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Reviews

Chimie Douce Approaches to the Synthesis of Metastable Oxide Materials†

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While thermodynamically stable metal oxides and other solids could be prepared by conventional high-temperature (ceramic) methods, syntheses of the more important metastable oxide materials of current interest, such as the zeolites and other microporous solids as well as layered and framework oxides of various kinds require mild, chemistry-based routes that occur at relatively low temperatures. In this review, we present a brief survey of the emerging chimie douce (soft-chemical) routes which enable synthesis of a wide variety of metastable oxide materials. A distinction is made between topochemical and nontopochemical routes. Ion exchange, intercalation, redox insertion/extraction, and pillaring are examples of topochemical routes; syntheses using sol–gel, hydrothermal conditions, molten salt media, and acid leaching of appropriate precursor oxides belong to the nontopochemical category. In topochemically controlled synthesis, a thermodynamically stable phase is prefabricated by a high-temperature route, which is then transformed into a metastable phase by an appropriate soft-chemical route. Several examples of synthesis of metastable oxides, drawn from the recent literature as well as from the author's work, are discussed.

1. Introduction

Among the various inorganic materials of current interest,[1] metal oxides occupy a pivotal position. For many of the properties/phenomena of importance in solid-state science today, one can find prototypical examples from among the family of metal oxides. Thus, $SrRuO_3$ and $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba) are metallic ferromagnets, Bi_2WO_6 and $Bi_4Ti_3O_{12}$ are high-temperature ferroelectrics, $LiNbO_3$ and $KTiOPO_4$ are frequency-doubling nonlinear optical materials, Na β-alumina, $Na_3Zr_2PSi_2O_{12}$ (NASICON), and $Bi_4V_2O_{11}$ are fast-ion conductors, $LiCoO_2$ and $LiMn_2O_4$ are mixed conductors useful for electrode materials in solid-state batteries, members of zeolite and ALPO family of oxides are molecular sieves and catalysts for several commercially important organic reactions, and, last but not least, cuprates containing CuO_2 sheets are high-T_c superconductors. It is increasingly realized that progress in inorganic materials chemistry crucially depends on the synthesis of new solids possessing unique structures and

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properties.[2-4] Progress in the past largely depended on the chance discovery (serendipity) of new materials.[5] The current trend[2,6] is toward "rational design" of solids based on the accumulated knowledge of crystal chemistry, thermodynamics, and reactivity as well as the relationship between crystal structure and electronic properties. Rational design implies two steps: the first is to identify the right kind of crystal structure and probable chemical composition that would give rise to the desired property; the next step is to find an appropriate procedure to synthesize the material. Although we are far from the ultimate dream of "tailor-making" solid materials with specified structure and properties, rational design has been possible to a limited extent within selected families of solids. An early example[7] of rational design is that of the fast sodium ion conductor, NASICON. The composition of this material was predicted to be a three-dimensional sodium ion conductor on the basis of crystal chemical and other considerations. A recent example[8] of rational design is that of the zincosilicate (VPI-7) that has a low framework density. The synthesis of this solid was based on a correlation[9] between framework density and smallest ring size in tetrahedral networks.

Rational design of inorganic solids continues to remain a challenging task[10] not only because we are unable to predict definitively the structure, stability, and properties of solids but also because, very often, we do not know the correct method to synthesize a solid even if we knew the desired composition and probable structure. While it may be possible to predict the existence of new compositions within the same structural families by analogy with already known phases, guided by intuition based on previous experience, prediction of entirely new phases with unknown structure and properties is almost impossible at present. Even if we are able to predict the composition somehow, the problem of synthesis is equally formidable. This is illustrated by the two examples, viz., NASICON and VPI-7 cited above. While NASICON could be synthesized by the common method employed in solid-state chemistry, viz., the ceramic method, which involves reacting a polycrystalline mixture of reagents at elevated temperatures, VPI-7, on the other hand, was synthesized by the hydrothermal method which uses mild conditions. Certainly, VPI-7 could not have been prepared by the ceramic method for the simple reason that it is a metastable solid.

It is well-known that the ceramic method is a crude approach to the problem of synthesis of inorganic solids,[4,11] which stands in contrast to the sophisticated methods employed by organic chemists today.[12] While organic molecular synthesis relies on kinetic control of the synthetic pathways through reaction mechanism and unit-by-unit assembly of the final product, formation of solids by the high-temperature ceramic method is totally controlled by the diffusion of atomic/ionic species through reactants and products, rather than breaking and making of chemical bonds (reaction mechanism). Attempts have been made recently to eliminate the problem of diffusion control of solid synthesis[13] by using sequentially deposited thin films of reactant solids, which are reacted at relatively low temperatures (~500 °C). Under these conditions, nucleation rather than diffusion becomes the rate-limiting step. While the strategy has enabled the synthesis of metastable intermediates in chalcogenide and silicide systems, it has so far not been possible to extend it to metal oxide synthesis. Another innovative synthetic strategy[14] which overcomes the diffusion control of solid–solid reactions is the use of highly exothermic reactions, such as that between $MoCl_5$ and Na_2S, which enables rapid synthesis of inorganic solids. However, since the reaction is so rapid, generating high temperatures, the method is useful mostly for the synthesis of thermodynamically stable phases.

The limitation of being able to synthesize only the thermodynamically stable phases by the ceramic method is a serious one in the context of rational design, because most of the solid materials of current interest are metastable phases. Thus, zeolites and other microporous solids, high-T_c cuprates, intercalation compounds of various kinds, inorganic/organic nanocomposites, pillared layered materials, to name the obvious, are all metastable materials. The ordinary ceramic method is not the right choice for the synthesis of most of these solids.

Realizing the limitations of the conventional high-temperature ceramic route, conscious efforts have been made in recent years toward evolving alternative strategies for the synthesis of metastable inorganic solids. The efforts have led, among others, to the development of mild, chemistry-based, approaches, which occur at relatively low temperatures, where attention is paid to details of structure, stability, and mechanism of product formation. These approaches, pioneered mainly in France and the United States, go by the name *chimie douce* (soft-chemistry) methods. While these methods have undoubtedly led to the successful synthesis of several metastable solid materials, it should be mentioned that there are other not-so-soft routes, such as quenching of molten reactants from high temperatures, nonequilibrium chemical vapor deposition,[15] and pulsed laser ablation,[16] which have also led to the synthesis of novel metastable solids.

This article is mainly devoted to a discussion of soft-chemistry routes and synthesis of metastable oxide

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materials, as well as the associated thermodynamic aspects.

2. Thermodynamics of Metastability and Routes to Metastable Phases

Since many of the oxide materials of current interest are metastable phases, an understanding of the thermodynamics of metastability, in general, would be helpful in designing routes for their synthesis. A metastable phase, by definition, has a higher free energy than the corresponding stable phase(s) for the same chemical composition.[17] Thus, metallic glasses, superconducting or superionic conducting oxides, such as $BaPb_{0.75}Bi_{0.25}O_3$, $Li_{1+x}Ti_{2-x}O_4$ ($0 < x \leq 1/3$), $La_{1.85}Sr_{0.15}CuO_4$, and $Na_{1+x}Al_{11}O_{17+x/2}$, zeolites, and other microporous solids, doped semiconductors such as Si:P, and "monodispersed" fine particles of metal oxides are all metastable phases under normal conditions where their properties are investigated. The origin of metastability is however not the same in all these examples. Thus, metallic glasses, doped semiconductors, and sodium β-alumina are compositionally metastable,[17] the entropy arising from frozen-in disorder and defects contributing to the higher free energy content. In the superconducting oxides cited above, metastability may be due to both the compositional disorder as well as the electronic instabilities associated with the superconducting composition.[18] Zeolites and other microporous solids, on the other hand, are topologically metastable materials,[1] the structural variations arising from the innumerable ways in which the SiO_4, AlO_4, and PO_4 tetrahedra can be assembled. The single most important factor[19] that contributes to the rich structural diversity and metastability of zeolites seems to be the soft X–O–X (X = Si, Al, or P) bending potential that allows facile bending of these bonds over a wide range of angles. The metastability of fine particles of oxide materials, produced by sol–gel and other methods, is due to the excess free energy associated with fine particle morphology.

It is instructive to inquire, in the context of synthesis, why metastable phases form at all in the first place or, in other words, why does not a solid directly crystallize as the thermodynamically most stable phase when it is synthesized? An answer to this question was provided long ago by Wilhelm Ostwald, who observed that systems generally transform, when the option is available, to a metastable rather than to the most stable phase.[17] It appears that when a solid is synthesized, say by quenching a melt or crystallizing from a solution, several thermodynamically permissible avenues are available for structure evolution, including, of course, the one that would give the most stable phase. The kinetically favored structural evolution involves smallest correlations of atomic positions and motions. Accordingly, when the initial system is far from equilibrium, nucleation of a metastable phase may be energetically more favorable than the stable phase. It is indeed remarkable that Ostwald's ideas regarding metastability have such a wide applicability in diverse disciplines including metallurgy,[17] materials science, ceramics,[20] and even in atmospheric sciences.[21] For instance, the sequence of solid phases formed in stratospheric aerosols, consisting of H_2SO_4, HNO_3, and H_2O, have recently been shown to follow the Ostwald's rule.[21]

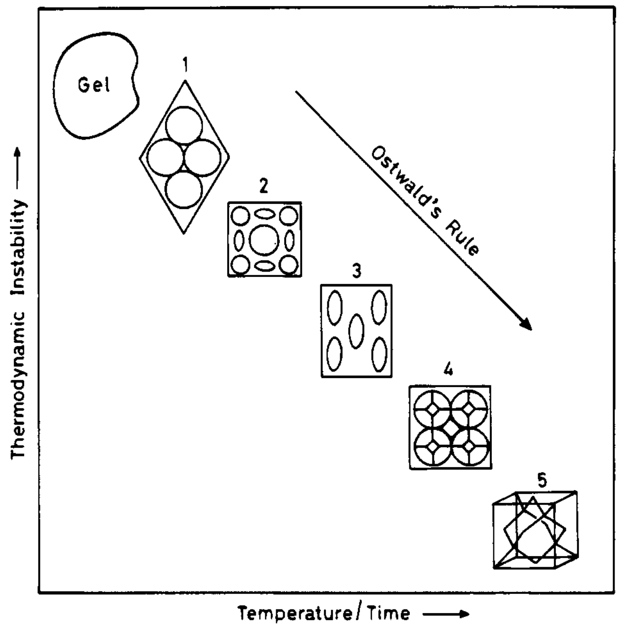

Figure 1. Schematic diagram showing the thermodynamics of zeolite synthesis. 1, 2, 3, and 4 denote zeolites of decreasing porosity. 5 denotes dense aluminosilicate.

We have already mentioned that a well-known family of metastable oxide materials are the zeolitic aluminosilicates and aluminophosphates.[22] Over the years, zeolite chemists have evolved methods for their synthesis.[23] Zeolites are generally synthesized from aluminosilicate gels under hydrothermal conditions (100–200 °C), often in the presence of certain organic additives at appropriate pH. Figure 1 shows the thermodynamics of zeolite synthesis schematically. The synthesis follows Ostwald's rule: the first phase to form is often not the most stable that is thermodynamically accessible. Accordingly, the phase dissolves and is replaced by a more stable second phase and so on, until the most stable phase is formed at the end. The thermodynamically most stable phases in this case are the dense forms of aluminosilicates (e.g., mullite), which are useless as microporous materials. Dense forms of aluminosilicates, such as cordierite, mullite and anorthite, are however useful microelectronic packaging materials, which have indeed been prepared by sintering appropriate zeolite precursors[24] around 1000 °C.

The principles we learn from zeolite synthesis (Figure 1) are useful for the synthesis of other metastable materials as well. We learn first that there are several metastable phases in a system, of which the one that crystallizes at the lowest possible temperature and at the shortest duration is most metastable. Since kinetic barriers exist between successive metastable phases, it is often possible to arrest the reaction by choosing

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appropriate experimental conditions to give the desired metastable product. In zeolite synthesis, addition of certain organic reagents stabilizes one metastable phase to the exclusion of others. Last, we learn that the duration of the reaction is an important variable in the synthesis of metastable materials.

Surprisingly, many of these principles seem to govern the formation of another important class of metastable materials, namely, the high-T_c superconducting cuprates. It is accepted that almost all the high-T_c cuprates are metastable phases at ordinary conditions.[18,25] A high entropy arising from point defects and other kinds of disorder stabilizes these phases at the synthesis condition. The 125 K superconductor[26] of the ideal composition, $Tl_2Ba_2Ca_2Cu_3O_{10}$, is a notorious example of a metastable cuprate, which cannot be prepared as a thermodynamic equilibrium phase under any combination of temperature, pressure and composition, since the phase actually decomposes under the same conditions at which it forms.[18] Accordingly, duration of synthesis becomes a stringent variable for the realization of this phase. A single-phase material is obtained at 890 °C in 1 h by reacting the component oxides in a sealed gold tube.[26] On the basis of this realization, we have recently synthesized[27] a new series of metastable high-T_c cuprates, $(Tl_{2-x}Cu_x)Ba_2CaCu_2O_8$, by carrying out the synthesis at lower temperatures and for shorter duration than those normally employed for the synthesis of $Tl_2Ba_2CaCu_2O_8$. The metastability of $(Tl_{2-x}Cu_x)Ba_2CaCu_2O_8$ is dramatically revealed by the observation that the phase, $(TlCu)Ba_2CaCu_2O_8$, (having the $Tl_2Ba_2CaCu_2O_8$ structure), synthesized by reaction at 650 °C for 2 h, is unstable with respect to the following decomposition at 850 °C:

$$2(TlCu)Ba_2CaCu_2O_8 \rightarrow Tl_2Ba_2Ca_2Cu_3O_{10} + 2BaCuO_2 + CuO + {}^1/_2O_2$$

Sleight[18] lists three different routes for the synthesis of metastable solids. The first route enables synthesis of materials that are metastable under ambient conditions but stable under some other conditions of temperature and pressure. The strategy is to synthesize the material under conditions where it is thermodynamically stable and then quench it to ambient conditions. If the phase possesses sufficient kinetic stability, it would be in a metastable state indefinitely under ambient conditions. Several solid solutions prepared at high enough temperatures, where entropy due to point defects contributes to the free energy of formation, are examples of synthesis by this route. A well-known example[28] is the solid solution between $BaPbO_3$ and $BaBiO_3$, where complete solid solubility obtains at temperatures above 880 °C. All the compositions including the superconducting ones are metastable. Synthesis by this route reveals that it is possible to adapt the ceramic method to obtain metastable phases by judicious choice of experimental conditions (temperature, time, cooling/quenching rates). Indeed, this method is similar to the bulk phase quenching commonly employed by metallurgists[17] for the synthesis of metastable alloys.

We employed this route for the synthesis of perovskite-like $BaPb_{1-x}Cu_xO_{3-x}$ and $BaBi_{1-x}Cu_xO_{3-x}$ solid solutions,[29] which could not be prepared by the ordinary ceramic route. The synthesis involved two steps. First, the constituent oxides, reacted at temperatures (1100–1150 °C) close to the melting point of the mixture, were quenched. The products were then annealed in oxygen at lower temperatures to obtain perovskite-like structure. We adopted a similar procedure for the synthesis of metastable $LiMMoO_6$ (M = Nb, Ta) trirutile oxides.[30]

The second route, which involves prefabrication of a thermodynamically stable phase which is then transformed to a metastable phase by a low-temperature, soft-chemical, operation such as dehydration, decomposition, ion exchange, intercalation/deintercalation, pillaring, etc., is relevant to the theme of the present article. We shall discuss several examples of synthesis of oxide materials by this route in the next section.

The third route consists of synthesis all the way under nonequilibrium conditions. The products are kinetically controlled metastable intermediates. A significant activation barrier prevents the phase from transforming into thermodynamic equilibrium products. Growth of diamond films which occurs under conditions far removed from equilibrium is a typical example. Syntheses of both bulk as well as films of high-T_c superconducting phases in the Hg, Tl, Bi/Ba, Sr, Ca/Cu/O systems also seem to be examples of this route.[16b,18]

Besides these direct solid-state approaches, other novel strategies that rely on, for example, direct conversion of molecules to solids,[31] molecular recognition at the inorganic/organic interfaces[32] and layer-by-layer assembly of heterostructures,[33] have been employed for the synthesis of a myriad variety of metastable phases that indeed form bridges between molecular chemistry on one hand and supramolecular and solid-state chemistry on the other.

3. Soft-Chemistry Routes for the Synthesis of Oxide Materials

3.1. Topochemical Routes. Although it has long been recognized[34] that several structural transformations in the solid state are governed by topotactic/topochemical considerations in the sense that "a definite and reproducible crystallographic orientation relationship" exists between the reactant and product phases, the mechanistic aspects of such transformations and their implications toward synthesis of metastable phases are being realized only in recent years. The late Professor Figlarz, one of the pioneering researchers in

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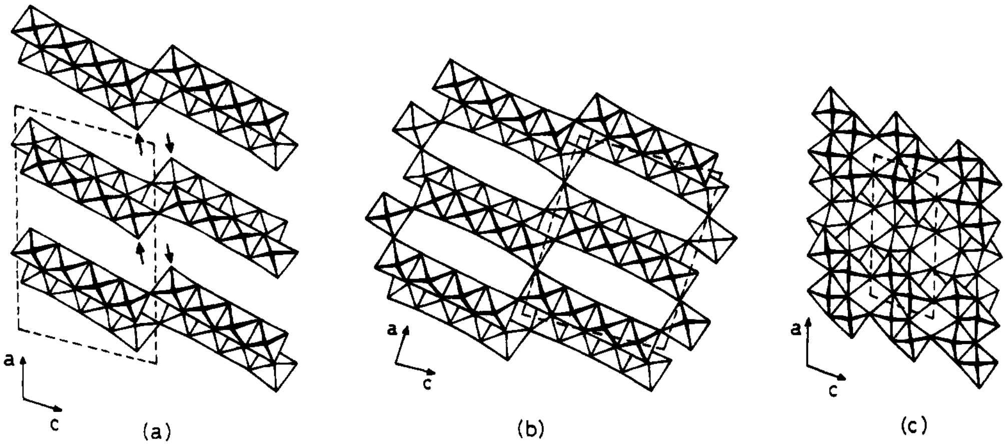

Figure 2. Covalent frameworks of (a) $K_2Ti_4O_9$, (b) $K_2Ti_8O_{17}$, and (c) TiO_2 (B) (after ref 38a). The most basic oxygen atoms are indicated by arrows.

this area, discusses in a seminal paper[35] the mechanistic aspects of topotactic reactions and their relevance to soft chemistry, taking the examples of oxidation and dehydration of $Ni(OH)_2$ and dehydration of $W_{1-x}Mo_xO_3\cdot{}^1/_3H_2O$. On the basis of a detailed investigation of the mechanism of these topotactic reactions, Figlarz et al.[35] come to the conclusion that the reactions proceed via oriented nucleation of the product on specific crystallographic planes (where nucleation is energetically favorable), followed by oriented growth of the nuclei at definite reactant/product interface. Accordingly, the nature of the solid product obtained in a chimie douce synthesis seems to depend not only on structural considerations but also on energetic (thermodynamic) considerations as well. The importance of the latter is exemplified by the dehydration of $WO_3\cdot{}^1/_3H_2O$ and $MoO_3\cdot{}^1/_3H_2O$. Although both the oxides are isostructural, $WO_3\cdot{}^1/_3H_2O$ dehydrates to give hexagonal WO_3, while the molybdenum analogue yields a ReO_3 type MoO_3. A knowledge of both the structural and mechanistic aspects of topochemical reactions is therefore essential to design new soft-chemistry routes based on topochemistry.

Over the past 10–15 years, chemistry-based topochemical methods have become popular for the synthesis of novel oxide materials, especially metastable ones. As we have already mentioned, the basic approach in many instances is to synthesize a thermodynamically stable phase by a high-temperature route followed by its transformation to a metastable phase by an appropriate soft-chemical route at relatively low temperatures. Typical examples of synthesis of this kind are ReO_3-like MoO_3 by dehydration of MoO_3 hydrates[36] or oxidation of Mo_4O_{11},[37] TiO_2(B) from layered titanates,[38] $A_2Ti_nO_{2n+1}$ (A = Na, K, Cs), by hydrolysis and subsequent dehydroxylation, TiO_2(H) by oxidation of hollandite-like $K_{0.25}TiO_2$,[39] $V_2(PO_4)_3$ possessing empty NASICON framework[40] by oxidative deintercalation of sodium from $Na_3V_2(PO_4)_3$, and superconducting $La_2CuO_{4+\delta}$. In the last example, the desired synthesis could be achieved by chemical[41] or electrochemical oxidation[42] of the parent La_2CuO_4. In all these examples, the syntheses are topochemically controlled in the sense the structures of the parent and product phases are related, but the mechanistic aspects largely remain unknown.

A dramatic example of the influence of structure on the reactivity is provided by the *ion exchange*[43] of Li in $LiAlO_2$. This oxide crystallizes in three different structures, α, β, and γ, of which only the α-modification, which adopts a rock salt superstructure where both Li and Al are octahedrally coordinated, undergoes facile exchange of Li^+ with H^+ in molten benzoic acid forming spinel-like $HAlO_2$. The β and γ forms of $LiAlO_2$, where Li occurs in tetrahedral oxygen coordination, do not exhibit a similar ion exchange. Hydrolytic proton exchange of $K_2Ti_4O_9$, first investigated by Tournoux and co-workers,[38a] is another important reaction that has great significance toward soft-chemical synthesis of metastable oxides. Hydrolysis of $K_2Ti_4O_9$ mainly yields two different products: partially hydrolyzed $K(H_2O)Ti_4O_8(OH)$ and fully hydrolyzed $(H_2O)_2Ti_4O_7(OH)_2$. Dehydration of the former yields a novel octatitanate, $K_2Ti_8O_{17}$, while that of the latter, a metastable modification of titanium dioxide, TiO_2(B) (Figure 2). Formation of the octatitanate from $K(H_2O)Ti_4O_8(OH)$ implies that protonation of $K_2Ti_4O_9$ is selective, occurring first at the most basic corner oxygens. The reactivity of $LiAlO_2$ and $K_2Ti_4O_9$ toward hydrolytic proton exchange has been theoretically examined with the help of semiempirical electronic structure calculations,[44,45] shedding new light on the problem of acidity and basicity of metal oxides in general.

Although ion exchange in zeolites and layered clay minerals has been known for a long time,[46] its full

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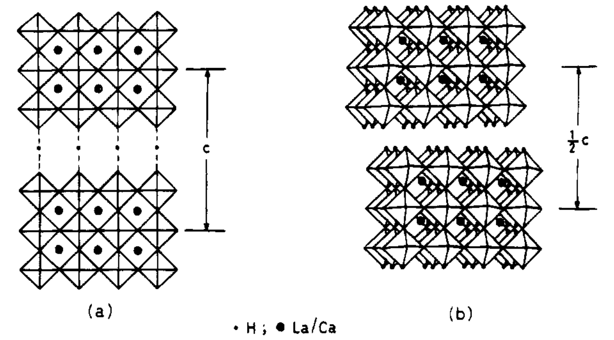

Figure 3. Schematic representation of the structures of (a) $HCa_2Nb_3O_{10}$ and (b) $H_2La_2Ti_3O_{10}$.

potential as a route for the synthesis of metastable solids has been recognized only in recent years.[47] Contrary to the general misconception that ion exchange requires fast mobility of ionic species, it has been shown that even when the diffusion coefficients are in the range of $\sim 10^{-11}$ cm^2 s^{-1}, exchange proceeds at considerable rates facilitating the use of ion exchange in solids as a synthetic technique.[47] Contrary to another common belief that facile ion exchange requires nonstoichiometry and mobile ion vacancy, ion exchange is common among several stoichiometric solids, typical examples being $LiAlO_2$ and $K_2Ti_4O_9$ which we have already discussed.

We have employed ion exchange to prepare several protonated layered perovskite oxides of the general formula, $H_yA_2B_3O_{10}$ (A = La/Ca; B = Ti/Nb; $0 < y \leq 2$), that exhibit transition-metal atom (Ti/Nb) and structure-dependent Bronsted acidity of the interlayer protons.[48,49] $H_yA_2B_3O_{10}$ oxides adopt two different structures (Figure 3): for $y \leq 1$, the structure is primitive tetragonal, being isostructural with $CsCa_2Nb_3O_{10}$[50] and $HCa_2Nb_3O_{10}$;[51] for ($1 < y \leq 2$), the structure is body-centered tetragonal, being isostructural with $Sr_4Ti_3O_{10}$[52] (*I4/mmm*) and $K_2La_2Ti_3O_{10}$.[53] The difference between the two structures arises essentially from the stacking of triple perovskite slabs ($A_2B_3O_{10}$) in the *c* direction. While the adjacent perovskite slabs are displaced by $(a + b)/2$ translation giving the body-centered tetragonal structure for $Sr_4Ti_3O_{10}$, there is no displacement of the adjacent slabs in the $CsCa_2Nb_3O_{10}$ structure (Figure 3).

This difference in the stacking of perovskite slabs in $H_yA_2B_3O_{10}$ has a profound influence on their Bronsted acidity as revealed by intercalation of *n*-alkylamines and other organic bases. While $HCa_2Nb_3O_{10}$ and its isostructural derivatives behave as solid Bronsted acids intercalating a wide variety of organic bases including aniline (pK_a = 4.63) and pyridine (pK_a = 5.3), $H_2La_2Ti_3O_{10}$ and its isostructural derivatives, $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$, do not exhibit an obvious Bronsted acidity, as revealed by their inability to intercalate even strong bases such as piperidine (pK_a = 11.2) and guanidine (pK_a = 12.5). This lack of intercalation reactivity for the protons of $H_2La_2Ti_3O_{10}$ and $H_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ seems to be related to the special interlayer structure arising from the displacement of the perovskite slabs in the [110] direction and not due to an intrinsic difference in the acidity of protons as such between the two sets of oxides. This conclusion is supported by the lack of intercalation reactivity for $H_2Ca_2Nb_2TiO_{10}$, which is isostructural with $H_2La_2Ti_3O_{10}$. Had the difference in the intercalation reactivity between $H_2La_2Ti_3O_{10}$ (and its derivatives) and $HCa_2Nb_3O_{10}$ (and its derivatives) been due to the intrinsic acidity difference of the protons in the two sets of compounds, one would have observed a greater acidity (and hence amine intercalation) in $H_2Ca_2Nb_2TiO_{10}$, since the protons attached to NbO_6 octahedra would be more acidic than the protons attached to TiO_6 octahedra.

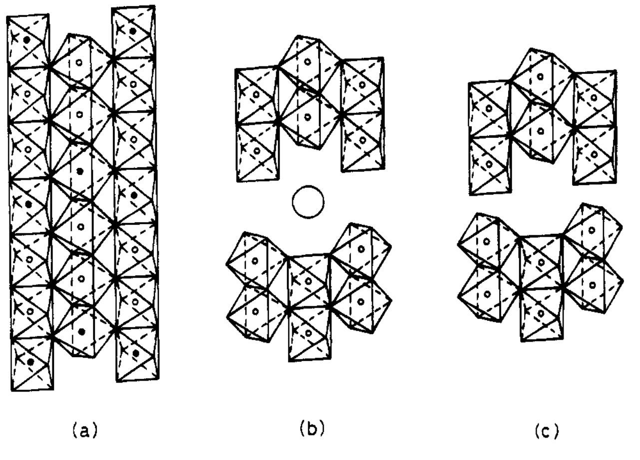

Figure 4. Schematic representation of the structures of (a) rutile-like $LiMWO_6$, (b) $HMWO_6{\cdot}nH_2O$, and (c) $HMWO_6$ (M = Nb, Ta).

We have prepared another series of layered perovskites[48] of the formula $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ ($0 \leq x \leq 2$), which are isostructural with $HCa_2Nb_3O_{10}$. In this series, we do observe a dramatic decrease in the intercalation reactivity as Nb is replaced by Ti: while the protons of $HCa_2Nb_3O_{10}$ are strongly acidic, $HLa_2Nb_2TiO_{10}$ is a weak Bronsted acid, intercalating piperidine (pK_a = 11.3) with great difficulty. It does not intercalate other bases with pK_a < 11.0. Since both the compounds are isostructural, this difference in intercalation reactivity truly reflects the intrinsic acidity difference of the protons attached to NbO_6 and TiO_6 octahedra.

$HMWO_6$ (M = Nb, Ta) and their hydrates are another set of new layered solids that we have synthesized[54] by ion exchange from their analogues, $LiMWO_6$. The latter crystallize in an ordered rutile structure (Figure 4) consisting of layers of LiO_6 octahedra alternating with WO_6 and MO_6 octahedra in the *c* direction. Since Li atoms are arranged in sheets perpendicular to the *c* direction, their removal by exchange with protons in aqueous acids results in a layered structure (Figure 4), where rutile-like MWO_6 slabs are interleaved by hydroxyl protons and water molecules. We have accord-

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ingly transformed by ion exchange the three-dimensional rutile-like structure of $LiMWO_6$ into a two-dimensional structure in $HMWO_6$ and their hydrates. Interestingly layered $HMWO_6$ are among the strongest solid acids containing metal–oxygen octahedra, intercalating a variety of organic amines[55] including weak Lewis bases like 4-nitroaniline ($pK_a = 1.0$) and quinoxaline ($pK_a = 0.56$). Recently, we have prepared the molybdenum analogues,[30] $HMMoO_6$ (M = Nb, Ta), which are even more acidic. We are at present investigating the acid–base as well as the redox intercalation chemistry of these novel oxides.

Reductive *intercalation* and oxidative *deintercalation* of atomic and molecular species in close-packed, layered and framework host materials are complementary strategies for the synthesis of several metastable metal oxides and chalcogenides that exhibit multiple oxidation states.[56] Reductive intercalation of alkali metals in layered MoS_2 and WS_2 was first reported by Rüdorff.[57] In more recent years, the technique has been widely explored and applied to several systems by Murphy,[58] Goodenough,[59] Whittingham,[60] and others[61] in the context of developing cathode materials for solid-state batteries. The best-known example is the lithium insertion into layered TiS_2 giving Li_xTiS_2 ($0 \le x \le 1.0$). The insertion can be achieved chemically or electrochemically. In chemical insertion, *n*-butyllithium dissolved in a hydrocarbon solvent is employed as lithiating agent. In the electrochemical method, a polycrystalline pellet of TiS_2 serves as cathode, a sheet of Li metal or LiAl alloy as anode and a solution of $LiClO_4$ in a polar organic solvent as electrolyte. Intercalation of lithium occurs during the discharge cycle. A major advance in this field is the development of the so-called "rocking chair" batteries[62] that make use of oxide materials such as $Li_{1+x}Mn_2O_4$ or $LiCoO_2$ as the positive electrode and a graphitic carbon as the negative electrode. Use of VO_2(B), a metastable oxide that is isostructural with TiO_2 (B) in place of graphite, has enabled the use of aqueous $LiNO_3$ as electrolyte for the first time,[63] making lithium rechargeable batteries safe and cost effective.

Besides the application of such redox systems as electrode materials in rechargeable batteries, reactions of this kind carried out chemically have proved to be of considerable value as soft-chemical avenues for the synthesis of several metastable materials that are inaccessible otherwise. Chemical insertion of lithium and other electropositive elements has been achieved in a variety of hosts.[58,60] We have shown that reaction of iodides of electropositive metals with WO_3, MoO_3, and V_2O_5 at relatively low temperatures (500–600 °C) affords a convenient route for the insertion of alkali and alkaline earth metals[64] yielding oxide bronzes. Use of tetrahydroborate salts[65] have enabled insertion of alkali metals and other cations such as R_4N^+ (R = alkyl) and $[(Ph_3P)_2Cu]^+$ into MoO_3, V_2O_5, FeOCl, and TaS_2. Tetrahydroborate reduction[66] has also been used for the synthesis of Na_xWO_3. The reducing power of BH_4^- seems to be intermediate between that of I^- and n-$C_4H_9^-$.

The possibility of oxidative deintercalation as a convenient route for the synthesis of metastable phases was first demonstrated by Murphy and co-workers.[67] They showed that lithium could be oxidatively extracted from $LiVS_2$ using I_2 in CH_3CN; the product VS_2 being metastable could not be prepared otherwise. Subsequently, we showed that the strategy is applicable to oxide hosts as well,[68] by deintercalating lithium from $LiVO_2$ and Li_2MoO_3. The deintercalation from oxide hosts however requires a stronger oxidizing agent, viz., Br_2 dissolved in $CHCl_3$ or CH_3CN. Unlike sulfides, the layered structure of the oxides is not preserved at higher levels of deintercalation.[69] In recent times Stacy and co-workers[70] have employed this method for the synthesis of Li_xNbO_2 and Na_xNbO_2. DiSalvo and co-workers,[71] in a systematic study of the various chemical reagents available for deintercalation, have shown that NO_2^+ in the form of NO_2PF_6 and MoF_6 are powerful oxidizing agents that can deintercalate lithium from $LiCoO_2$ and Li_2CuO_2.

We have recently extended the oxidative deintercalation route to framework phosphates containing transition metals like vanadium and titanium.[40,72] Thus, we could deintercalate sodium from NASICON phosphate, $Na_3V_2(PO_4)_3$, by using chlorine as the oxidizing agent. The product of complete deintercalation is a new metastable phosphate, $V_2(PO_4)_3$, that retains the NASICON framework. A similar deintercalation of sodium from $Na_3TiV(PO_4)_3$ proceeds to the extent of removal of two-thirds of the sodium giving $NaTiV(PO_4)_3$. Interestingly, we could not deintercalate potassium from the langbeinite phosphate, $K_2TiV(PO_4)_3$, by similar means. The lack of deintercalation reactivity of this phase in contrast to the facile deintercalation of sodium from $Na_3V_2(PO_4)_3$ and $Na_3TiV(PO_4)_3$ is presumably related to the structure. Langbeinite, being a true cage structure with small windows connecting the cages, does not permit mobility of potassium ions through the framework of $K_2TiV(PO_4)_3$, while NASICON, being a skeletal structure with an interconnected interstitial space (Figure 5) permits facile mobility of sodium ions through the framework resulting in deintercalation, provided, of course, the framework incorporates appropriate tran-

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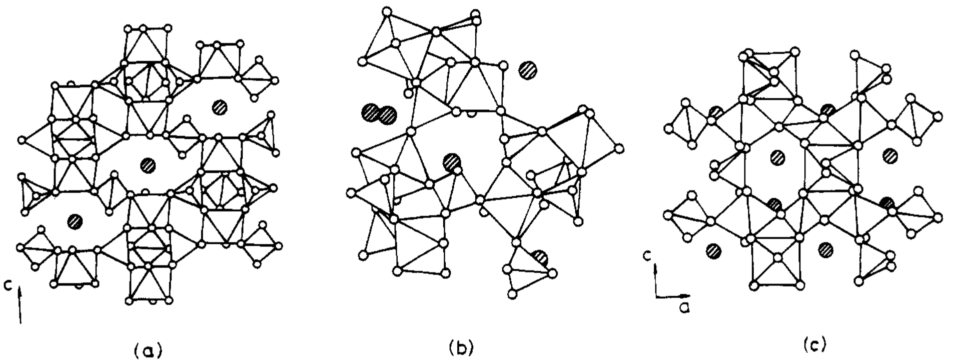

Figure 5. Covalent frameworks of (a) NASICON, (b) langbeinite, and (c) $KTiOPO_4$.

sition metal atoms such as Ti(III) and V(III) that can undergo oxidation.

More importantly, we have employed this technique to prepare new nonlinear optical (NLO) materials of the $KTiOPO_4$(KTP) type.[73] KTP is a framework phosphate containing one-dimensional channels parallel to [001] where the potassium ions reside (Figure 5). The structure allows mobility of potassium ions through the channels resulting in ion exchange and ionic conductivity. Accordingly, we envisaged that it would be possible to oxidatively deintercalate potassium from this structure by incorporating appropriate transition metal atoms in the framework. To realize this possibility, we prepared new KTP analogues, $KM_{0.5}M'_{0.5}OPO_4$ (M = Nb^{V}, Ta^{V}; M′ = Ti^{III}, V^{III}) and investigated oxidative deintercalation of potassium[74] using Cl_2. Typically, deintercalation proceeds as follows:

$$KNb^{V}{}_{0.5}Ti^{III}{}_{0.5}OPO_4 + {}^{1}\!/_{4}Cl_2 \rightarrow K_{0.5}Nb^{V}{}_{0.5}Ti^{IV}{}_{0.5}OPO_4 + {}^{1}\!/_{2}KCl$$

giving new KTP analogues. While the parent materials do not show second harmonic generation (SHG) of 1064 nm radiation, the deintercalated materials do show a SHG response. Both $K_{0.5}Nb^{V}{}_{0.5}Ti^{IV}{}_{0.5}OPO_4$ and $K_{0.5}Ta^{V}{}_{0.5}Ti^{IV}{}_{0.5}OPO_4$ prepared by this route show powder SHG intensities of 532 nm radiation comparable to that of KTP. The synthesis of these new KTP analogues reveals the importance of d^0 cations toward determining the SGH property of KTP and its derivatives.

Besides redox deintercalation/intercalation of alkali metals, intercalation chemistry, in general, has been used with ingenuity to synthesize a wide variety of metastable oxide materials. Thus, polymerizable organics such as aniline, pyrrole, and 2,2′-bithiophene have been *intercalated* and *polymerized* within the galleries of layered hosts such as 2:1 clay minerals,[75] FeOCl,[76] V_2O_5 gel,[77] and so on,[78] to yield inorganic/organic polymer composites. A distinction has to be made between two different types of intercalation–polymerization. When the host material contains a reducible transition metal ion as in FeOCl or V_2O_5 gel, intercalation, and oxidative polymerization of organic molecules occur simultaneously, resulting in synergistic modification of host–guest properties. A typical example is the polymerization of aniline in a V_2O_5 gel, which could be represented as

$$C_6H_5NH_2 + V_2O_5{\cdot}xH_2O \rightarrow {}^{1}\!/_{n}(-C_6H_4NH-)_nH_2V_2O_5{\cdot}xH_2O$$

In host materials such as 2:1 clays and α-$Zr(HPO_4)_2$, monomer intercalation occurs first through an acid–base interaction; subsequent polymerization is achieved through an external oxidizing agent[78] such as Cu^{2+}, $(NH_4)_2S_2O_8$, or oxygen. Aniline intercalated to layered MoO_3 has been polymerized[79] using $(NH_4)_2S_2O_8$, whereas the same reaction in layered $HUO_2PO_4{\cdot}4H_2O$ occurs by merely heating the monomer intercalate in air[80] at 130 °C. We have polymerized aniline in the layered perovskite $HCa_2Nb_3O_{10}$ by $(NH_4)_2S_2O_8$ oxidation.[81] Polymerization of this kind has also been achieved in zeolites and mesoporous MCM-41 yielding conducting filaments of polyaniline (molecular wires) encapsulated in the channels of insulating hosts.[82]

Exfoliation of layered (or chain) materials to yield single layer (or chain) colloidal dispersions and their subsequent *restacking* in the presence of large guest molecules afford another new strategy to synthesize novel metastable materials.[83] Although originally exfoliated dispersions were obtained for certain clays and layered dichalcogenides[84] (MoS_2, TaS_2), a wide variety of layered oxides have now been dispersed into single or multiple layers of atomic dimensions.[83] While these dispersions are thermodynamically unstable with respect to flocculation, they can be rendered sufficiently stable by appropriate choice of cation/solvent combination or by addition of surfactants. A recent example[33] of the use of dispersions for the synthesis of composite materials is the layer-by-layer assembly of α-$Zr(HPO_4)_2$ and a variety of polymeric or oligomeric cations such

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as poly(allylamine) hydrochloride (PAH), $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ (Al_{13}^{7+}), and cytochrome *c*. When the acidic protons of α-$Zr(HPO_4)_2$ are partially exchanged with tetra-*n*-butylammonium ions, the material spontaneously exfoliates into single layers that remain dispersed indefinitely in water. When the dispersion is placed in contact with a protonated amine-modified surface, the inorganic layers are anchored on to the surface on which polymeric or oligomeric cations are then deposited. By repeating the sequence, well-defined two-dimensional heterostructures of considerable thickness have been prepared.

Pillaring is another intercalation reaction that enables synthesis of metastable oxide materials.[85] Pillaring refers to intercalation of robust, thermally stable, molecular species that prop the layers apart so as to convert the two-dimensional interlayer space into micropores of molecular dimension, somewhat similar to the pores present in zeolites. Smectite clays,[85] layered $Zr(HPO_4)_2$,[86] α-MoO_3,[87] layered perovskites,[88] and layered double hydroxides (LDHs)[89] are among the hosts that have been pillared by cationic/anionic species such as alkylammonium ions, polyoxocations (e.g., $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$) and isopoly and heteropolyanions (e.g., $Mo_7O_{24}^{6-}$, $V_{10}O_{28}^{6-}$, and $PV_3W_9O_{40}^{6-}$).

3.2. Nontopochemical Routes. Among the nontopochemical routes for synthesis of metastable oxides, sol–gel method, hydrothermal method, synthesis using molten salts and acid-leaching are noteworthy. The *sol–gel method* is probably the oldest[90] soft-chemical route that enables synthesis of several technologically important ceramics and glasses.[91] The method involves hydrolysis and condensation of molecular or ionic precursors to form an oxide network directly from a solution. The essential steps in a sol–gel synthesis are formation of a sol from a multicomponent ionic/molecular solution, gelation of the sol, and desiccation and heat treatment to transform the gel to a ceramic/glass.[92,93] The method is necessarily nontopochemical, since there is no direct relationship between the crystal structure of the final product and the precursor.

Metal alkoxides, such as tetraethyl orthosilicate, aluminum isopropoxide, and tetrabutyl titanate, are common molecular precursors for the sol–gel synthesis of SiO_2-, Al_2O_3-, and TiO_2-based ceramics. At present, efforts are being made to design new alkoxide precursors as well as modify the reactivity of known precursors.[94,95] For example, facile synthesis of multicomponent ceramics containing two or more cations is achieved more easily from a *single* molecular precursor having the required cation stoichiometry than from a mixture of precursors. Thus, heterometallic alkoxides $LiNb(OEt)_6$ and $Mg[Al(OR)_4]_2$ are ideal precursors for the synthesis of $LiNbO_3$ and $MgAl_2O_4$. As a general rule, hydrolysis and condensation reactivity of an alkoxide increases with decreasing electronegativity and increasing size of the central atom. $PO(OEt)_3$ and $VO(OEt)_3$ are illustrative examples; while the former cannot be hydrolyzed under ambient conditions, the latter readily hydrolyzes into a gel. High reactivity metal alkoxides can be "tamed", as it were, by replacing some of the alkoxy groups by other groups such as acetate or acetylacetonate. It is even possible to replace alkoxy groups by alkyl groups to give new precursors such as diethoxydimethylsilane, which contains nonhydrolyzable Si–C bonds. Sol–gel synthesis employing such organically modified precursors[91] (ormosils) yields novel hybrid ceramics possessing useful optical and mechanical properties.

Besides organic molecular precursors, several inorganic (cationic or anionic) species in aqueous medium[96] have been used as precursors in the sold–gel synthesis of oxide materials. Here, the sol–gel process essentially involves olation (formation of hydroxyl bridges) and oxolation (formation of oxygen bridges) which are controlled by pH and concentration. Formation of V_2O_5 gels from aqueous vanadate solutions is a typical example. Monomeric VO_4^{3-}, which is predominant at high pH, transforms to V_2O_5 gel through a complex process that involves protonation, hydration, olation, and oxolation, as the pH is lowered. The sol–gel route using vanadate or vanadium alkoxide precursors is the most reliable method for the synthesis of this metastable oxide material,[97] which possesses a semicrystalline layered structure related to V_2O_5. The combination of acidic and redox properties together with the layered structure makes it a unique electronic material finding application in humidity sensors, electrochromic displays, and microbatteries. Several other metal oxides and hydrous metal oxides including those of Al, Fe, Ti, and Zr have been prepared[98] in monodispersed fine particle morphology through the sol–gel route using inorganic precursors in aqueous media.

The *hydrothermal method*, which is a well-established means of synthesizing zeolites,[23] has in recent times enabled synthesis of a wide variety of metastable materials that include aluminum phosphates (ALPOs) and other microporous transition metal phosphates that contain metal–oxygen octahedra/other polyhedra and PO_4 tetrahedra, transition metal polychalcogenides, and so on. Unlike zeolites, synthesis of ALPOs requires acidic or mildly basic conditions and no alkali metal cations. A typical ALPO synthesis mixture[23] consists of alumina, H_3PO_4, water, and an organic additive such as quaternary ammonium salt or an amine. The use of fluoride ions, instead of hydroxide ions as mineralizer, allows synthesis of novel microporous solids[99] (e.g., cloverite and ULM series of Al/Ga phosphates). Under acidic conditions, the fluoride ions are either trapped in the smallest cages or built in as a part of the inorganic framework.

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The role of organic additives in hydrothermal synthesis has been much discussed.[23] Besides templating, organic additives can also act as space fillers and structure-directing agents. Structure direction implies that a specific structure is synthesized using a particular additive. An example of structure direction[100] is provided by the synthesis of hexagonal faujasite using 1,4,7,10,13,16−hexaoxacyclooctane (18-crown-6). A true example of templating[101] is provided by $C_{18}H_{36}N^+$-triquaternary amine, which is specific to the synthesis of ZSM-18. Tetraalkylammonium salts are common structure directing agents in the synthesis of high-silica zeolites.

On the basis of the accumulated knowledge on various aspects of hydrothermal synthesis, a rational design of microporous solids is becoming possible. For example, recognizing a correlation between minimum framework density and smallest ring size, Annen et al.[8] have synthesized a zincosilicate (VPI-7) that is topologically related to lovdarite containing three-membered rings and a low framework density. The synthesis of mesoporous silicates[102] (MCM-41) with adjustable pore sizes in the range ~15 to ≥100 Å is a step in the direction of rational synthesis. Synthesis of these materials is achieved by an entirely new strategy that makes use of a self-assembled molecular array, instead of an isolated molecule or ion, as templating agent. Typically, quaternary ammonium salts of the type n-$C_nH_{2n+1}(CH_3)_3N^+$-OH/Cl$^-$ (n = 12−16), which are known to form micelles in aqueous solution are used as templates in the synthesis. Formation of mesoporous solids of this kind seems to involve a "liquid crystal templating" mechanism wherein the inorganic silicate/aluminate ions build "walls" around organic template assemblies which are already ordered in the gel. It is significant that while the arrangement of pores is very regular in these materials, considerable disorder exists in the inorganic "walls" that form the porous structure. Stucky and coworkers[103] have generalized this approach to enable the synthesis of periodic mesoporous materials of a variety of metal oxides including tungsten, antimony, lead, aluminum, iron, and zinc. Their strategy is to use cationic surfactants as templates for anionic inorganic species and anionic surfactants for cationic inorganic species.

The hydrothermal method has enabled synthesis of oxide materials that contain tetrahedra and octahedra and other polyhedra. A variety of phosphates of molybdenum and vanadium synthesized by Haushalter and co-workers[104] are examples of this kind. An interesting example[105] is the hydrothermal synthesis of an inorganic double helix, $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$. This solid containing double helices formed from VO_6 octahedra, VO_5 square pyramids, and PO_4 tetrahedra and crystallizing in a chiral structure (space group $P4_3$ or its enantiomorph, $P4_1$) illustrates the power and potential of the hydrothermal method for the synthesis of complex inorganic solids.

Use of molten salts as *reactive fluxes* is another nontopochemical route that has enabled synthesis of metastable phases, especially at temperatures (~200−500 °C) intermediate between those accessible by the hydrothermal route and conventional ceramic route. The method, introduced by Ibers and co-workers[106] and elaborated by Kanatzidis and co-workers[107] for the synthesis of ternary and quaternary metal chalcogenides, essentially consists in reacting metallic elements in low melting alkali metal polychalcogenide fluxes, A_2Q_n (Q = S, Se, Te). The polychalcogenide functions not only as a classical flux in the sense of promoting the reaction at low temperatures but also as a source of the alkali metal and chalcogen/polychalcogen in the final product.

For the synthesis of oxide materials by this route, alkali metal hydroxides, NaOH and KOH, are the obvious choices. These are relatively low melting solids forming an eutectic at 175 °C. A molten alkali hydroxide melt contributes to the synthesis in two ways. The acid−base equilibrium existing in the melt, viz., $2OH^- \rightleftharpoons H_2O + O^{2-}$, enables in general dissolution of metal oxides in wet (acidic) fluxes and their recrystallization in dry (basic) fluxes. The highly electropositive environment in the melt stabilizes highest oxidation states for many metals. Both these attributes have been exploited in the synthesis and growth of crystals of several superconducting oxides such as $La_{2-x}M_xCuO_4$ (M = Na, K),[108] $Ba_{1-x}K_xBiO_3$,[109] and twin-free $EuBa_2Cu_3O_{7-x}$.[110] We have synthesized[111] several oxides of the formula, $A_2BB'O_7$ (A = La, Nd; BB′ = Pb, Sn, Bi) crystallizing in the pyrochlore structure, by the use of molten KOH. Significantly, the pyrochlore oxides, $La_2Pb_2O_7$, $La_2Bi_2O_7$, and La_2PbBiO_7 containing Pb(IV) and Bi(V) are insulators, unlike the perovskite oxides, Ba(Pb,Bi)O_3 and (Ba,K)BiO_3, which are metallic and superconducting. Anhydrous $KBiO_3$ has been synthesized electrochemically from a KOH melt.[112]

A nontopochemical route that has been little explored for the synthesis of metastable oxides is *acid leaching*. Acid leaching is known in geology as a means of transforming rocky silicates to clays and soil minerals.[113] An early example of synthesis using acid leaching[114] is that of PrO_2 from Pr_6O_{11} and Pr_7O_{12}, which has

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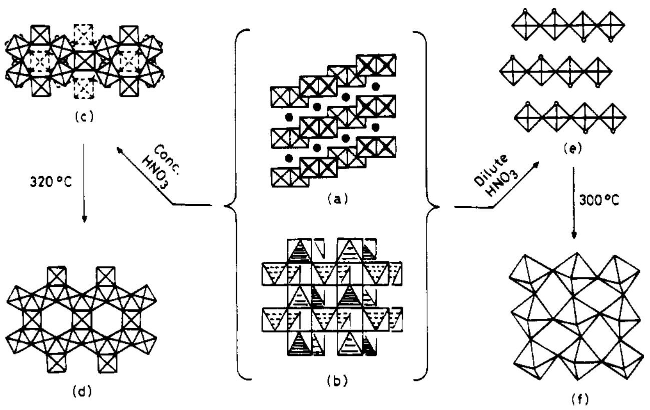

Figure 6. Schematic representation of the structures of oxides obtained by acid leaching of (a) $LiVWO_6$ and (b) $LiAlW_2O_8$, (c) $WO_3{\cdot}{}^1/_3H_2O$, (d) hexagonal WO_3, (e) $WO_3{\cdot}H_2O$, and (f) monoclinic WO_3.

attracted recent attention.[115,116] Interestingly, the leaching reaction

$$Pr_6O_{11} + 6H^+ \rightarrow 4PrO_2 + 2Pr^{3+} + 3H_2O$$

is accompanied by acoustic emission.[115] $Tb_{11}O_{20}$,[117] Pb_3O_4, and Mn_3O_4 are some of the other oxides that undergo similar leaching in acids. In recent times, acid leaching of $AVMoO_6$ (A = Li, Na) brannerites investigated by Davies and co-workers[118] has enabled the synthesis of new hexagonal vanadium–molybdenum oxides possessing a microporous tunnel structure. Subsequently, we explored[119] acid leaching of layered $LiVWO_6$ and three-dimensional $LiMW_2O_8$ (M = Al, Fe) in an attempt to understand the nature of leaching of oxides of this kind. Our investigations reveal that the solid product obtained by acid leaching is determined more by the hydrolytic tendency of the cations present and the acid strength, rather than the exact crystal structure of the parent oxides. Thus, leaching of both $LiVWO_6$ and $LiMW_2O_8$ (M = Al, Fe) in dilute HNO_3 yields layered $WO_3{\cdot}2H_2O/WO_3{\cdot}H_2O$-related products, while leaching in concentrated HNO_3 yields $WO_3{\cdot}{}^1/_3H_2O$-like products (Figure 6). However, while the products obtained by leaching of $LiVWO_6$, viz., $H_{0.125}V_{0.125}W_{0.875}O_3{\cdot}1.5H_2O$ and $H_{0.33}V_{0.33}W_{0.67}O_3{\cdot}{}^1/_3H_2O$, retain a considerable amount of vanadium, the leached products of $LiMW_2O_8$ are pure $WO_3{\cdot}H_2O$ and $WO_3{\cdot}{}^1/_3H_2O$ free from Al or Fe. The retention or otherwise of the additional metal (V^{5+}, Fe^{3+}, Al^{3+}) in the leached product presumably depends on the hydrolytic behavior[120] of the respective cations. Accordingly, while the less acidic Al^{3+} is completely leached out (together with Li^+) from $LiAlW_2O_8$, yielding pure $WO_3{\cdot}H_2O$ or $WO_3{\cdot}{}^1/_3H_2O$, leaching of the more acidic V^{5+} from $LiVWO_6$ is incomplete in aqueous HNO_3, yielding vanadium-substituted derivatives of $WO_3{\cdot}2H_2O$ or $WO_3{\cdot}{}^1/_3H_2O$. In general, acid leaching seems to be governed by the following principle: A binary or multinary oxide containing two or more cations (of the same or different metals) that differ in their basicity preferentially leaches out cation(s) of higher basicity into aqueous acid, leaving behind a new solid phase containing the more acidic cation(s). We believe acid leaching is a potentially useful soft-chemical route that deserves greater attention in the future.

4. Concluding Remarks

The brief survey of the soft-chemical routes for the synthesis of metastable oxide materials as well as the associated thermodynamic aspects presented in this article is illustrative rather than exhaustive, revealing the immense potential of this approach. An exhaustive coverage of this area is available in the Proceedings of the International Symposium on Soft-Chemistry Routes to New Materials.[121] Considering the tremendous ongoing interest and significant effort invested in this area of research, there is no doubt that newer and more efficient soft-chemistry routes will be discovered in the years to come, based on a better understanding of the structural and thermodynamic aspects, that will eventually enable rational design of solid materials with specified structure and properties.

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