Chemical approaches to the design of inorganic materials

C.N.R. Rao

Solid State & Structural Chemistry Unit and
CSIR Centre of Excellence in Chemistry,
Indian Institute of Science, Bangalore 560012, India

Chemical methods of synthesis play a crucial role in designing and discovering new inorganic materials and also in providing better and less cumbersome methods for preparing known materials. We discuss here the various methods along with several examples, paying special attention to soft chemistry routes. Besides the conventional ceramic method, the methods examined are the precursor method, topochemical reactions, intercalation reactions, ion-exchange method, alkali flux method and electrochemical methods. We discuss cuprate superconductors as a case study in chemical synthesis.

1. INTRODUCTION

Considerable chemical ingenuity is required in the synthesis of solid materials. Although tailor-making materials of the desired structure and properties remains the main goal of materials science, it is not always possible to do so by conventional methods. Rational synthesis has indeed provided a variety of materials, SIALON, NASICON and the large number of microporous materials being typical examples. 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 inorganic solid materials. We shall discuss the various methods with examples and specially examine soft chemistry routes.

2. VARIANTS OF THE CERAMIC METHOD

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. One of these relates to decreasing the diffusion path lengths. In a poly-

crystalline mixture of reactants, the individual particles are approximately 10 μm in size, representing diffusion distances of roughly 10,000 unit cells. By using freeze-drying, spray-drying, coprecipitation and 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 reactants. In coprecipitation, the required metal cations taken as soluble salts (e.g. nitrates) are coprecipitated from a common medium, usually as hydroxides, carbonates, oxalates or citrates. In actual practice, one takes oxides or carbonates of the relevant metals, digests them with an acid (usually HNO_3) 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 temperatures employed in the ceramic method.

3. 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 the synthesis involves a reaction in solution. A few 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 $H_2Ti_4O_9 \cdot xH_2O$, 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 $Ni(OH)_2 \cdot xH_2O$ with a large inter-sheet distances of 7.8 Å by the hydrolysis of $NaNiO_2$, followed by the subsequent reduction of $NiOOH$. Similar transformations of Fe and Co doped $Ni(OH)_2 \cdot xH_2O$ have been studied [4]. Intercalation and deintercalation reactions are soft chemical routes for the synthesis 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.

Intercalation reactions involve the insertion of a guest species into a solid host lattice without any major rearrangement of the solid structure [1,5]. There are many examples of intercalation reactions, 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.). Deintercalation of Li^+ or such ions from the intercalated materials gives oxides and other materials in unusual metastable structures. 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 reactions to prepare bronzes and Chevrel compounds have been described in recent years. Novel materials can be obtained by restacking single-layer MoS_2 with molecular units included between the layers. A variety of organic molecules have been included between MoS_2 and other layered chalcogenides [6].

The sol-gel method may be considered to be a soft chemical route. Many of the topochemical reactions are gentle, although some of them may occur entirely in solid state.

4. TOPOCHEMICAL REACTIONS

Intercalation reactions are generally topochemical in nature. In topochemical reactions, reactivity is controlled by the crystal structure and there is orientational relationship between the product and the parent just as in martensitic reactions [1]. Dehydration of $\beta-Ni(OH)_2$ to NiO as well as the oxidation of $Ni(OH)_2$ to NiOOH are both topochemical [7]. $\gamma-FeOOH$ topochemically transforms to $\gamma-Fe_2O_3$ on treatment with an organic base. Dehydration of many hydrates such as $VOPO_4.2H_2O$ and $HMoO_2PO_4.H_2O$ is topochemical. The topochemical nature of dehydration has been exploited to prepare MoO_3 in the metal stable ReO_3 type structure [8]. $WO_3.1/3 H_2O$ gives WO_3 in different structures depending on the temperature of dehydration [7].

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 $LaNiO_3$.

5. 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. 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 $(NH_4)_2-M(CrO_4)_2.6H_2O$ and $LaCo(CN)_6.5H_2O$ from $LaCoO_3$. Hydrazinate precursors have been employed to prepare several complex oxides.

Specially noteworthy are the carbonate solid solutions of calcite structure which, on decomposition, give the oxide with the desired cation ratios [9]. A variety of complex oxides have been prepared by this method and many of these cannot be prepared otherwise. Hydroxide, nitrate and cyanide solid solutions have also been employed as precursors for oxides. Recently a precursor has been found to prepare Chevrel phases [10] of the type $A_xMo_6S_8$ by the reaction, $2A_x(NH_4)_yMo_3S_9 + 10H_2 \rightarrow A_{2x}Mo_6S_8 + 10H_2S + 2yNH_3 + yH_2$. Precursors for the synthesis of $YBa_2Cu_3O_7$ have been discussed [11]. It should be noted that organometallic precursors have been found to be ideal to make non-oxide ceramics such as Si_3N_4, SiC etc.

6. ION-EXCHANGE AND ALKALI FLUX METHODS

Ion exchange is an important property of fast ion conductors such as β-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 certain complex 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 $HTaO_3$.

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 $La_2CuO_{4+\delta}$ [11].

7. 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). Electrochemical method provides the best means of preparing oxides where a transition metal ion is required to be in a high oxidation state. Thus, superconducting $La_2CuO_{4+\delta}$ as well as $SrFeO_3$ type oxides have been prepared electrochemically [12]. There is much to be done in the area of electrochemical oxidation of metal oxide systems.

8. 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 $Y_{3-x}Ba_{3+x}Cu_6O_{14}$ [13]. 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 [11]. 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.

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 ($T_c \sim 60K$) the alkali flux method. 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. Oxygen stoichiometry is, however, not a problem with the bismuth cuprates. 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-} replace the CuO_4 units in 123 as well as other cuprates[14-17].

9. 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. The presence of wrong sequences 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. Many systems forming ordered intergrowth structures have come to be known in recent years [18]. These systems generally exhibit homology. What is amazing is that such periodicity occurs in three-dimensional solids. 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.

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C.N.R. Rao obtained the M.Sc degree from the Banaras Hindu University, Ph.D. degree from the Purdue University and the D.Sc. degree from the University of Mysore. He is a Fellow of the Science Academies in India and of the Royal Society, London. He is a Foreign Associate of the U.S. National Academy of Sciences and a Foreign Member of the Science Academies of several countries including Russia. He is an honorary member of the American Academy of Arts and Sciences and a Member of the Pontifical Academy of Sciences. He is also Founder-fellow of the Third World Academy of Sciences of which he is now Vice-President. He is the recipient of many prizes and medals including the Marlow Medal of the Faraday Society, Solid State Chemistry Medal of the Royal Society of Chemistry, Hevrovsky medal of the Czech Academy of Sciences, SN Bose and MN Saha medals of the Indian National Science Academy. He has received D.Sc (honoris Causa) from 21 universities including Purdue, Novosibirsk, Bordeaux and Wroclaw and is on the editorial boards of several international journals including J. Solid State Chemistry, Chemical Physics Letters, J. Materials Chemistry, Materials Research Bulletin and Solid State Communication. His main research interests

are in solid state chemistry, surface science, spectros-
copy and molecular structure.   He was President of the
International Union of Pure and Applied Chemistry and is
an Honorary Fellow of the Royal Society of Chemistry,
London.