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LOW-TEMPERATURE SYNTHESIS OF NOVEL METAL OXIDES BY TOPOCHEMICAL REACTIONS*†

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Synthesis of a variety of novel metal oxides has been achieved at low temperatures by topochemical reactions. Thus topochemical dehydration of $Mo_{1-x}W_xO_3.H_2O$ provides a convenient route for the synthesis of $Mo_{1-x}W_xO_3$ in ReO_3-type structure. Dehydration of $HMoO_2PO_4.H_2O$ to $HMoO_2PO_4$ results in a topotactic transformation of the parent chain structure to a layered structure in the product. Exchange of lithium with protons in $LiNbWO_6$ and $LiTaWO_6$ results in a novel structural transformation from the rutile to the ReO_3 structure of the product phases, $HNbWO_6$ and $HTaWO_6$. Topotactic reduction of $LaNiO_3$ and $LaCoO_3$ yields new vacancy-ordered perovskite-related phases, $La_3Ni_2O_5$ and $La_2Co_2O_5$ that cannot be synthesized otherwise. Hydrogen can be inserted topotactically into $LaNiO_3$ and $LaCoO_3$ around ambient temperatures in the presence of Pt-catalyst to yield H_xLaNiO_3 and H_xLaCoO_3. Insertion of bismuth into WO_3 yielding *intergrowth tungsten bronzes*, Bi_xWO_3, can also be viewed as a topotactic process. The investigations reveal that it is possible to design imaginative routes for the synthesis of metal oxides at low temperatures making use of topochemical reactions.

Key Words : Synthesis of Metal Oxides; Topochemical Reactions; Dehydration; Ion-Exchange; Reduction; Insertion/Extraction.

INTRODUCTION

SYNTHESIS and structural characterization of solids constitute an important activity of solid state chemists.[1] Conventionally, solid state synthesis is carried out by the ceramic method which involves mixing the reactants and heating them at high temperatures. The limitations of this crude approach are too well known to be recounted here.[2] In recent years, efforts have been made to design imaginative routes for solid state synthesis based on novel chemical reactions.[3] A number of common chemical reactions involving inorganic solids such as dehydration, decomposition, oxidation, and reduction are known to proceed *topochemically* to yield well-defined products that bear definite structural relationships with the starting materials.[4,5] Reversible insertion and extraction of atomic and molecular species into layered solids *via* redox and ion-exchange processes is another topochemical reaction that is being increasingly investigated.[6,7] Topochemical relationship has recently been shown to exist between NiO and Ni when the oxide is reduced to the metal.[8] Such topochemical reactions which occur at relatively mild conditions provide 'soft' (low-temperature) routes for solid state synthesis.

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Synthesis of solids at low temperatures has several attractive features. Homogeneous and pure products with large surface areas can be obtained with relative ease. Metastable phases that cannot be prepared by high temperature methods can be stabilized by low temperature methods. More importantly, in view of the structural relationships existing between the parent and product solids in topochemical reactions, it is possible to engineer the synthesis *via* topochemical reactions, to yield solids possessing the desired structures.

We have made use of topochemical dehydration, ion-exchange, oxidative deintercalation, reduction and insertion of atomic species (H, Bi) into oxide hosts to synthesize a variety of novel metal oxides. Thus topochemical dehydration of $Mo_{1-x}W_xO_3.H_2O$ and $HMoO_2PO_4.H_2O$ has enabled the synthesis of ReO_3-like $Mo_{1-x}W_xO_3$ and layered $HMoO_2PO_4$. Exchange of lithium with protons in $LiNbWO_6$ and $LiTaWO_6$ has resulted in the formation of ReO_3-like $HNbWO_6$ and $HTaWO_6$, the ion-exchange being accompanied by a topotactic structural transformation from rutile to ReO_3 structure. Oxidative deintercalation of lithium from $LiVO_2$ an Li_2MoO_3 possessing ordered rocksalt structure has yielded new $Li_{1-x}VO_2$ and $Li_{2-y}MoO_3$ members where the cubic close packed anion array is preserved. An interesting example of solid state synthesis of metastable phases is that of $La_2B_2O_5$ (B = Co, Ni) from $LaBO_3$ perovskites *via* topochemical reduction. Significantly, when the same parent oxides are treated with hydrogen in the presence of platinum at room temperature, hydrogen-insertion products, H_xLaBO_3, are obtained instead of anion deficient phases. Similar hydrogen insertion has also been carried out with $HNbWO_6$, $HTaWO_6$ and $Mo_{1-x}W_xO_3$ to yield hydrogen bronzes. Another interesting example of topochemical insertion is that of Bi into WO_3 yielding *intergrowth tungsten bronzes* (ITBs) wherein WO_3 slabs of finite width intergrow coherently with strips of HTB structure. The results of these investigations presented in this paper reveal that it is possible to design imaginative methods for the synthesis of a variety of metal oxides based on topochemical reactions.

Experimental

$Mo_{1-x}W_xO_3.H_2O$ ($0 < x \leqslant 1$) solid solutions were prepared by adding a solution of MoO_3 and WO_3 in aqueous ammonia to hot (60 °C) 6M HNO_3 under constant stirring.[9] $HMoO_2PO_4.H_2O$ was prepared by adding a viscous solution of MoO_3 (10g) in concentrated H_3PO_4 (30ml) to 250ml of concentrated nitric acid.[10] On evaporation, white crystals of $HMoO_2PO_4.H_2O$ separated out. $LiNbWO_6$ and $LiTaWO_6$ of trirutile structures were prepared by reacting the required quantities of Li_2CO_3, WO_3, Nb_2O_5/Ta_2O_5 at 800 °C for 24h. $LiVO_2$ was prepared by reacting Li_2CO_3 and V_2O_5 in hydrogen atmosphere, first at 500 °C for 4h and then at 700 °C for 10h. Li_2MoO_3 was prepared by hydrogen-reduction of Li_2MoO_4 at 650 °C.[10a] $LaCoO_3$ and $LaNiO_3$ were prepared by methods reported in the literature.[11] Bi_xWO_3 ($x \leqslant 0.1$) were prepared by heating Bi metal with WO_3 in sealed evacuated silica tubes at 900 °C.[11a]

Dehydration and reduction reactions involving a weight loss were followed thermogravimetrically using a Sartorious Microbalance at heating rates of 2–5°

per minute. Proton-exchange of lithium in $LiNbWO_6$ and $LiTaWO_6$ was carried out by refluxing the solids in hot aqueous H_2SO_4 (9–13M). Delithiation of $LiVO_2$ and Li_2MoO_3 was carried out by treating the oxides with Br_2 in $CHCl_3$ at room temperature. Hydrogen insertion into $LaNiO_3$, $LaCoO_3$ and $Mo_{1-x}W_xO_3$ was carried out at 30–100 °C by passing hydrogen over the oxides dispersed with 0.5 per cent Pt by weight.

The solids were characterized by X-ray diffraction, electron diffractron and i.r. absorption spectroscopy. X-ray powder diffraction patterns were recorded with a JEOL JDX-8P diffractometer or a Philips diffractometer (PW 1050/70) using CoK_α or CuK_α radiation. Electron diffraction patterns were recorded with a JEOL 200CX electron microscope.

Results and Discussion

Topochemical Dehydration

Dehydration of several inorganic solids is known to proceed topochemically, typical examples being the transformation of brucite $[Mg(OH)_2]$ to periclase (MgO)[12] and $MoO_3.2H_2O$ to anhydrous MoO_3.[13] We have investigated the topochemical dehydration of $Mo_{1-x}W_xO_3.H_2O$ and $HMoO_2PO_4.H_2O$ which has enabled the preparation of $Mo_{1-x}W_xO_3$ and $HMoO_2PO_4$, possessing novel structures.

MoO_3 crystallizes in a layered structure (Fig. 1) involving corner-and edge-shared MoO_6 octahedra, while the analogous WO_3 adopts a ReO_3-like structure where the WO_6 octahedra share all corners. Although both the structures are related,[14] it has not been possible to transform MoO_3 to the WO_3 structure (or *vice-versa*). Nevertheless, it is known that MoO_3 can be stabilized in the WO_3 structure by partially substituting molybdenum by tungsten.[15] Unfortunately, the preparation of $Mo_{1-x}W_xO_3$ by the ceramic technique is difficult due to the difference in volatilities of the parent oxides. The solid solution between the hydrated oxides, $Mo_{1-x}W_xO_3.H_2O$, could however be readily prepared by a wet method, since $MoO_3.H_2O$ and $WO_3.H_2O$ are isostructural.[16] $Mo_{1-x}W_xO_3.H_2O$ adopt the same layered structure as $MoO_3.H_2O$ and $WO_3.H_2O$ with a monoclinic unit cell ($a\sim7.5$, $b\sim10.7$, $c\sim7.3$Å, $\beta\sim91°$). The hydrate solid solutions undergo dehydration around 230 °C to yield $Mo_{1-x}W_xO_3$ which crystallize in the monoclinic WO_3 structure ($a\sim7.3$, $b\sim7.4$, $c\sim3.9$Å, $\beta\sim91°$). The topotactic transformation of the hydrates to anhydrous solid solutions involves a collapse of the layers along the *b*-direction, the structure remaining essentially the same in the *ac*-plane (Fig. 1). The crystallographic orientational relationships between the parent and product oxides as established by electron diffraction are $(010)_{hydr} \parallel (010)_{oxide}$, $[100]_{hydr} \parallel [001]_{oxide}$ and $[001]_{hydr} \parallel [100]_{oxide}$. Interestingly, even the yellow $MoO_3.H_2O$ undergoes dehydration to yield a metastable ReO_3-like MoO_3 which subsequently transforms to the layered variety.[9]

Oxides possessing corner-connected network of octahedra and of tetrahedra are of considerable current interest,[17,18] typical examples being the vanadyl and

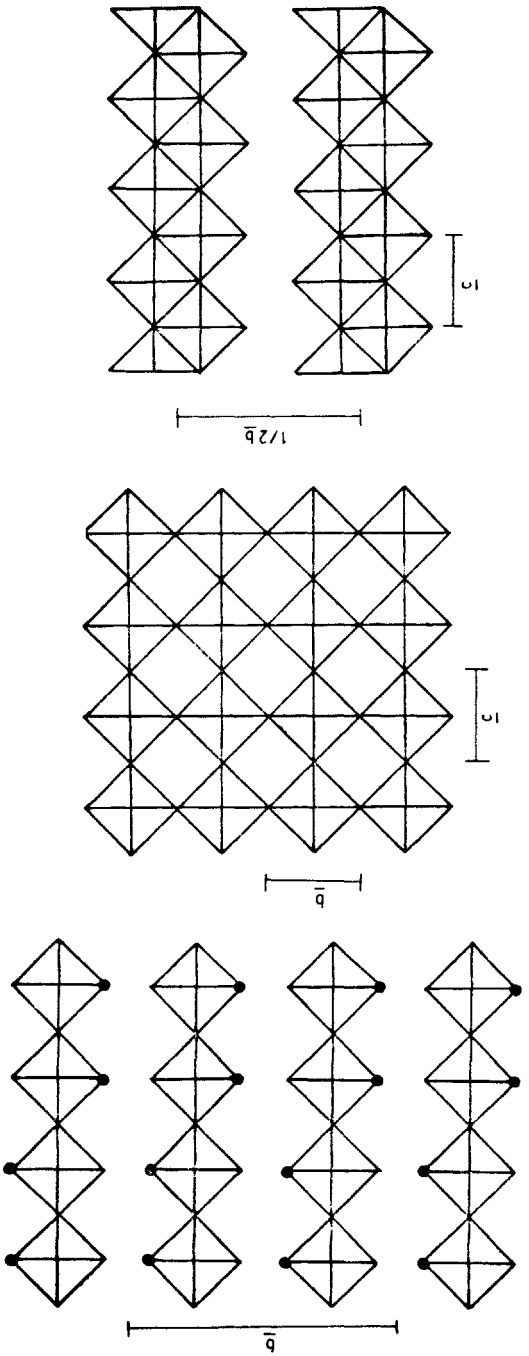

FIG 1 Schematic representation of the structures of $Mo_{1-x}W_xO_3.H_2O$ (left), ReO_3-like $Mo_{1-x}W_xO_3$ (middle) and layered MoO_3 (right).

molybdenyl phosphates. $VOPO_4.2H_2O$ is the prototype of this family of solids adopting a layered structure.[19] Each VO_6 octahedron shares its equatorial oxygens with phosphorus; the two remaining axial oxygens consist of a vanadyl (V=O) oxygen and a water molecule coordinated *trans* to it. The structure is tetragonal ($a=6.215$, $c=7.40$Å). $VOPO_4.2H_2O$ readily loses water topotactically to yield anhydrous $VOPO_4$ wherein the structural features of the parent are essentially preserved.

$HMoO_2PO_4.H_2O$ is an interesting molybdenyl phosphate which adopts a chain structure (monoclinic, $a=6.73$, $b=6.32$, $c=7.03$Å, $\beta=110.2°$) consisting of alternating MoO_6 and PO_4 polyhedra; each MoO_6 and PO_4 share three vertices forming double chains (Fig. 2) which run parallel to the b-direction.[20] The chains

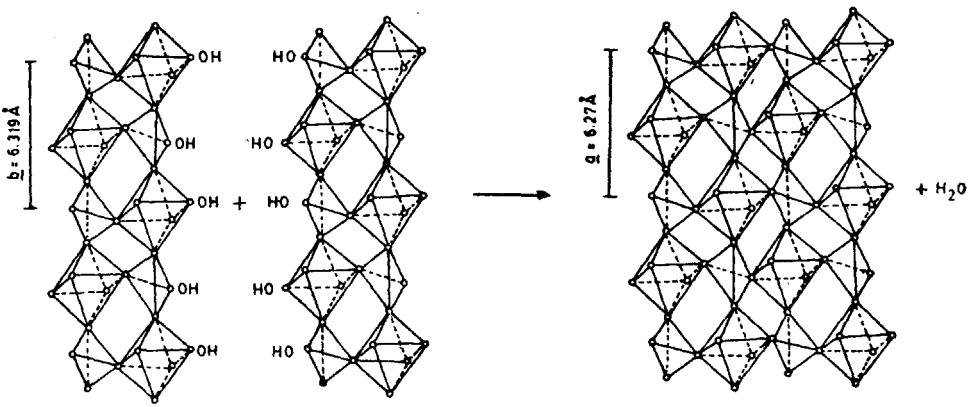

FIG 2 Schematic representation of the topotactic dehydration of $HMoO_2PO_4.H_2O$ (left) to layered $HMoO_2PO_4$ (right).

are held together by hydrogen bonding. The position of hydrogen atoms are not known in this structure, but it is likely that they are attached to the unshared oxygen atoms of MoO_6 and PO_4. Accordingly, the compound may be formulated as $Mo(OH)_3PO_4$ or $MoO(OH)_2HPO_4$. Since the building unit of this structure viz, alternating tetrahedra and octahedra, is essentially the same as that in $VOPO_4.2H_2O$, we visualized that it may be possible to transform $HMoO_2PO_4.H_2O$ to a layered structure similar to $VOPO_4.2H_2O$, by topotactic elimination of water. We found that $HMoO_2PO_4.H_2O$ readily loses one water molecule around 250 °C yielding a new phase. X-ray diffraction pattern of the dehydration product (Table I) is different from that of starting material and could be indexed on a tetragonal cell with $a=6.27$ and $c=4.91$Å. The new phase which could be written as $MoO(OH)PO_4$ or $MoO_2(HPO)_4$ is likely to possess a layered structure similar to $VOPO_4.2H_2O$, having been formed by linking up the double chains laterally through elimination of water (Fig. 2). During the topochemical transformation, the structure essentially remains the same in the b-direction ($b=6.32$Å in the parent becomes $a=b=6.27$Å in the product).

TABLE I

X-ray powder diffraction pattern of $HMoO_2PO_4$ prepared by topochemical dehydration of $HMoO_2PO_4.H_2O$

hkl	d_{obs}(Å)(I)	$d^{(a)}_{calc}$ (Å)
001	4.91 (60)	4.91
110	4.49 (30)	4.43
101	3.92 (40)	3.87
111	3.31 (10)	3.29
200	3.13 (100)	3.13
002	2 42 (5)	2.45
220	2.21 (5)	2.22
112	2.16 (8)	2.15
221	2.01 (5)	2.02
310	1.97 (5)	1.98
311	1.81 (5)	1.84
320	1.76 (3)	1.74

(a) $a = 6.27$, $c = 4.91$Å

Topochemical Ion-Exchange

Many complex metal oxides containing alkali metals undergo ion-exchange in aqueous or molten salt media retaining their structural features.[21] An interesting example of an ion-exchange reaction which is accompanied by a topotactic structural transformation is that of proton-exchange of $LiNbO_3$ and $LiTaO_3$.[22] The exchange results in the formation of cubic $HNbO_3$ and $HTaO_3$ possessing a ReO_3-type structure. We have investigated the proton-exchange of lithium in $LiNbWO_6$ and $LiTaWO_6$ in aqueous acid solutions.[23] The exchange results in the formation of $HNbWO_6$ and $HTaWO_6$ which adopt cubic ReO_3-like structure.

The primary products of proton-exchange of $LiNbWO_6$ and $LiTaWO_6$ are $HNbWO_6.H_2O$ and $HTaWO_6.H_2O$ as revealed by chemical analysis of tungsten and thermogravimetric analysis of water content. Both the phases are isomorphous adopting a simple cubic structure of ReO_3 type. The unit cell parameters derived from X-ray powder diffraction patterns (Fig. 3) are $a = 3.783$ (1)Å for the niobium compound and $a = 3.807(2)$Å for the tantalum compound. The hydrated phases lose water to give anhydrous $HMWO_6$ (M = Nb or Ta) around 400 °C and $MWO_{5.5}$ around 600 °C. Both $HMWO_6$ and $MWO_{5.5}$ also possess cubic ReO_3-type structures (Fig. 3). It is indeed curious that $MWO_{5.5}$ adopts the ReO_3 structure since the composition is anion-deficient. On annealing the cubic $NbWO_{5.5}$ at 900 °C for 12 hours, the phase transforms to a tetragonal structure (Fig. 3) with $a = 24.3$ and $c = 3.92$Å. The tetragonal phase appears to be related to tetragonal tungsten bronzes possessing a pentagonal column structure.[24]

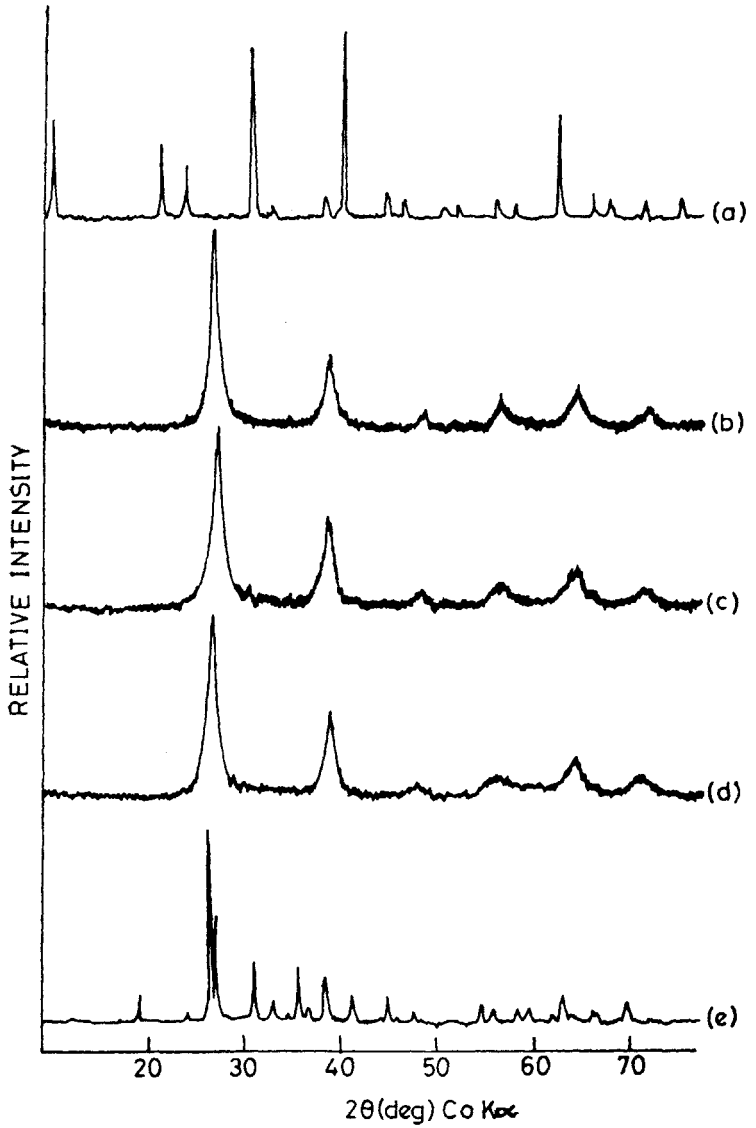

FIG 3 X-ray powder diffraction patterns of (*a*) $LiNbWO_6$ (trirutile), (*b*) $HNbWO_6.H_2O$, (*c*) $HNbWO_6$, (*d*) $NbWO_{6\cdot5}$ and (*e*) $NbWO_{6\cdot5}$ after heating at 900 °C for 12 hrs. Patterns (b)-(d) are cubic ReO_3-like and pattern (*e*) is TTB-like.

Ion-exchange of $LiMWO_6$ to give $HMWO_6$ is accompanied by a transformation from the trirutile to the ReO_3 structure. A plausible mechanism for the rutile-ReO_3 transformation is shown in Fig. 4. On ion-exchange, the tetragonal close packed anion array of the rutile structure transforms first to the HCP array; subsequently cation rearrangement occurs to give a MWO_6 network that is similar

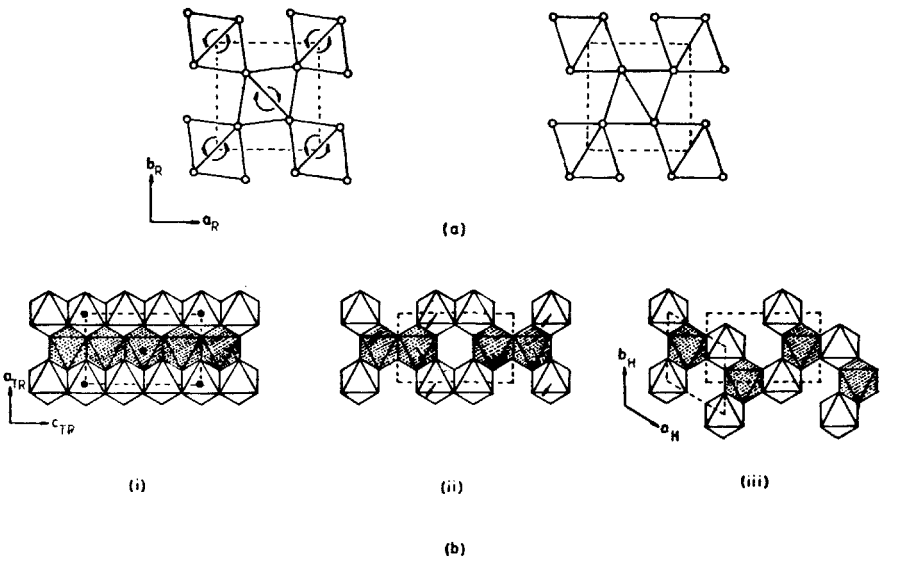

FIG 4 Plausible topotactic mechanism for the transformation of trirutile structure of $LiNbWO_6$ to ReO_3 structure of $HNbWO_6$. (*a*) shows transformation of tetragonal close packed anion array to hexagonal close packed (HCP) array by rotation of occupied octahedra. (*b*) shows rearrangement of $NbWO_6$ framework in trirutile to that of NbO_3 in $LiNbO_3$. (*i*) $LiNbWO_6$ trirutile; Li-occupied octahedra are shown with a filled circle. (*ii*) $NbWO_6$ framework after removal of lithium. (*iii*) $NbWO_6$ framework after rearrangement to $LiNbO_3$ structure.

to the NbO_3 network in the $LiNbO_3$ structure. The network may then transform to the ReO_3 structure by a mechanism similar to that proposed by Rice and Jackel[22] for the transformation of $LiNbO_3$ to $HNbO_3$. The latter involves rotation of the octahedra by $\sim 60°$ about the c_H which rearranges the hexagonal close packed anion array to 3/4 cubic close packed anion array of the ReO_3 structure. We believe that this is the first instance of a transformation of a rutile structure to ReO_3 structure, occurring topotactically on ion-exchange at low temperatures.

Topochemical Delithiation

Reversible topotactic insertion/extraction of lithium and sodium into/from layered metal oxides and chalcogenides has been extensively investigated in view of the importance of such systems as positive electrode materials in high-energy density solid state batteries.[25] Insertion/extraction of alkali metal atoms can also be achieved chemically through suitable reducing/oxidizing agents and this offers an attractive route for the synthesis of solids.[26] Thus extraction of lithium from $LiVS_2$ using I_2/CH_3CN has enabled the synthesis of metastable VS_2.[27] We have investigated the topochemical extraction of lithium from $LiVO_2$[23] and Li_2MoO_3. Both the oxides crystallize in layered structures related to rocksalt (Fig. 5).

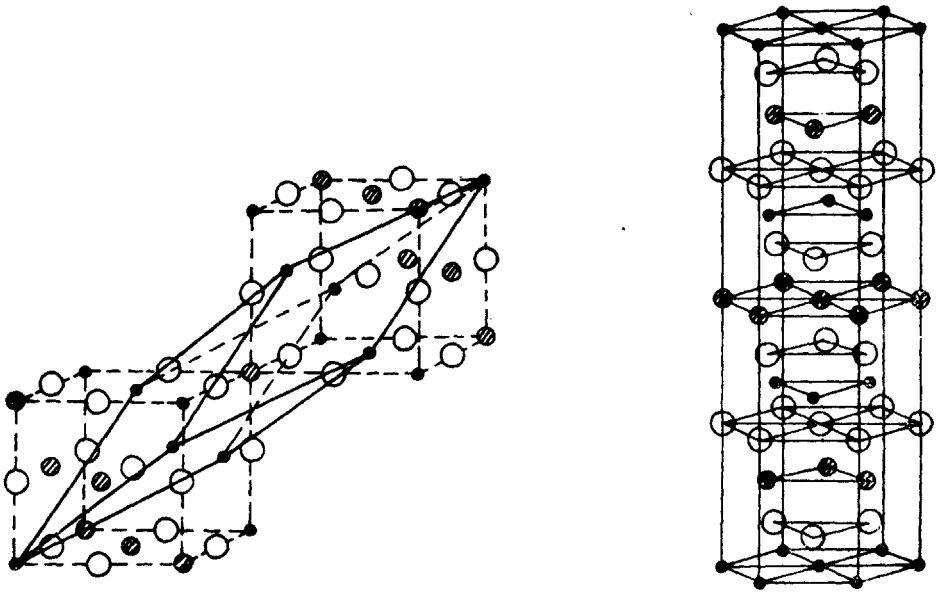

FIG 5 Structure of $LiVO_2$. (*a*) shows ordering of Li^+ and V^{3+} in alternate (111) cation planes of the rocksalt structure; (*b*) hexagonal unit cell of $LiVO_2$. Li_2MoO_3 possesses essentially the same structure except that V^{3+}-planes are replaced by planes containing both Li^+ and Mo^{4+} in the ratio 1:2.

In $LiVO_2$ which adopts the α-$NaFeO_2$ structure, Li^+ and V^{3+} ions are ordered in alternate (111) cation planes of the rocksalt structure, while in Li_2MoO_3, entirely Li^+ containing cation planes alternate with those containing Li and Mo in the ratio 1 : 2.

We have been able to extract lithium from $LiVO_2$ and Li_2MoO_3 using Br_2 in $CHCl_3$ as oxidizing agent.

$$LiVO_2 + \frac{x}{2} Br_2 \rightarrow Li_{1-x} VO_2 + xLiBr$$

$$Li_2MoO_3 + \frac{y}{2} Br_2 \rightarrow Li_{2-y} MoO_3 + yLiBr$$

In both the cases, delithiation proceeds topotactically yielding $Li_{1-x}VO_2$ and $Li_{2-y}MoO_3$ series of oxides (Figs. 5 and 6). Extent of delithiation can be easily followed by determining the oxidation states of the transition metal ion. In $Li_{1-x}VO_2$, there is a marked decrease in c and a slight increase in a as x increases (Table II). The diffraction pattern of $Li_{.10}VO_2$ (Fig. 6) is indexable on a cubic unit cell with $a = 8.17$Å. The changes in X-ray diffraction patterns of $Li_{1-x}VO_2$ are indicative

TABLE II

Chemical compositions and unit cell parameters of $Li_{1-x}VO_2$ and $Li_{2-y}MoO_3$ obtained by topochemical delithiation

Composition	Oxidation state of V/Mo	Littice parameters(Å)	
		a_H	c_H
$LiVO_2$	3.00	2.84	14.79
$Li_{0.65}VO_2$	3.35	2.84	14.80
$Li_{0.45}VO_2$	3.55	2.86	14.54
$Li_{0.25}VO_2$	3.75	2.89	14.31
$Li_{0.1}VO_2$	3.90	2.89	14.24
Li_2MoO_3	4.00	2.88	14.93
$Li_{1.3}MoO_3$	4.70	2.89	14.94
$Li_{0.95}MoO_3$	5.05	2.91	14.89
$Li_{0.5}MoO_3$	5.46	2.93	14.77

of a cation rearrangement while retaining the anion subarray. de Picciotto *et al.*[29] who have investigated the system subsequently have found structural evidence for the rearrangement of vanadium atoms; in $Li_{0.22}VO_2$ approximately one-third of the vanadium atoms is located in octahedral sites left vacant in the lithium layer. $Li_{1-x}VO_2$ members formed by delithiation appear to be metastable; thus rocksalt-like $Li_{0.5}VO_2$ transforms to LiV_2O_4 spinel and a VO_2 obtained by nearly complete delithiation of $LiVO_2$ transforms to the monoclinic (rutile-type) VO_2 at high temperatures (Fig. 6).

In the $Li_{2-y}MoO_3$ system, delithiation proceeds readily up to $y = 1.5$ yielding $Li_{0.5}MoO_3$ as the final product. All the intermediate phases up to $y = 1.5$ retain the parent structure (Fig. 7). Complete removal of lithium is not achieved under the conditions employed. It appears that lithium ions present in alternate (111) cation planes are removed while those present in the planes along with molybdenum are not readily extracted. It should be interesting to determine the structure of $Li_{0.5}MoO_3$ which would reveal whether cation rearrangement occurs or not.

Topochemical Reduction

Topochemical redox reactions are well known, typical examples being the transformation of iron oxides between rocksalt and spinel structures.[5] Reduction of WO_3 to yield W_nO_{3n-1} and W_nO_{3n-2} series of crystallographic shear phases may also be regarded as topotactic process since the relationship to the parent ReO_3 structure can be traced in the products. Similar topotactic reduction of perovskite oxides has not been investigated extensively, although a large number of superstructures derived from anion vacancy ordering in perovskite oxides is known.[30] Reduction of $CaMnO_3$ to $Ca_2Mn_2O_5$ has been found to be a topotactic reaction.[31]

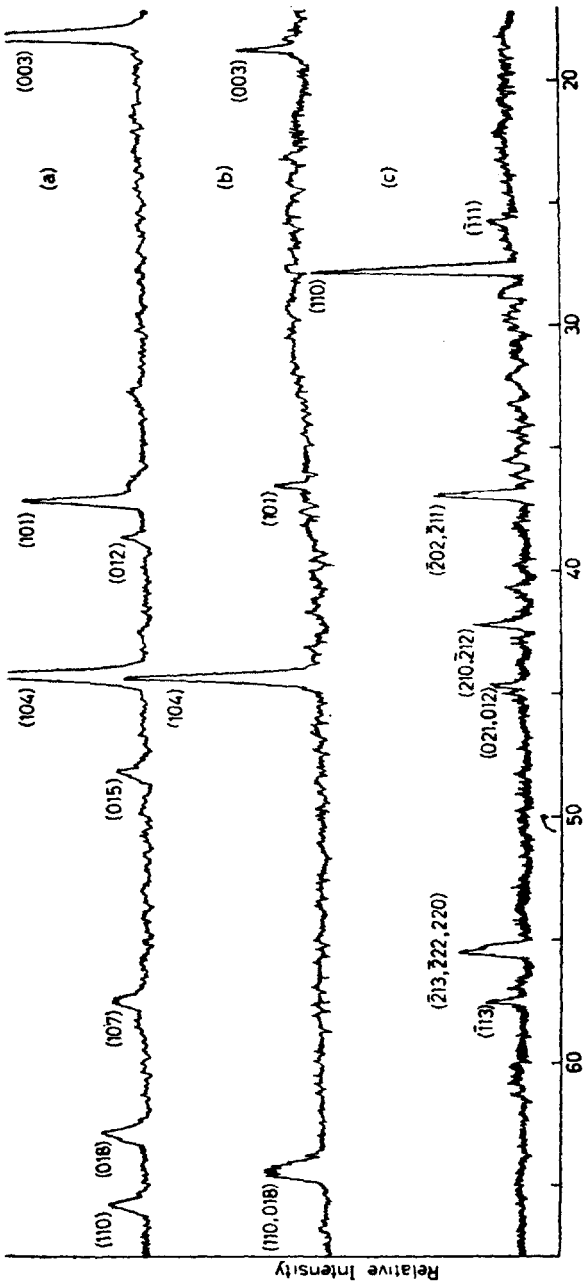

FIG 6 X-ray powder diffraction patterns of (*a* $LiVO_3$, (*b*) $Li_{0.1}VO_3$ and (*c*) monoclinic VO_2 (CuKα radiation).

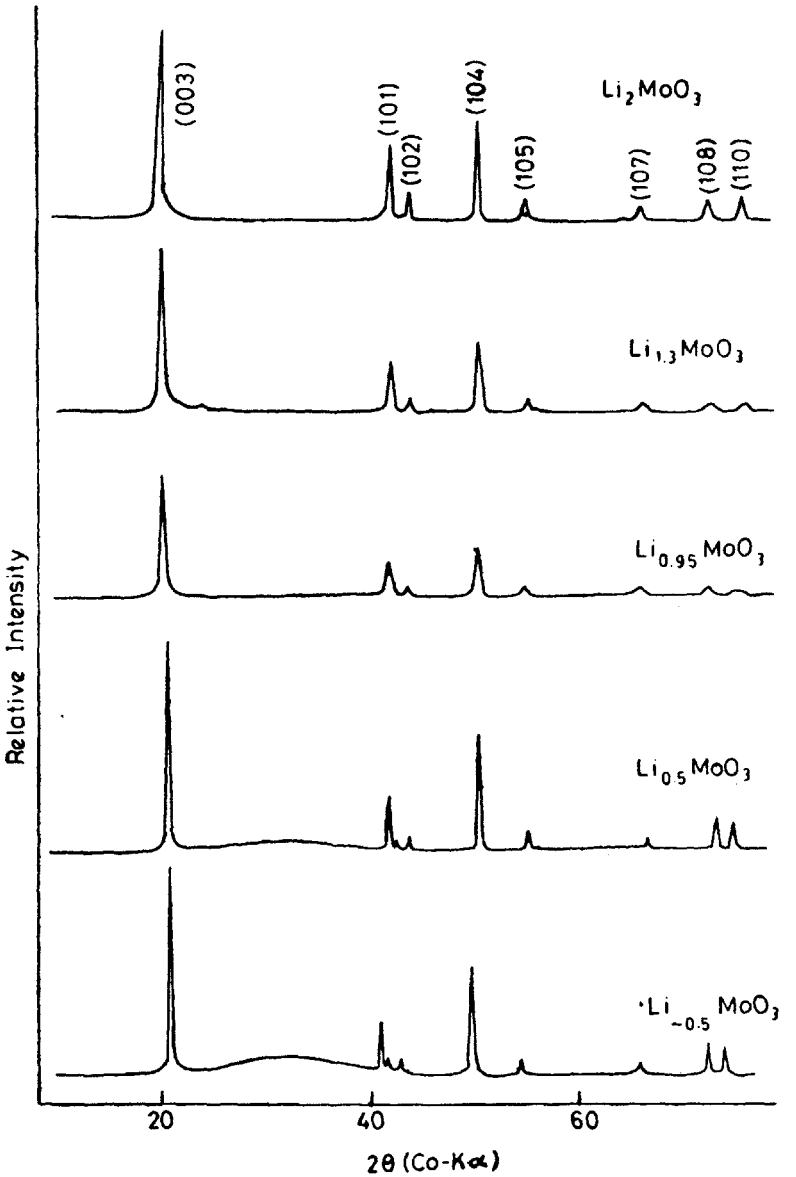

FIG 7 X-ray powder diffraction patterns of $Li_{2-y}MoO_3$.

Gai and Rao[32] who have investigated the nonstoichiometry of $LaNiO_3$ by thermogravimetry have proposed the formation of $La_nNi_nO_{3n-1}$ series. We have recently investigated the reduction of $LaNiO_3$ and $LaCoO_3$ under controlled conditions.[33] We have found that the reduction proceeds to give metastable phases of composition $La_2Ni_2O_5$ and $La_2Co_2O_5$. What is interesting is that both the oxides can be oxidized back to the parent perovskites indicating that the reversible reduction-oxidation is

indeed a topochemical reaction. X-ray and electron diffraction data (Figs. 8 and 9) reveal that while $La_2Co_2O_5$ adopts a brownmillerite structure, $La_2Ni_2O_5$ exhibits a new type of anion vacancy ordering in the perovskite structure involving octahedral and square-planar coordination of Ni^{2+}. The difference between the structures of compositionally similar $La_2Ni_2O_5$ and $La_2Co_2O_5$ can be attributed to the differences in site preferences of Co^{2+} and Ni^{2+}; when the ions are forced to accept four-fold anion coordination, Co^{2+} would prefer a tetrahedral geometry while Ni^{2+} would favour a square-planar geometry.

Topochemical Insertion of Hydrogen and Bismuth in Transition Metal Oxides

Hydrogen atoms can be inserted topotactically into a variety of inorganic solids.[7] Insertions of hydrogen into MoO_3 and MnO_2 yielding H_xMoO_3 and H_xMnO_2 are some of the early examples of this type of reaction.[34,35] Hydrogen insertion is a redox process involving electron transfer from the hydrogen atom to the reducible cation of the host solid. Hydrogen insertion has so far been investigated mainly with the binary transition metal oxides such as WO_3, MoO_3, ReO_3 and V_2O_5. We have found that hydrogen can be readily inserted into $LaNiO_3$ and $LaCoO_3$ perovskites at low temperatures in the presence of platinum which acts as a hydrogen-spillover catalyst. The compositions of the insertion compounds are $H_{0.85}LaNiO_3$ and $H_{0.50}LaCoO_3$ as determined by chemical analysis of oxidation states of nickel and cobalt. The insertion products possess essentially the same perovskite structure as the parent material (Fig. 10) with a slight increase in lattice parameter (pseudocubic unit cell parameter of $H_{0.85}LaNiO_3$ is 3.880Å, while the corresponding value for $LaNiO_3$ is 3.826Å). The hydrogen insertion compounds exhibit a much higher resistivity than the parent perovskites. Thus, while the resistivity of a compressed pellet of $LaNiO_3$ at room temperature was around 1ohm cm, the resistivity of the same pellet after hydrogen insertion was $\sim 10^4$ ohm cm. These results are consistent with the reduction of the transition metal ions to the divalent state on hydrogen insertion. Further work is in progress to characterize the structure and properties of hydrogen-insertion compounds derived from perovskite oxides.

We have been able to insert hydrogen into $HMWO_6$ (M = Nb or Ta) as well as in $Mo_{1-x}W_xO_3$ using Pt as the catalyst. $H_{1-x}MWO_6$ ($x \sim 0.3$) phases are isostructural with the parent $HMWO_6$ adopting cubic ReO_3-type structure. The phases are deep blue in colour and exhibit a much lower resistivity ($\sim$30 ohm. cm) than the the parent oxides ($\sim 10^6$ ohm cm.) The blue colour and the low resistivity reveal partial reduction of W^{6+} to W^{5+} on hydrogen insertion. With $Mo_{1-x}W_xO_3$, hydrogen insertion results in an increase of the symmetry of the structure, becoming tetragonal and cubic with increasing hydrogen content. Powder diffraction patterns of $Mo_{0.5}W_{0.5}O_3$ and $H_{0.2}Mo_{0.5}W_{0.5}O_3$ are compared in Fig. 11. The pattern of the hydrogen insertion compound can be indexed on a tetragonal cell with $a = 5.210$ and $c = 3.91$Å.

WO_3 forms a variety of tungsten oxide bronzes, A_xWO_3 (A = electropositive metal) which can be regarded as insertion compounds.[36] The structures

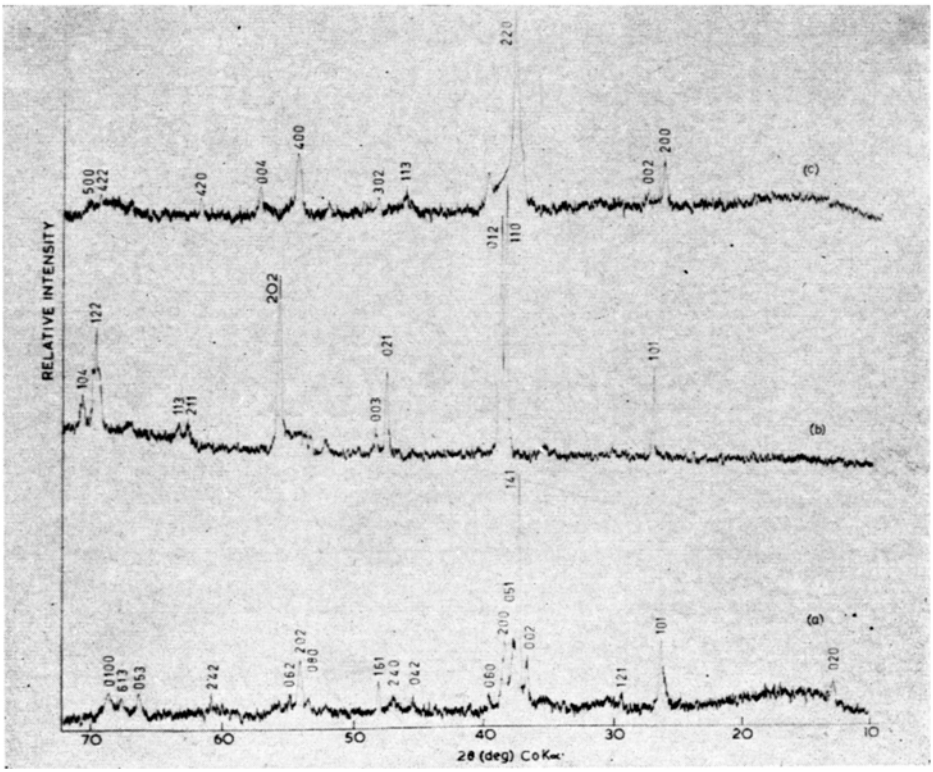

FIG 8 X-ray powder diffraction patterns of (*a*) $La_2Co_2O_5$, (*b*) $LaCoO_3$ obtained by oxidizing $La_2Co_2O_5$ and (*c*) $La_2Ni_2O_5$.

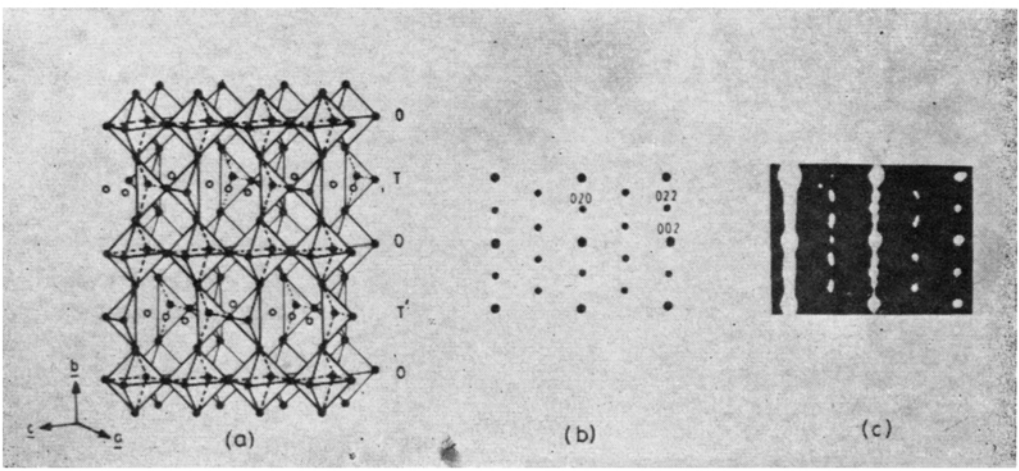

FIG 9 The structure and electron diffraction pattern of $La_2Co_2O_5$ in [100] zone axis—(*a*) brownmillerite structure, (*b*) the diffraction pattern expected and (*c*) the diffracted pattern observed.

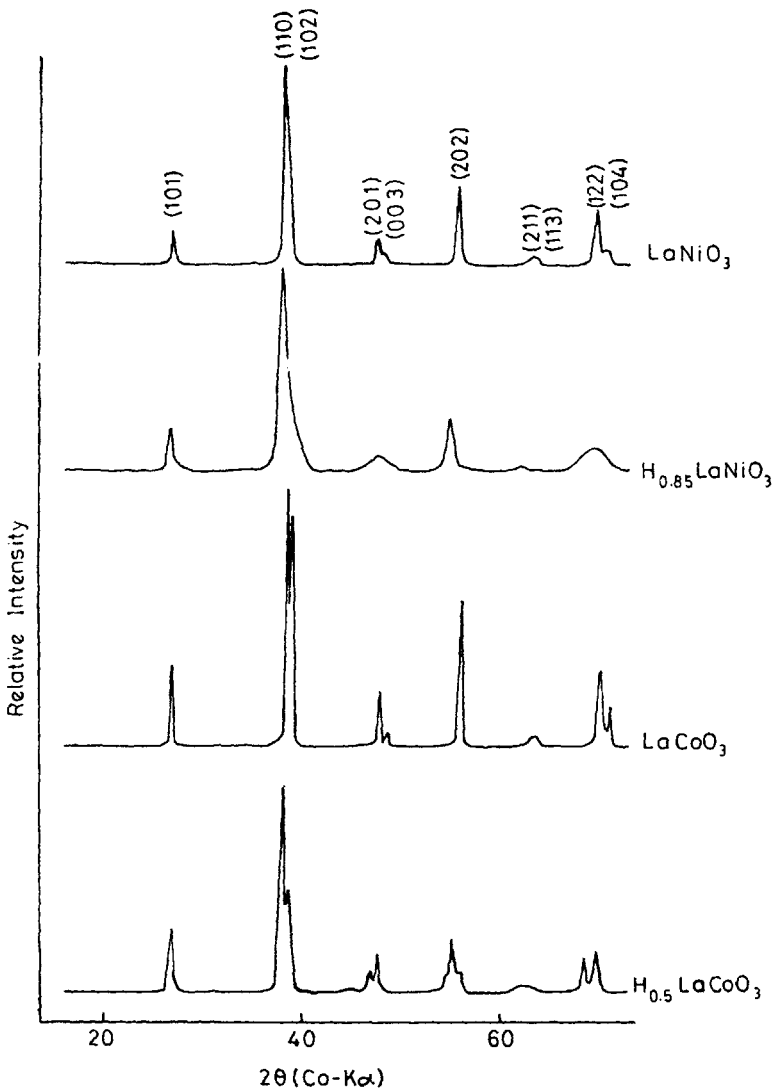

FIG 10 X-ray powder diffraction patterns of $LaNiO_3$, $LaCoO_3$ and their hydrogen insertion products.

of these compounds depend on the identity of A as well as the value of x. In addition to the three well-known tungsten bronzes, viz., cubic (perovskite-like), tetragonal (TTB) and hexagonal (HTB), a new type of tungsten bronze, called intergrowth tungsten bronze (ITB), has been discovered for small x values of A = K, Rb or Cs.[37] We have found that reaction of bismuth with WO_3 in sealed tubes around 900 °C results in insertion of bismuth atoms into WO_3, yielding ITBs, Bi_xWO_3 ($x \leqslant 0.07$). Detailed investigations of Bi_xWO_3 have shown that each bismuth transfers three electrons to the WO_3 host.[11a] The intergrowth structure of

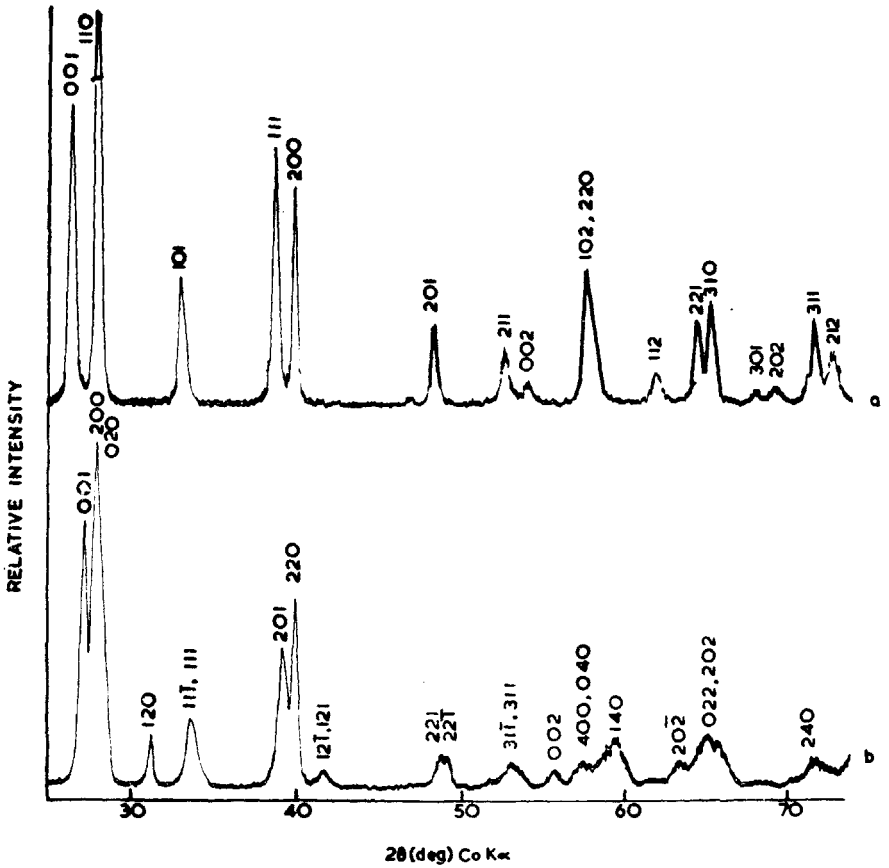

FIG 11 X-ray powder diffraction patterns of (a) $Mo_{0\cdot3}W_{0\cdot5}O_3$ and (b) $H_{0\cdot2}Mo_{0\cdot5}W_{0\cdot5}O_3$.

the bronzes, consisting of slabs of WO_3 strips of HTB units, one tunnel wide, has been revealed by high resolution electron microscopy (Fig. 12). Formation of the ITB structure can be viewed as a topochemical process since insertion of bismuth rearranges the octahedral network of the parent WO_3 to produce hexagonal tunnels to accommodate bismuth without breaking the W-O bonds in the parent oxide.

CONCLUDING REMARKS

The results reported in the paper show that it is possible to exploit topochemical reactions of inorganic solids, which occur at relatively low temperatures, to design new strategies for the synthesis of metal oxides. It should be interesting to extend topochemical methods for the synthesis of other classes of inorganic solids such as metal halides and metal chalcogenides. Synthesis of VS_2 by extraction of lithium from $LiVS_2$, of MFe_2S_4 (M = Ca, Sr, Ba) starting from $KFeS_2$ by ion-exchange and of Mo_6S_8 from $Cu_xMo_6S_8$ by acid leaching are some of the examples of topochemical synthesis of metal sulphides.[27,38] The significance of the present

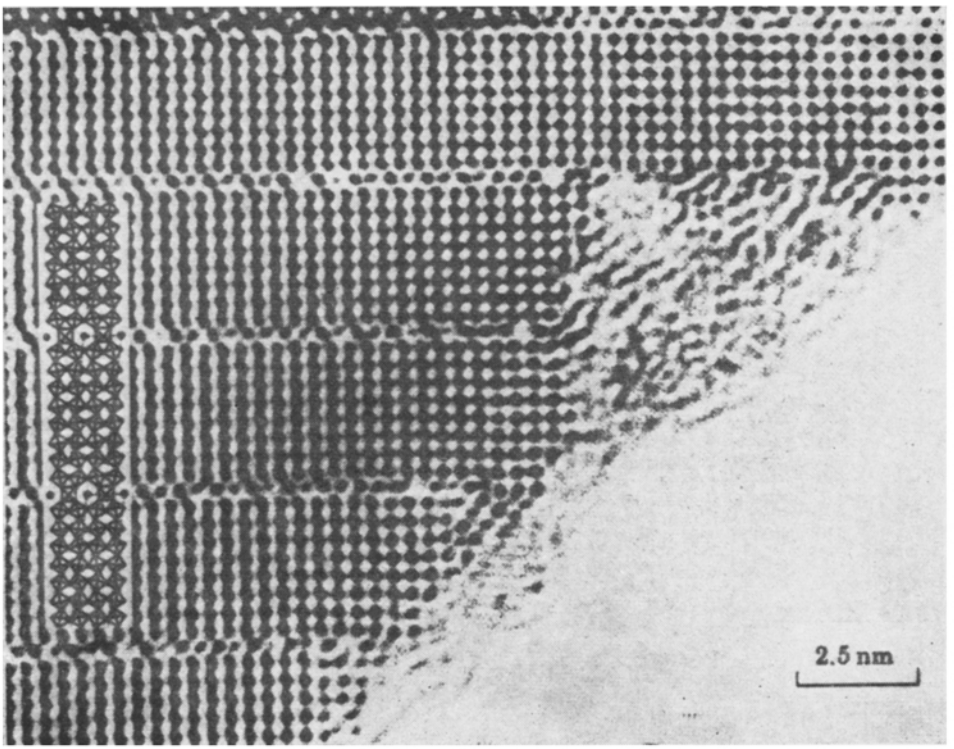

FIG 12 High resolution electron microscope (500 kV) image of $Bi_{n-1}WO_{3n}$ revealing the ITB structure. Slabs of WO_3 and HTB strips where Bi atoms are located are clearly seen in the image.[11a]

work extends beyond solid state synthesis. It is not known, for instance, why in some topochemical reactions the structure is essentially retained, while a structural transformation accompanies the reaction in others, as in the case of conversion of $LiNbO_3$ to $HNbO_3$. The role of electronic configuration of the transition metal atom and the nature of bonding in the solid on the course of topochemical reactions are not clear at precent. Thus it is not known why $LiNbO_3$ undergoes facile proton-exchange in aqueous acids, while the structurally related $LiSbO_3$ does not. Similarly, it is not known why lithium insertion into ReO_3 giving $LiReO_3$ and Li_2ReO_3 is accompanied by a structural transformation[39] while a similar transformation is not seen when lithium is extracted from Li_2MoO_3. These aspects deserve further investigation.

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