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SYNTHESIS AND REACTIONS OF SOME NOVEL METAL OXIDE SYSTEMS*

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Metal oxides formed by the recurrent intergrowth of two structurally similar but compositionally different units are discussed. Synthesis of complex metal oxides by the decomposition of precursors is presented. Interesting examples of metastable oxides prepared by topotactic reduction of parent oxides or topotactic dehydration of the parent hydroxides are described.

Key Words : Metal Oxides; Intergrowth Phenomena; Topotactic Reactions

INTRODUCTION

SYNTHESIS of inorganic solids possessing novel structures and properties constitutes a major facet of modern solid state chemistry. In this article, I shall briefly present some recent studies of solid state synthesis and reactions carried out in the author's laboratory. First, we shall examine some aspects of inorganic solids exhibiting novel structural features due to random or recurrent intergrowth.[1-3] Polytypic solids such as ZnS, CdI_2, TaS_2 and perovskite oxides (ABO_3) possessing close-packed or layered structures and exhibiting unit cells which differ in dimension along one of the three axes of the crystal are well documented in the literature[3-5]; the unit cell parameter in the unique direction in polytypes falls anywhere between a few Angstroms to a few thousand Angstroms. Long-period polytypes show evidence for considerable disorder with different polytypic forms being present in different regions of the same crystal. Long periodicities in crystals have been observed in other situations as well. What is of special interest to us here is the discovery of an increasing number of inorganic materials forming long-period structures entailing recurrent intergrowth of two or more chemically distinct but structurally related units. Such intergrowths may be considered to constitute a new class of inorganic compounds. We shall discuss a few of the intergrowth structures investigated.

The second aspect of solid state synthesis that we shall discuss pertains to novel routes and low-temperature methods for the synthesis of unusual inorganic oxides. Solid state chemists generally prepare complex metal oxides by the ceramic method which involves mixing of the component oxides or suitable decomposable

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salts such as nitrates and carbonates and heating them to high temperatures. Reactions in ceramic preparations entail large diffusion distances ($\sim$ 100,000Å) between reacting species and therefore, require repeated grinding and heating. Ceramic reactions are often incomplete yielding inhomogeneous products. More importantly, the ceramic method does not lend itself to the synthesis of metastable and low-temperature phases. There has been considerable interest in the last few years to develop alternative methods of synthesis of solid. One approach is based on the use of compound or solid solution precursors which reduces the diffusion distance to $\sim$ 10Å. Solid solutions of isostructural inorganic solids, such as nitrates and carbonates of divalent metals are excellent precursors for the synthesis of complex metal oxides.[6,7] The solid solution precursor method enables continuous variation of cation ratios and hence the synthesis of any desired composition of a given oxide system. A variety of novel metal oxides has been synthesized in this laboratory by the solid solution precursor method. For example, by employing carbonates of divalent metals of calcite structure, monoxides, $Mn_{1-x}M_xO$ (M=Mg, Co, Cd), of rocksalt structure and several perovskite derived oxides (*e.g.* $Ca_2Co_2O_5$, Ca_2FeCoO_5 and $Ca_3Fe_2MnO_8$) possessing anionvacancy ordered superstructures[8] have been synthesized. Some of the metal oxides prepared by the precursor route are useful as starting materials for the synthesis of interesting new oxides. A noteworthy case is the synthesis of oxides of the type $Ca_2Fe_{2-x}Mn_xO_5$ by the topotactic reduction of $Ca_2Fe_{2-x}Mn_xO_{6-y}$ ($0 < y < 1$) perovskites, the latter having been prepared by the decomposition of calcite carbonate precursors. Members of the $Ca_2Fe_{2-x}Mn_xO_5$ series which may be regarded as solid sloutions between $Ca_2Fe_2O_5$ (with octahedral and tetrahedral coordination of Fe) and $Ca_2Mn_2O_5$ (with square pyramidal coordination of Mn) exhibit novel anion-vacancy ordered superstructures of the perovskite, based on octahedral, tetrahedral and square-pyramidal coordinations of the transition metal ions. We have also prepared several oxides by making use of hydroxide, nitrate and cyanide precursors.

Simple topotactic reactions involving metal oxides have been exploited to prepare several new solids. For example, $LaBO_3$ (B = Ni or Co) can be reduced topotactically to yield the $n = 2$ members of the homologous series[9] $La_nB_nO_{3n-1}$ which cannot be prepared by the ceramic route. Topotactic dehydration of isostructural $Mo_{1-x}W_xO_3.H_2O$ ($0 \leqslant x \leqslant 1$) is found to yield $Mo_{1-x}W_xO_3$ solid solutions of ReO_3 structure which are difficult to prepare by the ceramic route. By employing the dehydration route, it has been possible to obtain metastable MoO_3 in the ReO_3 structure instead of the stable layered structure. The investigations described in the paper serve to illustrate how one can design ingenious routes for the synthesis of novel oxides based on a knowledge of the structural chemisry.

Intergrowth Structures

Several systems form chemically well-defined recurrent ordered intergrowth structures with large periodicities, rather than random solid solutions with variable composition. However, the ordered intergrowth structures themeselves frequently show the presence of wrong sequences (Fig. 1). The presence of wrong sequences

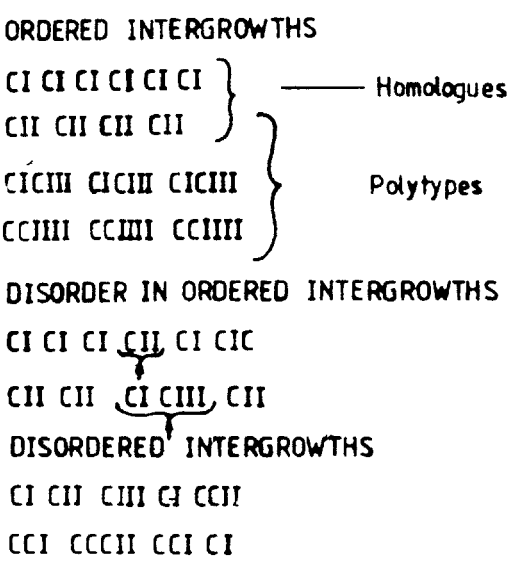

FIG 1 Different types of intergrowth structures formed by the component units C and I. Arrow indicates faulted sequence.

or lamellae is best revealed by a technique that is more suited to the study of local structure. 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.[1,2] Selected area electron diffraction which forms an essential part of HREM provides useful information (not generally provided by X-ray diffraction) regarding the presence of supercells due to intergrowth or defect ordering.

Many systems forming ordered intergrowth structures have come to be known in recent years. These systems generally exhibit homology. In some of the systems, magnetic or electrostatic interactions may be more important rather than interactions arising from the structural characteristics of the component units. The intergrowth structures formed by oxides of the Aurivillius family of oxides studied by us however seem to be genuine ordered intergrowth structures. There is little doubt that such ordered structures are equilibrium structures rather than accidents of random stacking during growth.

If the perovskite structure is cut parallel to the (110) planes, slabs of the composition $A_{n-1}B_nO_{3n+2}$ are obtained; if these slabs are stacked, an extra sheet of A gets introduced giving rise to the family of oxides of the general formula $A_nB_nO_{3n+2}$. Typical members of this family[10] are Ca_2NbO_7 ($n = 4$) $NaCa_4Nb_5O_{17}$ ($n = 5$) and $Na_2Ca_4Nb_6O_{20}$($n = 6$). HREM and X-ray studies show that an ordered intergrowth structure with $n = 4.5$ with the composition Na $Ca_8Nb_9O_{31}$ corresponds to alternate stacking of $n = 4$ and $n = 5$ lamellae, although occasionally...44554455...type of stacking is also encountered. Between $n = 4$ and 4.5, a

large number of ordered solids are found with the b parameter of unit cell ranging anywhere from 58.6Å in the $n = 4.5$ compound to a few thousand angstroms in longer period structure. These solids seem to belong to the class of infinitely adaptive structures described by Anderson.[11]

Aurivillius[12] has described the family of oxides of the general formula $Bi_2A_{n-1}B_nO_{3n+3}$ where the perovskite slabs, $(A_{n-1}B_nO_{3n+1})^{2-}$, n octahedra thick, are interleaved by $(Bi_2O_2)^{2+}$ layers. Typical members of this family are $Bi_2WO_6(n = 1)$, $Bi_3Ti_{1.5}W_{0.5}O_9$ $(n = 2)$, $Bi_4Ti_3O_{12}$ $(n = 3)$ and $Bi_5Ti_3CrO_{15}$ $(n = 4)$ and they have been investigated in detail by HREM. These oxides form intergrowth structures[13,14] 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 simply involves heating the component oxides/carbonates of metals. Ordered intergrowth structures with (m, n) values of (1, 2), (2, 3) and (3, 4) have been fully characterized by X-ray diffraction and HREM. What is most amazing is that such intergrowth structures with long range order are indeed formed while either member (m and n) can exist as a stable entity. Preparations with stacking of the type (3, 3, 4) have not been possible, but short stretches with such sequences have been noticed in the electron micrographs. These materials seem to be truly representative of recurrent ordered intergrowth since other factors such as magnetic interactions and the possibility of infinitely adaptive structures do not manifest themselves. The impressive periodicity found in the recurrent intergrowth solids formed by the Aurivillius family of oxides is illustrated by the high resolution electron micrograph in Fig. 2 where the structural projection as well as the computer-simulated image are shown. This micrograph almost appears to be the ultimate in resolution since we can clearly see the interface of Bi atoms between the $n = 3$ and $n = 4$ members of the Aurivillus family of oxides as well as the heavy atoms constituting the perovskite layers.

The relative ease with which WO_3 forms tetragonal, hexagonal or perovskite-type bronzes by interaction with alkali and other metals is well known.[15,16] The new family of intergrowth tungsten bronzes (ITB) involving the intergrowth of nWO_3 slabs and one to three strips of the hexagonal tungsten bronze (HTB) is of relevance to our discussion here. In these intergrowth tungsten bronzes of the general formula M_xWO_3, x is generally 0.1 or less and depending on whether the HTB strip is one or two-tunnel wide, ITB's are classified as belonging to $(0, n)$ and $(1, n)$ series. HTB strips of two tunnel width seem to be most stable in ITB's and many ordered sequences of the $(0, n)$ and the $(1, n)$ series have been identified. Recently, ITB phases of Bi have been characterized and in this system the HTB strips are always one-tunnel wide[17] (Fig. 3). Displacement of adjacent tunnel rows due to the tilting of WO_3 octahedra often results in the doubling of the long-period axis of the ITB. Evidence for the ordering of the intercalating Bi atoms in the tunnels has been found in terms of satellites around the superlattice spots in the electron diffraction patterns. Among the other systems exhibiting ordered intergrowth, special mention must be made of hexagonal barium ferrites[18] M_pY_q ($M = BaFe_{12}O_{19}$ and $Y = Ba_2Me_{12}O_{22}$, where Me is Zn, Ni, Mg etc.). A large number of intergrowth structures of this family have been identified.

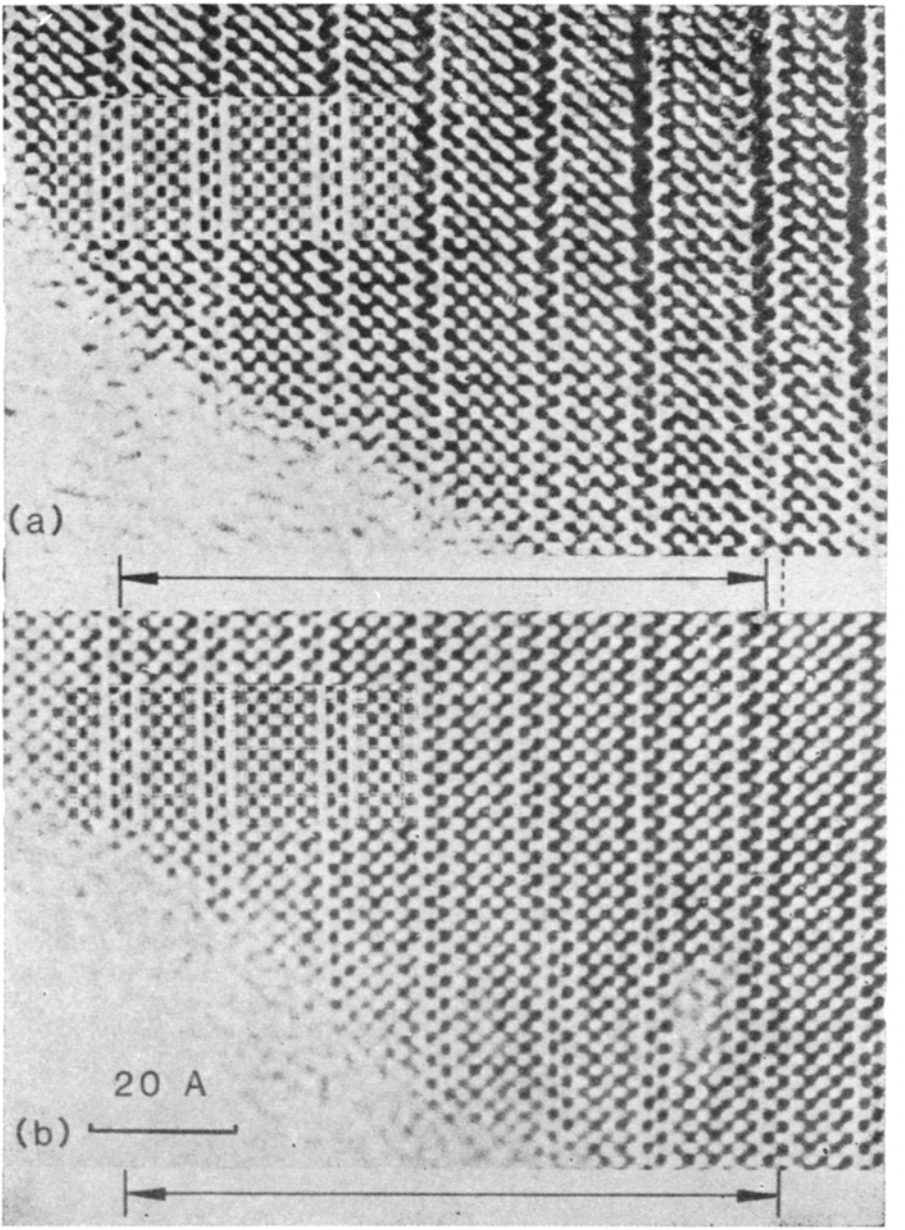

FIG 2 500kV high-resolution electron microscopic images of (*a*) $Bi_9Ti_6CrO_{27}$ and (*b*) $BaBi_8Ti_7O_{27}$ in [110] projection with computer simulations (inset). These are ordered intergrowth structures with (*m*, *n*) values of (3, 4). The marker indicates the length of three cell units in each case, the length of the *c*-parameter being greater in (*b*) by 0.7Å. (*a*) is formed by the intergrowth of $Bi_4Ti_3O_{12}$ and $Bi_5Ti_3CrO_{15}$ while (*b*) is formed by the intergrowth of $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$.

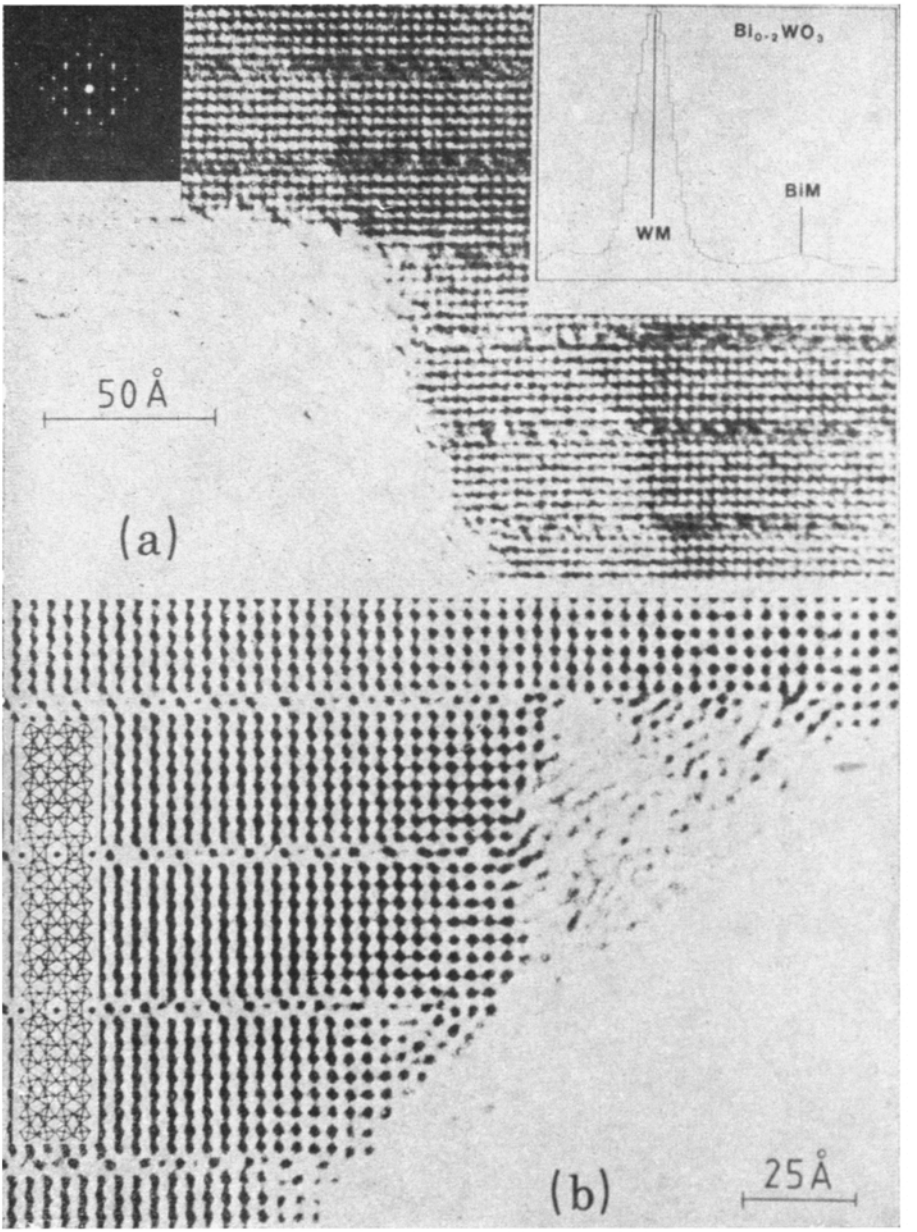

FIG 3(*a*) HREM image of a crystal of composition $Bi_{0\cdot067}WO_3$ obtained with a 200kV microscope. Selected area electron diffraction and X-ray emission spectrum are shown. The image corresponds to [001] projection.

(*b*) HREM image of Bi_xWO_3 ($x < 0.05$) in the [001] projection. Empty or underoccupied Bi tunnel sites can be seen. Structural model is shown; dark circles in the projection are Bi atoms.

Disordered intergrowth is a phenomenon commonly encountered in diverse systems. Accordingly, intergrowth tungsten bronzes show considerable disorder. In oxides of the general formula $A_{n+1}B_nO_{3n+1}$, ordered intergrowths of neighbouring members are rarely found; instead, disordered intergrowth of different members occurs, typical of these systems is La-Ni-O. In the HREM images of $La_3Ni_2O_7$ and $La_4Ni_3O_{10}$, we see lamellae of other members of the La_{n+1} Ni_nO_{3n+1} series[19] (Fig. 4). In β-alumina, as well as in the corresponding gallia, β and β″ forms intergrow randomly and the latter form is generally not found in the pure state.[20] Disordered intergrowth affects stoichiometry (unless the component units are polytypic) and this is the case in all the systems discussed in this article. It is thus possible for crystals of such materials to exhibit variations in composition and structure along a particular direction. The mechanism of formation of long-period intergrowth structures is likely to involve elastic strain. Changes in the atomic positions at the interface as well as in the perovskite lamellae of the intergrowth structures formed by Aurivillius oxides (investigated by HREM) provide direct evidence for elastic strain effects.[21]

Novel Metal Oxides Prepared by the Decomposition of Precursor Solid Solutions

Synthesis of complex oxides by the decomposition of compound precursors has been known for sometime. For example, thermal decomposition of LaCo $(CN)_6 5H_2O$

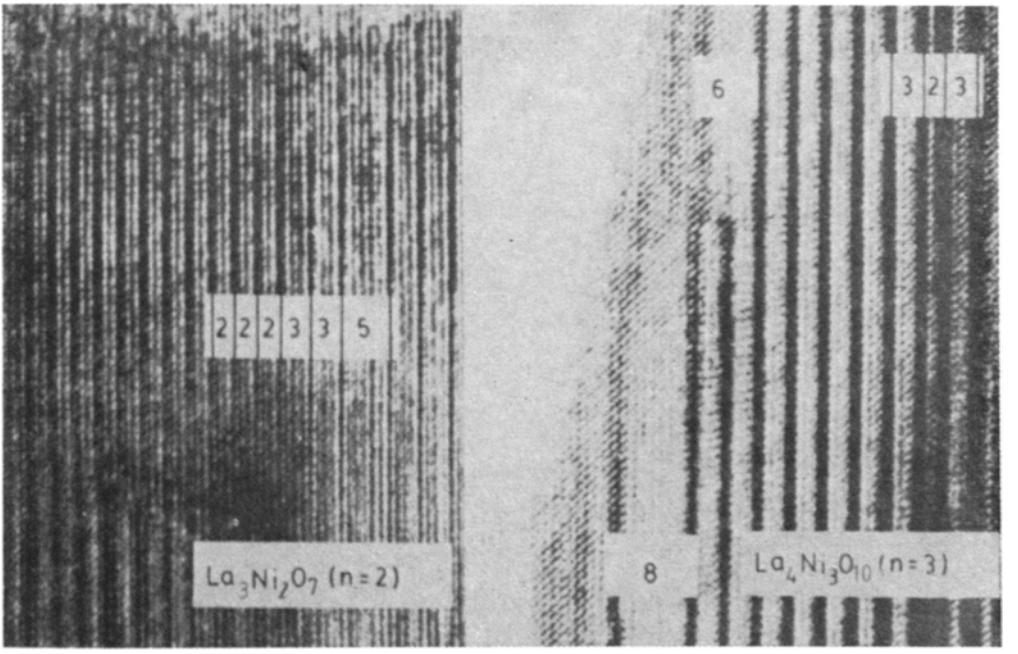

FIG 4 HREM images of the $n = 2$ and $n = 3$ members of the $La_{n+1}Ni_nO_{3n+1}$ series showing the intergrowth of different members.

and $LaFe(CN)_6 6H_2O$ in air readily yield $LaCoO_3$ and $LaFeO_3$ respectively. $BaTiO_3$ can be prepared by the thermal decomposition of Ba $[Ti\ O(C_2O_4)_2]$ while $LiCrO_2$ can be prepared from Li $[Cr(C_2O_4)_2(H_2O)_2]$. Unfortunately, compound precursors are not always easy to find.

Carbonates of metals such as Ca, Mg, Mn, Fe, Co, Zn and Cd are isostructural, possessing the calcite structure. We can therefore prepare carbonate solid solutions containing two or more cations in different proportions. The rhombohedral a_R of the carbonate solid solutions varies systematically with the weighted mean cation radius. The carbonate solid solutions are ideal precursors for the synthesis of monoxide solid solutions of rocksalt structure. The carbonates can be decomposed in vacuum or in flowing nitrogen, to yield single-phase solid solutions of monoxides of the type $Mn_{1-x}M_xO$ (M = Mg, Ca, Co or Cd) of rocksalt structure. Oxide solid solutions of M = Mg, Ca or Co would require 770-970 K for their formation, while those containing cadimium are formed at still lower temperatures. The facile formation of rocksalt oxides by the decomposition of calcite carbonates is due to the close (possibly topotactic) relationship between the structures of calcite and rocksalt. Monoxide solid solutions of rocksalt strcture have been characterized by esr spectroscopy (in the case of $Mn_{1-x}M_xO$ and magnetic susceptibility, besides X-ray powder diffraction. The monoxide solid solutions can be used as precursors for preparing spinels and other complex oxides.

Besides monoxide solid solutions, a number of ternary and quaternary oxides of novel structures could be prepared by decomposing the carbonate precursors in air or oxygen. Thus we have been able to prepare $Ca_2Fe_2O_5$ and $CaFe_2O_4$ by heating the corresponding carbonate solid solutions in air at 1070 and 1270 K respectively for about 1h. $Ca_2Fe_2O_5$ has the well-known brownmillerite structure with Fe^{3+} ions in alternate octahedral and tetrahedral sites (Fig. 5.) Two new oxides of similar compositions, $Ca_2Co_2O_5$ and $CaCo_2O_4$, were alone prepared by decomposing the appropriate carbonate precursors in oxygen atmosphere around 940 K. Unlike $Ca_2Fe_2O_5$ (brownmillerite), $Ca_2Co_2O_5$ crystallizes in an orthorhombic structure[7] related to $Ca_2Mn_2O_5$ (Fig. 5), where the anionvacancy ordering in the pervoskite lattice gives a squarepyramidal coordination[22] around the transition metal ion. $CaCo_2O_4$ adopts a monoclinic structure related[23] to $Ca_2Mn_3O_8$. We have also synthesized quaternary oxides Ca_2FeCoO_5, $Ca_2Fe_{1.6}Mn_{0.4}O_5$, $Ca_3Fe_2MnO_8$ etc. belonging to the $A_nB_nO_{3n-1}$ family[24] by the carbonate precursor route. In the Ca-Fe-O system, there are several othere 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.

A good example of a multistep solid state synthesis achieved starting from carbonate solid solution precursors is provided by the $Ca_2Fe_{2-x}Mn_xO_5$ series of oxides.[25] The structures of both the end members, $Ca_2Fe_2O_5$ and $Ca_2Mn_2O_5$, are derived from that of the perovskite. $Ca_2Fe_2O_5$ possesses the brownmillerite structure wherein the anion-vacancy ordering confers octahedral and tetrahedral coordination

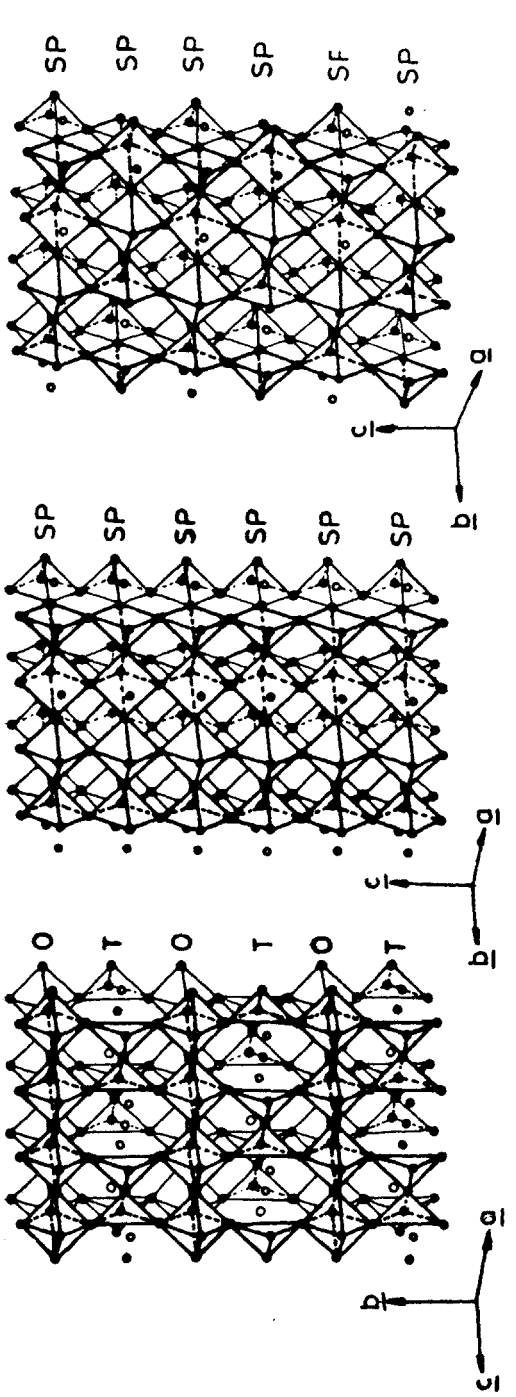

FIG 5 Structures of (*a*) $Ca_2Fe_2O_5$ (brownmillerite) (*b*) $Ca_2Mn_2O_5$ and (*c*) $Ca_2Co_2O_5$. Oxygen vacancies are shown by open circles.

to Fe^{3+}, while in $Ca_2Mn_2O_5$, vacancy ordering results in square-pyramidal coordination around Mn^{3+} (Fig. 5). Solid solutions between the two oxides which would be expected to show oxygen vacancy ordered superstructures with Fe^{3+} in octahedral (O) and tetrahedral (T) coordinations and Mn^{3+} in square-pyramidal (SP) coordination, cannot be prepared by the ceramic method. These solid solutions have been prepared starting from the carbonate solid solutions $Ca_2Fe_{2-x}Mn_x(CO_3)_4$ ($x = 2/3$, 1, 4/3). The carbonates decompose in air around 1200–1350 K to give perovskite-like phases, $Ca_2Fe_{2-x}Mn_xO_{6-y}$ ($y < 1$). The compositions of the three perovskite-like oxides prepared by us are $Ca_3Fe_2MnO_8$(I), $Ca_3Fe_{1.5}Mn_{1.5}O_{8.1}$(II) and $Ca_3FeMn_2O_{8.35}$(III). X-ray and electron diffraction patterns show that they are members of the $A_nB_nO_{3n-1}$ homologous series of anion-vacany ordered superstructures with $n = 3$ ($A_3B_3O_{8+z}$).

Selective reduction of the oxides I–III in dilute hydrogen at 600 K yields $Ca_2Fe_{4/3}Mn_{2/3}O_5 \equiv Ca_3Fe_2MnO_{7.5}$(IV), $Ca_2FeMnO_5 \equiv Ca_3Fe_{1.5}O_{7.5}$(V) and $Ca_2Fe_{2/3}Mn_{4/3}O_5 \equiv Ca_3FeMn_2O_{7.5}$(VI) respectively. During this step, only Mn^{4+} in the parent oxides is reduced to Mn^{3+} and Fe^{3+} remains unreduced. X-ray and electron diffraction patterns of IV show the unit cell to be orthorhombic being related to the $Ca_2Mn_2O_5$ cell as follows : a (IV) $= a_0$, b (IV) $= 3\,c_0$ and c (IV) $= b_0$, where a_0, b_0 and c_0 are the unit cell parameters of $Ca_2Mn_2O_5$. The most probable superstructure of the oxide therefore involves SP, O and T polyhedra along the b-direction (Fig. 6). This structure results from the topotactic reduction of the O layers of Mn^{4+} in I to SP layers of Mn^{3+} in IV, the anion vacancies being ordered along the 100_I direction as in $Ca_2Mn_2O_5$. The topotactic relation between I and IV can be expressed as $(100)_I \| (100)_{IV}$; $(010)_I \| (010)_{IV}$ and $(001)_I \| (002)_{IV}$. X-ray diffraction patterns reveal that oxides V and VI also possess similar orthorhombic structures suggesting the presence of O, T and SP polyhedra. It is really interesting that the oxides IV–VI transform to the brownmillerite structure on heating at 870 °C in vacuum (Fig. 6). This thermal transformation reveals that the $Ca_2Fe_{2-x}Mn_xO_5$ oxides containing O, SP and T polyhedra are metastable phases being formed because of the topotactic nature of the reduction of Mn^{4+} to Mn^{3+} which converts $Mn^{4+}O_6$ octahedra to $Mn^{3+}O_5$ square-pyramids.

A number of ternary and quaternary metal oxides of perovskite and related structures can be prepared by employing hydroxide, nitrate and cyanide solid solution precursors as well.[26] For example, hydroxide solid solutions of the general formula $Ln_{1-x}M_x(OH)_3$ (where Ln = La or Nd and M = Al, Cr, Fe, Co or Ni) and $La_{1-x-y}M'_xM''_y(OH)_3$ (where M' = Ni and M'' = Co or Cu) crystallizing in the rare earth trihydroxide structure can be decomposed at relatively low temperatures ($\sim$ 870 K) to yield $LaNiO_3$, $NdNiO_3$, $LaNi_{1-x}Co_xO_3$, $LaNi_{1-x}Cu_xO_3$ etc.

Making use of the fact that anhydrous alkaline earth metal nitrates $A(NO_3)_2$ (A = Ca, Sr, Ba) and Pb $(NO_3)_2$ are isostructural, we have prepared nitrate solid solutions[26] of the formula $A_{1-x}Pb_x$ $(NO_3)_2$ which are ideal precursors for the preparation of ternary oxides such as $BaPbO_3$, Ba_2PbO_4 and Sr_2PbO_4. Quaternary oxides of the type $LaFe_{0.5}Co_{0.5}O_3$ and $La_{0.5}Nd_{0.5}CoO_3$ which cannot be made

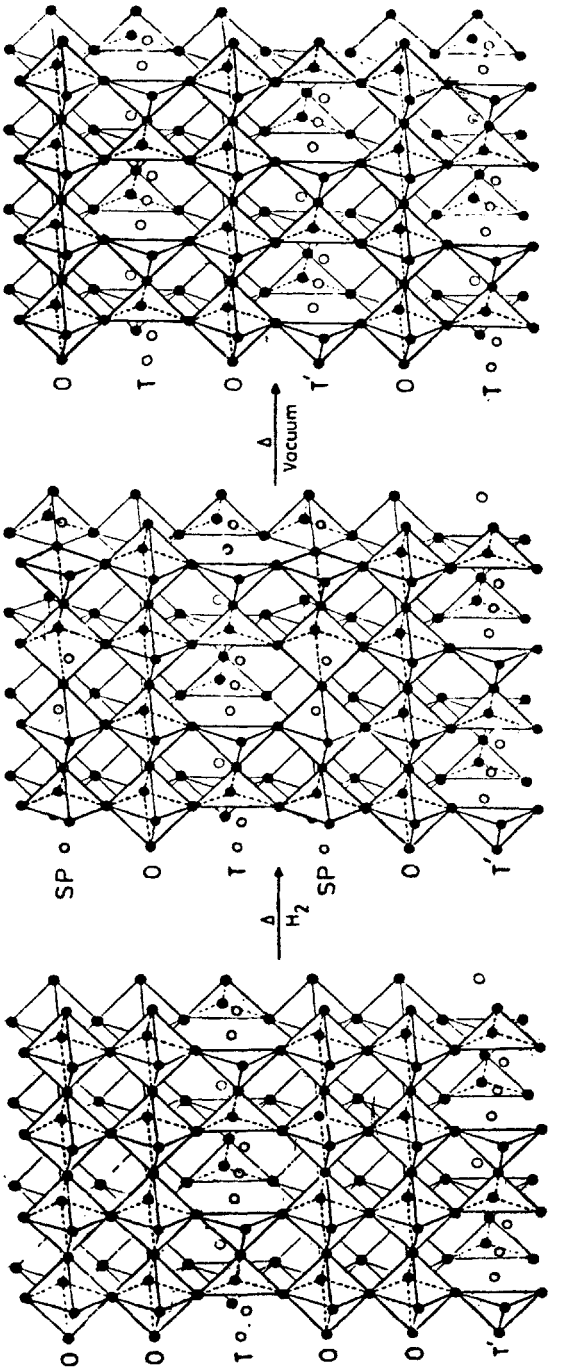

FIG 6 $Ca_3Fe_2MnO_8$ (I) of the $A_nB_nO_{3n-1}$ family is reduced topotactically to give $Ca_2Fe_{4/3}Mn_{4/3}O_5$ (IV) possessing SP, O and T polyhedra of the transition metal ions. IV transforms to the brownmillerite structure (*see* $Ca_4Fe_2O_5$ in Fig. 5) possessing only O and T polyhedra.

readily by the ceramic method have been prepared by the decomposition of cyanide solid solutions $La\ Fe_{0.5}Co_{0.5}(CN)_6 5H_2O$ and $La_{0.5}Nd_{0.5}\ Co(CN)_6.5H_2O$ respectively.

$La_2Co_2O_5$ and $La_2Ni_2O_5$

Both $LaNiO_3$ and $LaCoO_3$ crystallize in the rhomoherdral perovskite structure and the anion-deficient non-stoichiometry of these oxides seems interesting. Gai and Rao[9] proposed the homologous series $La_nNi_nO_{3n-1}$ on the basis of a thermogravimetric study of the decomposition of $LaNiO_3$; it is not known whether a similar series exists in the case of cobalt. Controlled reduction of $LaNiO_3$ and $LaCoO_3$ in hyrogen shows the formation of $La_2Ni_2O_5$ and $La_2Co_2O_5$ representing the $n = 2$ members of the homologous series $La_nB_nO_{3n-1}$ (B = Co or Ni). $La_2Ni_2O_5$ can be prepared by the reduction of $LaNiO_3$ at 600 K in pure or dilute hydrogen,[27] but $La_2Co_2O_5$ can only be prepared by the reduction of $LaCoO_3$ in dilute hydrogen at 670 K. Both the oxides can be oxidized back to the parent perovskites at low temperatures. Neither $La_2Ni_2O_5$ nor $La_2Co_2O_5$ can be prepared by the solid state reaction of La_2O_3 and the transition metal oxide. Both X-ray and electron diffraction data reveal that $La_2Co_2O_5$ adopts the brownmillerite structure (Fig. 7).

The X-ray diffraction pattern of $La_2Ni_2O_5$ is different from that of $La_2Co_2O_5$, but could be indexed on a tetragonal cell related to cubic perovskite. Electron diffraction patterns reveal a new type of vacancy ordering in $La_2Ni_2O_5$, the most likely structure being one where the oxygen vacancies are ordered along the $[110]_p$ direction in the (001) LaO planes of the perovskite lattice. Such an ordering of oxygen vacancies results in planes of $LaO_{0.5}\square_{0.5}$ ($\square$ = vacancy) and NiO_2 stacked alternately parallel to the c-direction, giving rise to square-planar and octahedral coordinations of Ni^{2+} (Fig. 8). The topotactic relationship between $La_2Ni_2O_5$ and

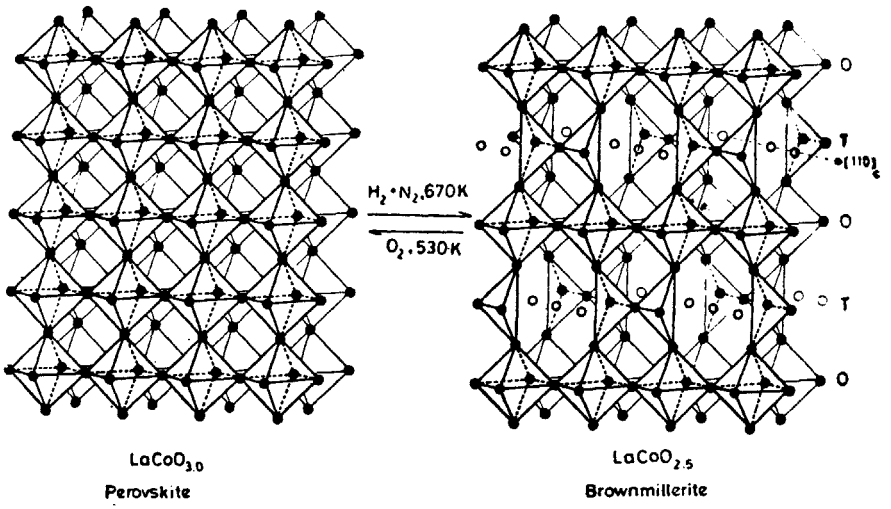

FIG 7 Reversible transformation of $LaCoO_3$ and $La_2Co_2O_5$. La_2CoO_5 has ordered, alternate octahedra and tetrahedra (brownmillerite structure).

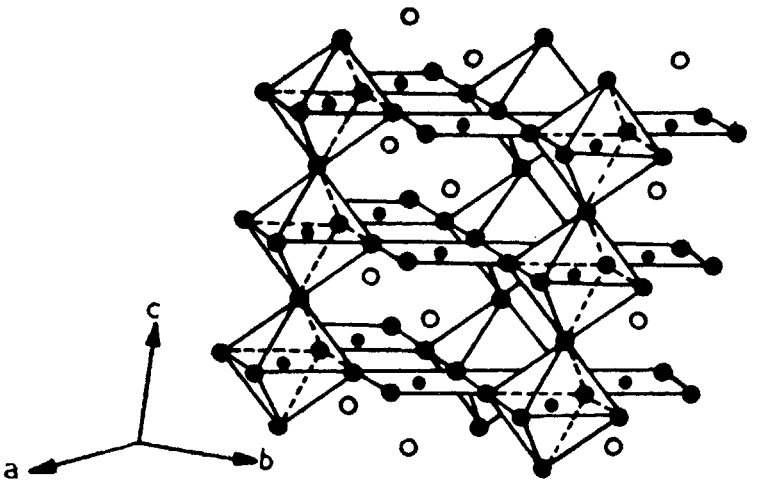

FIG 8 Proposed structure of $La_2Ni_2O_5$.

$LaNiO_3$ may be expressed as : $(200)_t \| (100)_c$ and $(002)_t \| (001)_c$. The difference between the structures of $La_2Co_2O_5$ and $La_2Ni_2O_5$ may be due to the difference in the site-preference energies of Co^{2+} and Ni^{2+}.

$Mo_{1-x}W_xO_3$ ($O \leqslant x \leqslant 1$)

Many of the modern developments in solid state chemistry owe much to the investigations carried out on MoO_3 and WO_3, the crystallographic shear planes being a major discovery. WO_3 crystallizes in a ReO_3-like structure, but MoO_3 possesses a layered structure. MoO_3 can be stabilized in the WO_3 structure by partly substituting tungsten for molybdenm .[28] These solid solutions can be pre-prepared by the ceramic method (by heating MoO_3 and WO_3 in sealed tubes around 870 K) or by the thermal decomposition of mixed ammonium metallates. These methods however do not always yield monophasic products owing to the difference in volatilities of MoO_3 and WO_3. We therefore sought to prepare $Mo_{1-x}W_xO_3$ by the topotactic dehydration of $Mo_{1-x}W_xO_3.H_2O$. Since yellow $MoO_3.H_2O$ and WO_3H_2O are isostructural, the solid solutions between them are prepared readily by adding a solution of MoO_3 and WO_3 in ammonia to hot 6M HNO_3. The hydrates, $Mo_{1-x}W_xO_3.H_2O$, crystallize in the same structure as $MoO_3.H_2O$ and $WO_3.H_2O$ with a monoclinic unit cell (Fig. 9). The hydrate solid solutions undergo dehydration around 500 K yielding $Mo_{1-x}W_xO_3$ which crystallize in the ReO_3-related structure of WO_3 (Fig. 9).

It is interesting that thermal dehydration of $WO_3.H_2O$ as well as $Mo_{1-x}W_xO_3.H_2O$ gives rise to oxides of ReO_3 structure. MoO_3 obtained by the dehydration of $MoO_3.H_2O$ however has a layered structure; this reaction is reported to be topotactic. We have investigated the nature of the dehydration reaction by an *in situ* electron diffraction study where the decomposition occurs due to beam heating.[29] Electron diffraction patterns clearly show how $WO_3.H_2O$ transforms to

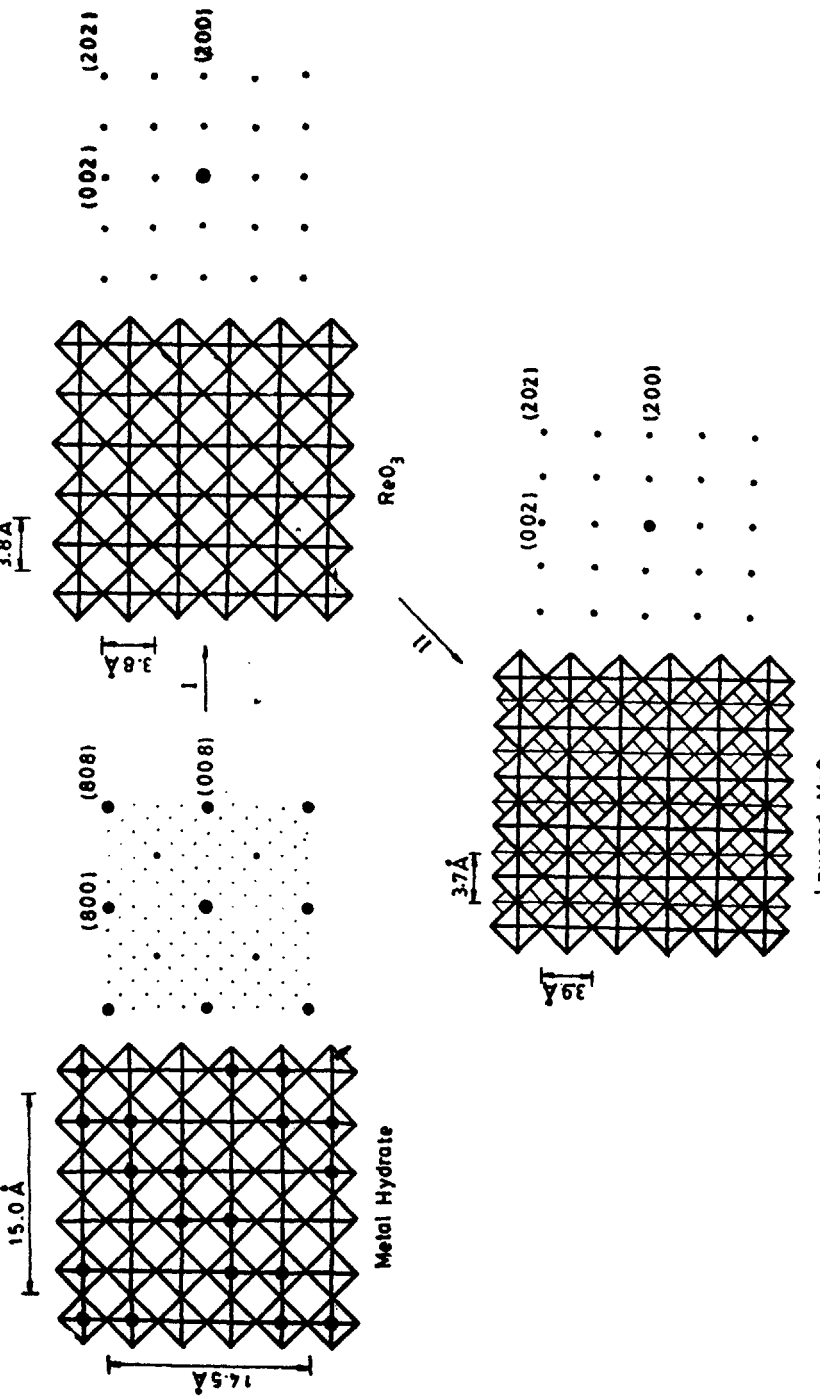

FIG 9 Structural projection of isostructural $Mo_{1-x}W_xO_3.H_2O$ ($0 \leqslant x \leqslant 1$) along with the projection of cubic $ReO_3(WO_3)$ and layered MoO_3 structures. Schematic representation of electron diffraction patterns is also shown.

WO_3 topotactically with the following orientational relationships; $(010)_{hydr} \| (010)_{oxide}$, $[100]_{hydr} \| [001]_{oxide}$ and $[001]_{hydr} \| [100]_{oxide}$. The mixed metal hydrates, $Mo_{1-x}W_xO_3.H_2O$, also undergo topotactic dehydration with similar orientational relations. What is more interesting is that when the dehydration of $MoO_3.H_2O$ is carried out under similar conditions, we clearly see evidence of MoO_3 in the ReO_3 structure (Fig. 9) instead of the expected layered structure. The ReO_3 structure of MoO_3 is metastable and is produced only by topotactic dehydration under mild conditions. Samples of MoO_3 obtained by careful dehydration in a thermogravimetric balance showed most crystallites to be in the layered structure, but a few of them did possess ReO_3 structure. We believe that the observation of Re_3O-like MoO_3 is significant. Relations between the structures of the metal hydrates, $WO_3(ReO_3)$ and layered MoO_3 are shown in Fig. 9. The present study suggests that dehydration of all the hydrates may occur by route I. In the case of $NoO.H_2O$, the initially formed ReO_3 structure transforms to the layered MoO_3 structure (route II).

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