Chemical approaches to the design of oxide materials

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Abstract: Chemical methods of synthesis play a crucial role in de-
signing and discovering new and novel materials and in providing less
cumbersome methods for preparing known materials. Chemical methods
also enable the synthesis of metastable materials which are otherwise
difficult to prepare. In this presentation, the various innovative
chemical methods of synthesising oxide materials will be briefly
reviewed with emphasis on soft-chemical routes. Electrochemical
synthesis, ion-exchange method, alkali-flux method and some of the
intercalation reactions will be highlighted, besides topochemical
aspects of solid state synthesis. Cuprate superconductors as well as
intergrowth structures will also be examined.

Introduction

Considerable chemical ingenuity is required in the synthesis of solid materi-
als. Tailor-making materials of the desired structure and properties is one of the
main goals of materials chemistry, but it is not always possible to do so by conven-
tional methods. Rational synthesis has indeed provided a variety of materials,
SIALON, NASICON and the large number of microporous materials being typical exam-
ples. Rational approach to materials synthesis generally gives thermodynamically
stable materials, but may miss new and novel metastable ones. In this presentation,
we shall be mainly concerned with chemical approaches to the synthesis of oxides and
shall discuss the various methods with examples and specially examine soft chemistry
routes.

Ceramic Procedures

The most common method of preparing inorganic solid materials is by the
reaction of the component materials in the solid state at high temperatures (1). In
some instances, as in the preparation of chalcogenides or of materials where the
products or reactants are volatile, the reaction is carried out in sealed tubes. In
preparing oxides, one generally pelletizes the reacting materials and repeats the
grinding, pelletizing and heating operations several times. Yet, the completion of
the reaction or the phasic purity of the product are not assured. The ceramic
method suffers from several disadvantages. Various modifications of the ceramic
technique have been employed to overcome some of the limitations. An important
effort has been to decrease diffusion path lengths. In a polycrystalline mixture of
reactants, individual particles are approximately 10 μm in size, representing diffu-
sion distances of roughly 10,000 unit cells. By using freeze-drying, spray-drying,
coprecipitation, sol-gel and other techniques, it is possible to reduce the particle
size to a few hundred angstroms and thus effect a more intimate mixing of the react-
ants. In coprecipitation, the required metal cations taken as soluble salts (e.g.
nitrates) are coprecipitated from a common medium, usually as hydroxides, car-
bonates, oxalates or citrates. In actual practice, one takes oxides or carbonates
of the relevant metals, digests them with an acid and then the precipitating reagent
is added to the solution. The precipitate obtained after drying is heated to the
required temperature in a desired atmosphere to produce the final product. The
decomposition temperatures of the precipitates are generally lower than the temper-
atures employed in the ceramic method.

Soft Chemistry Routes

      Soft chemistry routes essentially employ simple reactions that can be carried
out under mild conditions at relatively low temperatures. Generally, at least one
of the steps of synthesis involves a reaction in solution. A few illustrative
examples would help to understand the spirit of soft chemistry. Tournoux et al (2)
prepared a new form of TiO_2 by the dehydration of $H_2Ti_4O_9.xH_2O$, obtained from
$K_2Ti_4O_9$ by exchange of K^+ by H^+. Raveau and coworkers [3] prepared $Ti_2Nb_2O_9$ by the
dehydration of $HTiNbO_5$, which in turn was prepared by cation exchange with $ATiNbO_5$
(A = K, Rb). Delmas et al prepared $Ni(OH)_2.xH_2O$ with a large intersheet distance of
7.8 Å by the hydrolysis of $NaNiO_2$, followed by the subsequent reduction of NiOOH.
Similar transformations of Fe and Co doped $Ni(OH)_2.xH_2O$ have been examined (4).
Intercalation and deintercalation reactions are soft chemical routes for the syn-
thesis of many solids. Thus, deintercalation of $LiVS_2$ gives VS_2 which cannot be
prepared otherwise; deintercalation of $LiVO_2$ similarly gives metastable VO_2.
Recently, we have used deintercalation of amine intercalates of WO_3 to prepare WO_3
in perfect cubic form (ReO$_3$ type) and also in other metastable forms. In Fig.1 we
show the x-ray diffraction patterns of stable WO_3, $WO_3.0.5NEt_3$ and WO_3 (cubic).
Heating WO_3 (cubic) at 770K transforms it to the stable monoclinic form. Acid
leaching the NEt_3 intercalate gives another metastable form of WO_3 as shown in
Fig.2.

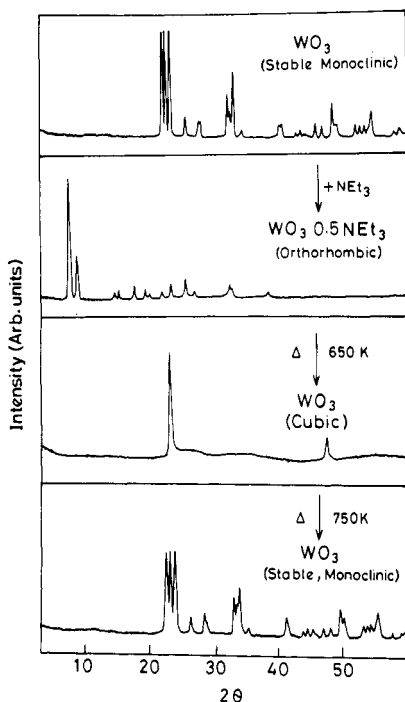Fig. 1. X-ray diffraction patterns of
stable (monoclinic) WO_3, $WO_3.0.5NEt_3$,
cubic WO_3 (ReO$_3$ type) obtained by
thermal deintercalation of $WO_3.0.5NEt_3$
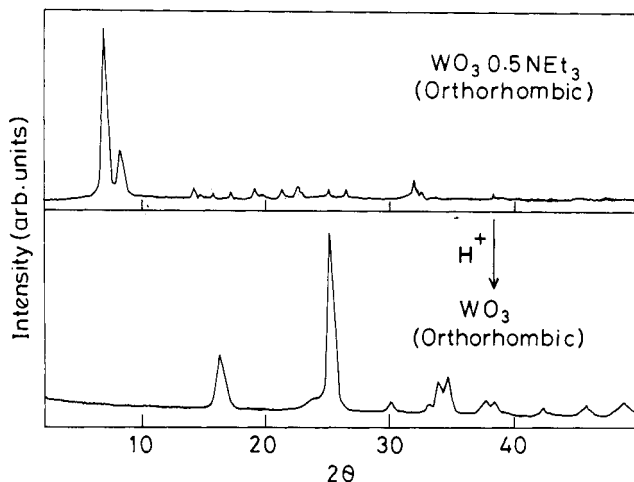and WO_3 (monoclinic) obained by heating
the metastable cubic WO_3 phase.

Fig.2. X-ray diffraction patterns
showing formation of a metastable
orthorhombic phase of WO_3 by the acid
leaching of the intercalated amine in
$WO_3.0.5NEt_3$ at room temperature.

      Intercalation reactions involve the insertion of a guest species into a solid
host lattice without any major rearrangement of the solid structure (1,5). Many
intercalation reactions are known, with a variety of host materials which include
graphite, oxides and chalcogenides. Thus, Li^+ has been intercalated in large
number of hosts (VS_2, TiS_2, VO_2, Fe_2O_3, Fe_3O_4, MnO_2 etc.). Tungsten bronzes may be
considered to be intercalation compounds. Chevrel phases are also intercalation

compounds since Cu and such cations can be leached out to produce the chalcogenides. Novel materials can be obtained by restacking exfoliated single-layer MoS_2 and other layered materials with molecular units between the layers. A variety of molecules have been incorporated between such single layers of MoS_2, MoO_3 and other layered materials (6). Many of the topochemical reactions are gentle, although they may occur entirely in the solid state.

Precursor Methods

The best way of reducing diffusion distances in solid state synthesis, in particular by ceramic procedures, is to have precursors wherein the relevant metal ions are a short distance apart (Fig.3). Precursor compounds to prepare a variety of perovskite oxides have been known for some time (e.g. $Ba[TiO(C_2O_4)_2]$ for $BaTiO_3$, $Li[Cr(C_2O_4)_2.(H_2O)_2]$ for $LiCrO_2$, MCr_2O_4 from $(NH_4)_2M(CrO_4)_2.6H_2O$ and $LaCoO_3$ from $LaCo(CN)_6.5H_2O$. Hydrazinate precursors have been employed to prepare several complex oxides.
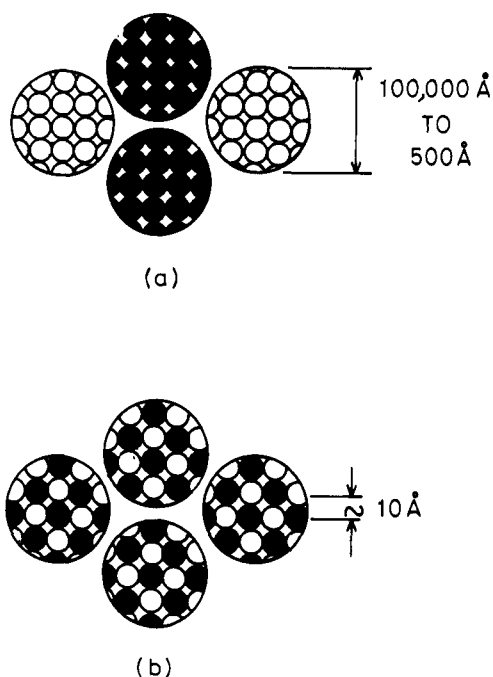

(a)

(b)

Fig.3. Large diffusion distances involved in ceramic
preparations involving two types of cations (closed
circles and open circles represent two cations) com-
pared to a precursor (the two cations are present in
proximity).

Specially noteworthy are the carbonate solid solutions of calcite structure which on decomposition give the oxide with the desired cation ratios (7). A variety of complex oxides have been prepared by this method and many of these cannot be prepared otherwise.

A large number of carbonate solid solutions of calcite structure containing two or more cations in different proportions and these solid solutions are excellent precursors for the synthesis of oxides since the diffusion distances are consider-ably lower than in the ceramic procedure. The rhombohedral unit cell parameter, a_R, of the carbonate solid solutions varies systematically with the weighted mean cation radius. Carbonate solid solutions are ideal precursors for the synthesis of monox-ide solid solutions of rock-salt structure. For example, the carbonates are decom-posed in vacuum or in flowing dry nitrogen, to obtain monoxides of the type $Mn_{1-x}M_xO$ (M = Mg, Ca, Co or Cd) of rock-salt structure. Oxide solid solutions of M = Mg, Ca

and Co would require 770-970K for their formation while those containing cadmium are
formed at still lower temperatures.   The facile formation of oxides of rock-salt
structure by the decomposition of carbonates of calcite structure is due to the
close (topotactic) relationship between the structures of calcite and rock-salt.
The monoxide solid solutions can be used as precursors for preparing spinels and
other complex oxides.

      A number of ternary and quarternary oxides of novel structures have been
prepared by decomposing carbonate precursors containing the different cations
in the required proportions.   Thus, one can prepare $Ca_2Fe_2O_5$ and $CaFe_2O_4$ by
heating the corresponding carbonate solid solutions in air at 1070 and 1270K
respectively for about 1h. $Ca_2Fe_2O_5$ is a defect perovskite with ordered oxide
ion vacancies and has the well-known brownmillerite structure with the Fe^{3+}
ions in alternate octahedral (0) and tetrahedral (T) sites.   Cobalt oxides of
similar compositions, $Ca_2Co_2O_5$ and $Ca_2Co_2O_4$, have been prepared by decomposing
the approrpiate carbonate precursors around 940K.   Unlike in $Ca_2Fe_2O_5$, anion-
vacancy ordering in $Ca_2Mn_2O_5$ gives rise to a square-pyramidal coordination
(SP) around the transition metal ion.   One can also synthesize quarternary
oxides, Ca_2FeCoO_5, $Ca_2Fe_{1.5}Mn_{1.5}O_{8.25}$, $Ca_3Fe_2MnO_8$ etc. belonging to the $A_nB_nO_{3n-1}$
family, by the carbonate precursor route (Fig.4).   In the Ca-Fe-O system, there are
several other oxides such as $CaFe_4O_7$, $CaFe_{12}O_{19}$ and $CaFe_2O_4(FeO)_n$ (n = 1,2,3) which
can, in principle, be synthesized starting from the appropriate carbonate solid
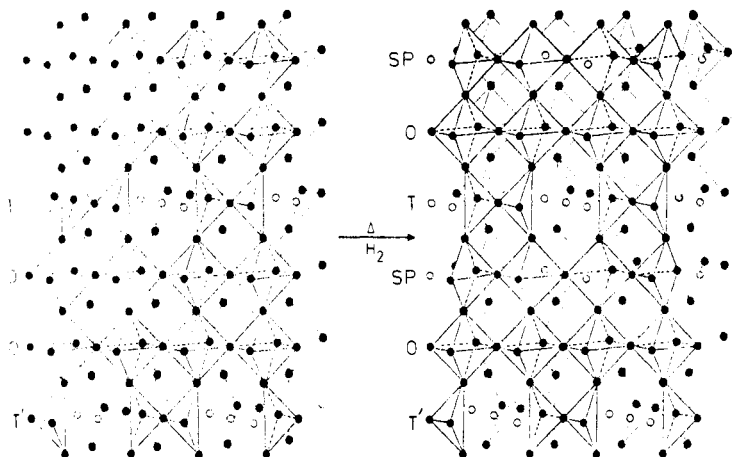solutions and decomposing them in a proper atmosphere.

Fig. 4. $Ca_3Fe_2MnO_{7.5}$ with three types of transition
metal coordinations obtained by the topochemical
reduction of $Ca_3Fe_2MnO_8$ with only octahedral and
tetrahedral coordinations. The latter oxide is ob-
tained by the thermal decomposition of the precursor
carbonate, $Ca_2Fe_{4/3}Mn_{2/3}(CO_3)_4$.

      Hydroxide, nitrate and cyanide solid solutions have also been employed as
precursors for oxides.   Recently a precursor has been found to prepare Chevrel
phases (8) of the type $A_xMo_6S_8$ by   the reaction, $2A_x(NH_4)_yMo_3S_9 + 10H_2 \longrightarrow$
$A_{2x}Mo_6S_8 + 10H_2S + 2yNH_3 + yH_2$.   Precursors for the synthesis of $YBa_2Cu_3O_7$ have been
described (9).

Topochemical Reactions

      Intercalation reactions are generally topochemical in nature.   In topochemical
reactions, the reactivity is controlled by the crystal structure and there is orien-
tational relationship between the product and the parent just as in martensitic
transformations (1).   Dehydration of ß-Ni(OH)$_2$ to NiO as well as the oxidation of
Ni(OH)$_2$ to NiOOH are both topochemical (10). Y-FeOOH topochemically transforms to

γ-Fe_2O_3 on treatment with an organic base. Dehydration of many hydrates such as $VOPO_4 \cdot 2H_2O$ and $MoO_3 \cdot H_2O$ is topochemical. The topochemical nature of dehydration has been exploited to prepare MoO_3 in the metal stable ReO_3 type structure (12). $WO_3 \cdot 1/3\ H_2O$ gives WO_3 in different structures depending on the temperature of dehydration (10). Topochemical reduction and oxidation reactions are known. Thus, the reduction of $YBa_2Cu_3O_7$ to $YBa_2Cu_3O_6$ is topochemical. $La_2Ni_2O_5$ can only be made by the topochemical reduction of $LaNiO_3$; $La_2Co_2O_5$ can similarly be prepared only from $LaCoO_3$ (11).

Ion-Exchange and Alkali Flux Methods

Ion-exchange is an important property of fast-ion conductors such as ß-alumina. Ion exchange also provides a means of preparing other materials. Typical examples are the preparation of $LiCrO_2$ from $NaCrO_2$ and $LiNO_3$, $AgAlO_2$ from $KAlO_2$ and $AgNO_3$ and $CuFeO_2$ from $LiFeO_2$ and $CuCl$. These reactions are carried out in molten state or in aqueous solution. It is through proton exchange with oxide materials containing alkali metal ions (specially Li^+) that one obtains several materials used as precursors to prepare some of the oxides. We examined some examples while discussing soft chemistry routes. Another example is the conversion of $LiNbO_3$ and $LiTaO_3$ to $HNbO_3$ and $HTaO_3$ (13).

Use of strong alkaline media in the form of solid fluxes or molten solutions is helpful in preparing oxides, specially if one of the metal ions is required in a high oxidation state. Thus $Pb_2(Ru_{2-x}Pb_x)O_{7-y}$ with Pb in 4+ state is prepared in a highly alkaline media. Molten alkali has been used to prepare superconducting $La_2CuO_{4+\delta}$ (9).

Electrochemical Methods

Electrochemistry in aqueous or molten media has yielded a large number of inorganic materials including carbides, borides, silicides, oxides and sulfides. Many of the oxide bronzes are prepared electrochemically, just as other alkali metal intercalation compounds (e.g. Li_xMS_2). The electrochemical method provides the best means of preparing oxides where a transition metal ion is required to be present in a high oxidation state. Thus, superconducting $La_2CuO_{4+\delta}$ as well as $SrFeO_3$ type oxides have been prepared electrochemically [14]. Recently, Pouchard et al have prepared oxygen-excess $La_8Ni_4O_{17}$ with unusual oxygen species electrochemically (15) while we have prepared ferromagnetic, cubic $LaMnO_{3+\delta}$ with > 40% Mn^{4+} content. In Fig.5 we show the progressive oxidation of $LaMnO_3$ from the orthorhombic phase to the cubic phase _via_ the rhombohedral phase.

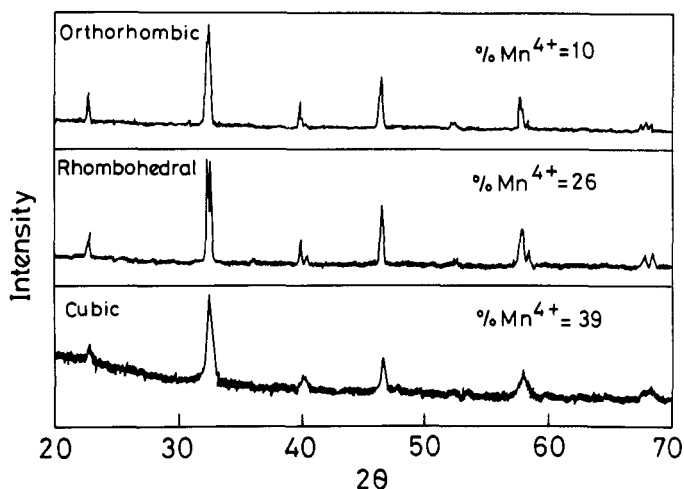Fig. 5. Rhombohedral and cubic $LaMn^{+3}Mn_x^{4+}O_{3+\delta}$ obtained by the electrochemical oxidation of orthorhombic $LaMnO_3$.

Nebulized spray pyrolysis

Pyrolysis of sprays is a well-known method for depositing films. Thus, one can obtain films of oxidic materials such as CoO, ZnO and $YBa_2Cu_3O_7$ by the spray pyrolysis of solutions containing salts (e.g. nitrates) of the cations. A novel improvement in this technique is the so-called pyrosol process or nebulized spray pyrolysis involving the transport and subsequent pyrolysis of a spray generated by an ultrasonic atomizer as demonstrated by Joubert and coworkers (16). Wold and coworkers as well as Rao and coworkers have employed this method to prepare films of a variety of oxides. When a high frequency (100 kHz-10MHz range) ultrasonic beam is directed at a gas-liquid interface. a geyser is formed and the height of the geyser is proportional to the acoustic intensity. Its formation is accompanied by the generation of a spray, resulting from the vibration at the liquid surface and cavitation at the liquid-gas interface. The quantity of spray is a function of the intensity. Ultrasonic atomization is accomplished by using an approrpiate transducer made of PZT located at the bottom of the liquid container. A 500-1000 kHz transducer is generally adequate. The atomized spray which goes up in a column fixed to the liquid container is deposited on a suitable solid substrate and then heat-treated to obtain the film of the concerned material. The flow rate of the spray is controlled by the flow-rate of air or any other gas. The liquid gas is heated to some extent, but its vaporization should be avoided. In Fig. 6 we show the appratus employed in the pyrosol method.
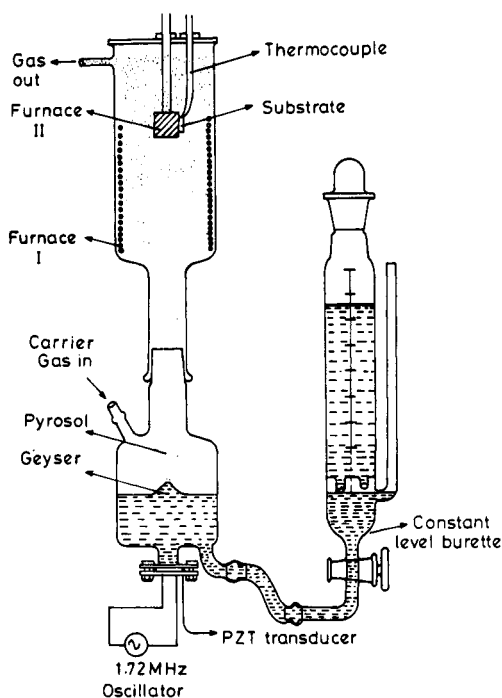

Fig. 6. Apparatus for nebulized pyrolysis.

The source liquid would contain the relevant cations in the form of salts dissolved in an organic solvent. Organometallic compounds (e.g. acetates, alkoxides, ß-diketonates etc.) are generally used for the purpose. Proper gas flow is crucial to obtain satisfactory conditions for obtaining a good liquid spray. Nebulized spray pyrolysis is somewhere between MOCVD and spray pyrolysis, but the choice of source compounds for the pyrosol process is much larger than available for MOCVD. Furthermore, the use of a solvent minimizes or eliminates the difficuslties faced in MOCVD. Films of a variety of oxide materials such as $(PB,Zr)TiO_3$, $YBa_2Cu_3O_7$ and $LaNiO_3$ have been obtained by the pyrosol method. The pyrosol method is truly inex-

pensive compared to CVD/MOCVD. The thickness of pyrosol films can be anywhere between a few hundred angstroms to a few microns.

Cuprate Superconductors

The discovery of a superconducting cuprate with T_c above 77K created a sensation in early 1987. Wu et al. who announced this discovery first made measurements on a mixture of oxides containing yttrium, barium and copper obtained in their efforts to obtain the yttrium-analogue of $La_{2-x}Ba_xCuO_4$. In this laboratory, we worked independently on the Y-Ba-Cu-O system on the basis of solid state chemistry. We knew that Y_2CuO_4 could not be made and that substituting yttrium by barium in this cuprate was not the way to proceed. We therefore tried to make $Y_3Ba_3Cu_6O_{14}$ by analogy with the known $La_3Ba_3Cu_6O_{14}$ and varied the yttrium barium ratio as in $Y_{3-x}Ba_{3+x}Cu_6O_{14}$ (17). By making $x = 1$, we obtained $YBa_2Cu_3O_7$ ($T_c \approx$ 90K). We knew the structure had to be that of a defect perovskite from the beginning, because of the route we adopted for the synthesis.

Preparative aspects of the various types of cuprate superconductors have been recently reviewed (9). The cuprates are ordinarily made by the traditional ceramic method (mix, grind and heat), which involves thoroughly mixing the various oxides and/or carbonates in the desired proportion and heating the mixture at a high temperature. The mixture is ground again after some time and reheated until the desired product is formed, as indicated by X-ray diffraction. This method may not always yield the product with the desired structure, purity or oxygen stoichiometry. Variants of this method are often employed. For example, decomposing a mixture of nitrates has been found to yield a better product in the case of the 123 compounds by some workers; others prefer to use BaO_2 in place of $BaCO_3$ for the synthesis. One of the problems with the bismuth cuprates is the difficulty in obtaining phasic purity (minimizing intergrowth of the different layered phases). The glass or the melt route has been employed to obtain better samples. Sealed tube reactions are essential in the case of thallium and mercury cuprates.

Heating oxidic materials under high oxygen pressures or in flowing oxygen often becomes necessary to attain the desired oxygen stoichiometry. Thus, La_2CuO_4 and $La_2Ca_{1-x}Sr_xCu_2O_6$ heated under high oxygen pressures become superconducting with T_c values of 40 and 60K respectively. We have prepared an analogous cuprate with two CuO_2 sheets (T_c - 60K) by using $KClO_3$ in the preparation. In the case of the 123 compounds, one of the problems is that they lose oxygen easily. It is necessary to heat these materials in an oxygen atmosphere below the orthorhombic-tetragonal transition temperature. The 124 superconductors were first prepared under high oxygen pressures, but it was later found that heating the oxide or nitrate mixture in the presence of Na_2O_2 in flowing oxygen is sufficient to obtain 124 compounds. Superconducting lead cuprates, however, can only be prepared in the presence of very little oxygen. In the case of the electron superconductor $Nd_{2-x}Ce_xCuO_4$, it is necessary to heat the material in an oxygen-deficient atmosphere. Many of the thallium cuprates have to be heated in vacuum, N_2 or H_2 atmospheres to make them superconducting.

The sol-gel method has been conveniently employed for the synthesis of 123 and bismuth cuprates. Materials prepared by such low-temperature methods have to be heated under suitable conditions to obtain the desired oxygen stoichiometry as well as the characteristic high T_c value. 124 cuprates, lead cuprates and even thallium cuprates have been made by the sol-gel method; the first two are particularly difficult to make by the ceramic method. Coprecipitation of all the cations in the form of a sparingly soluble salt such as carbonate in a proper medium (e.g. using tetraethylammonium oxalate), followed by thermal decomposition of the dried precipitate has been employed by many workers to prepare cuprates. Several other novel strategies employed for the synthesis of superconducting cuprates were mentioned while discussing the various methods. Strategies where structure and bonding considerations are involved in the synthesis are generally more interesting. One such example is the synthesis of modulation-free superconducting bismuth cuprates. Special mention should be made of oxyanion derivatives of cuprates, some of which are superconducting. Anions such as CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and BO_3^{3-} replace the CuO_4 units in 123 as well as other cuprates (18-22).

Intergrowth Structures

There are several metal oxides exhibiting well-defined recurrent intergrowth structures with large periodicities, rather than forming random solid solutions with variable composition. Such ordered intergrowth structures themselves however frequently show the presence of wrong sequences. High resolution electron microscopy (HREM) enables a direct examination of the extent to which a particular ordered arrangement repeats itself, the presence of different sequences of intergrowths, often of unit cell dimensions. Many systems forming ordered intergrowth structures have come to be known in recent years (23). These systems generally exhibit homology. The Aurivillius family of oxides of the general formula $Bi_2A_{n-1}B_nO_{3n+3}$ form intergrowth structures of the general formula $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$ involving alternate stacking of two Aurivillius oxides with different n values. The method of preparation involves simply heating a mixture of the component metal oxides at ~1000K. Ordered intergrowth structures with (m,n) values of (1,2), (2,3) and (3,4) have been fully characterized. Intergrowth bronzes and hexagonal barium ferrites are also examples of ordered intergrowths. What is surprising is that such periodicity occurs even when either units involved in the integrowth is stable by itself.

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