

version of the lipids from the gel state to the liquid crystal state.

The different results obtained with 1-palmitoyllysophosphatidylcholine and 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) are indicative of differential degrees of self-association of gramicidin A. In the case of the stoichiometric 1-palmitoyllysophosphatidylcholine/gramicidin A model membrane the  $^2\text{H}$  NMR data suggest that gramicidin A forms a rigid two-dimensional array of peptides, thereby excluding any lateral or rotational diffusion in the plane of the membrane and also tryptophan ring flipping motions. On the other hand, the interstices between the gramicidin A are apparently large enough to allow an almost unhindered lipid motion and to create a normal lipid bilayer order profile. The tendency of self-association is much reduced in bilayers of 1,2-dimyristoyl-*sn*-glycerol-3-phosphocholine as evidenced by the observation of mobile components in the  $^2\text{H}$  NMR spectrum of gramicidin A. Since 1:4 1-palmitoyllysophosphatidylcholine/gramicidin A bilayers form preferentially regardless of the initial lipid/gramicidin ratio,<sup>10</sup> the differences in gramicidin mobility between DMPC and lysophosphatidylcholine membranes must be due to more than simply their different lipid/protein ratios.

At present,  $^2\text{H}$  NMR of membrane proteins is at an early stage. The studies on the gramicidin model

membrane suggest that in this particular membrane it is the irregular outer contour of the peptide which matches with the inherent disordering tendency of the lipids. In other cases, yet to be investigated, the outer surface of the protein in the membrane may however be fluidlike, providing a fluid mechanical match with the fluid lipid bilayer.<sup>6</sup>

Most important, however, if a deuterium labeling of the active site of membrane proteins could be achieved,  $^2\text{H}$  NMR might provide insight into the mechanistic aspects of such proteins.

### Concluding Remarks

$^2\text{H}$  NMR can provide insights into the structural and dynamic properties of each membrane component. Studies of the lipid hydrocarbon chains and headgroups have revealed the nature and rates of motions undergone and the effects of proteins, other lipids, and ions. Future work will be directed toward more closely defining the roles of specific interactions in membrane functioning. Studies of membrane proteins, while still relatively new, should provide detailed insights into the motions of proteins and their constituents, how they are affected by lipids and other factors, and, most promisingly, into the mechanism of catalysis and transport.

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## Synthesis of Complex Metal Oxides by Novel Routes<sup>†</sup>

C. N. R. RAO\* and J. GOPALAKRISHNAN

*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*

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### Introduction

A variety of inorganic solids have been prepared in recent years by employing a wide range of conditions such as irradiation by laser or electron beams, use of high pressures, high vacuum, or hydrothermal conditions, rapid quenching of melts, melting in a water-cooled copper container using rf power (skull melting) or in an arc, and so on.<sup>1</sup> Several ways of accomplishing synthesis under mild conditions have been explored,

and of special importance are the energy-saving routes involving low temperatures. In this article we shall present some of the important innovations in the synthesis of complex metal oxides, hoping that the article will also serve to illustrate how solid-state chemists pursue synthesis often employing seemingly simple techniques.

Innovations in the synthesis of complex metal oxides and related materials are necessary for tailor-making solids with the desired structure and properties. It is only by employing ingenious methods that one can prepare solids that are ordinarily metastable or unstable. Low-temperature methods enable the synthesis of several such materials (e.g.,  $\text{ReO}_3$ -like  $\text{MoO}_3$ ,  $\text{La}_2\text{Co}_2\text{O}_5$ ,  $\text{Ca}_2\text{Mn}_2\text{O}_5$ ,  $\text{Pb}_2\text{Ru}_{2-x}\text{Pb}_x\text{O}_{7-y}$ ,  $\text{VS}_2$ ,  $\text{Mo}_6\text{S}_8$ , and so on). Besides being of academic interest, novel synthesis of metal oxides is of great relevance because of possible applications in crucial sectors such as electronics, communication, and energy. Active metal oxides with controlled particle size are important in catalysis. Metal

C. N. R. Rao obtained his Ph.D. degree from Purdue University in 1958 and worked as a research associate at the University of California, Berkeley, before starting his academic career in India. He was Professor of Chemistry at the Indian Institute of Technology, Kanpur, for several years and was later founder Chairman of the Solid State and Structural Chemistry Unit and the Materials Research Laboratory at the Indian Institute of Science, Bangalore, of which he is now Director. Of the many professional honors he has received, mention must be made of the D.Sc. (honoris causa) from Purdue University and the A.C.S. Centennial Foreign Fellowship. He is Fellow of the Royal Society, London, and an Honorary Foreign Member of the American Academy of Arts and Sciences. His main research interests are solid-state chemistry, surface science, chemical spectroscopy, and molecular structure.

J. Gopalakrishnan obtained his Ph.D. degree in Inorganic Chemistry from the Indian Institute of Science. After working as a Lecturer at the Department of Chemistry, Indian Institute of Technology, Madras, and as a Fellow of the Alexander von Humboldt Foundation at the Technical University, Berlin, he joined the Solid State and Structural Chemistry Unit, Indian Institute of Science, where he is now a Professor and Chairman of the Unit. Synthesis and structural characterization of metal oxides and chalcogenides are his primary areas of research interest.

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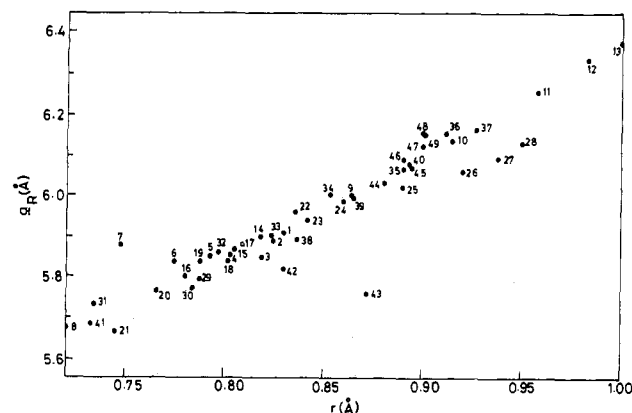
oxides show unusual electronic properties ranging anywhere between insulating behavior at one extreme and metallic behavior at the other. Some of the oxides also exhibit transitions from a nonmetallic to the metallic state (e.g.,  $V_2O_3$ ,  $La_2NiO_4$ ). Many of the important magnetic materials are metal oxides (e.g.,  $BaFe_{12}O_{19}$ ,  $Y_3Fe_5O_{12}$ ); so are materials with high dielectric constants (e.g.,  $BaTiO_3$ ,  $Bi_4Ti_3O_{12}$ ). Oxides exhibit interesting optical properties as well (e.g.,  $PbZr_{1-x}Ti_xO_3$ ), while some others are fast ion conductors (e.g., sodium  $\beta$ -alumina,  $Na_{1+x}Al_{11}O_{17+x/2}$ , and Nasicon,  $Na_3Zr_2PSi_2O_{12}$ ). We can cite many such examples of complex metal oxides with fascinating properties of technological value.

The most widely used solid-state synthetic technique has been the ceramic method which involves mixing the solid components and reacting the mixture at elevated temperatures. By its very nature, the method requires large diffusion distances (up to  $10^5$  Å) of the reacting species and is therefore of disadvantage. Furthermore, the method does not always yield a single-phase product. Diffusion distances can be cut down through a reduction in the size of the reacting particles by means of spray-drying and freeze-drying or by the sol-gel technique. The sol-gel method, which generally involves hydrolysis and polymerization of ionic species in aqueous media, has been widely used in the past few years as an energy-minimizing means of synthesizing a variety of oxides and other materials.<sup>2</sup> Chemically speaking, the most attractive alternative to the ceramic method is the precursor method where the starting material is a monophasic compound containing the required species in the right proportion.<sup>3</sup> We shall discuss the precursor method in some detail in this article and also refer to some aspects of the sol-gel method.

Solid-state reactions where the crystal structure controls the reactivity<sup>4</sup> (topochemical reactions) yield unusual products which cannot otherwise be prepared by conventional methods. We shall examine a few interesting topochemical reactions employed in the synthesis of novel metal oxides. Intercalation involving the insertion of neutral or ionic species (by an ion-exchange or a redox mechanism) into layered solids, where the atomic arrangement is essentially two-dimensional like in graphite, is a topochemical process which has led to the synthesis of a large number of inorganic solids. Intercalation chemistry<sup>5</sup> has emerged to become a major aspect of solid-state chemistry. While it would be beyond the scope of this article to do full justice to this vast subject, we shall describe some of the important reactions for the synthesis of metal oxides involving topochemical dehydration, reduction, atom insertion, and ion exchange.

### The Precursor Method

Any facile low-temperature method for preparing a monophasic metal oxide would require a homogeneous



**Figure 1.** Plot of rhombohedral lattice parameter  $a_R$  of calcite carbonate solid solutions vs. weighted mean cation radius  $r$ . (The numbers refer to the compositions of various solid solutions: 1–8, Mn–Mg system; 9–13, Mn–Ca system; 14–16, Mn–Fe system; 17–21, Mn–Co system; 22–28, Mn–Cd system; 29–31, Fe–Mg system; 32–37, Fe–Ca system; 38–40, Fe–Cd system; 41, Mg–Co system; 42 and 43, Co–Ca system; 44, Ca–Fe–Co system; 45, Ca–Mn–Co system; 46–49, Ca–Mn–Fe system.)

mixing of the component species on an atomic scale. Since this cannot be achieved in the conventional ceramic method or any of its modifications, one way to meet this requirement is to prepare a precursor compound<sup>3</sup> in which the reactants are present in the required stoichiometry. Typical examples of the use of such precursor compounds in the syntheses of oxides are  $BaTiO_3$  from  $BaTiO(C_2O_4)_2$ ,  $LnFeO_3$  ( $Ln = La, Y$ , or rare earth) from  $LnFe(CN)_6 \cdot 5H_2O$ ,  $LnCoO_3$  from  $LnCo(CN)_6 \cdot 5H_2O$ ,  $LnAlO_3$  from  $(NH_4)_3[Ln(OH)Al(C_6H_4O_7)_2]$ ,  $FeAlO_3$  from  $(NH_4)_3[Fe_{0.5}Al_{0.5}(C_2O_4)_3] \cdot 3H_2O$ , and  $(Al_{1-x}Cr_x)_2O_3$  from  $(NH_4)_3[Al_{1-x}Cr_x(C_2O_4)_3] \cdot 3H_2O$ . Optoelectronic materials such as  $PbZr_{0.5}Ti_{0.5}O_3$  and  $(PbLa)(ZrTi)O_3$  can be prepared from carboxylate precursors. A number of such examples of the use of metal-organic precursor compounds (generally salts of organic acids such as oxalates, citrates, etc.) for the preparation of oxides and other solids can be cited.<sup>3</sup> The disadvantage with this method is that it is not always possible to find suitable precursor compounds for the synthesis of complex metal oxides of all desired compositions. This can, however, be accomplished by resorting to precursor solid solutions (continuous series of isostructural solid solutions containing a common anion) as starting materials.<sup>6</sup> The best examples of such precursor solid solutions are carbonates of the type  $M_{1-x}A_xCO_3$  where  $M = Ca$  or  $Mg$  and  $A = Mn, Fe, Co$ , etc., which crystallize in the calcite structure. It is noteworthy that carbonates of  $Mg, Ca, Cd, Mn, Fe$ , and several other metals possess the calcite structure. We have prepared a variety of carbonate solid solutions containing two or more cations in different proportions.<sup>7</sup> The rhombohedral  $a_R$  of these carbonate solid solutions varies systematically with the weighted mean cation radius as shown in Figure 1, clearly depicting the formation of single-phase precursors in a wide variety of systems. The carbonate solid solutions are ideal precursors for the synthesis of monoxides of rock salt

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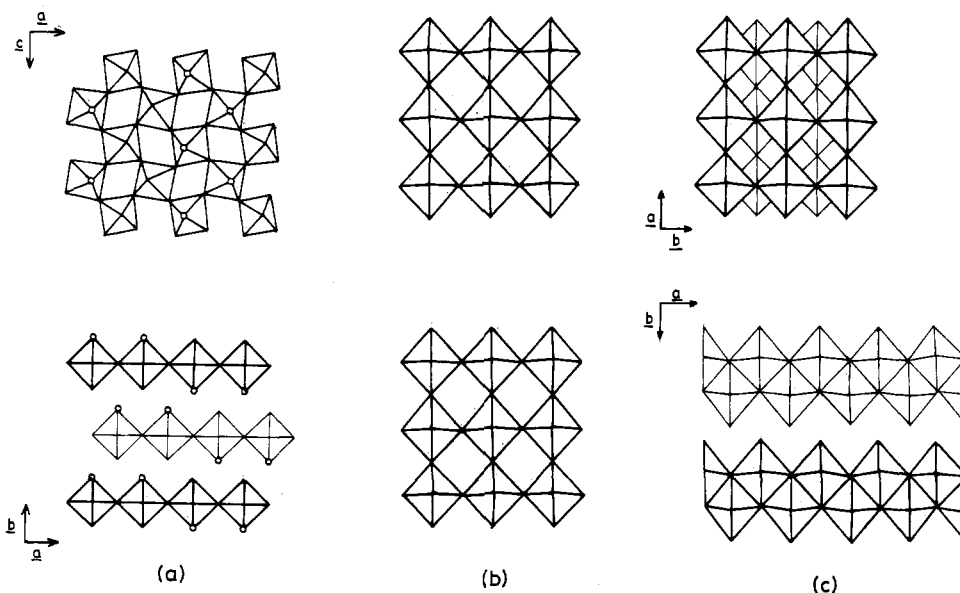
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**Figure 4.** Schematic representations of the structures of (a)  $\text{MoO}_3 \cdot \text{H}_2\text{O}$ , (b)  $\text{ReO}_3$ -like  $\text{MoO}_3$ , and (c) layered  $\text{MoO}_3$ . Pure  $\text{MoO}_3$  first forms the  $\text{ReO}_3$ -type phase which on further heating goes to the layered structure. The solid solutions  $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ , however, remain in the  $\text{ReO}_3$  structure.

possible to transform one into the other. Mono- as well as dihydrates of these oxides are however isostructural, and their dehydration is considered to proceed topochemically.<sup>16</sup> The mixed oxide hydrates,  $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$ , have the same structure as  $\text{W}(\text{Mo})\text{O}_3 \cdot \text{H}_2\text{O}$  and undergo topochemical dehydration to yield  $\text{Mo}_{1-x}\text{W}_x\text{O}_3$  in the  $\text{WO}_3$  structure<sup>17</sup> (Figure 4). The reaction involves a collapse of the layered structure in the  $b$  direction, the structure essentially remaining the same in the  $ac$  plane. Crystallographic (orientational) relationships are found between the parent hydrate and the product oxides as revealed by electron diffraction:  $(010)_{\text{hydr}} \parallel (010)_{\text{oxide}}$ ,  $[100]_{\text{hydr}} \parallel [001]_{\text{oxide}}$ , and  $[001]_{\text{hydr}} \parallel [100]_{\text{oxide}}$ . More importantly, we have shown that in situ dehydration of  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  in the electron microscope gives  $\text{MoO}_3$  in the  $\text{ReO}_3$  structure; this new form of  $\text{MoO}_3$  transforms into the layered  $\text{MoO}_3$  structure on further heating (Figure 4). After we established the formation of cubic  $\text{MoO}_3$  from the hydrate, other workers<sup>18</sup> have prepared  $\text{ReO}_3$ -like  $\text{MoO}_3$  by dehydrating spray-dried molybdic acid or  $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ .

An interesting feature of  $\text{Mo}_{1-x}\text{W}_x\text{O}_3$  solid solutions prepared by topotactic dehydration of the monohydrates is that they undergo facile reduction to yield a variety of products.<sup>7b,17</sup> When the reduction is carried out in a  $\text{CO}_2$  atmosphere ( $\sim 530^\circ\text{C}$ ), nonstoichiometric oxides belonging to the  $\text{M}_n\text{O}_{3n-1}$  Magneli series with crystallographic shear planes are formed. Reduction of  $\text{Mo}_{1-x}\text{W}_x\text{O}_3$  in hydrogen yields monoclinic  $\text{Mo}_{1-x}\text{W}_x\text{O}_2$  at  $360^\circ\text{C}$ . When  $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$  is directly reduced in hydrogen at  $750^\circ\text{C}$ , monophasic Mo-W alloys are formed, providing a convenient route for the synthesis of these alloys.

Oxides possessing a network of octahedra and tetrahedra are of considerable current interest,<sup>19</sup> VOP-

$\text{O}_4 \cdot 2\text{H}_2\text{O}$  adopting a layered structure<sup>20</sup> being a typical example of this family. This solid dehydrates topochemically to give the monohydrate and the anhydrous  $\text{VOPO}_4$ .  $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  possessing a chain structure with alternating  $\text{MoO}_6$  octahedra and  $\text{PO}_4$  tetrahedra<sup>21</sup> transforms into  $\text{MoO}(\text{OH})\text{PO}_4$ , possibly with a layered structure, by topotactic elimination of water. The infrared spectrum of  $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  reveals the presence of both OH and  $\text{H}_2\text{O}$ , suggesting that the formula is  $\text{MoO}(\text{OH})\text{PO}_4 \cdot \text{H}_2\text{O}$ .

Topochemical oxidation-reduction reactions are common among inorganic solids, a well-known example being the transformation of iron oxides between rock salt and spinel structures. A topochemical relationship exists between  $\text{NiO}$  and  $\text{Ni}$  when the oxide is reduced to the metal.<sup>22</sup> Reduction of  $\text{WO}_3$  to yield  $\text{W}_n\text{O}_{3n-1}$  or  $\text{W}_n\text{O}_{3n-2}$  with crystallographic shear planes<sup>23</sup> may also be regarded as a topotactic process since the relationship with the parent  $\text{WO}_3$  structure can be traced in the products. Topotactic reduction of perovskite oxides has, however, not been investigated extensively although superstructures derived from anion vacancy ordering in perovskite oxides are known<sup>24</sup> (Figure 5).

Some time ago, Gai and Rao<sup>25</sup> investigated the nonstoichiometry of  $\text{LaNiO}_3$  and proposed the formation of a  $\text{La}_n\text{Ni}_n\text{O}_{3n-1}$  homologous series. Our recent work<sup>26</sup> has shown that both  $\text{LaNiO}_3$  and  $\text{LaCoO}_3$  are reduced by hydrogen at relatively low temperatures ( $350\text{--}400^\circ\text{C}$ ) to give metastable  $\text{La}_2\text{Ni}_2\text{O}_5$  and  $\text{La}_2\text{Co}_2\text{O}_5$ . These solids cannot be prepared by direct reaction of the component oxides (e.g.,  $\text{La}_2\text{O}_3$  and  $\text{NiO}$ ), but they get readily oxidized to yield the starting perovskite oxides.

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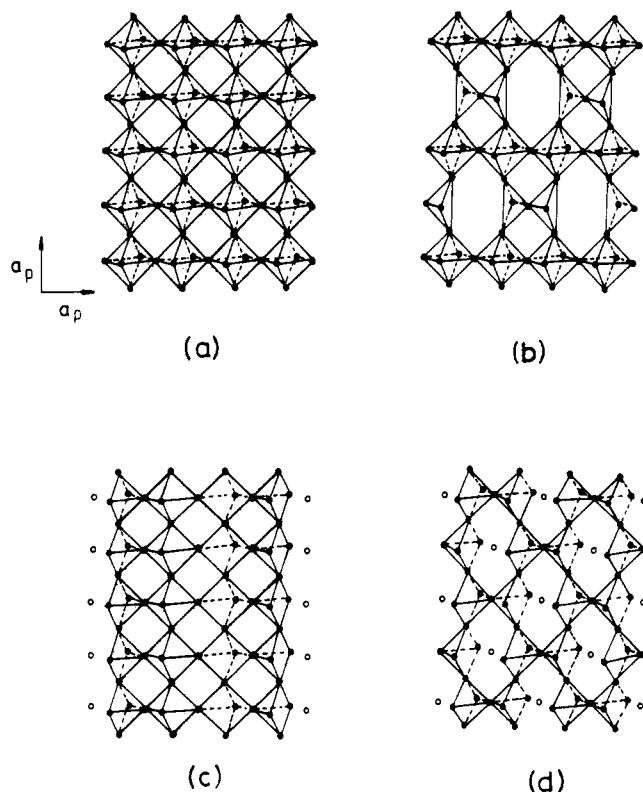
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**Figure 5.** Anion vacancy-ordered superstructures derived from the perovskite structure: (a) perovskite, (b)  $\text{Ca}_2\text{Fe}_2\text{O}_5$  (brownmillerite), (c)  $\text{Ca}_2\text{Mn}_2\text{O}_5$ , and (d)  $\text{Ca}_2\text{Co}_2\text{O}_5$ .

$\text{La}_2\text{Ni}_2\text{O}_5$  adopts a perovskite-related structure involving  $\text{Ni}^{2+}$  in octahedral and square-planar coordination, while  $\text{La}_2\text{Co}_2\text{O}_5$  is formed in the brownmillerite structure. The difference between the structures of compositionally similar  $\text{La}_2\text{Ni}_2\text{O}_5$  and  $\text{La}_2\text{Co}_2\text{O}_5$  is most likely due to the difference in site preferences of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ ; when the ions are forced to adopt fourfold oxygen coordination,  $\text{Co}^{2+}$  ( $d^7$ ) prefers tetrahedral coordination while  $\text{Ni}^{2+}$  ( $d^8$ ) favors square-planar geometry.

$\text{Ca}_2\text{Mn}_2\text{O}_5$  is synthesized by topotactic reduction of  $\text{CaMnO}_3$  at relatively low temperatures<sup>27,28</sup> ( $\sim 300^\circ\text{C}$ ). The oxide possesses an unusual anion vacancy ordered superstructure of the perovskite where  $\text{Mn}^{3+}$  exhibits square-pyramidal anion coordination (Figure 5). A good example of synthesis achieved by the precursor route followed by topochemical reduction is that of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ , the structure of the end members  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{Ca}_2\text{Mn}_2\text{O}_5$  being derived from the perovskite.<sup>29</sup> The  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  system is indeed quite interesting since the transition-metal ions can take up O, T, and SP coordinations; we have been able to prepare members of this family starting from the carbonate precursor,  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x(\text{CO}_3)_4$ . The carbonates decompose in air to give the perovskite-related phases,  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_{6-y}$  ( $y < 1.0$ ). Reduction of the oxides in dilute hydrogen around  $330^\circ\text{C}$  results in the desired solids,  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ ; in this step,  $\text{Mn}^{4+}$  ions in the parent oxides are selectively reduced to  $\text{Mn}^{3+}$ . The orthorhombic structure of  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  is related to

the cubic perovskite as  $a \approx 2^{1/2}a_c$ ,  $b \approx 3a_c$ , and  $c \approx 2(2^{1/2}a_c)$ . Electron diffraction investigations reveal that the superlattice ordering in  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  involves features of both the end members, suggesting the presence of O, T, and SP polyhedra along the  $b$  direction. Formation of such a unique structure is evidently due to the topotactic nature of the reduction (Figure 6) which converts  $\text{Mn}^{4+}\text{O}_6$  octahedra to  $\text{Mn}^{3+}\text{O}_5$  square pyramids. Oxides of the  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$  system are unstable and transform into the brownmillerite structure on heating at  $\sim 900^\circ\text{C}$ . It is noteworthy that these metastable oxides can only be prepared starting from the precursor carbonates and not by the ceramic method employing a mixture of the component binary oxides.

Insertion of atomic species into inorganic host solids<sup>30</sup> is an interesting topochemical reaction, insertion of hydrogen into  $\text{WO}_3$  and of lithium into  $\text{TiS}_2$  being typical examples. Such atom insertion involves electron transfer from the guest atom to the host solid, resulting invariably in the reduction of the transition metal in the host. A number of oxides resulting from alkali-metal insertion-extraction are known (Figure 7) [e.g.,  $\text{Li}_x\text{MO}_2$  ( $M = \text{V}, \text{Co}, \text{Ni}$ ) and  $\text{Na}_x\text{MO}_2$  ( $M = \text{Ti}, \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}$ )]. Deintercalation (extraction) of alkali metals from  $\text{AMO}_2$  ( $A = \text{Li}, \text{Na}$ ) carried out under mild oxidizing conditions is a useful route for the synthesis of  $\text{A}_x\text{MO}_2$  that cannot be prepared by direct means (e.g.,  $\text{Li}_x\text{VO}_2$  from  $\text{LiVO}_2$ ). It is known that hydrogen can be inserted into a variety of binary metal oxides<sup>30</sup> such as  $\text{MnO}_2$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{ReO}_3$ , and  $\text{V}_2\text{O}_5$ . We find that hydrogen can be readily inserted into perovskite oxides such as  $\text{LaNiO}_3$  and  $\text{LaCoO}_3$  at room temperature in the presence of platinum catalyst. The insertion compounds,  $\text{H}_{0.85}\text{LaNiO}_3$  and  $\text{H}_{0.5}\text{LaCoO}_3$ , possess essentially the same structure as the parent perovskites with a slight increase in the lattice parameter.  $\text{H}_{0.85}\text{LaNiO}_3$  is an insulator ( $\rho \sim 10^4$  ohm.cm at 300 K) and is paramagnetic, unlike  $\text{LaNiO}_3$  which is a Pauli paramagnetic metal. The results are consistent with electron transfer from the hydrogen atom to  $\text{LaNiO}_3$ , reducing  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$  in the insertion product.

Formation of tungsten oxide bronzes by the reaction of elements like K, Rb, or Cs with  $\text{WO}_3$  in the absence of oxygen at elevated temperatures is another instance of atom insertion reaction.<sup>31</sup> We have established that bismuth reacts with  $\text{WO}_3$ , yielding intergrowth tungsten bronzes (ITBs)<sup>32</sup> of the formula  $\text{Bi}_x\text{WO}_3$  ( $0.02 < x \leq 0.07$ ). The structure of  $\text{Bi}_x\text{WO}_3$  consists of slabs of  $\text{WO}_3$  and strips of hexagonal tungsten bronze, one tunnel wide, intergrowing coherently with each other (Figure 7). Formation of such a ITB structure is a topochemical process since the insertion of bismuth rearranges the octahedral network of  $\text{WO}_3$  to produce hexagonal tunnels to accommodate bismuth without breaking W-O bonds of the parent oxide. We have found recently that it is possible to insert alkali and other electropositive metals into  $\text{WO}_3$  and other similar oxides by reaction with the corresponding metal iodides, thus providing a very convenient low-temperature route for the syn-

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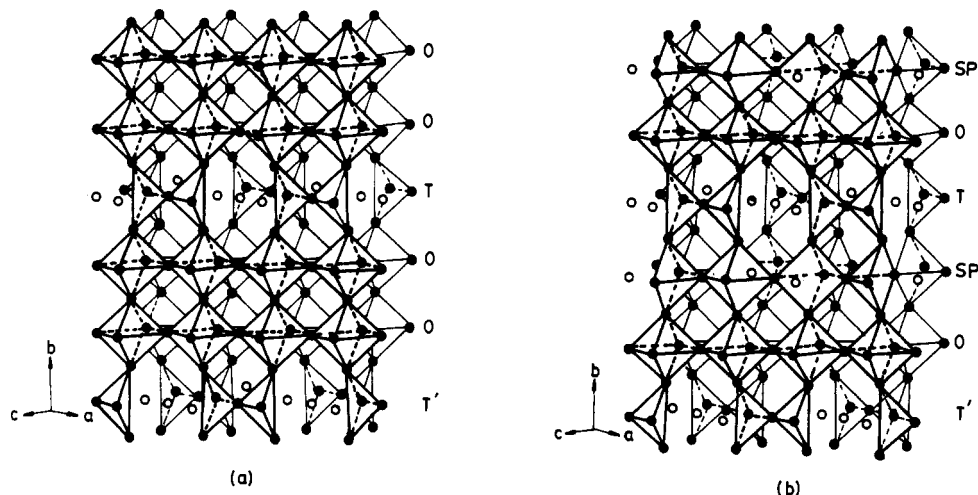


Figure 6. Topotactic reduction of (a) perovskite-related  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  to (b)  $\text{Ca}_3\text{Fe}_2\text{MnO}_{7.5} \equiv \text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$ .

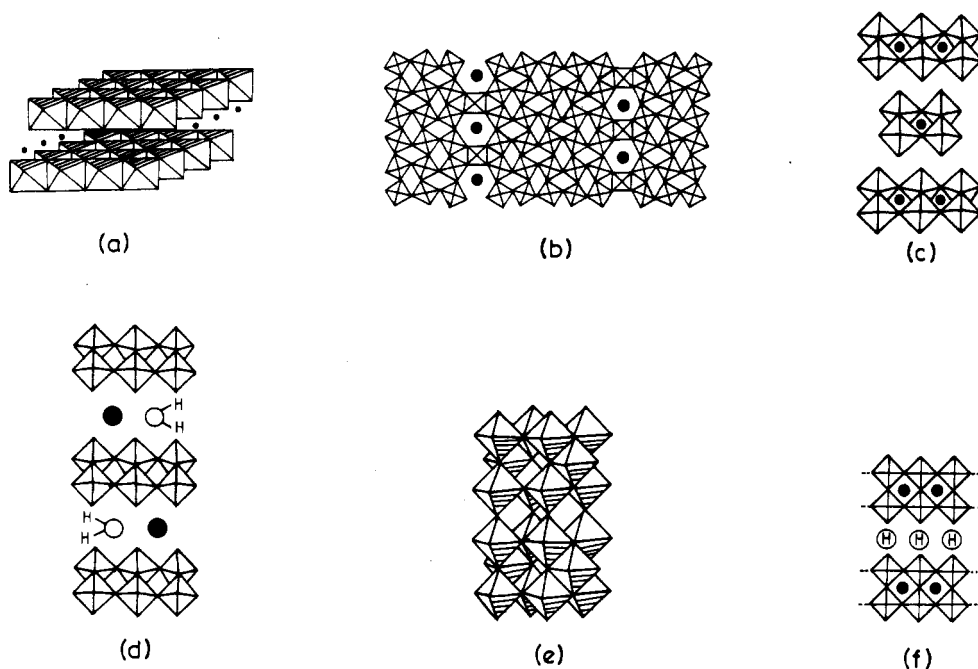


Figure 7. Schematic representation of the structures of some novel oxides prepared by atom insertion/extraction and ion-exchange methods: (a) Layered  $\text{Li}_x\text{MO}_2$  ( $M = \text{V}, \text{Co}, \text{Ni}$ ); filled circles in between the layers denote alkali-metal atoms. (b)  $\text{Bi}_x\text{WO}_3$  (ITB); filled circles in the hexagonal tunnels denote Bi atoms. (c) Layered molybdenum oxide bronzes,  $\text{A}_x\text{MoO}_3$  ( $A = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ ); filled circles within  $\text{MoO}_3$  layers denote alkali-metal atoms. (d)  $[\text{A}(\text{H}_2\text{O})]_x\text{MoO}_3$  ( $A = \text{Rb}, \text{Cs}$ ); filled circles in between  $\text{MoO}_3$  layers denote alkali-metal atoms. (e)  $\text{MoO}_3$  network built up of  $\text{MoO}_6$  octahedra in the "blue" bronze,  $\text{K}_{0.3}\text{MoO}_3$ ; potassium atoms which lie between such  $\text{MoO}_3$  slabs are not shown. (f) Layered  $\text{HLaNb}_2\text{O}_7$ ; filled circles within octahedral layers denote lanthanum atoms.

thesis of a variety of oxide bronzes.<sup>33,34</sup> This simple method has enabled us to make not only the well-known oxide bronzes (e.g.,  $\text{K}_{0.3}\text{MoO}_3$ ) but also some unusual ones. Thus, interaction of  $\text{MoO}_3$  with alkali metal iodides at relatively low temperatures ( $\sim 300^\circ\text{C}$ ) yields novel layered molybdenum oxide bronzes; these bronzes are different from the ones reported recently<sup>35</sup> where water is also intercalated between the  $\text{MoO}_3$  layers (Figure 7). New bronzes of  $\text{Mo}_{1-x}\text{W}_x\text{O}_3$  possessing the hexagonal tungsten bronze structure have also been prepared by the reaction of the oxide solid solution with KI at low temperature ( $\sim 300^\circ\text{C}$ ).<sup>34</sup>

Many metal oxides containing alkali and other metals undergo ion exchange in aqueous or molten salt media

retaining their structural features,<sup>36</sup> providing a low-temperature route for the synthesis of new oxides. An example<sup>37</sup> of such a reaction accompanied by a topotactic structural transformation is that of exchange of lithium by protons in  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ , giving rise to cubic  $\text{HNbO}_3$  and  $\text{HTaO}_3$ . Proton exchange of lithium in the rutile oxides,  $\text{LiNbWO}_6$  and  $\text{LiTaWO}_6$ , leads to  $\text{ReO}_3$ -like  $\text{HNbWO}_6$  and  $\text{HTaWO}_6$ .<sup>38</sup> Exchange of alkali-metal ions by protons is common in layered oxides;<sup>36,39</sup>  $\text{HTiNbO}_5$ ,  $\text{H}_2\text{Ti}_3\text{O}_7$ ,  $\text{H}_2\text{Ti}_4\text{O}_9$ , and  $\text{HCa}_2\text{Nb}_3\text{O}_{10}$  are some of the oxides prepared in this manner. Interest in this family of oxides stems from the fact that

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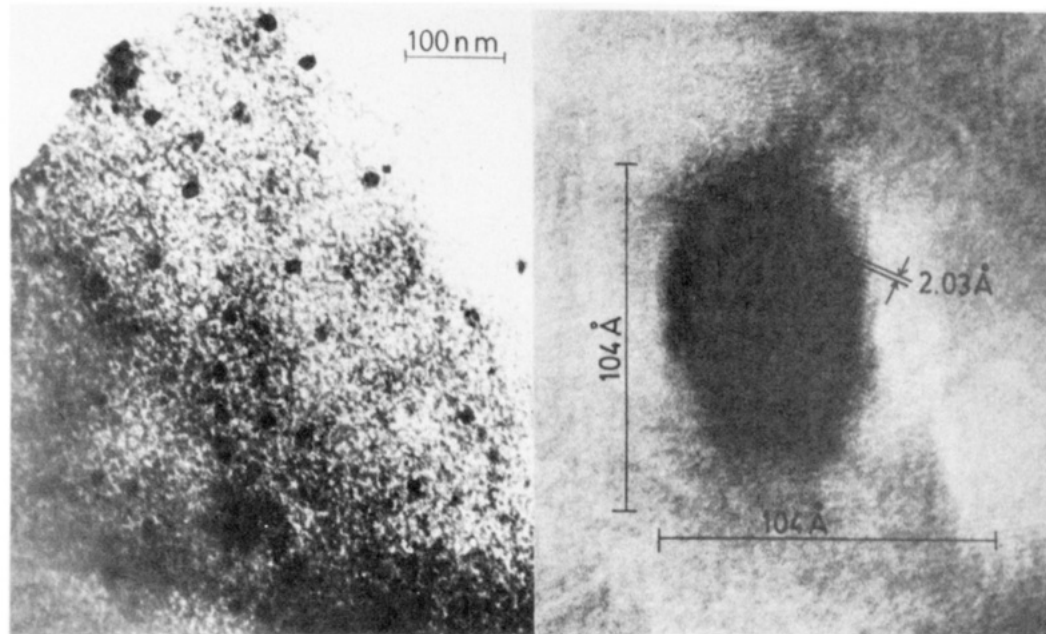
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**Figure 8.** Electron micrograph showing distribution of Ni particles (seen as dark spots) in 5 wt % Ni/Al<sub>2</sub>O<sub>3</sub> composite. Lattice resolution of a particle is also shown.

they show sufficient Brønsted acidity to react with organic bases such as *n*-alkylamines to form intercalation compounds.<sup>40</sup> The protonated oxides dehydrate at low temperatures (300–350 °C) to form new metastable oxides, an example<sup>41</sup> being the formation of a new polymorphic modification of titanium dioxide, TiO<sub>2</sub>(B), from H<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>. HLaNb<sub>2</sub>O<sub>7</sub> (Figure 7) and HLa<sub>2</sub>Ti<sub>2</sub>NbO<sub>10</sub> prepared from the alkali-metal analogues by the ion-exchange method exhibit Brønsted acidity and intercalation behavior.<sup>42</sup> Potentialities of exchange reactions for synthetic purpose appear to be immense; thus, it appears that all the three components of ternary oxides, A<sub>x</sub>M<sub>y</sub>O<sub>z</sub>, can be exchanged, giving rise to new solids.<sup>43</sup>

### Sol-Gel Route

A sol is a dispersion of discrete colloidal particles, and a gel is a colloidal solid normally containing a fluid component as well with a network internal structure in a manner that both the fluid and the solid components are in a highly dispersed state. The term xerogel is used to describe dry gels. The sol-gel method of preparing solid materials has gained importance in the past few years.<sup>44,45</sup> Gels have been used to prepare highly reactive submicron particles, to increase the homogeneity of multicomponent systems, and so on. Advantages of the sol-gel method have lately been exploited by Roy, Livage, and others to prepare diverse materials including ceramics, glasses, and composites, many of which have technological importance.<sup>45–47</sup> The sol-gel

process itself is better understood today with regard to the mechanism of gelation, desiccation, and sintering. A novel class of materials prepared recently is that of diphasic nanoscale composites where the heterogeneity is on the nanoscale (i.e., with the phases in the 1–10-nm range).<sup>48</sup> Typical of such composites are SiO<sub>2</sub>-AgCl, SiO<sub>2</sub>-PbCrO<sub>4</sub>, and SiO<sub>2</sub>-CdS. Another interesting class of materials prepared by the sol-gel route is that of metal-ceramic composites where the small metal particles (e.g., Ni and Pt) are dispersed in the bulk of a ceramic oxide (e.g., Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>).<sup>49</sup> These metal-ceramic composites provide a unique way of investigating divided metals.<sup>50,51</sup> In Figure 8 we show a transmission electron micrograph of Ni-Al<sub>2</sub>O<sub>3</sub> composite to illustrate how the metal particles are distributed in the ceramic; the metal particles also show lattice resolution in high-resolution images. In Ni-Al<sub>2</sub>O<sub>3</sub> composite with low metal content, Ni is not ferromagnetic;<sup>50</sup> magnetic properties provide a means of probing the nature of such small metal particles.

### Concluding Remarks

We have presented some important aspects of oxide synthesis by novel routes, citing several examples from our own work. There are a few other methods that we have not touched upon. For instance, precipitation of metal hydroxides from aqueous solutions followed by removal of water has been a common method for the synthesis of “active” oxides.<sup>52</sup> The method is useful not only for the synthesis of binary ceramics such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> but also for multinary oxides such as MnZn ferrites and PLZT, where the desired metal ions are coprecipitated from aqueous solutions by proper control of pH and temperature followed by appropriate thermal treatment. The coprecipitated solids

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are, however, not single phases, unlike in the precursor method. The so-called alkoxide process where water-sensitive metal alkoxides are hydrolyzed to give an intimate mixture of hydroxides is an extension of the coprecipitation method. The sol-gel route also involves hydrolysis and polycondensation of inorganic species,<sup>2</sup> but the conditions are so adjusted that precipitation is avoided; the condensed species are slightly charged, stabilizing them as a colloid.<sup>46</sup> The sol-gel method has been extended to synthesize gels of  $V_2O_5$  and  $WO_3$ <sup>46</sup> as well as complex oxides such as Nasicon.<sup>2</sup> Oxides such as  $ZrO_2$  obtained by the sol-gel method or from hydrolysis of salts are often stabilized in the high-temperature form; thus, cubic  $ZrO_2$  (ordinarily formed above 2000 °C) is obtained at room temperature by these methods. An interesting instance of a low-temperature synthesis of a ternary oxide<sup>53</sup> is that of  $BaTiO_3$  achieved by the reaction of  $Ba(OH)_2$  and  $TiO_2$  gel (formed by the in situ hydrolysis of a titanium alkoxide) at 120 °C/2 atm. Synthesis of complex oxides of pyrochlore structure such as  $Pb_2[Ru_{2-x}Pb_x^{4+}]O_{7-y}$  and  $Bi_2[Ru_{2-x}Bi_x^{5+}]O_{7-y}$  directly from a strong alkaline medium under oxidizing conditions is a novel low-temperature method<sup>54</sup> which may have wider applicability.

We referred earlier to the use of organometallic compounds as precursors in the synthesis of aluminosilicates and related solids. Organometallic compounds increasingly find use in the synthesis of oxide materials. Tin-doped indium oxide, used as a transparent electrode in optoelectronic devices, can be prepared by thermal decomposition of 2-ethyl hexanoates of tin and indium.<sup>55</sup> Open framework transition metal phosphates,  $Fe_5P_4O_{20}H_{10}$  and  $NaFe_3P_3O_{12}$ , which are isostructural with the minerals hureaulite and alluaudite, have been synthesized by a hydrothermal procedure using organometallic precursors.<sup>56</sup> The hydrothermal method and its variants also provide a low-temperature means of synthesizing metal oxides and other solids.<sup>57,58</sup>

Solid-state chemists have also designed ingenious low-temperature methods for the synthesis of a variety of solids other than metal oxides. We shall mention here a few examples from the recent literature. Molybdenum sulfides with different molybdenum/

chalcogen ratios are prepared by reacting various molybdenum halides with hexamethyldisilthiane in methylene chloride.<sup>59</sup> Polymetallic sulfides containing molybdenum (e.g.,  $M_x(NH_4)_yMo_3S_9$  where  $M = Cu, Pb, La, \text{ or } Gd$ ) prepared by precipitation from an ammonium thiomolybdate solution have been found to be convenient precursors for the synthesis of Chevrel phases.<sup>34</sup> Alloys of platinum metals (Pt-Ru, Pt-Rh, and Pt-Pd) have been prepared<sup>60</sup> by reduction of coprecipitated metal sulfides around 800 °C.

Novel routes for the synthesis of known as well as new types of metal oxides and other solids continue to provide exciting research opportunities of academic interest and technological value. Undoubtedly, many new oxides with fascinating properties will be discovered in the years to come. In fact, the recent sensational discovery of high-temperature superconductivity in complex metal oxides is illustrative of the tremendous possibilities arising from metal oxide chemistry. It was hitherto believed that metallic systems and organic or organometallic compounds are the more appropriate candidates for high-temperature superconductivity. This myth is now exploded by oxides of the type  $La_{2-x}Sr_x(Ba_x)CuO_4$ , possessing the  $K_2NiF_4$  structure showing onset of superconductivity in the 30–40 K range.<sup>61,62</sup> Even more staggering is the discovery of Y-Ba-Cu oxides which become superconducting (with zero resistance) well above liquid nitrogen temperature.<sup>63,64</sup> It has just been established<sup>65</sup> that the oxide responsible for this high-temperature superconductivity is  $Y_2Ba_4Cu_6O_{14+\delta}$ . It would be worthwhile preparing such oxides by employing the precursor and other routes since stoichiometry and hence the  $Cu^{2+}/Cu^{3+}$  ratio are crucial factors in determining their properties. It is expected that oxide materials which become superconducting even at higher temperatures will be forthcoming in the near future.

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