Journal of Alloys and Compounds, 203 (1994) 289–295
JALCOM 896

Structural studies of Li_5ReO_6, Li_4NpO_5 and Li_5NpO_6 by neutron and X-ray powder diffraction

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(Received July 19, 1993)

Abstract

This paper reports on the preparation of Li_5ReO_6, Li_4NpO_5 and Li_5NpO_6 by solid-state reactions, the results of X-ray and neutron powder diffraction measurements on all three compounds, and the determination of the structures of Li_5ReO_6 and Li_4NpO_5 from the neutron data. The neutron powder diffraction refinement for Li_5ReO_6 confirms a recent single-crystal X-ray diffraction study: monoclinic, space group *C2/m*. This structure is retained by Li_5ReO_6 between 298 K and 10 K. The neutron powder diffraction refinement for Li_4NpO_5 confirms earlier X-ray powder diffraction results: tetragonal, space group *I4/m*, $a = 6.698$ Å, $c = 4.415$ Å. The lithium and oxygen positional parameters of Li_4NpO_5 have been refined: coordination about Np is an extended octahedron, with each Np ion surrounded equatorially by four oxygen ions at 2.00 Å and axially by two oxygen ions at 2.21 Å. Li_5NpO_6 shows an X-ray powder pattern consistent with the original report, but the neutron diffraction data set could not be refined in terms of the originally proposed space group or any other plausible model structure.

1. Introduction

Complex oxides of alkali metals with f elements are of great interest because of their bonding and electronic properties. The first syntheses of lithium uranates (VI) [1] and other lithium oxometallates [2] provided evidence that it should be possible to synthesize lithium oxometallates with transuranium ions in high oxidation states. Keller and coworkers pioneered the syntheses and structural characterization of alkali metal oxoneptunates, oxoplutonates and oxoamericiates [3, 4]. The synthesis of Li_5NpO_6, reported in 1969 as the first crystalline Np (VII) compound [5], epitomized the potential of actinide oxometallates to display the highest actinide oxidation states. Extensive structural studies had been carried out on lithium oxometallates by this time, almost all by X-ray powder diffraction [2–4, 6].

As part of a search for oxyfluorides of Np (VII), we had the opportunity to repeat the synthesis of Li_5NpO_6. The structure of Li_5NpO_6 was described as "$R\bar{3}$?" [5] on the basis of the similarity of its X-ray powder pattern to that of other lithium oxometallates Li_xMO_6 [2, 6]. During the years since the original preparation of Li_5NpO_6, a single-crystal synthesis of Li_5ReO_6 and redetermination of its structure was carried out by Betz and Hoppe [7]. They found it to be monoclinic rather than hexagonal, as had earlier been reported on the basis of X-ray powder diffraction [8]. The monoclinic structure of Li_5ReO_6 casts doubt upon the assignment of space group $R\bar{3}$ to Li_5NpO_6. Synthesis conditions as well as safety requirements made it impractical to attempt to prepare single crystals of Li_5NpO_6. We therefore synthesized a sufficiently large polycrystalline sample of this compound to collect a neutron powder diffraction data set in order to establish its structure. For completeness we synthesized Li_5ReO_6 and Li_4NpO_5 as powders on the same scale and carried out parallel powder-diffraction studies.

Among the ternary neptunium oxides synthesized by Keller *et al.* was Li_4NpO_5 [4]. As has been the case for most complex oxides, this was a polycrystalline sample. Its structure was inferred from that of the corresponding uranium oxide Li_4UO_5, the structure of which had been described as tetragonal, space group *I4/m* [9]. The structures of Li_4UO_5 and Na_4UO_5 were the first of complex actinide oxides to be determined by powder X-ray and neutron diffraction [10]; neutron diffraction confirmed the space group and established the oxygen positions for both compounds. The structure, which was confirmed by infrared spectra of both compounds, revealed extended octahedral $UO_4O_{2/2}$ units with square-planar equatorial U–O bonds at 1.99 Å and longer axial U–O bonds. ($O_{2/2}$ refers to the two axial oxygen atoms, each of which is bonded to two uranium atoms). The oxygens at the axial positions are

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SSDI 0925-8388(93)00896-7

shared with identical octahedra above and below. This structure was the first of several to show that complex uranium oxides do not necessarily retain the short U–O bonds of the $[O=U=O]^{2+}$ ion. As part of our project we decided to confirm by neutron powder diffraction that Li_4NpO_5 is isostructural with Li_4UO_5 and that the coordination about neptunium is similar to that about uranium.

Thermochemical studies of many complex oxides of the hexavalent actinides have determined the magnitude of the stabilization effect represented by the solid-state reaction

$$3BaO(s) + MO_3(s) \longrightarrow Ba_3MO_6(s) \quad (1)$$

For M ≡ Np, $\Delta H(1) = -372$ kJ mol^{-1} [11, 12]. These enthalpy effects, and the trends as alkali/alkaline-earth and actinide cations are changed, have been interpreted in terms of (acidic oxide)–(basic oxide) relationships. Very few thermodynamic data are known for lithium oxometallates because they are often synthesized with an excess of lithium oxides. The existence of compounds such as Li_5NpO_6, Li_5PuO_6 and Li_6AmO_6 confirms that acid–base stabilization of high actinide oxidation states by lithium oxide is also effective.

2. Experimental section

We chose to carry out our neptunium oxide syntheses with highly reactive Li_2O_2 and low-fired NpO_2 powder in order to optimize solid-state reactions such as

$$5/2Li_2O_2(s) + NpO_2(s) = Li_5NpO_6(s) + 1/2O_2(g) \quad (2)$$

In order to collect optimum neutron diffraction data sets, lithium-7 is preferred over natural lithium which contains 6% ^{6}Li because ^{6}Li has a very large neutron-absorption cross-section. Lithium-7 was obtained as $^7LiOH \cdot H_2O$ (enriched as 99 at.% ^{7}Li) from ISOTEC, Inc., Miamisburg, Ohio (USA). The $^7LiOH \cdot H_2O$ was converted to $^7Li_2O_2$ by a modification of a published procedure [13]. The product Li_2O_2 was assayed for Li by inductively coupled plasma atomic emission spectroscopy and found 30.5 ± 1.5 mass % *vs.* calculated value of 30.43 mass %.

Li_5ReO_6 was synthesized by thoroughly mixing finely divided Re powder (Aldrich 99.995%) with a stoichiometric amount of Li_2O_2, heating the mixture gradually to 375 °C, regrinding, heating to 600 °C, regrinding, and heating to 725 °C – each time under flowing oxygen in an Al_2O_3 boat. Thermogravimetric analysis confirmed that the product retained constant weight when heated to this temperature, but slowly lost weight above 730 °C. X-ray and neutron diffraction data sets were collected on the golden-yellow product, which was handled in air.

Synthesis of Li_4NpO_5 was begun by grinding by hand for 30 min Li_2O_2 (prepared as above) and reactive (low-fired) NpO_2 (prepared by heating Np (V) oxalate slowly in air to 405 °C) in the mole ratio $Li_2O_2/NpO_2 = 2.1$, in 1 g batches using a mortar within an inert-atmosphere glovebox (water content <1 p.p.m.). The mixture was transferred to an alumina boat and slid into a quartz tube of rectangular cross-section, open at both ends, for safe transport through the glovebox antechamber. This assembly was then inserted horizontally into a quartz reaction vessel outside the glovebox but within a "hood" surrounding the glovebox antechamber. The quartz reaction vessel was equipped with an O-ring seal and inlet and outlet gas fittings through which a continuous flow of dry O_2 was maintained, so that the reaction mixture was exposed to air for less than 1 min during loading. The vessel was heated by a horizontal tube furnace to bring the sample to 700 °C. After 4–20 h heating, the furnace was cooled down, and the sample was returned to the interior of the inert-atmosphere glovebox after pumpdown in the antechamber, reground for 30 min, and reheated. This procedure was repeated until four batches had been prepared. The completeness of reaction to Li_4NpO_5 was verified by powder X-ray diffraction.

After the neutron diffraction data for Li_4NpO_5 had been obtained, the neptunium was recovered by dissolving the sample in dilute aqueous HNO_3, precipitating Np (V) oxalate with excess oxalic acid solution, and centrifuging and washing the precipitate thoroughly to remove lithium. The Np oxalate was reconverted to reactive NpO_2 by slow heating to 405 °C in air. X-ray powder diffraction confirmed that the black product was NpO_2.

Synthesis of Li_5NpO_6 was carried out by a procedure similar to that for Li_4NpO_5, beginning with $^7Li_2O_2$ and reactive NpO_2 in the mole ratio $Li_2O_2/NpO_2 = 3.0$. The ground mixture was heated in O_2 to only 400–410 °C, the temperature recommended by Keller and Seifert, and reground and reheated twice. We confirmed by thermogravimetry that a lower temperature is insufficient to achieve an adequate reaction rate, while a higher temperature, even to 420 °C, leads to significant decomposition to Li_4NpO_5. The completeness of reaction to Li_5NpO_6 was verified by powder X-ray diffraction; it was also determined by placing a weighed amount of the product into a spectrophotometer cuvette within the inert-atmosphere glovebox, which was then removed from the box, and the oxide dissolved in a known volume of 1.0 mol dm^{-3} NaOH(aq), so that its Np (VII) content could be found from the absorption at 618 nm ($\epsilon = 393$ M^{-1} cm^{-1}) [14]. By acidifying the solution within the cuvette and adding $NaNO_2$, all of the Np was reduced to Np (V), which was determined from its absorption at 980 nm ($\epsilon = 403$ M^{-1} cm^{-1})

[15]. In this way 92% of the Np was found to be Np(VII).

X-ray powder diffraction patterns of Li_5ReO_6 were obtained by the Debye–Scherrer method with Ni-filtered Cu radiation at room temperature. After loading and sealing quartz capillaries with Li_4NpO_5 and Li_5NpO_6 in the inert-atmosphere glovebox, X-ray Debye–Scherrer powder diffraction films of these oxides were also obtained at room temperature. For neutron powder diffraction, 3–4 g samples were loaded into thin-walled vanadium cans (double-encapsulated for neptunium compounds) as conventionally used at the General-Purpose Powder Diffractometer (GPPD) at Argonne's Intense Pulsed Neutron Source. As before, Li_4NpO_5 and Li_5NpO_6 were handled only in the inert-atmosphere glovebox. Neutron diffraction data sets were collected for Li_5ReO_6 at 298 K, 100 K and 10 K. Data sets for Li_4NpO_5 and Li_5NpO_6 were collected at 298 K. Diffraction data from $2\Theta = 148°$ detector banks were used for highest resolution and accuracy.

3. Results and discussion

The X-ray and neutron powder diffraction data for Li_5ReO_6 were all indexed in space group *C2/m*. To confirm the structural determination of Betz and Hoppe [7], we refined the 298 K and 10 K neutron powder diffraction data sets in this space group. Final refinements were done with a total of 47 parameters: four unit cell parameters, an overall scale factor, three peak-shape factors, an absorption parameter, five background parameters, seven positional parameters, and 26 anisotropic thermal parameters. Since very weak neutron diffraction peaks of Li_2CO_3 were observed, the unit cell parameters, an overall temperature parameter, and a scale factor for Li_2CO_3 were also refined for this second phase; the scale factors for the two phases indicated that the abundance of Li_2CO_3 was 2 mol.% in Li_5ReO_6. The final weighted profile *R* factor

$$100\left[\frac{\Sigma w(y_{obs}-y_{calc})^2}{\Sigma w(y_{obs})^2}\right]$$

was 5.45% at 298 K and 5.65% at 10 K. The refined parameters are shown in Table 1, and the Rietveld profile plot of the 10 K data appears in Fig. 1.

To confirm the X-ray powder indexing and lattice parameters found by Keller *et al.* [3, 4] for Li_4NpO_5, we refined the data set in space group *I4/m* as chosen by Hoekstra and Siegel [10]: 8 Li in (*h*) *x*, *y*, 0; 2 Np in (*a*) 0, 0, 0; 2 O in (*b*) 0, 0, 1/2; 8 O in (*h*) *x*, *y*, 0. Final refinement was done with 28 parameters: two unit cell parameters, an overall scale factor, three peak-shape factors, an absorption parameter, five background parameters, four positional parameters, and 12 anisotropic thermal parameters. The final weighted profile *R* factor was 5.6% at 298 K. The refined parameters are shown in Table 2, and the Rietveld profile plot appears in Fig. 2. No unindexable peaks were found for Li_4NpO_5. The strongest peaks for Li_5NpO_6 ($d = 2.14$ Å) and NpO_2 ($d = 1.918$ Å) are visible in Fig. 2.

It is of interest to consider how the Np–O coordination in Li_4NpO_5 (Fig. 3) changes from the U–O coordination in Li_4UO_5. To a first approximation one would predict that the bond distances in any Np compound should be slightly smaller than in an isostructural U compound. As is the case in Li_4UO_5, coordination about Np in Li_4NpO_5 is an extended octahedron. It appears from Table 2 that the average bond distance is the same in both compounds, with the octahedron slightly less distorted in Li_4NpO_5 than in Li_4UO_5. Unfortunately, Hoekstra and Siegel [10] did not give uncertainties for any of their results on Li_4UO_5, and they gave insufficient details to permit an assessment of the uncertainties of their positional parameters. Therefore the bond distances in Li_4UO_5 have insufficient precision to permit a meaningful comparison. The Np and O2 temperature factors are nearly isotropic, whereas the O1 thermal ellipsoid is oblate.

We note that a recent X-ray powder diffraction and vibrational spectroscopic study of the structures of β-Na_4UO_5 and β-Na_4NpO_5 has been published [16]. Our results are consistent with this work as well as with the original X-ray powder diffraction studies of these compounds [3, 4, 10]. It is likely that the compounds $(Li, Na)_4(U, Np, Pu, Am)O_5$ are all isostructural. There are also references to a face-centered cubic (f.c.c.) form α-Na_4UO_5 and α-Na_4NpO_5 [1, 17].

Attempts were made to refine the neutron powder diffraction data for Li_5NpO_6 on the basis of several model structures. One model is the trigonal space group $R\bar{3}$ used for the original lattice-parameter refinement of Li_5NpO_6. The model in this space group (as well as in related space groups) has hexagonal-closest-packed layers of oxygens that yield *N* octahedral holes and 2*N* tetrahedral holes for *N* oxygen atoms. The tetrahedral holes are partly filled with Li^+ if compounds such as Li_nMO_6 ($n = 4$, 5, 6, 7 or 8) adopt this structure. This model was originally proposed by Scholder [2] and has recently been applied by Trömel and Hauck [18] to determine the structure of Li_8SnO_6. In 1969 Hauck included Li_5ReO_6 in a large list of compounds Li_nMO_6 to which this model could be applied. A second model is the monoclinic space group found by Betz and Hoppe [7] for Li_5ReO_6, and confirmed for that compound by neutron diffraction in this paper. This model is related to that above, except that the octahedral coordination about Re, and to a greater extent the tetrahedral coordination about Li, are quite distorted.

TABLE 1. Li_5ReO_6 crystallographic results at 298 K and 10 K [a]

	Single-crystal X-ray, 298 K [7]	Powder X-ray, 298 K (this work)	Powder neutron, 298 K (this work)	Powder neutron, 10 K (this work)
a (Å)	5.0679(6)	5.0621(54)	5.0649(1)[c]	5.0433(1)[c]
b (Å)	8.7315(8)	8.7387(86)	8.7314(1)[c]	8.7058(1)[c]
c (Å)	5.0293(6)	5.0326(46)	5.0277(1)[c]	5.0071(1)[c]
β/deg	110.24(1)	110.299(62)	110.187(1)[c]	110.029(1)[c]
Li1 *y*	0.669(3)		0.6661(7)	0.6672(7)
Li1 U_{11} (Å²)	0.019(5)		0.020(3)	0.017(3)
Li1 U_{22} (Å²)	[b]		0.020(2)	0.015(2)
Li1 U_{33} (Å²)	[b]		0.025(2)	0.022(2)
Li1 U_{13} (Å²)	[b]		0.007(2)	0.007(2)
Li2 U_{11} (Å²)	0.026(10)		0.014(3)	0.003(2)
Li2 U_{22} (Å²)	[b]		0.012(3)	0.009(3)
Li2 U_{33} (Å²)	[b]		0.018(3)	0.010(3)
Li2 U_{13} (Å²)	[b]		−0.004(3)	−0.002(2)
Li3 *y*	0.324(4)		0.3237(6)	0.3235(5)
Li3 U_{11} (Å²)	0.024(7)		0.012(2)	0.006(2)
Li3 U_{22} (Å²)	[b]		0.012(2)	0.006(1)
Li3 U_{33} (Å²)	[b]		0.011(2)	0.004(1)
Li3 U_{13} (Å²)	[b]		0.011(2)	0.006(1)
Re U_{11} (Å²)	0.007(1)		0.004(1)	0.002(1)
Re U_{22} (Å²)	0.010(1)		0.004(1)	0.001(1)
Re U_{33} (Å²)	0.008(1)		0.007(1)	0.003(1)
Re U_{13} (Å²)	0.002(1)		0.004(1)	0.002(1)
O1 *x*	0.271(2)		0.2715(2)	0.2703(3)
O1 *y*	0.348(9)		0.3476(1)	0.3471(1)
O1 *z*	0.764(2)		0.7666(2)	0.7661(2)
O1 U_{11} (Å²)	0.014(3)		0.006(1)	0.003(1)
O1 U_{22} (Å²)	0.010(3)		0.003(1)	0.001(1)
O1 U_{33} (Å²)	0.011(4)		0.005(1)	0.002(1)
O1 U_{12} (Å²)	−0.003(1)		−0.002(1)	−0.001(1)
O1 U_{13} (Å²)	0.004(3)		0.000(1)	−0.005(3)
O1 U_{23} (Å²)	0.000(3)		−0.001(1)	−0.004(3)
O2 *x*	0.276(3)		0.2729(3)	0.2727(3)
O2 *z*	0.228(3)		0.2250(3)	0.2261(3)
O2 U_{11} (Å²)	0.016(5)		0.005(1)	0.001(1)
O2 U_{22} (Å²)	0.016(5)		0.006(1)	0.003(1)
O2 U_{33} (Å²)	0.012(6)		0.007(1)	0.004(1)
O2 U_{13} (Å²)	0.006(4)		0.003(1)	0.001(1)

[a] Numbers in parentheses are estimated standard deviations. Where no entry is shown in the table, no value was reported (by others) or determined (by us).

[b] Not refined in reference 7.

[c] We estimate the lattice parameters refined from neutron data to have an overall accuracy of about ± 0.025%.

A third model is the hexagonal space group $P3_112$ originally proposed by Hauck for Li_5ReO_6 [8]. This model is related to NaCl, with cation (5Li+Re) and anion (6O) f.c.c.-related sublattices. Oxygen atoms form an f.c.c. (cubic closest packed) array. Octahedral holes formed by this array are all occupied, 5/6 by Li and 1/6 by Re, in alternating layers (3Li) and (2Li+Re). This model has been elaborated further by Hauck [19, 20].

Yet a fourth model is that recently found by X-ray single-crystal diffraction of α-Li_6UO_6 [21]. This is the trigonal space group $R\bar{3}$ of the first model, but with a different unit cell.

X-ray and neutron powder diffraction intensities were calculated with the program LAZY PULVERIX [22] for each of these models, and refinement was attempted with each using the Argonne Rietveld refinement package. In no case was the refinement adequate. In the best case (monoclinic *C2/m*, second model), six observed peaks were not found when using the model structure. These peaks were at *d*-spacings (in Å) 2.751w, 2.667w, 2.511w, 2.310w, 2.179w, and 1.856m (medium, weak). They did not match possible impurities such as Li_2O, Li_2O_2, Li_2CO_3, NpO_2, Li_4NpO_5, Cd or V. (The two last 'impurities' are actually shielding and container metals in the GPPD.) Other models have been suggested

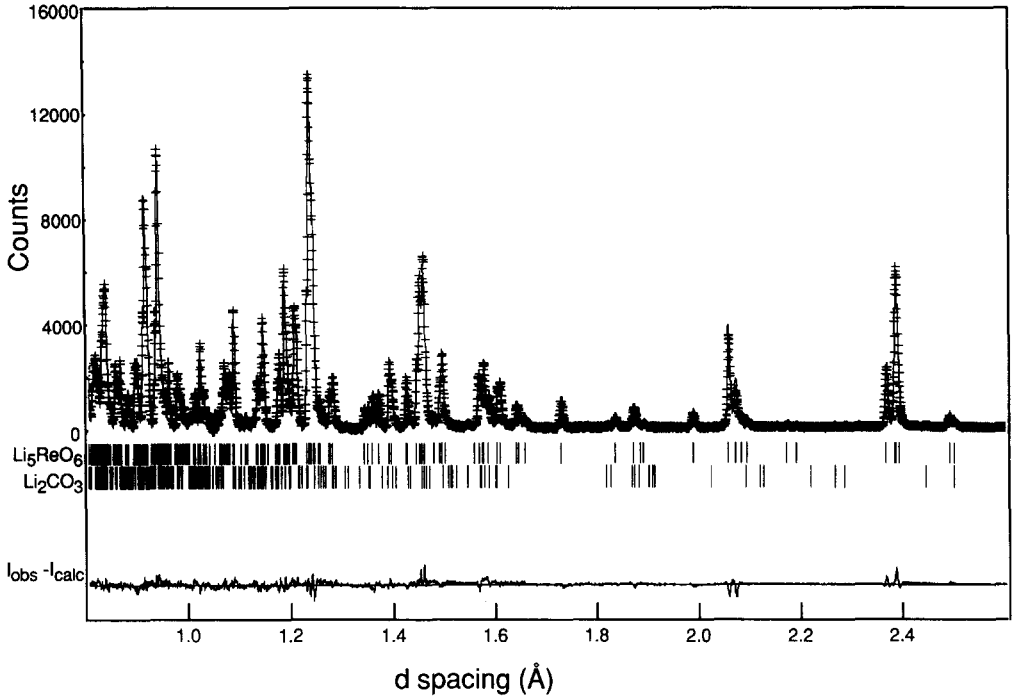

Fig. 1. Powder neutron diffraction profile for Li_5ReO_6 (10 K). The two sets of vertical lines are allowed reflections for Li_5ReO_6 (top) and Li_2CO_3 (bottom). The lower plot is the difference profile ($I_{obs} - I_{calc}$).

TABLE 2. Li_4MO_5 powder diffraction results at 298 K [a]

	Li_4UO_5		Li_4NpO_5		
	X-ray [10]	Neutron [10]	X-ray [3,4]	X-ray (this work)	Neutron (this work)
a (Å)	6.720	6.736	6.698	6.698(3)	6.6999(1)[b]
c (Å)	4.451	4.457	4.432	4.415(2)	4.4199(1)[b]
Li x		0.197			0.1881(8)
Li y		0.383			0.4094(9)
Li U_{11} (Å²)					0.013(2)
Li U_{22} (Å²)					0.024(3)
Li U_{33} (Å²)					0.025(1)
Li U_{12} (Å²)					0.007(2)
Np U_{11} (Å²)					0.006(1)
Np U_{33} (Å²)					0.006(1)
O1 U_{11} (Å²)					0.011(1)
O1 U_{33} (Å²)					0.008(1)
O2 x		0.280			0.2856(3)
O2 y		0.097			0.0867(3)
O2 U_{11} (Å²)					0.008(1)
O2 U_{22} (Å²)					0.010(1)
O2 U_{33} (Å²)					0.009(1)
O2 U_{12} (Å²)					0.001(1)
M-O(axial) (Å)		2.23			2.210(1)
(equatorial) (Å)		1.99			2.000(2)

[a] Numbers in parentheses are estimated standard deviations. Where no entry is shown in the table, no value was reported (by others) or determined (by us).

[b] We estimate the lattice parameters refined from neutron data to have an overall accuracy of about ± 0.025%.

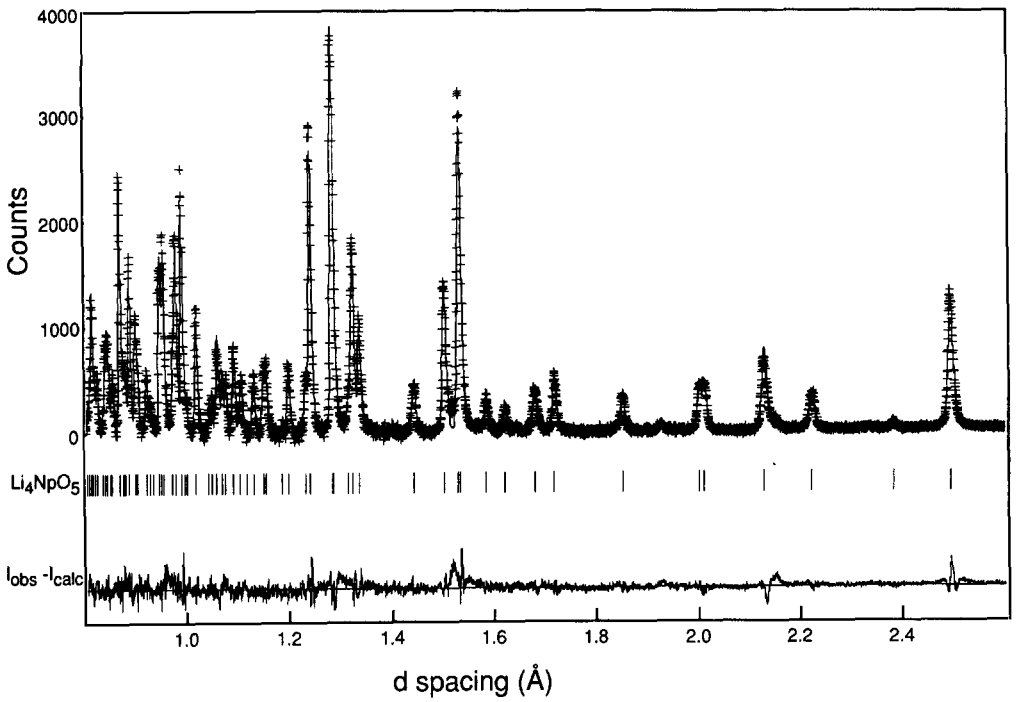

Fig. 2. Powder neutron diffraction profile for Li_4NpO_5 (298 K). The lower plot is the difference profile ($I_{obs}-I_{calc}$).

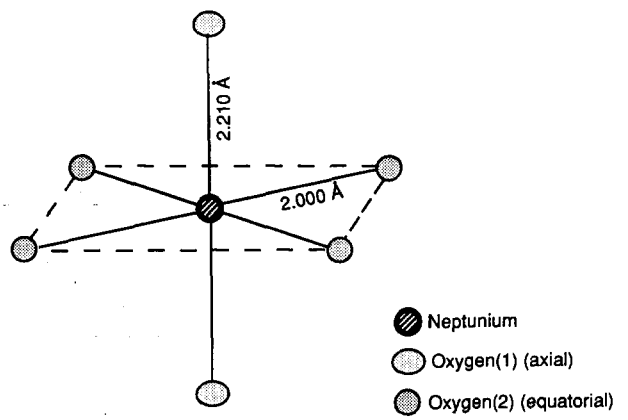

Fig. 3. Np–O coordination in Li_4NpO_5.

to us by Hauck, and solution of the Li_5NpO_6 structure may yet be possible

4. Conclusions

We have confirmed by powder neutron diffraction that the structure of Li_5ReO_6 at room temperature is monoclinic, space group *C2/m*, and that there is no structural phase transition between 298 K and 10 K. We have determined the structure of Li_4NpO_5 to be the same as that of Li_4UO_5 and have refined the positional parameters by powder neutron diffraction. We have collected powder neutron diffraction data for Li_5NpO_6; these data do not fit any known models of other compounds Li_nMO_6.

Acknowledgments

The authors thank F.J. Rotella and J.W. Richardson (Argonne Intense Pulsed Neutron Source Division) for guidance and assistance in collecting and interpreting the neutron diffraction data. They also thank J. Hauck (Kernforschungsanlage Jülich) for helpful suggestions regarding alternative models for Li_5NpO_6. This work was performed under the auspices of the United States Department of Energy, Divisions of Chemical and Materials Sciences, under contract W-31-109-ENG-38. In addition, R.R.G. acknowledges support from the Teacher Research Associates Program of the Department of Energy, administered through the Argonne Division of Educational Programs.

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