

Toward rational synthesis of transition metal oxides

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Abstract. Transition metal oxides display structural diversity crystallizing into a variety of framework, layer and tunnel structures. The electronic and structural properties of these can be fine-tuned due to their ability to reversibly accept metal cations and protons into their internal void spaces and electron-charge-transfer equivalents into their conduction bands. It is essential to prepare them in suitable form (powders, thin film or single crystal) with well-defined stoichiometry and morphological characteristics to be employed as 'intelligent materials'. Traditional solid state reactions however lead to thermodynamically stable products with more compact structures (sometimes multiphasic) which are not suitable for different applications.

The trend in modern solid state synthesis is therefore directed towards developing low-temperature reactions using appropriate molecular precursors that can react either as a molten metal or salt (the flux method) or in a molecular solvent (the hydrothermal method). Mild hydrothermal reactions in the temperature range from 100–300°C at low pH are found to be ideal conditions to crystallize novel vanadium, molybdenum and tungsten oxides and hydrates with layer or 3-D framework structures. The paper will focus mainly on the synthesis and structural properties of some selected materials. Effect of pH, time, temperature and nature of reactants on the structure of the products will be discussed. The approach used here is an attempt at synthesizing rationally designed transition metal oxides.

Keywords. Transition metal oxides; intercalation chemistry, metal coordination sites; distorted perovskite structure; redox reactions; X-ray diffractograms.

1. Introduction

Research into solid-state materials has grown dramatically in the past decade (Rao and Gopalakrishnan 1989). Motivation for this research includes the search for new inorganic solids with two- or three-dimensional network structures in connection with their applications in the areas of catalysis, chemical storage of energy and high temperature superconductivity. As such, progress in this area crucially depends upon synthesis of new materials possessing unusual structures and properties. In recent years there is considerable interest in the use of molecular species as precursors for the formation of inorganic materials.

Conventionally, solids are prepared through reactions proceeding at high temperatures under equilibrium conditions. Such efforts are often hampered by slow diffusion kinetics and incomplete reactions, rendering it difficult to obtain pure, single phase materials. Self-assembly, the formation of highly ordered structures, is currently playing an important role in biosynthesis and organic synthesis. However, assembling

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of small, soluble building blocks into inorganic crystalline solids is still unknown, probably due to lack of well-defined reaction chemistries. Recent studies have shown that through hydrothermal synthesis several complicated inorganic materials such as molybdenum and vanadium phosphates can be self-assembled from structurally simple precursors (Haushalter and Mundi 1993; Sohomonian *et al* 1993). The hydrothermal medium is attractive for ceramic powder synthesis because the combined effects of solvent, temperature, and pressure on ionic reaction equilibria can stabilize desirable products while inhibiting the formation of unwanted products. Also, it is possible to grow single crystals for structural analysis.

Vanadium, molybdenum and tungsten oxides and their alkali intercalated products have attracted considerable attention because of the variety of structures they can take up and their electrochemical and electronic properties. The variety of ways in which these metal polyhedra can be interlinked, and the accessibility of more than one oxidation state of metal, are the main factors contributing to the diverse solid-state chemistry. While the generation of polyanions of vanadium, molybdenum and tungsten in solution has been known for several years, only a limited number of them have been successfully crystallized (Pope 1983). These polyoxometallates invariably adopt complex cage (Keggin type) or cluster (Schlenker type) structures consisting of high-nuclear metal oxygen cluster anions formed by highly symmetrical core assemblies of MO_x units ($M = V, Mo, W$). Intercalation chemistry is however impossible in case of Keggin and Schlenker clusters as the cage framework blocks access to metal coordination sites.

An interesting example is that of tungsten trioxides. Through recent developments in low-temperature synthesis two metastable forms, a hexagonal and a cubic phase of tungsten trioxide, have been reported (Figlarz 1989) in addition to the well-known ReO_3 -related phase. Both phases possess a rigid tungsten-oxygen framework built of layers containing distorted corner-shared WO_6 octahedra and arranged to form six-membered rings (figure 1). In hexagonal WO_3 , the layers are stacked along $[001]$ axis, giving one-dimensional tunnels. In cubic pyrochlore WO_3 (figure 1), the layers are linked along the $[111]$ direction to form interconnected three-dimensional tunnels. These three tungsten oxides provide interesting sets to study the effect of structure on chemical reactivity and physical properties. In addition, it allows one to determine the impact of the openness of the structure on its behaviour. Also the cubic pyrochlore structure has expanded about 26% above that of the simple structure which is itself relatively open, being a distorted perovskite, ABO_3 , with all the A-sites vacant. WO_3 is not unique in this behaviour, TiO_2 is known to show an even larger number of structures (Tournoux *et al* 1986).

1.1 Hydrothermal reactions at autogeneous pressures

Hydrothermal reactions are becoming a popular route for the synthesis of transition metal oxides. This aqueous process is generally effected above room temperature and at high pressures. Typically the temperature varies from the boiling point to the critical point of water, 100–374°C and the pressures can be as high as 15 M Pa. In some cases, subsequent thermal treatment is required to crystallize the fine material.

Recently, we succeeded in obtaining two novel sodium tungstates in hexagonal and pyrochlore structures depending on the pH of the initial solution before hydrothermal treatment (Reis *et al* 1990, 1991b, 1992). Sodium present in the 3-D tunnels of the pyrochlore structure could be easily ion-exchanged for hydrogen, potassium, rubidium,

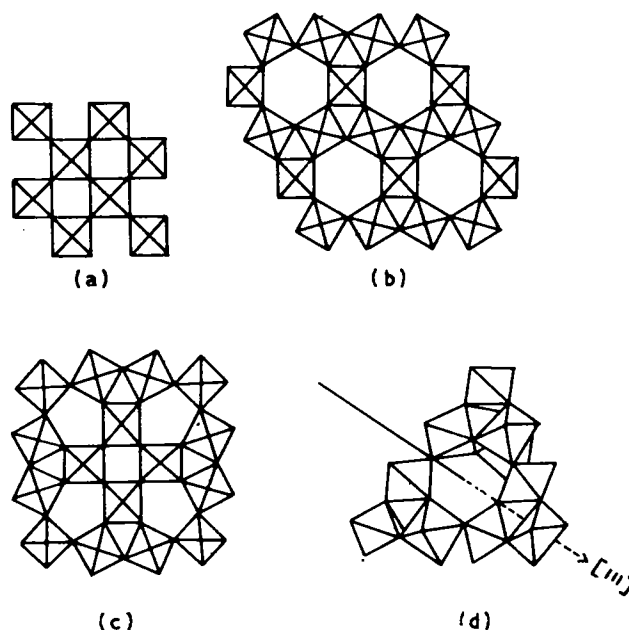


Figure 1. Structures of (a) ReO_3 , (b) hexagonal, (c) tetragonal and (d) pyrochlore tungsten oxides.

cesium, thallium, silver and ammonium. In contrast to the pyrochlore phase, the sodium occurring in the 1-D tunnels cannot readily diffuse out of this structure due to blockage. All these tungsten oxides undergo redox reactions with lithium to form reduced intercalation compounds. It is surprising to note that the pyrochlore structure is only reduced to W(V), whereas in the hexagonal lattice the tungsten can be reduced to W(IV). We also had success in preparing partially reduced metallic conductors such as $(\text{NH}_4)_x\text{WO}_3$ using organic-based solvents during the synthesis (Reis *et al* 1991a).

In aqueous solution vanadium, molybdenum and tungsten are known to occur in different oxidation states. They all undergo complex hydrolysis behaviour forming several ionic species (Baes and Mesmer 1976). Figure 2 shows the potential versus pH diagram of dilute vanadium, molybdenum and tungsten solutions at 25°C. In order to crystallize some of these reduced oxides we have employed a hydrothermal technique in our study. The present investigation is intended to offer a unified view of synthesizing metal oxides from aqueous solution.

2. Experimental

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and NaVO_3 were obtained from Alpha and SD Chemicals. In a typical experiment, 20 ml of 1M alkali metallate solution was acidified with required amounts of 1M HCl to give pH values in the range 1.0 to 6.0. The solutions were heated at specified temperatures and autogeneous pressures for a few days in Parr 4745 stainless steel acid digestion reactors. Prolonged standing of the acidified solutions can lead to precipitation, hence they are sealed and heated within one hour of preparation. Reductions of the metal ions are effected by reacting the

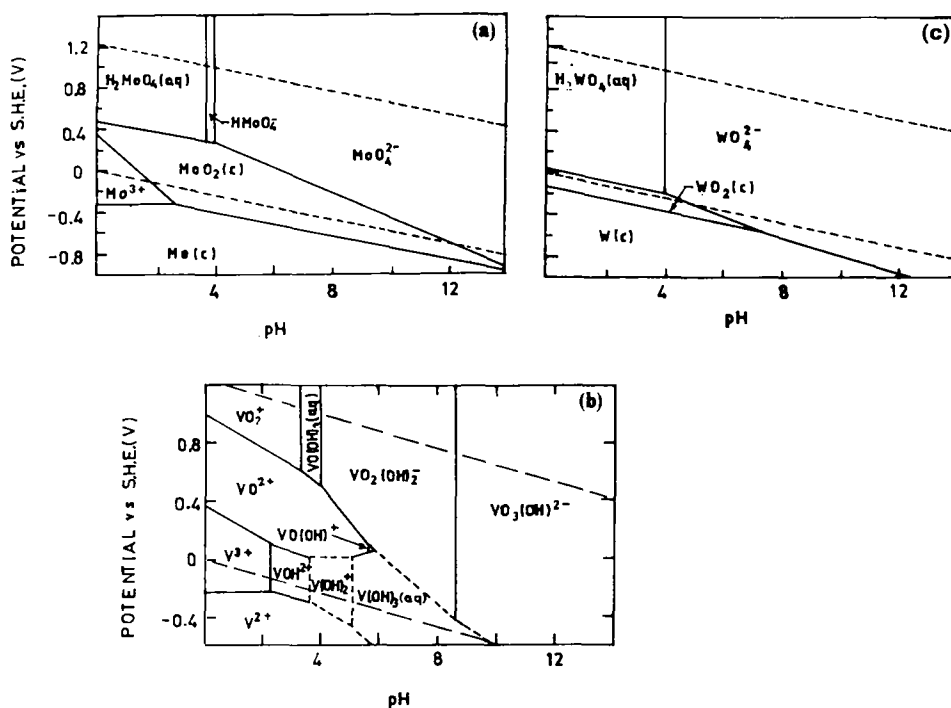


Figure 2. Potential versus pH for dilute vanadium (a), molybdenum (b) and tungsten (c) solutions at 298 K.

metallates with stoichiometric amounts of lower valent metal powder. The microcrystalline products obtained after the reaction were filtered, washed with ethanol and dried in air.

X-ray diffractograms were recorded on a Rigaku or Philips powder diffractometer employing Ni-filtered CuK radiation. X-ray powder diffraction patterns were analysed using several programs TREOR, PULVERIX and CELL. Thermal gravimetric analysis was performed on a Stanton Redcraft in an N_2 atmosphere. FTIR spectra were recorded using a Nicolet 5DX spectrometer. Scanning electron microscopic studies were made using Philips model 515 and EDAX (Philips Model PV 9900) for elemental analysis of various metals present. The quantitative analysis of sodium ions in these materials was also done using AAS, ICPS and flame photometry.

3. Results and discussion

3.1 Synthesis of tungsten oxide bronzes

X-ray powder diffraction patterns of the samples crystallized from acidified tungstate solutions showed the occurrence of a pyrochlore phase ($a \sim 10.3 \text{ \AA}$) when the initial pH was around 4 and a hexagonal phase ($a \sim 7.3$ and $c \sim 3.9 \text{ \AA}$) at pH 2 in addition to unreacted tungsten metal. Although the solids were pale blue in colour, it appears from our chemical analysis that reduction could not be achieved even to a limited extent by using tungsten metal under these conditions.

3.2 Synthesis of molybdenum oxide bronzes

X-ray powder diffractograms of the samples obtained in Na-Mo-O system under reduced conditions were altogether different from the tungstate system. Most of the samples prepared showed the formation of dark violet coloured crystals when pH was in the range 2–4. A careful analysis of the powder pattern of the sample prepared around pH = 2 showed that it was crystalline and did not contain any lines due to the presence of known molybdenum oxide hydrates, molybdenum oxides or known sodium molybdenum oxide bronzes. The pattern could however be completely indexed on a monoclinic cell (table 1) with $a = 7.723$, $b = 7.895$ and $c = 7.635$ Å and $\beta = 102.02^\circ$. The cell parameters and powder pattern suggest that it may probably belong to a distorted perovskite structure. It should be noted that our phase was very different from ReO₃-type MoO₃ reported in the literature. Also our samples are partly reduced. The oxidation state of molybdenum was estimated to be around + 5. Since the sample always contains a small amount of unreacted Mo metal, we are unable to ascertain its exact value. Though we have confirmed the presence of sodium in this phase, we could not estimate it quantitatively. IR spectrum of the samples showed characteristic features due to water and metal hydroxyl groups. In our reactions only the above phase seems to form in pH range 4–2. Single crystal analysis is needed to ascertain the exact nature of this phase.

3.3 Synthesis of vanadium oxide bronzes

When acidified sodium vanadate solutions were treated with vanadium metal, a blue solution was obtained which on aging at room temperature for a week resulted in a bluish-green powder. X-ray diffraction pattern of this phase (figure 3a) showed it to be amorphous in nature. On the other hand when the blue solution acidified to appropriate pH was subjected to hydrothermal treatment at 150–200°C for 2 days (refer table 2),

Table 1. X-ray powder diffraction pattern of NaMoO.

<i>h</i>	<i>k</i>	<i>l</i>	2TH-obs	2TH-calc	D-obs	<i>I</i> / <i>I</i> ₀
2	0	0	23.50	23.53	3.782	24
–2	0	1	24.10	24.06	3.689	4
2	1	0	26.10	26.13	3.411	100
0	2	2	33.00	32.99	2.712	10
			36.40		2.466	26
2	2	1	36.71	36.69	2.446	46
–1	3	1	37.31	37.31		
–1	1	3		37.34		
1	0	3	40.41	40.41	2.230	39
–3	1	2		40.42		
2	0	3	47.72	47.72	1.904	9
–1	2	4	53.31	53.24	1.717	40
4	2	0		53.76		
1	3	3	53.81	53.83	1.702	26
0	3	4	60.81	60.77	1.522	9
–2	1	4	60.84			

Cell parameters are based on $a = 7.723$; $b = 7.789$; $c = 7.635$ Å and $\beta = 102.02^\circ$

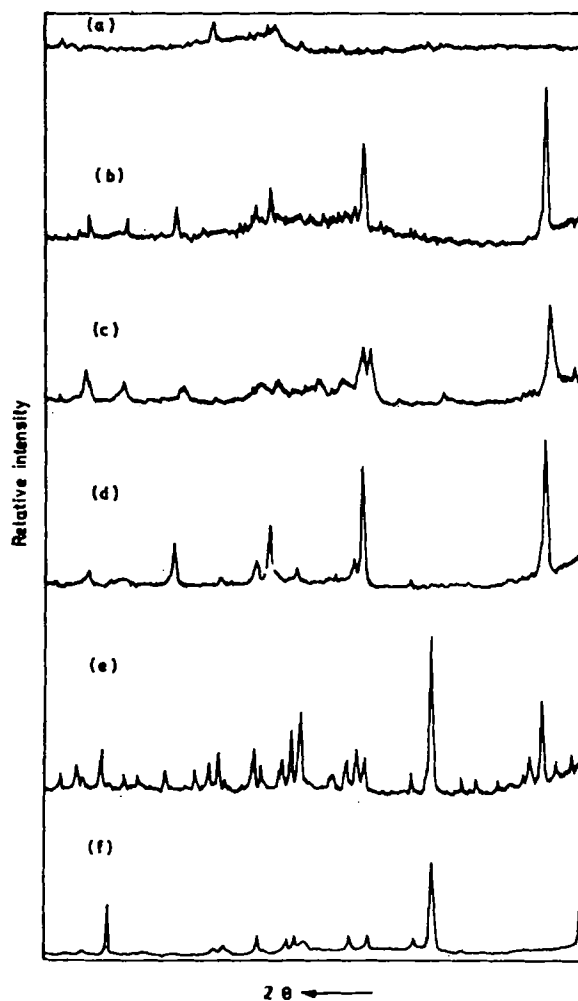


Figure 3. X-ray diffraction patterns of reduced sodium vanadates obtained under hydrothermal conditions: (a) pH 1.5 and 308 K, (b) pH 1.5 and 473 K, (c) pH 2, (d) pH 2.5, (e) pH 4 and (f) pH 6 and 423 K.

several crystalline phases were obtained as shown by X-ray diffraction patterns (figure 3). From these X-ray diffractograms we could distinctly differentiate the appearance of two different phases – one predominantly occurring in the pH range 4–6 and the other forming when pH is 2 to 4. We are not able to index these patterns on any known fully oxidized or reduced vanadium oxide/hydroxide hydrates. The oxidation state of vanadium is around +4 in all the cases. IR spectra and thermal analysis data support the presence of water as well as hydroxyl groups in the structure. Single crystal X-ray analysis is being carried out to ascertain the structure and composition of these phases.

Our results on Na-Mo-O and Na-V-O systems have shown that it is possible to synthesize new oxide bronzes under hydrothermal conditions. We expect that these possess unusual structures and intercalation chemistry.

Table 2. Reaction conditions and TGA data of oxide bronzes.

System	Reactants	pH	Reaction conditions		Colour	Wt. loss (%)
			Temp. (°C)	Days		
Na-W-O	5Na ₂ WO ₄ :W	2	130	2	Violet	
		4	130	2	Violet	
Na-Mo-O	5Na ₂ MoO ₄ :Mo	4	130	2	Violet	4
Na-V-O	4NaVO ₃ :V	1.5	35	2	Green	9
		1.5	200	2	Green	12
		2	200	2	Green	11.7
		2.5	200	2	Green	10.1
		4	200	2	Dark green	9.5
		6	200	2	Dark green	7.1

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