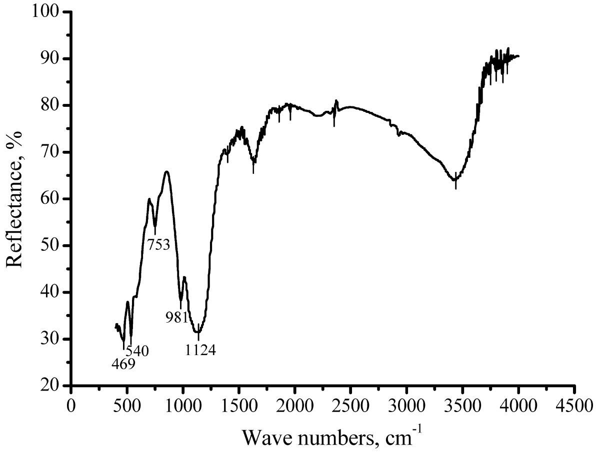

FIGURE 2 DRIFT spectrum of cubic ReP_2O_7.

$P_2O_7^{4-}$ modes; the vibrations of Re–O bonds (located 400 cm^{-1}) are not observed in the spectrum recorded here.[22,23] The adsorption bands located at 469 cm^{-1}, 540 cm^{-1}, 753 cm^{-1}, 981 cm^{-1} and 1124 cm^{-1} are assigned to $\delta_s(PO_3)$, $\delta_{as}(PO_3)$, ν_s(P—O—P), ν_{as}(P—O—P), and the sum of $\nu_s(PO_3)$ and $\nu_{as}(PO_3)$ vibrations, respectively. An estimation of the P—O—P angle based on an empirical factor Δ[19] and a correlation table[20] according to the equation reported in.[19]

$$100\Delta = (\nu_{as}(\text{P—O—P}) - \nu_s(\text{P—O—P}))/(\nu_{as}(\text{P—O—P}) + \nu_s(\text{P—O—P})), \quad (1)$$

where ν_{as}(P—O—P) and ν_s(P—O—P) are the P—O—P vibration frequencies, led to a value for the P—O—P angle of about 141° to be compared to 146° obtained from XRPD data in Birkedal et al.,[14] which corresponds to a normal P—O (bridging) distance of about 1.52 Å.

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