Preparative solid state chemistry. Recent developments

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Abstract. A survey of recent developments in preparative solid state chemistry shows that, with a knowledge of structural chemistry and reactivity patterns of solids, it is possible to synthesize a variety of new solids possessing novel structures. A distinction is made between synthesis of *new solids* and synthesis of solids by *new methods*. Three new routes to solid state synthesis are recognized: the precursor method, and topochemical methods involving redox and ion-exchange reactions. The low-temperature topochemical methods enable synthesis of metastable phases that are inaccessible by the high temperature route. Several illustrative examples of solid state synthesis from the recent literature are presented.

Keywords. Preparative solid state chemistry; new methods; new solids.

1. Introduction

Solid state chemistry is essentially concerned with synthesis of solids and study of their structures and properties (Rao 1982). As such progress in this area crucially depends upon synthesis of new solids possessing unusual structures and properties. A recent US Panel Report (1979) has drawn attention to this fact. Table 1, adopted from this report, lists some of the landmark syntheses of solids which have opened up new avenues of research in solid state science as well as resulted in technical application in some cases (Warren and Geballe 1981).

We can distinguish four categories of preparation of solids depending on the purpose and aim of the investigator: (i) Preparation of known solids in specified quality, quantity, crystallinity, shape etc. Preparation of crystals of Si, Ge and III-V semiconductors belongs to this category. (ii) Preparation of a series of compounds in order to study a specific property. For example, preparation of an isostructural series of spinel ferrites for screening their magnetic characteristics, or a series of perovskite oxides to understand their electronic structure belongs to this category. (iii) Preparation of unknown members in a structurally related class of solids for purpose of extension and extrapolation of structure-property relationships. Systematic measurements of physical properties in a related series form the basis for testing and extending already known models. Examples under this category would be the synthesis of new A15 alloys or new layered dichalcogenides to examine their superconducting behaviour. This category overlaps with category (ii), but the role of synthesis is more important here. (iv) Synthesis of entirely new class of compounds. This is the most challenging and interesting category of all and generally preceeds the earlier categories. Preparations of this type provide new structures, with the promise of new properties, new phenomena and new concepts. Preparative solid state chemistry is concerned with categories (iii) and (iv), which deal with the preparation of new solids. Preparative

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Table 1. Some important solid state preparations leading to major developments in solid state science.

Prototype solid	First reported by and year	Subsequent development
ZrO_2 (Y_2O_3)	Nernst in 1900	Fuel cell; oxygen sensor
ZrO_2 (CaO)	Ruff in 1929	
Na β-alumina	Stillwell in 1926	Solid electrolytes: Na-S battery
$LiNbO_3$	Süe in 1937	Ferroelectrics; nonlinear optical materials
$BaFe_{12}O_{19}$	Adelskold and Schrewelis in 1938	Ferrites; memory devices
$LnNi_5$	Klemm in 1943	Strong magnets; hydrogen
(Ln = rare earth)		storage materials
Amorphous Si	Konig in 1944	Solar cells
$BaTiO_3$	Tammann in 1925	
$Bi_4Ti_3O_{12}$	Aurivillius in 1949	Ferroelectrics
H_xMoO_3	Glemser in 1951	Proton conductors; electrochromic displays
$K_{0.5}MoS_2$	Rüdorff in 1959	Intercalation chemistry; battery cathodes
K_2 [Pt $(CN)_4$] $X_{0.3}$	Krogmann in 1968	One-dimensional conductors
MMo_6X_8 (X = S, Se)	Chevrel in 1971	High-field superconductors
$(CH)_x$	Chiang and others in 1977	Molecular metals
Sialon	Jack in 1978	High temperature ceramics
(Si, Al)$_3$ (N, O)$_4$		

efforts of this sort which require a knowledge of structural chemistry and reactivity patterns of solids are particularly amenable to chemists.

Preparation of solids is however not an isolated field of activity; preparative efforts in solid state chemistry will be most rewarding when there is a close interaction among preparation, characterization and property evaluation (Honig and Rao 1981; Wold 1980). This interrelationship between preparation and characterization of structure and properties is being increasingly recognized by workers in this area and this has led to significant advances.

2. Preparation of new solids

That a remarkable number of new solid phases has been discovered even in supposedly simple systems reveals that presumably a much larger number of phases remains undiscovered, probably because they have not been sought. In many systems, it is possible to predict the existence of new phases by analogy with already known phases, but they remain unknown either because the rate of formation under known set of conditions is extremely slow or the system does not permit the use of extreme conditions (such as high temperatures or high pressures) because of the inherent instability of phases under these conditions (Brewer 1958). A good example is W_6S_8, the tungsten analogue of Mo_6S_8 Chevrel phase. The tungsten phase probably exists but could not be synthesized so far ostensibly because the phase is unstable at temperatures which would be required for its synthesis. Instances such as this call for innovative synthetic efforts.

In discussing the recent developments in preparative solid state chemistry, it is helpful to make a distinction between preparation of *new solids* and preparation of

solids by *new methods*. Preparation of a new solid need not necessarily involve a new method. A number of instances can be cited where preparation of new solids with novel structures and properties is achieved by routine procedures. Typical of them are $Na_3Zr_2PSi_2O_{12}$ (NASICON), $Na_{1+x}Al_{11}O_{17+x/2}$ (β-alumina), $BaFe_{12}O_{19}$ and MMo_6S_8 Chevrel phases. All these phases are prepared by ordinary method of reacting easily available constituents at elevated temperatures (ceramic method). In the last case, the reaction is carried out in closed ampoules for obvious reasons, but in others even this precaution is unnecessary. The importance of such preparations lies not in the method, but in selecting the right constituents in the right proportion, bearing in mind their chemistry and the structure and properties desired in the new phase. This aspect is illustrated by the synthesis of $Na_3Zr_2PSi_2O_{12}$, a fast sodium-ion conductor, wherein the composition was chosen keeping in mind the coordination preferences of the atoms involved, stability of their oxidation states, nature of network that would be formed and whether the network would permit three-dimensional mobility of sodium ions (Goodenough *et al* 1976). Another example of innovative synthesis by design is the preparation of 'synthetic' bone material for prosthetic application (Roy 1977). Here the problem is not only the synthesis of the chemical compound constituting the human bone, *viz* calcium hydroxyapatite, but also having it with the 100% connectivity and porosity of the natural bone. The synthesis could be accomplished because of two realizations: certain marine corals ($CaCO_3$) possessed the same porosity and connectivity as the human bone and aragonite form of $CaCO_3$ can be topotactically converted to calcium hydroxyapatite in a hydrothermal reaction. Thus reaction of marine corals with phosphoric acid under hydrothermal conditions produces synthetic bone material. A number of similar examples of synthesis of solids by design for specific purposes can be cited from the recent literature (Hagenmuller 1983).

Synthesis of new solids is not always achieved by design. Scientific research would be uninteresting if there is no room for serendipity. Preparative solid state chemistry has its share of serendipitous discovery of new materials. The discovery of $NaMo_4O_6$, the prototype of metal cluster chain compounds, is a recent example of this category (Torardi and McCarley 1979). The discovery resulted from a most innocent experiment aimed at preparing $NaZn_2Mo_3O_8$, the sodium-analogue of the lithium-containing cluster compound, $LiZn_2Mo_3O_8$. For this purpose, a mixture of Na_2MoO_4, ZnO, MoO_2 and Mo was sealed in a molybdenum tube and heated at $1100°C$. The product turned out to be shiny needles of $NaMo_4O_6$ instead of the expected $NaZn_2Mo_3O_8$. The crystal structure of $NaMo_4O_6$ turned out to be one of the most unique and astonishing of oxide structures consisting of infinite chains of Mo_6 octahedral clusters sharing opposite edges (figure 1). Another recent example of unintentional synthesis of a new phase is that of $Rb_xP_8W_{32}O_{112}$, a phosphorus-tungsten bronze (Giroult *et al* 1980). The new phase was obtained unexpectedly during the preparation of a rubidium tungsten bronze in a silica ampoule. The fact that the phase could not be prepared when platinum container was used led to the suspicion that one of the constituents of the silica ampoule, namely phosphorus, was incorporated into the phase. This was later confirmed by other investigations. This piece of accidental synthesis of a new phase has led to the discovery of a whole new family of phosphorus tungsten oxides of the general formula, $A_xP_4O_8$ $(WO_3)_{2m}$ ($4 \leqslant m \leqslant 10$) (Hervieu and Raveau 1982). An example of unintentional synthesis of new phases from our laboratory is that of $BiMWO_6$ (M=Cr, Fe) crystallizing in pyrochlore and tetragonal tungsten bronze (TTB) structures (Ramanan *et al* 1983). The phases were obtained during an investigation of structural
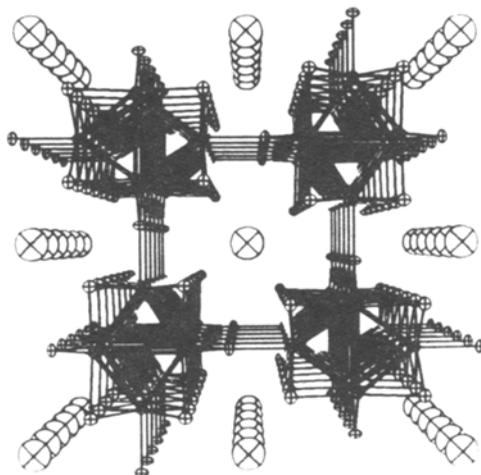
Figure 1. Structure of $NaMo_4O_6$ showing condensed Mo_6 octahedral metal clusters (from Torardi and McCarley 1979).

changes in Bi_2WO_6 when bismuth was substituted by iron or chromium. The phases represent first examples of MWO_6 (M=Cr, Fe) pyrochlore and TTB networks.

3. Preparation of solids by new methods

As already pointed out, we could predict the existence of a number of new phases in several systems, but they remain unknown because conventional synthetic methods are inadequate for their synthesis. Even in cases where conventional methods (*e.g.* ceramic method) are useful, preparative efforts are often hampered by slow diffusion kinetics and incomplete reactions, rendering it difficult to obtain pure, single-phase, materials. There have been significant attempts in recent years to overcome the limitations of conventional synthetic methods, resulting in alternative routes for solid state synthesis. The new methods not only have enabled synthesis of known solids in a state of high purity and homogeneity at far lower temperatures than the conventional methods, but in addition have resulted in the synthesis of unknown phases. Among these alternative strategies, the following three methods, which rely on the knowledge of structural chemistry and reactivity patterns of solids, have proved significant: (i) the solid-state precursor method, (ii) methods based on topochemical redox reactions and (iii) topochemical ion-exchange reactions. The emphasis in all the three methods is in achieving the synthesis at *low temperatures* such that the products obtained are in a finely divided state with high surface areas—a feature essential for catalysis and other applications. More importantly, synthesis at temperatures considerably lower than the sintering temperatures of solids preserves the essential features of the parent structure with minimal structural reorganization. It is for this reason that we have called methods (ii) and (iii) topochemical methods. Synthesis by topochemical methods often yields metastable phases that cannot be obtained by conventional methods. We now discuss the principle and potentialities of each one of these methods with appropriate examples from the recent literature.

3.1 *The solid-state precursor method*

The ideal condition for the preparation of a pure, single-phase, solid in the shortest time at the lowest possible temperature is to ensure homogeneous mixing of the reactants on an atomic scale. Obviously this cannot be achieved in a conventional ceramic method or modifications thereof (Johnson 1981). The only way to meet the ideal condition is to prepare a single solid phase (a chemical compound) in which the reactants are built-in in the required stoichiometry. Such a solid phase is known as the *precursor* which often on heating gives the desired product in a stoichiometric and homogeneous state. The compound precursor method has been employed for the synthesis of several complex metal oxides (Wold 1980). Spinel-type ferrites, MFe_2O_4 (M=Mg, Mn, Co, Ni), have been prepared by thermal decomposition of acetate precursors of the general formula M_3Fe_6 $(CH_3COO)_{17}O_3OH \cdot 12 C_5H_5N$. The advantage of the method is that the precursors can be prepared as crystalline solids in a state of high purity, possessing the desired M/Fe ratio. Other examples of synthesis of metal oxides through the compound precursor route are: preparation of chromites, MCr_2O_4, by the decomposition of dichromates, $(NH_4)_2 M(CrO_4)_2 \cdot 6H_2O$, preparations of $BaTiO_3$ and $LiCrO_2$ by the decomposition of $Ba[TiO(C_2O_4)_2]$ and $Li[Cr(C_2O_4)_2 (H_2O)_2]$ and of $LaFeO_3$ by the decomposition of La $[Fe(CN)_6]$. An interesting variation of the precursor method is the synthesis of ceramic oxides by the hydrolysis of metal alkoxides (Mazdiasni *et al* 1967).

It is not always possible to find suitable precursors for the synthesis of all the desired compositions because the stoichiometry of the precursor may not correspond to that of the product desired. Recently Horowitz and Longo (1978) and Longo and Horowitz (1981) have developed a solid-solution precursor method which retains all the advantages of compound precursors, but avoids the stoichiometry problem. The strategy is to make use of isostructural compounds containing a common anion so that they form a continuous series of solid solutions. The method has been used for the synthesis of several ternary oxides in the Ca-Mn-O system such as $Ca_2Mn_3O_8$, $CaMn_3O_6$, $CaMn_4O_8$ and $CaMn_7O_{12}$ by thermal decomposition of carbonate solid-solutions, $Ca_{1-x}Mn_xCO_3$, having the calcite structure. Vidyasagar *et al* (1984) have extended the method to prepare phases in the Ca-Fe-O, Ca-Co-O as well as Ca-M-M'-O (M, M'=Mn, Fe, Co) systems. Solid solution precursors have several advantages: (i) the reacting cations are uniformly blended together thereby avoiding the diffusion problem and compositional inhomogeneities in the final product. (ii) the product is formed at a much lower temperature than in a conventional ceramic synthesis thus permitting an examination of subsolidus regions of the phase diagram which would otherwise be inaccessible. The products formed at lower temperatures possess larger surface areas which is an important requirement in catalyst preparations.

The solid-solution precursor method has recently been used for the low temperature synthesis of Mo-W alloys (Cheetham 1980) by hydrogen-reduction of $(NH_4)_6-$ $[Mo_{7-x}W_xO_{24}]$. The precursor first decomposes to give a MoO_3-WO_3 solid-solution which undergoes subsequent reduction with hydrogen to give the alloy. Synthesis of lower valence transition metal oxides such as $LaVO_3$, $CaThV_2O_6$, $ZnMoO_3$ etc by hydrogen-reduction of the corresponding fully oxidized phases also belongs to this category (Palanisamy *et al* 1975; Vidyasagar and Gopalakrishnan 1982a; Manthiram and Gopalakrishnan 1980). A number of transition metal sulphides have been prepared, starting from a variety of compound precursors such as oxides, sulphates,

chlorides or even complex salts such as $(NH_4)_3RhCl_6$, $(NH_4)_2RuCl_6$ and $[Co\,(NH_3)_6]$ Cl_2 by reaction with H_2S or CS_2 vapours (Murugesan *et al* 1982; Passaretti *et al* 1981; Corino *et al* 1982).

3.2 *Methods involving topochemical redox processes*

Several transition metal oxides and chalcogenides, MX_n, can be intercalated at room temperature with lithium and other alkali metals to give reduced phases, A_xMX_n (A = Li, Na or K). The formation of such phases was first reported by Rüdorff (1959). The process has several features which make it attractive both as a preparative technique as well as in application as battery cathodes (Murphy and Christian 1979): (i) the reaction is reversible and can be brought about chemically or electrochemically; (ii) the reaction is topochemical in nature occurring with minimal structural reorganization of the host, MX_n and (iii) both A cations as well as electrons transferred to the host possess considerable mobility in A_xMX_n phases rendering them mixed ionic/electronic conductors. It is this last feature that makes them useful as cathode materials in solid-state batteries. The best-known example of alkali metal intercalation is that of lithium into TiS_2 to give Li_xTiS_2 ($0 < x \leqslant 1$) (Whittingham 1978; Whittingham and Chianelli 1980). The intercalation can be carried out by two methods. In the first, a chemical reagent, usually *n*-butyl lithium dissolved in a hydrocarbon solvent such as hexane, is employed as the lithiating agent: $xC_4H_9Li + TiS_2 \rightarrow Li_xTiS_2 + x/2C_8H_{18}$. Since the major byproduct is octane, Li_xTiS_2 can be readily obtained by filtration. The reaction must however be carried out in inert atmosphere. The second method for synthesizing lithium intercalates involves electrochemical reduction of TiS_2 in a cell of the type shown in figure 2. A polycrystalline sample of TiS_2 bonded into an electrode form is immersed into a polar organic solvent (*e.g.* dioxolane) in which lithium perchlorate is dissolved; a sheet of lithium metal or LiAl serves as the anode. On shorting the two electrodes, lithium ions intercalate TiS_2, the charge-compensating electrons passing through the external circuit. Electrochemical intercalation is particularly advantageous because the rate of the reaction can be controlled by imposing an external voltage across the cell; when the voltage exceeds the value
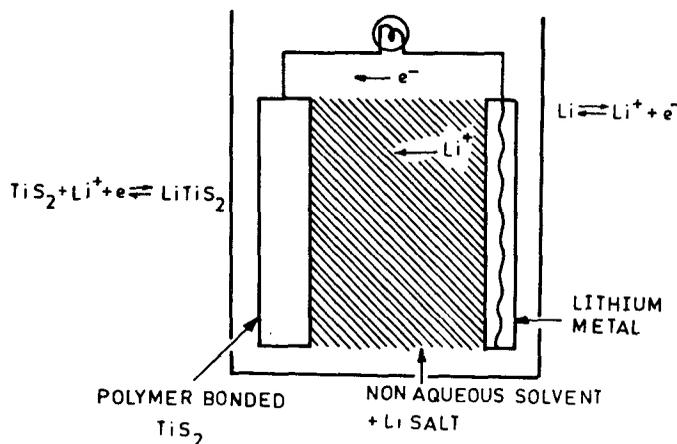

Figure 2. Schematic diagram of electrochemical cell for lithium intercalation into TiS_2.

corresponding to the free energy change ΔG of intercalation reaction, reverse reaction namely deintercalation occurs.

Intercalation of lithium has been achieved in a variety of MX_n hosts. Deintercalation of lithium has also been done both electrochemically and chemically. Deintercalation of lithium from $LiMX_n$ using mild oxidizing agents such as I_2/CH_3CN and $Br_2/CHCl_3$ offers a low temperature route for the synthesis of Li_xMX_n and MX_n phases that are otherwise impossible to prepare, such as Li_xVS_2 and Li_xVO_2 (Murphy *et al* 1977; Vidyasagar and Gopalakrishnan 1982b). In table 2 we list representative examples of lithium intercalation as well as deintercalation. From the table, it is evident that lithium intercalation occurs in a wide variety of oxide and sulphide hosts possessing one-, two-, and three-dimensional structures. In most cases, the gross structural features of the host is retained. In some cases, there are specific structural changes which can be accounted for within the framework of a topochemical mechanism, *e.g.* $LiReO_3$ and Li_2ReO_3 (Cava *et al* 1982). In both $LiReO_3$ and Li_2ReO_3, the ReO_3 host made exclusively of corner-shared octahedra undergoes significant change on lithium insertion without breaking bonds. The 12-coordinated cavities in the ReO_3 framework become each two octahedral cavities which are occupied by lithium. Lithium insertion in close-packed oxides such as Fe_2O_3, Fe_3O_4, Mn_3O_4 and TiO_2 results in interesting structural changes

Table 2. Intercalation and deintercalation of lithium into MX_n hosts

| MX_n host	Remarks	References
TiS_2	Li_xTiS_2: $0 < x \leqslant 1$. Phase is homogeneous over the entire composition	Whittingham (1978)
VS_2	Li_xVS_2: $0 \leqslant x \leqslant 1$. Phases obtained by deintercalation of lithium from $LiVS_2$ using I_2/CH_3CN. Three different phase regions: $0.25 \leqslant x \leqslant 0.33$; $0.48 \leqslant x \leqslant 0.62$ and $0.85 \leqslant x \leqslant 1$ apart from VS_2	Murphy *et al* (1977)
NbS_2 (3R)	$Li_{0.5}NbS_2$ and $Li_{0.70}NbS_2$	Whittingham (1978)
TiS_3	Li_2TiS_3 and $Li_{2+x}TiS_3$ $(0 < x \leqslant 1)$	Whittingham (1978)
MoS_3	Li_xMoS_3 $(0 < x \leqslant 4)$	Jacobson *et al* (1979)
MO_2 (rutile)	Li_xMO_2 $(x \geqslant 1)$ (M = Mo, Ru, Os or Ir)	Murphy *et al* (1978)
TiO_2 (anatase)	Li_xTiO_2 $(0 < x \leqslant 0.7)$. $Li_{0.5}TiO_2$ transforms irreversibly to $LiTi_2O_4$ spinel at $500°C$	Murphy *et al* (1982)
CoO_2	Li_xCoO_2 $(0 < x < 1)$: Phases obtained by electrochemical delithiation of $LiCoO_2$	Mizushima *et al* (1980)
VO_2	Li_xVO_2 $(0 < x < 1)$: Phases obtained by chemical delithiation of $LiVO_2$ using $Br_2/CHCl_3$	Vidyasagar and Gopalakrishnan (1982b)
VO_2 (B)	Li_xVO_2 $(0 < x < 2/3)$: chemical lithiation using *n*-butyl lithium	Murphy and Christian (1979)
Fe_2O_3	$Li_xFe_2O_3$ $(0 < x < 2)$: Anion array transforms from hcp to ccp on lithiation	Thackeray *et al* (1982)
Fe_3O_4	$Li_xFe_3O_4$ $(0 < x < 2)$: Fe_2O_4 subarray of the spinel structure remains intact	Thackeray *et al* (1982)
Mn_3O_4	$Li_xMn_3O_4$ $(0 < x < 1.2)$: Lithium insertion suppresses tetragonal distortion of Mn_3O_4	Thackeray *et al* (1983)
MoO_3	Li_xMoO_3 $(0 < x < 1.55)$	Dickens and Pye (1982)
V_2O_5	$Li_xV_2O_5$ $(0 < x < 1.1)$: intercalation of lithium by using LiI	Dickens *et al* (1979)
ReO_3	Li_xReO_3 $(0 < x \leqslant 2)$: three phases $0 \leqslant x \leqslant 0.35$; $x = 1$ and $1.8 \leqslant x \leqslant 2$	Murphy *et al* (1981) Cava *et al* (1982)
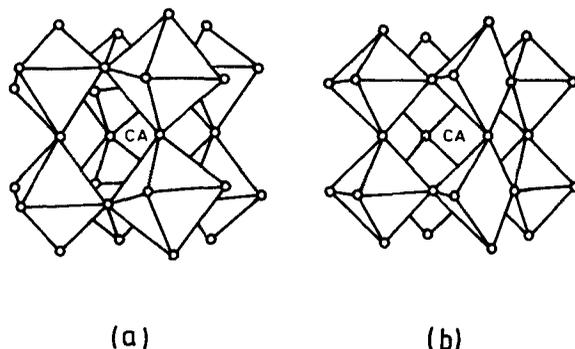
Figure 3. Structures of (a) $CaMnO_3$ and (b) $CaMnO_{2.5}$ (from Poeppelmeier *et al* 1982).

(Thackeray *et al* 1982, 1983; Murphy *et al* 1982). Lithium insertion changes the anion array of Fe_2O_3 from hexagonal to cubic close packing. Lithium insertion suppresses the cooperative Jahn-Teller distortion of Mn_3O_4. Lithium-inserted anatase, $Li_{0.5}TiO_2$, transforms to the superconducting spinel $LiTi_2O_4$ around 500°C. These examples reveal that low temperature intercalation-deintercalation of lithium and other alkali metals provides an important route for the synthesis of new solid phases.
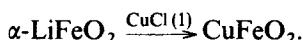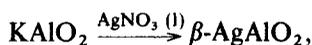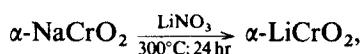
Several transition metal oxides can be topochemically reduced at relatively. low temperatures to yield metastable phases wherein the structural identity of the parent phases is preserved. Reduction of $CaMnO_3$ to $CaMnO_{2.5}$ and $CaMnO_{3-x}$ $(0 < x < 0.5)$ is a typical example (Poeppelmeier *et al* 1982). The reduction can be carried out by a variety of reducing agents such as H_2, NH_3, C_2H_4 and C_3H_6 between 300 and 500°C. The reduced phases possess structures closely related to the perovskite $CaMnO_3$ (figure 3). A number of similar preparations making use of the hydrogen reduction method have been carried out in this laboratory: Ln_2TiMoO_8 (scheelite) → Ln_2TiMoO_7 (pyrochlore) (Ln = rare earth); $Ln_2Mo_3O_{12}$ (scheelite-type) → $Ln_2Mo_3O_9$ (anion-deficient scheelite) and Ln_2MoO_6 (distorted fluorite) → Ln_2MoO_5 (anion-deficient fluorite) (Gopalakrishnan and Manthiram 1981; Manthiram and Gopalakrishnan 1978). A significant feature of these reduced phases is that they can be reversibly oxidized to their parent phases, a feature that is of significance with regard to their potential use as oxidation catalysts.

3.3 *Topochemical ion-exchange methods*

A number of inorganic solids having a layered or three-dimensional network structures exhibits fast cation transport. Sodium β- and β''- aluminas are typical examples. Sodium ions in these solids move rapidly in layers which provide a number of empty sites and easy pathways for the ionic motion. Diffusion coefficients are typically of the order of 10^{-7} cm^2 sec^{-1}. Fast cation conductors such as β-aluminas are good ion-exchangers. The exchange can be carried out easily at room temperature in both aqueous and molten salt conditions. Thus sodium β-alumina has been exchanged with H^+, H_3O^+, NH_4^+ and other monovalent and divalent cations giving rise to different β-aluminas (Farrington and Briant 1978; Tofield 1982). Ion-exchange in inorganic solids is a general phenomenon not being restricted to fast ion conductors alone. The kinetic and thermodynamic aspects of ion-exchange in inorganic solids have been examined by

England *et al* (1983). Their results reveal that ion-exchange is quite a widespread phenomenon occurring even when the diffusion coefficients are as small as $\sim 10^{-12}\,cm^2\,sec^{-1}$, at temperatures far below the sintering temperatures of solids. Substantial concentrations of mobile ion vacancies (introduced by nonstoichiometry or doping) are not required; ion-exchange could occur at considerable rate even in stoichiometric solids. The importance of such ion-exchange lies in the fact that since exchange is carried out at temperatures far below the sintering temperature of solids, the framework is not altered substantially during the exchange (topochemical exchange); this enables preparation of metastable phases that are inaccessible by high temperature reactions. England *et al* (1983) have shown that a variety of metal oxides having layered, tunnel and close-packed structures can be ion-exchanged in aqueous solutions or molten salt conditions to produce new phases.

Some of the exchange reactions are:

$$\alpha\text{-}NaCrO_2 \xrightarrow[300°C;24\,hr]{LiNO_3} \alpha\text{-}LiCrO_2,$$

$$2\,Na_2Ti_6O_{13} \xrightarrow[900°C;12\,hr]{Li_2SO_4} 2\,Li_2Ti_6O_{13} \rightarrow Li_4Ti_5O_{12} + 7\,TiO_2,$$
$$\text{metastable}$$

$$Li_4Ti_5O_{12} \xrightarrow[500°C;4\,days]{ZnCl_2} Li_2Zn\,[\square\,Ti_5]\,O_{12},$$

$$KAlO_2 \xrightarrow{AgNO_3\,(l)} \beta\text{-}AgAlO_2,$$

$$\alpha\text{-}LiFeO_2 \xrightarrow{CuCl\,(l)} CuFeO_2.$$

The structure of the framework is largely retained during the ion-exchange except for minor changes to accommodate the structural preferences of the incoming ion. Thus when α-LiFeO$_2$ is converted to CuFeO$_2$ by exchange with molten CuCl, the structure changes from α-NaCrO$_2$ to delafossite to provide a linear anion coordination for Cu$^+$ (figure 4). Similarly when KAlO$_2$ is transformed to β-AgAlO$_2$ by ion-exchange, there is a structure change from cristobalite to ordered wurtzite. The change probably occurs to provide a tetrahedral coordination for Ag$^+$.

An interesting ion-exchange reaction reported by Rice and Jackel (1982) is the conversion of LiNbO$_3$ and LiTaO$_3$ to HNbO$_3$ and HTaO$_3$ by treatment with hot aqueous acid. The exchange of Li$^+$ by protons is accompanied by a topotactic transformation of the rhombohedral LiNbO$_3$ structure to the cubic perovskite structure of HNbO$_3$. The mechanism suggested for the transformation is the reverse of the mechanism of transformation of cubic ReO$_3$ to rhombohedral LiReO$_3$ and Li$_2$ReO$_3$ (Cava *et al* 1982), involving a twisting of the octahedra along $[111]_{cubic}$ direction so as to convert the 12-coordinated perovskite tunnel sites to two six-
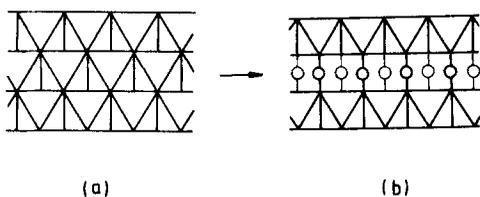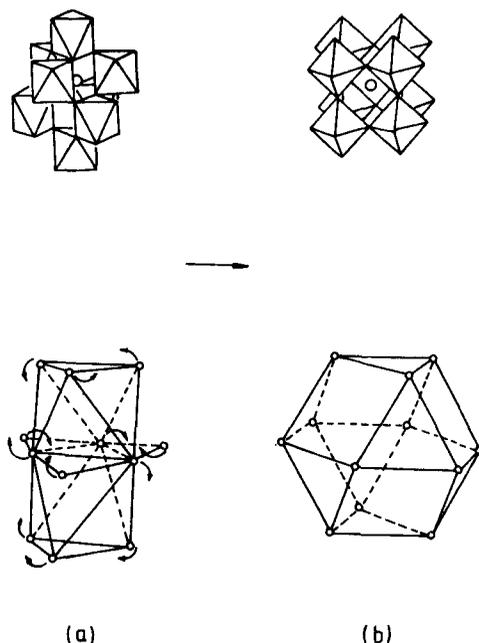

Figure 4. Topochemical transformation of (a) α-LiFeO$_2$ (α-NaCrO$_2$ structure) to (b) CuFeO$_2$ (delafossite structure) (from England *et al* 1983).

(a)   (b)

Figure 5. Topochemical transformation of (a) rhombohedral $LiNbO_3$ to (b) cubic $HNbO_3$. The NbO_6 octahedra are shown at the top. Conversion of two octahedral sites in the rhombohedral structure to a cubooctahedral site in the perovskite structure is shown at the bottom (from Rice and Jackel 1982).

coordinated sites in the rhombohedral structure (figure 5). Another interesting structural change accompanied by ion-exchange is reported in $Na_{0.7}CoO_2$ by Delmas *et al* (1982). $Na_{0.7}CoO_2$ is a layer oxide wherein the anion layer sequence is ABBAA; cobalt ions occur in alternate interlayer octahedral sites and sodium ions in trigonal prismatic coordination in between the CoO_2 units. When this material is ion-exchanged with LiCl, a new form of $LiCoO_2$ possessing the layer sequence ABCBA is obtained. In this unusual structure LiO_6 octahedra share a face with one CoO_6 octahedron and three edges with three other octahedra belonging to the next layer. Accordingly, the phase is metastable and transforms irreversibly to the stable $LiCoO_2$ (ABCABC) structure around 250°C.

A variety of inorganic solids has been exchanged with protons to give new phases some of which exhibit high protonic conduction: typical of them are $HTaWO_6 \cdot H_2O$ (Groult *et al* 1982); $HMO_3 \cdot xH_2O$ (M=Sb, Nb, Ta) pyrochlores and $HSbO_3 \cdot xH_2O$, cubic $KSbO_3$ structure (Chowdhry *et al* 1982); $HTiNbO_5$, layer structure (Rebbah *et al* 1982) and so on. Ion-exchange has also been reported in metal sulphides. For instance, $KFeS_2$ undergoes topochemical exchange of potassium in aqueous solutions of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} to give new phases in which the $[FeS_{4/2}]_\infty$ tetrahedral chain is preserved:

$$KFeS_2 + 0.5A^{2+} + xH_2O \rightarrow A_{0.5}^{2+}(H_2O)_x[FeS_2]^- + K^+$$
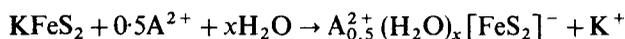
where $A = Mg^{2+}$, Ca^{2+}, Sr^{2+} or Ba^{2+}.

4. Conclusions

The present survey of some of the recent developments in preparative solid state chemistry has revealed that with knowledge of structural chemistry and reactivity patterns of solids, it has been possible to synthesize a variety of new solids possessing novel structures. The emphasis has been on low-temperature methods which enables synthesis of metastable phases that are inaccessible by the high-temperature route. A distinction is made between synthesis of *new solids* that may not involve new methods and synthesis by *new methods*. Three different routes to solid state synthesis have been recognized: the precursor method, the topochemical redox method and the topochemical ion-exchange method. Several illustrative examples are given for each category. The survey is however not complete in that it has not included all the recent developments in preparative solid state chemistry. For instance preparation of solids by vapour transport and deposition routes (Warren and Geballe 1981; Honig and Rao 1981), preparation of lower valence metal compounds by electrolytic reduction in molten salt media (McCarrol *et al* 1983), synthesis using low melting metals as solvents (Espinosa 1980) and synthesis of solids at high pressures (Joubert and Chenavas 1975) as well as chemical simulation of high pressure effects by suitable substitution are some of the aspects of preparative solid state chemistry that have not been discussed here.

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