

Chemical design of solid inorganic materials

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Abstract: Newer strategies for the synthesis of inorganic solids have made a great impact on present-day materials chemistry. In this article, typical case studies of synthesis involving new methods and soft chemical routes are discussed besides recent results from nebulized spray pyrolysis and synthesis of nanoscale metal and alloy particles.

Introduction

Strategies for the synthesis of inorganic solids are being increasingly recognized as crucial for the design and development of materials. This aspect of materials chemistry has been dealt with in some recent publications(1-3). It is convenient to categorize synthetic strategies in the solid state under the three following headings: (a) Strategies involving the traditional ceramic procedure and its variants as well as improvements directed towards decreasing diffusion distances, (b) Novel reactions and methods to prepare known and sometimes new solids and (c) Soft chemical routes generally yielding new, metastable solids. We shall briefly examine these three categories of synthesis with examples mainly chosen from the work carried out in the author's laboratory. We shall also discuss some of the recent results on oriented oxide films obtained by nebulized spray pyrolysis and some efforts to synthesize nanoscale particles of metals and alloys.

Modifications of the traditional ceramic procedure

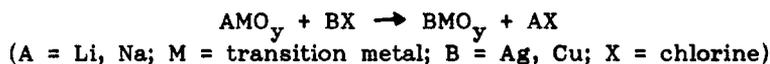
The traditional method of synthesizing inorganic solids has been the ceramic procedure involving the reaction of mixtures of solid materials containing the relevant metal ions at high temperatures. In spite of some of the limitations, a large variety of solids have been successfully prepared by this method. Thus, most of the high-temperature superconducting cuprates have been prepared by the ceramic method. Several modifications of the ceramic method have been employed to overcome the limitations, specially to decrease the diffusion distances. Two of the techniques used to obtain small particles are spray-drying and freeze drying. Coprecipitation is also commonly employed to reduce diffusion distances. Coprecipitation helps to get the required cations in closer proximity and lowers the temperature of decomposition, just as the sol-gel method. A variety of cuprate superconductors have thus been prepared by coprecipitation of carbonates or oxalates(4).

Precursors have been used extensively to reduce diffusion distances in solid state synthesis. Precursors can be single compounds containing all the relevant cations in the required proportion or solid solutions of carbonates, nitrates, cyanides and the like. Carbonate solid solutions as well as alkoxide precursors have been used widely for the synthesis of oxides and the subject has been reviewed adequately(1,3). Precursors have been specially useful in the synthesis of silicon carbide and related materials as well as semiconductor materials(1).

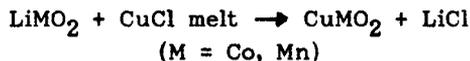
Besides the precursor method, there are a few other strategies employed extensively for the synthesis of complex oxides. The sol-gel route is one of them. Since this method has been reviewed widely, we shall not discuss it here. The combustion method or self-propagating high-temperature synthesis is becoming somewhat popular(1,5). The method gives oxide powders in fine particulate form. Sulfides, nitrides and many other solids have also been prepared by this method. What is to be noted is that in most of the modifications discussed hitherto such as the combustion method as well as the precursor, coprecipitation and sol-gel methods, one ultimately heats the product to a desired temperature just as in the traditional ceramic method, although the temperature may be somewhat lower.

Novel methods for the synthesis of known and occasionally new solids

Many of the methods under this category employ soft chemistry routes, two typical ones being ion exchange and the alkali-flux method. These methods yield known solids by a milder route and occasionally some new solids. Several oxides have been prepared by ion exchange(1) by employing the general reaction:



K.M. Bhat in this laboratory has prepared $CuCoO_2$ and $CuMnO_2$ by this method.



$CuCoO_2$ so prepared has the delafossite structure and contains low-spin Co(III) ions. $CuMnO_2$ has the monoclinic crednerite structure and is antiferromagnetic. There has been partial success in preparing $Cu(I)Cu(III)O_2$ by the reaction of $ACuO_2$ with $CuCl$.

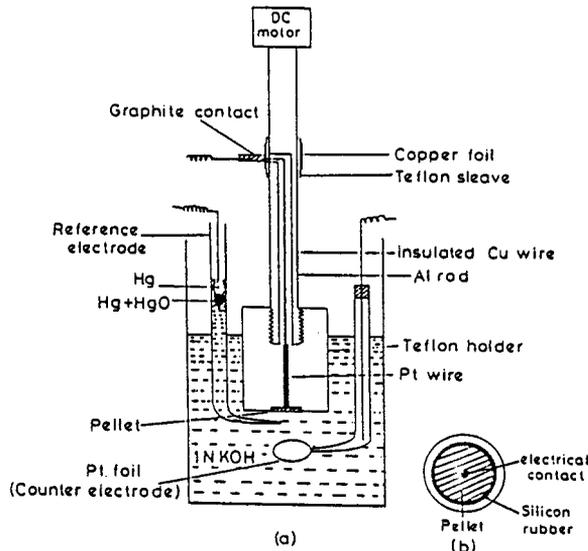


Fig. 1 (a) An electrochemical cell with (b) the rotating disc electrode

Electrochemical methods have been effectively used to prepare oxides containing transition metals in high oxidation states (e.g. $SrFeO_3$, $SrCoO_3$, $LaMnO_3$), avoiding the use of high oxygen pressures. A typical electrochemical cell is shown in Fig. 1. There are several examples of electrochemical oxidation in the recent literature(1). Let us consider the case of the superconducting cuprate system, $La_{2-x}A_xCuO_4$ (A = Sr or Ba). When $x = 0.0$, the material as prepared is insulating. On electrochemical

oxidation, the oxygen content (hole concentration) increases and the material becomes superconducting. The hole-concentration and superconducting properties of $\text{La}_{2-x}\text{A}_x\text{CuO}_4$ ($x > 0.0$) are significantly affected after electrochemical oxidation (Fig. 2).

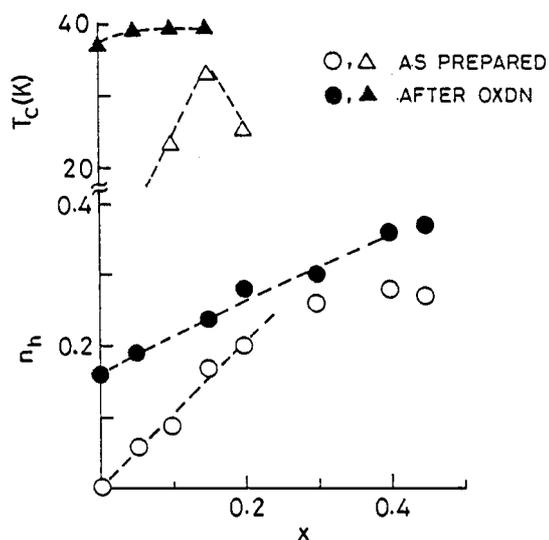


Fig. 2 Variation of the hole concentration, n_h , and the T_c with x in $\text{La}_{1-x}\text{A}_x\text{CuO}_4$ before and after electrochemical oxidation (from K.R. Kannan)

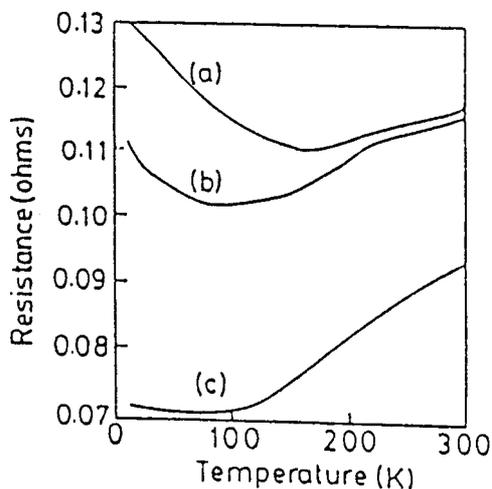


Fig. 3 Electrical resistance of (a) as-prepared $\text{NdNiO}_{3-\delta}$ and (b) of the sample after electrochemical oxidation for 24 hr. and (c) for 48 hr.

An interesting example of electrochemical oxidation is provided by NdNiO_3 . As prepared, NdNiO_3 is oxygen deficient and shows a metal-insulator transition. Many workers have studied this transition without realizing that it arises from the non-stoichiometry. The stoichiometric NdNiO_3 prepared by electrochemical oxidation is however metallic down to low temperatures(6) as shown in Fig.3.

Soft chemical routes for the synthesis of novel solids

Soft chemical routes often give entirely new, often metastable solids. Many examples of such synthesis can be cited. Preparation of $\text{Ti}_2\text{Nb}_2\text{O}_9$ by the dehydration of HTiNbO_5 (obtained from ion exchange with ATiNbO_5), of layered Ni hydroxide from NaNiO_2 and a new form of TiO_2 from $\text{H}_2\text{Ti}_4\text{O}_9 \cdot x\text{H}_2\text{O}$ are some examples(see refs.1 & 3). Soft chemical routes for the synthesis of solids has been reviewed recently(1,7,8). Hydrothermal synthesis has emerged to become an excellent method to produce a variety of microporous solids and related materials(1). Intercalation and deintercalation, acid leaching and ion exchange are some of the important reactions employed in soft chemistry. We shall cite one example from recent work in this laboratory. Ayyappan et al(9) have prepared cubic and other metastable forms of WO_3 and MoO_3 by first intercalating amines into them and then removing the amines thermally or by acid leaching (Fig. 4 and 5). Hydrogen bronzes such as H_xWO_3 and H_xMoO_3 have been prepared by refluxing the parent oxides in an alcohol or in ethylene glycol(10).

Complex oxides by nebulized spray pyrolysis

Pyrolysis of atomized sprays containing organometallic precursors provides a method of preparing nanomaterials in bulk quantities and also oriented films of complex oxides on solid substrates (11). Recently, oriented films of LaNiO_3 , $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{La}_3\text{Ni}_2\text{O}_7$ have been prepared and characterized. Oriented films of ferroelectrics

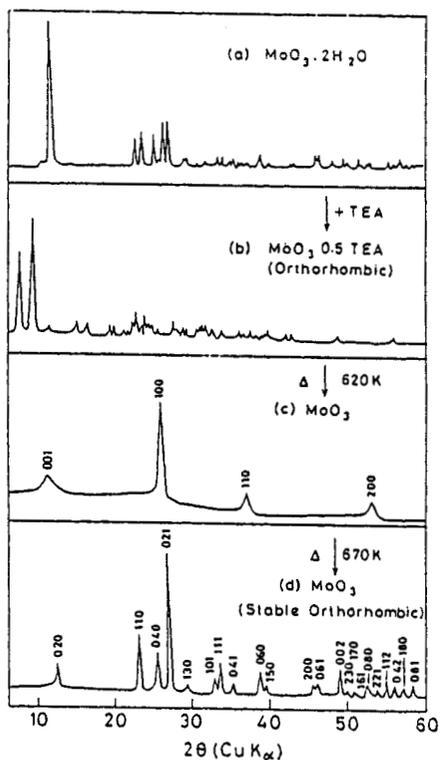


Fig. 4 XRD patterns of (a) MoO₃·2H₂O, (b) MoO₃·0.5TEA, (c) metastable ReO₃ type MoO₃ obtained by heating the amine adduct and (d) the stable orthorhombic MoO₃ (layered structure) obtained by heating Cubic MoO₃.

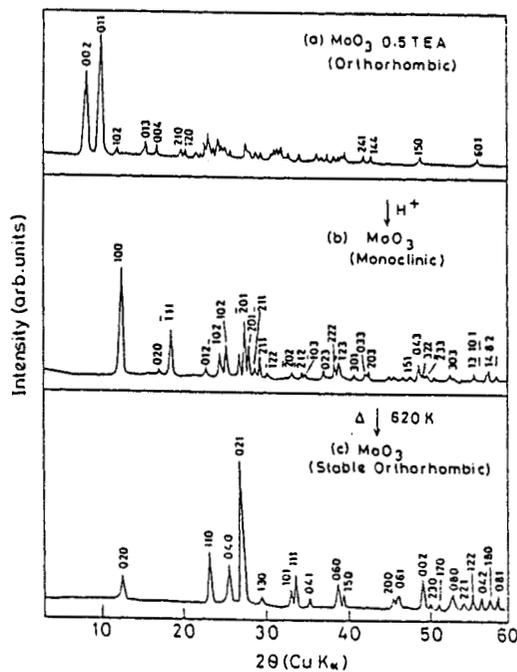


Fig. 5 XRD patterns of (a) MoO₃·0.5TEA (b) Monoclinic MoO₃ obtained by acid leaching the amine adduct and (c) stable MoO₃ obtained by heating the monoclinic form.

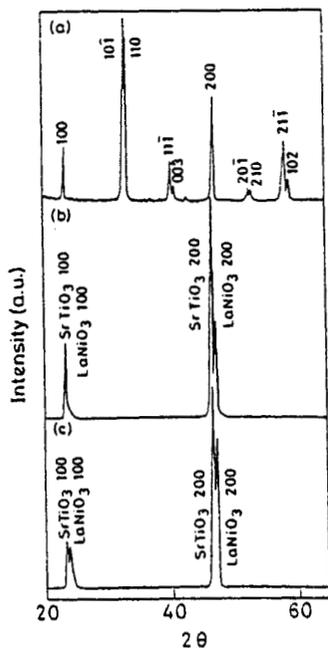


Fig. 6 XRD patterns of (a) polycrystalline LaNiO₃ and (b), (c) oriented films of LaNiO₃ on SrTiO₃ (100)

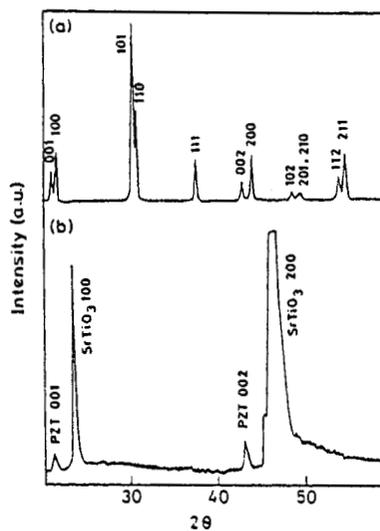


Fig. 7 XRD patterns of (a) polycrystalline PZT and (b) oriented film of PZT on SrTiO₃ (100)

such as PbTiO_3 and PZT have also been prepared by this technique. The films actually appear to be epitaxial and this chemical method has great promise. In Fig. 6 and 7, we show the x-ray diffraction patterns of LaNiO_3 and PZT obtained on a $\text{SrTiO}_3(100)$ substrate.

Synthesis of nanoparticles of metals and alloys

Metal colloids with nanometer dimensions have been prepared by employing a variety of methods. The method usually involves the reaction of metal salt solutions with certain reducing agents (e.g. alcohols and glycols) in the presence of a polymer, such as PVP, to prevent agglomeration(1). There have been a few attempts to prepare bimetallic alloy particles as well. H.N. Vasan in this laboratory has prepared nanoscale Ag-Pd and Cu-Pd alloys by the reaction of methanol (or ethanol) with a $\text{PdO}_x + \text{AgNO}_3$ or $\text{CuO}_x + \text{PdO}_x$ mixtures (obtained by the decomposition of nitrate mixtures of the appropriate composition). In Fig. 8, we show how a typical Cu-Pd alloy is obtained from such a reaction. In Fig. 9, we show the x-ray diffraction

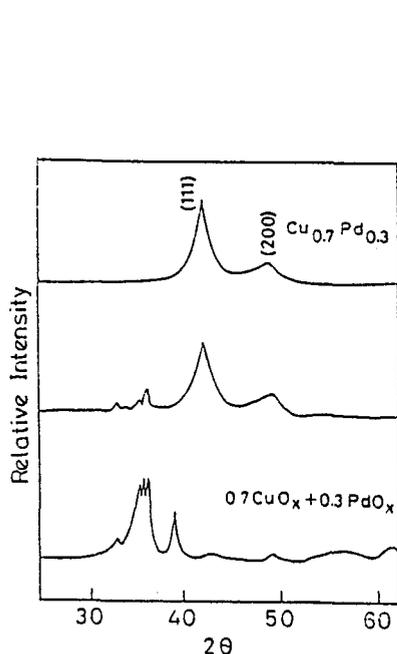


Fig. 8 X-ray diffraction patterns showing the formation of the Cu-Pd alloy by the reaction of $\text{CuO}_x + \text{PdO}_x$ on refluxing with dry ethanol under nitrogen.

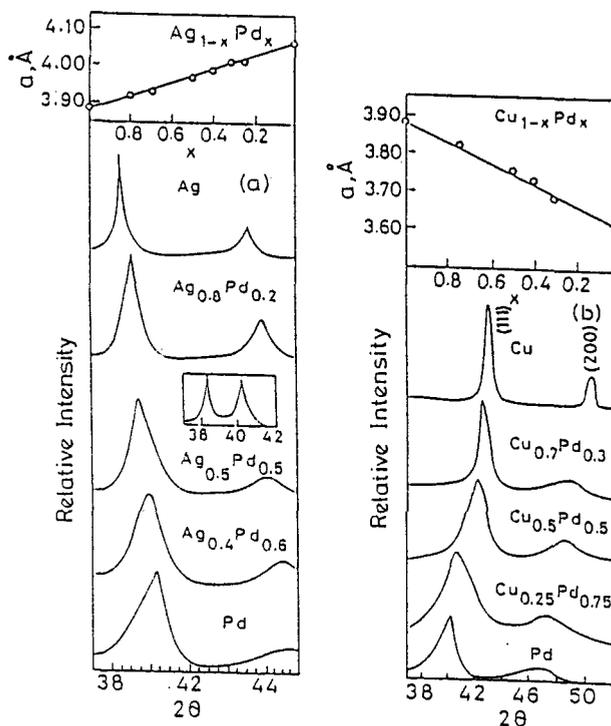


Fig. 9 X-ray diffraction patterns showing the (111) and (200) reflections of the (a) Ag-Pd and (b) Cu-Pd nanoparticles. Vegard law behaviour is seen.

patterns of alloy particles of different compositions prepared in this manner. All the alloy compositions have the FCC structure and the particle diameters are in the 5-40 nm range.

Nanoparticles of metals can be incorporated into clays, by first intercalating the clays with metal salts and then reducing them with alcohols or glycols. S. Ayyappan and S. Gopalan have incorporated Ni, Co, Cu, Pd and Ag into clays in this manner with the particle size varying anywhere between 3 and 40 nm. In Fig. 10 we show

the electron micrograph of a clay showing $\sim 16\text{\AA}$ layers with nickel particles in them. Typical x-ray diffraction patterns of the clay with different amounts of nickel (of different particle sizes) are shown in Fig. 11.

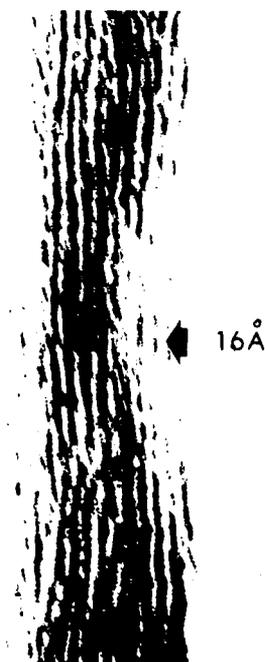


Fig. 10 Electron micrograph showing 16\AA layers in montmorillonite containing nickel.

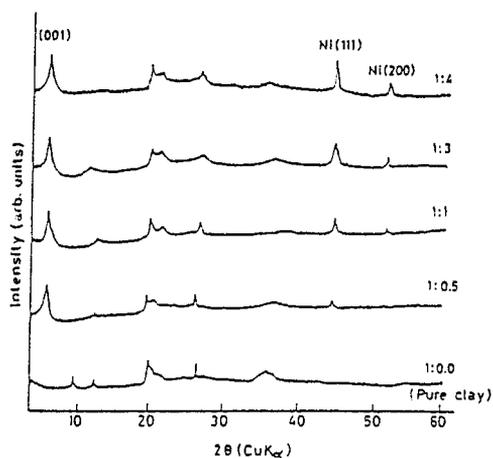


Fig. 11 X-ray diffraction patterns of nickel-incorporated montmorillonite. The starting clay to nickel acetate wt. ratios are shown. Metallic nickel reflections can be seen.

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REFERENCES

1. C.N.R. Rao, *Chemical Approaches to the Synthesis of Inorganic Materials*, John Wiley, New York, 1994.
2. J. Corbett in *Solid State Chemistry* (A.K. Cheetham and P. Day, eds.), Clarendon Press, Oxford, 1992.
3. C.N.R. Rao, *Pure Appl. Chem.*, **66**, 1765 (1994).
4. C.N.R. Rao, R. Nagarajan and R. Vijayaraghavan, *Supercond Sci. Tech.*, **6**, 1 (1993).
5. M. Merzhanov in *Chemistry of Advanced Materials* (C.N.R. Rao, ed.), Blackwell, Oxford, 1991.
6. R. Mahesh, K. R. Kannan and C.N.R. Rao, *J. Solid State Chem.* **114**, 294 (1995).
7. J. Rouxel, M. Tournoux and R. Bree (eds), *Soft Chemistry Routes to New Materials*, Trans Tech Publications, Switzerland, 1994.
8. J. Gopalakrishnan, *Chem. Mater.* (1995) in Print.
9. S. Ayyappan, G.N. Subbanna and C.N.R. Rao, *Chem. Eur. J.*, **1**, 165 (1995).
10. S. Ayyappan and C.N.R. Rao, *Mater. Res. Bull* (1995) in Print.
11. A.R. Raju, H.N. Aiyer and C.N.R. Rao, *Chem. Mater.*, **7**, 225 (1995).