JOURNAL OF SOLID STATE CHEMISTRY **63**, 278–283 (1986)

$HNbWO_6$ and $HTaWO_6$: Novel Oxides Related to ReO_3 Formed by Ion Exchange of Rutile-Type $LiNbWO_6$ and $LiTaWO_6$[1]

VASUDEVA BHAT AND J. GOPALAKRISHNAN[2]

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

Received July 24, 1985; in revised form November 25, 1985

Both $LiNbWO_6$ and $LiTaWO_6$ undergo ion exchange in hot aqueous H_2SO_4 yielding the hydrates $HMWO_6 \cdot H_2O$ (M = Nb or Ta). The reaction is accompanied by a structural transformation from the rutile to the ReO_3 structure. The cell constants are $a = 3.783(3)$ Å for $HNbWO_6 \cdot H_2O$ and $a = 3.785(5)$ Å for $HTaWO_6 \cdot H_2O$. The ReO_3 structure is retained by the dehydration products $HMWO_6$ and $MWO_{5.5}$ as well. $HMWO_6$ phases yield $H_{1+x}MWO_6$ hydrogen bronzes on exposure to hydrogen in the presence of platinum catalyst.

1. Introduction

Several complex metal oxides containing alkali metals undergo ion exchange in aqueous or molten salt media retaining their structural features. Such ion-exchange reactions provide low-temperature routes for the synthesis of new solids that cannot be prepared by high-temperature methods (*1*, *2*). An interesting example of ion-exchange reaction accompanied by a structural transformation is that of proton exchange of $LiNbO_3$ and $LiTaO_3$ (*3*). The exchange results in the formation of cubic $HNbO_3$ and $HTaO_3$ possessing an ReO_3-type structure. We have been interested in investigating the possible occurrence of a similar exchange of lithium in oxides crystallizing in different structures. We have found that when $LiNbWO_6$ and $LiTaWO_6$ are refluxed with aqueous H_2SO_4, $HNbWO_6$ and $HTaWO_6$ are formed. The reaction is accompanied by a transformation from the rutile to the ReO_3 structure. We believe that this is the first instance of such a transformation occurring at low temperatures. In this paper, we report the preparation and structural characterization of $HNbWO_6$ and $HTaWO_6$ from their lithium analogues and suggest a possible mechanism for the rutile-ReO_3 transformation.

2. Experimental

$LiNbWO_6$ and $LiTaWO_6$ were prepared by reacting the required quantities of Li_2CO_3, WO_3, and Nb_2O_5/Ta_2O_5 at 800°C for 24 hr. Both the oxides crystallize in trirutile structure as revealed by X-ray powder diffraction. Their lattice parameters ($a = 4.677(6)$ and $c = 9.27(1)$ Å for the niobium compound and $a = 4.673(2)$ and $c = 9.309(5)$ Å for the tantalum compound) agree with the values reported in the literature (*4*).

---

[1] Contribution No. 315 from the Solid State and Structural Chemistry Unit.

[2] To whom correspondence should be addressed.

0022-4596/86 $3.00

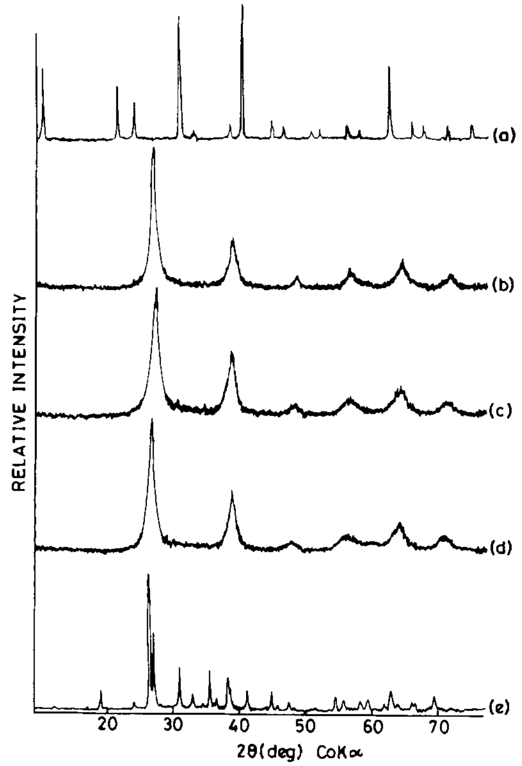

FIG. 1. X-Ray powder diffraction patterns of (a) $LiNbWO_6$, (b) $HNbWO_6 \cdot H_2O$, (c) $HNbWO_6$, (d) $NbWO_{5.5}$, and (e) $NbWO_{5.5}$ after heating at 900°C for 12 hr.

Ion exchange of lithium in $LiNbWO_6$ and $LiTaWO_6$ was investigated by refluxing the solids in hot aqueous H_2SO_4 and HNO_3. The reaction was monitored by the flame test of the filtrate and X-ray diffraction of the solid. Exchange was not significant with HNO_3 but facile exchange occurred with 9–13 M H_2SO_4 at 150–210°C, the tantalum compound requiring higher concentrations of the acid. The reaction was complete with $LiNbWO_6$ in 24 hr in 9 M H_2SO_4 while it required about a week with $LiTaWO_6$ in 13 M H_2SO_4. The solid products were filtered, washed with water, and air-dried at 110°C. Their composition as determined by chemical analysis of tungsten and thermogravimetry was $HMWO_6 \cdot H_2O$ (M = Nb or Ta).

The protonated oxides were characterized by X-ray diffraction, thermogravimetry and IR absorption spectroscopy. X-ray diffraction patterns were recorded with a JEOL JDX-8P powder diffractometer using Fe-filtered Co*Kα* radiation. Thermogravimetric curves were recorded using a Sartorius microbalance at a heating rate of 5°C per minute. Infrared spectra were recorded in KBr pellets and Nujol mull using a Perkin–Elmer 599 spectrometer.

3. Results and Discussion

Both $LiNbWO_6$ and $LiTaWO_6$ transform to the protonated oxides on treatment with hot aqueous H_2SO_4 as revealed by the presence of lithium in the filtrate and the changes in X-ray diffraction patterns of the solids. Chemical analysis of tungsten and thermogravimetric analysis of water content revealed that the composition of the solid products is $HMWO_6 \cdot H_2O$ (M = Nb or Ta). Both protonated phases are isomorphous adopting the simple cubic structure of ReO_3 (or perovskite) (Fig. 1). The X-ray reflections are broad indicating that the particle size of the products is much smaller than that of the parent $LiMWO_6$. The observed *d* spacings and intensities of $HNbWO_6 \cdot H_2O$ (together with other related niobium oxides) are given in Table I. The unit cell parameters of $HMWO_6 \cdot H_2O$ (a = 3.783(3) Å for the niobium compound and a = 3.785(5) Å for the tantalum compound) are comparable to $HNbO_3$ and $HTaO_3$ possessing ReO_3-related structure (*3*). Recently, Weller and Dickens (*5*) have reported a cubic cell of a = 7.622 Å for $HTaO_3$ on the basis of a powder X-ray and neutron diffraction study. The doubling of the cubic cell of the ReO_3 structure has been attributed to tilting of the TaO_6 octahedra. We do not see any evidence for such doubling of the unit cell in the diffraction patterns of $HMWO_6$.

Thermogravimetric analysis in air shows

TABLE I

X-RAY POWDER DIFFRACTION DATA OF $HNbWO_6 \cdot H_2O$, $HNbWO_6$, $NbWO_{5.5}$, AND $H_{\sim 1.3}NbWO_6$

hkl	$HNbWO_6 \cdot H_2O$[a]		$HNbWO_6$[b]		$NbWO_{5.5}$[c]		$H_{\sim 1.3}NbWO_6$[d]	
	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
100	3.779	100	3.773	100	3.779	100	3.773	100
110	2.672	45	2.681	42	2.691	42	2.675	55
111	2.181	7	2.199	5	2.214	5	2.203	8
200	1.891	14	1.894	13	1.910	12	1.884	11
210	1.691	22	1.696	18	1.702	18	1.695	22
211	1.545	9	1.548	10	1.553	9	1.546	11
220	1.337	3	1.340	3	1.347	3	1.340	3
221 300	1.261	5	1.263	4	1.270	4	1.263	6

[a] $a = 3.783(3)$ Å.
[b] $a = 3.79(1)$ Å.
[c] $a = 3.81(2)$ Å.
[d] $a = 3.79(1)$ Å.

that $HMWO_6 \cdot H_2O$ readily loses water of hydration to give anhydrous phases around 400°C (Fig. 2). The anhydrous compounds are stable up to about 600°C and suffer further weight loss. The second weight loss is likely to be due to the reaction

$$HNbWO_6 \rightarrow NbWO_{5.5} + \tfrac{1}{2}H_2O$$

The weight loss expected for the reaction is 2.41% and that found is 2.20%. Both the anhydrous $HMWO_6$ as well as $MWO_{5.5}$ retain the cubic ReO_3 structure (Figs. 1c and d). It is indeed surprising that $MWO_{5.5}$ possesses the ReO_3 structure since the composition is anion deficient. The anion vacancies are probably ordered at the microstructrual level which is not revealed by powder X-ray diffraction. On annealing the cubic $NbWO_{5.5}$ at 900°C for 12 hr, the phase transforms to a complex structure; its diffraction pattern (Fig. 1e) which could be indexed on a tetragonal cell with $a = 24.3$ and $c = 3.92$ Å is strikingly similar to the tetragonal tungsten bronzes possessing pentagonal column structures (*6*, *7*). $HTaWO_6 \cdot H_2O$, $HTaWO_6$, and $TaWO_{5.5}$ adopting defect pyrochlore structures have been reported (*8*).

We have recorded the IR spectra of $HNbWO_6 \cdot H_2O$, $HNbWO_6$, and the cubic $NbWO_{5.5}$ to find out the nature of water and

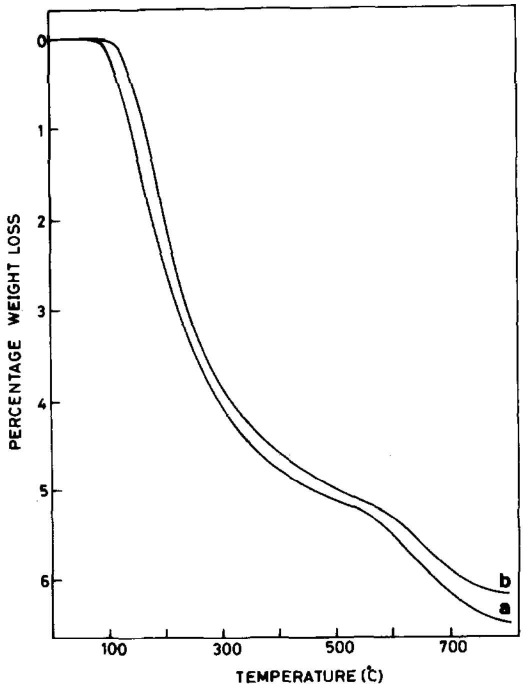

FIG. 2. Thermogravimetric curves of (a) $HNbWO_6 \cdot H_2O$ and (b) $HTaWO_6 \cdot H_2O$.

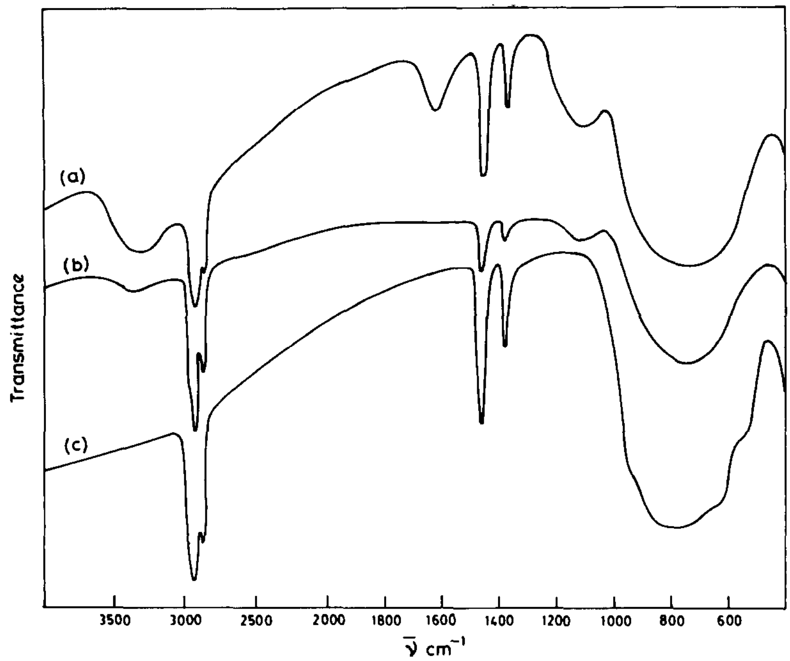

FIG. 3. Infrared spectra of (a) $HNbWO_6 \cdot H_2O$, (b) $HNbWO_6$, and (c) $NbWO_{5.5}$ recorded in Nujol mull.

the presence of OH groups (Fig. 3). $HNbWO_6 \cdot H_2O$ shows a strong, broad absorption between 3200 and 3500 cm^{-1} and a sharp absorption around 1625 cm^{-1} which are due to the stretching and bending modes of water, respectively. In addition, there is an absorption band around 1130 cm^{-1} which is probably due to *M*—OH bending. Metal hydroxides show absorption due to *M*—OH bending in this region (*9, 10*). In the IR spectrum of anhydrous $HNbWO_6$, the absorption at 1625 cm^{-1} disappears while the band around 1130 cm^{-1} is retained. This can be taken to indicate that the proton in $HNbWO_6$ occurs as an OH group. The compound has therefore to be formulated as $NbWO_5(OH)$ similar to other protonated oxides such as $HNbO_3$, $HTaO_3$, and HNb_3O_8 (*3, 11*). Both W and *M* as well as protons in $HMWO_6$ are apparently not ordered since the structure retains the cubic symmetry. In the IR spectrum of $NbWO_{5.5}$, all the absorption bands due to water and OH groups are absent. A broad and strong absorption centered around 800 cm^{-1} and another medium absorption around 340 cm^{-1} present in all the Nb—W oxides investigated are likely to be due to the internal modes of MO_6 and WO_6 octahedra.

The formation of $HMWO_6$ from $LiMWO_6$ on treatment with aqueous H_2SO_4 can take place by either a topotactic mechanism (similar to the formation of HMO_3 from $LiMO_3$) or a dissolution–recrystallization process. To distinguish between the two possibilities, we have refluxed a mixture of Nb_2O_5 and WO_3 in 9 M H_2SO_4 for 24 hr under conditions similar to the formation of $HNbWO_6 \cdot H_2O$ from $LiNbWO_6$. No $HNbWO_6$ was obtained in this reaction. It is possible that $HNbWO_6$ is not formed in this reaction because of the poor solubility of Nb_2O_5 in H_2SO_4. We have treated an

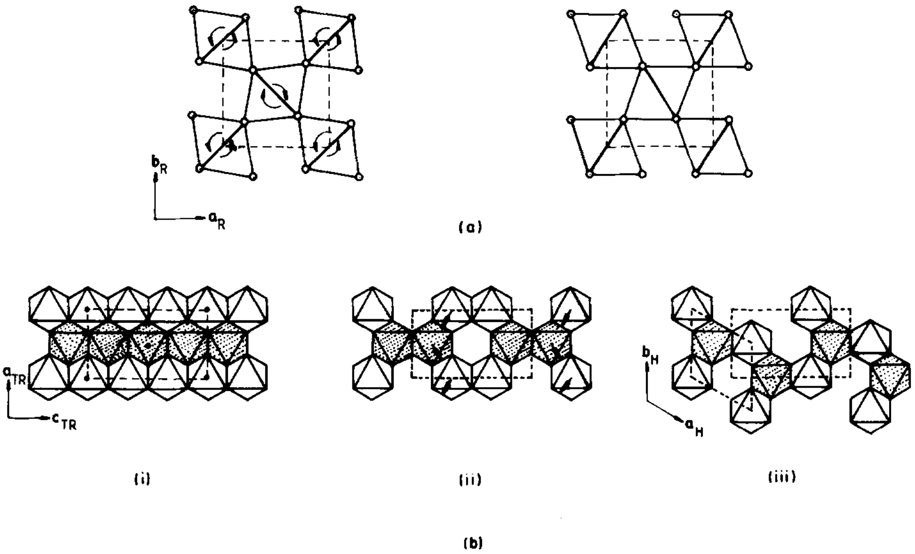

FIG. 4. Transformation of the tetragonal close-packed anion array to hexagonal close-packed (*hcp*) array by rotation of the occupied octahedra. (b) Transformation of $NbWO_6$ framework in $LiNbWO_6$ (trirutile) to NbO_3 framework of the $LiNbO_3$ structure. The oxygen array is idealized to *hcp*. Only occupied octahedra are shown. Shaded and unshaded octahedra are at different levels. (i) $LiNbWO_6$ trirutile. Li-occupied octahedra are shown with filled circles. (ii) $NbWO_6$ network after removal of lithium. Arrows indicate the direction of cation motion. (iii) $NbWO_6$ network after cation rearrangement. This network is equivalent to NbO_3 network in $LiNbO_3$.

equimolar mixture of $LiNbWO_6$ and $LiTaWO_6$ with 13 M H_2SO_4 for 1 week. The product obtained by this method showed an X-ray diffraction pattern similar to those of $HNbWO_6 \cdot H_2O$ and $HTaWO_6 \cdot H_2O$. We could not, however, decide from the pattern whether it is a mixture of $HNbWO_6 \cdot H_2O$ and $HTaWO_6 \cdot H_2O$ or a single-phase solid solution of the two, $HNb_{1-x}Ta_xWO_6 \cdot H_2O$. Formation of a single-phase solid solution would indicate that the reaction proceeds by a dissolution–recrystallization process. An EDAX analysis of the product in a scanning electron microscope by monitoring $K\alpha$ of Nb and $L\alpha$ of Ta revealed that the majority of the crystals contained both Nb and Ta although a few crystals did contain either Nb or Ta. The result seems to suggest that the formation of $HMWO_6 \cdot H_2O$ from $LiMWO_6$ on treatment with H_2SO_4 proceeds by a dissolution–recrystallization mechanism although a topotactic mechanism cannot be entirely ruled out.

We suggest a possible mechanism for the topotactic transformation of $LiMWO_6$ to ReO_3-like $HMWO_6$ in Fig. 4. On ion exchange, the tetragonal close-packed anion array of the rutile structure transforms first to the hexagonal close-packed (hcp) array. Subsequently cation rearrangement occurs to give a MWO_6 network that is similar to the NbO_3 network of the $LiNbO_3$ structure. The network then transforms to the ReO_3 structure by a mechanism similar to that proposed by Rice and Jackel (*3*) for the transformation of $LiMO_3$ to HMO_3. The latter involves rotation of the octahedra by ~60° about the c_H of $LiMO_3$ which rearranges the *hcp* anion array to the $\frac{3}{4}$ *ccp* anion array of the ReO_3 structure. Further work is needed to decide whether

$LiMWO_6$–$HMWO_6$ transformation occurs by a topotactic mechanism or a dissolution–recrystallization mechanism.

Since it is known that WO_3 forms stable hydrogen bronzes, H_xWO_3 (*12*), we expected that $HNbWO_6$ and $HTaWO_6$ would form similar hydrogen bronzes. We indeed found the formation of intense blue $H_{1+x}MWO_6$ (M = Nb or Ta) when anhydrous $HMWO_6$ dispersed with 0.5% of Pt was exposed to hydrogen at room temperature. Determination of the reducing power of the samples by oxidimetry revealed the formula of the bronzes to be $H_{\sim 1.3}MWO_6$. X-ray powder patterns of the blue bronzes are nearly identical with those of $HMWO_6$ indicating that the ReO_3 structure is retained in the bronzes. The observed d spacings and intensities of $H_{\sim 1.3}NbWO_6$ are given in Table I. The hydrogen bronzes exhibit a much lower resistivity (~30 ohm cm) for compressed polycrystalline pellets than the parent oxides (~10^6 ohm cm) at room temperature. The blue color and the low resistivity of the bronzes are indicative of partial reduction of W^{6+} to W^{5+} on hydrogen insertion. Unlike H_xWO_3, $H_{1+x}MWO_6$ bronzes are unstable under ambient conditions transforming to straw-white-colored parent oxides in ~30 min. The reaction is however reversible. The reversible insertion of hydrogen in $HMWO_6$ may be important in electrochromic devices.

Acknowledgments

Grateful thanks of the authors are due to Professor C. N. R. Rao, F.R.S. for valuable advice and encouragement. The authors thank the Department of Science and Technology, Government of India and the University Grants Commission, New Delhi, for support of this research.

References

1. W. A. England, J. B. Goodenough, and P. J. Wiseman. *J. Solid State Chem.* **49,** 289 (1983).
2. J. Gopalakrishnan, *Proc. Indian Acad. Sci. Chem. Sci.* **93,** 421 (1984).
3. C. E. Rice and J. L. Jackel, *J. Solid State Chem.* **41,** 308 (1982).
4. G. Blasse and A. D. M. dePauw, *J. Inorg. Nucl. Chem.* **32,** 3960 (1970).
5. M. T. Weller and P. G. Dickens, *J. Solid State Chem.* **58,** 164 (1985).
6. R. S. Roth and J. L. Waring, *J. Res. Natl. Bur. Stand. Sect. A* **70,** 281 (1966).
7. S. Iijima and J. G. Allpress, *Acta Crystallogr. Sect. A* **30,** 22, 29 (1974).
8. D. Groult, J. Pannetier, and B. Raveau, *J. Solid State Chem.* **41,** 277 (1982).
9. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed., Wiley, New York (1970).
10. R. A. Nyquist and R. O. Kagel, "Infrared Spectra of Inorganic Compounds," Academic Press, New York (1971).
11. F. Izumi and H. Kodama, *Z. Anorg. Allg. Chem.* **441,** 196 (1978).
12. P. G. Dickens and M. F. Pye, *in* "Intercalation Chemistry" (M. S. Whittingham and A. J. Jacobson Eds.), Academic Press, New York (1982).