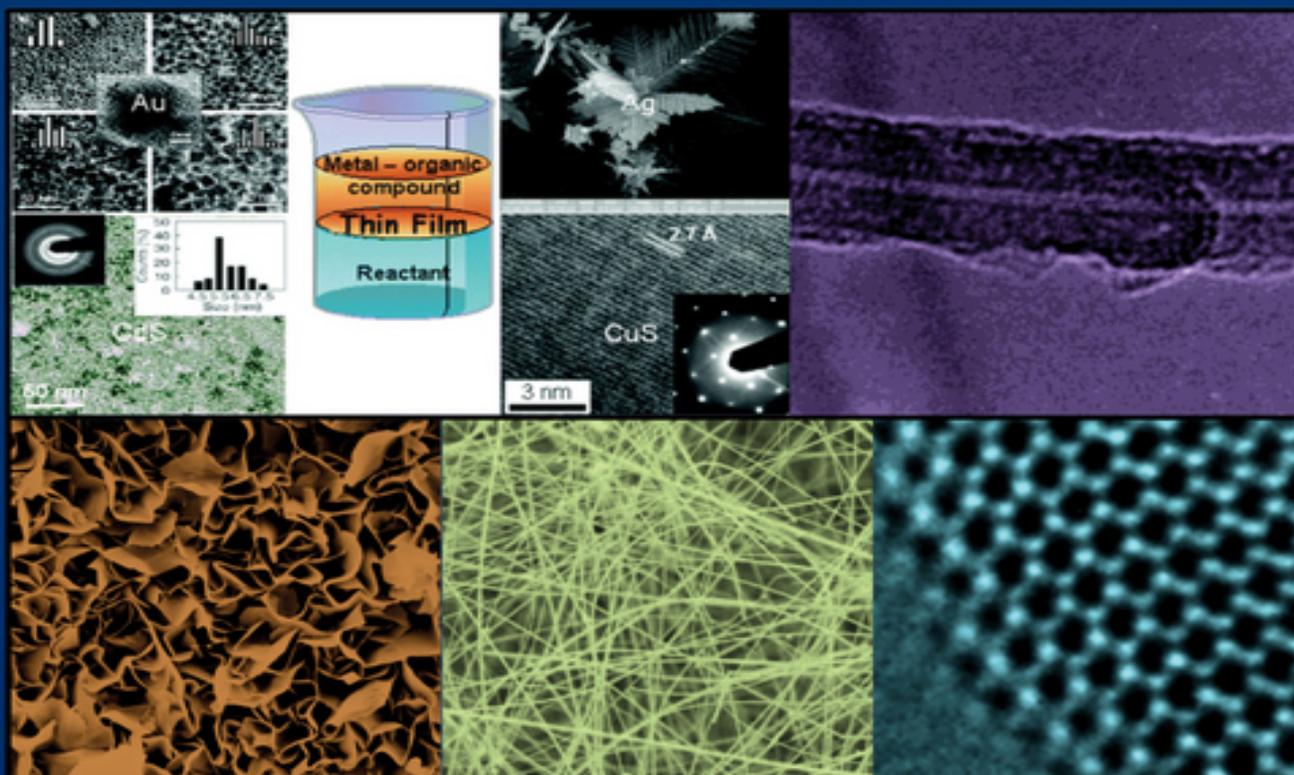


Essentials of Inorganic Materials Synthesis



C. N. R. Rao • Kanishka Biswas

WILEY

CONTENTS

COVER

TITLE PAGE

AUTHOR BIOGRAPHIES

PREFACE

1 INTRODUCTION

REFERENCES

2 COMMON REACTIONS EMPLOYED IN SYNTHESIS

2.1 SOFT-CHEMISTRY ROUTES

REFERENCES

3 CERAMIC METHODS

REFERENCES

4 DECOMPOSITION OF PRECURSOR COMPOUNDS

REFERENCES

5 COMBUSTION SYNTHESIS

REFERENCES

6 ARC AND SKULL METHODS

REFERENCES

7 REACTIONS AT HIGH PRESSURES

REFERENCES

8 MECHANOCHEMICAL AND SONOCHEMICAL
METHODS

8.1 MECHANOCHEMISTRY

8.2 SONOCHEMISTRY

REFERENCES

9 USE OF MICROWAVES

REFERENCES

10 SOFT CHEMISTRY ROUTES

10.1 TOPOCHEMICAL REACTIONS

REFERENCES

10.2 INTERCALATION CHEMISTRY

REFERENCES

10.3 ION EXCHANGE REACTIONS

REFERENCES

10.4 USE OF FLUXES

REFERENCES

10.5 SOL-GEL SYNTHESIS

REFERENCES

10.6 ELECTROCHEMICAL METHODS

REFERENCES

10.7 HYDROTHERMAL, SOLVOTHERMAL AND IONOTHERMAL SYNTHESIS

REFERENCES

11 NEBULIZED SPRAY PYROLYSIS

REFERENCES

12 CHEMICAL VAPOUR DEPOSITION AND ATOMIC LAYER DEPOSITION

REFERENCES

13 NANOMATERIALS

13.1 NANOPARTICLES

13.2 CORE-SHELL NANOCRYSTALS

13.3 NANOWIRES

13.4 INORGANIC NANOTUBES

13.5 GRAPHENE-LIKE STRUCTURES OF LAYERED INORGANIC MATERIALS

REFERENCES

14 MATERIALS

14.1 METAL BORIDES, CARBIDES AND NITRIDES

REFERENCES

14.2 METAL CHALCOGENIDES

REFERENCES

14.3 METAL HALIDES

REFERENCES

14.4 METAL SILICIDES AND PHOSPHIDES

REFERENCES

14.5 INTERGROWTH STRUCTURES AND MISFIT COMPOUNDS

REFERENCES

14.6 INTERMETALLIC COMPOUNDS

REFERENCES

14.7 SUPERCONDUCTING COMPOUNDS

REFERENCES

14.8 POROUS MATERIALS

REFERENCES

INDEX

END USER LICENSE AGREEMENT

List of Tables

Chapter 02

Table 2.1 Examples of chemical transport

Table 2.2 Examples of crystals grown by chemical transport

Chapter 04

[Table 4.1 Typical reactions of organometallic precursors employed in preparing semiconductors](#)

Chapter 05

[Table 5.1 Typical materials prepared by the combustion method](#)

Chapter 10

[Table 10.2.1 Examples of hosts and guests in intercalation compounds](#)

[Table 10.2.2 Intercalation compounds of lithium](#)

[Table 10.6.1 Typical electrochemical preparations](#)

Chapter 11

[Table 11.1 Typical films and 1D nanostructures prepared by NSP](#)

Chapter 14

[Table 14.5.1 Ordered intergrowth structure forming homologous series](#)

[Table 14.7.1 Synthesis of superconducting compounds](#)

List of Illustrations

Chapter 01

[Figure 1.1 Structure of \$\text{NaMo}_4\text{O}_{16}\$.](#)

[Figure 1.2 Crystal structure of Chevrel phases. \(a\) Type I with large cation in the origin \(eight rhombohedral unit cells\): each cation is surrounded by eight \$\text{Mo}_6\text{T}_8\$ blocks. The internal structure is shown for one of the blocks. Intercluster Mo-T₁ bond is marked in blue. \(b\) Three types of pseudocubic](#)

cavities between the Mo_6T_8 blocks. Cavities 1 and 2 form the diffusion channels in three directions (a channel in one of the directions is shown here). Sites for small cations in cavities 1 and 2 are presented separately on the right.

Figure 1.3 Structure of $\text{NaZr}_2(\text{PO}_4)_3$ which provided the design for NASICON: vacant trigonal-prismatic sites, p; octahedral Zr^{4+} sites, Z; and octahedral sites available for Na^+ , M. For each M, there are three Mo sites forming hcp layers perpendicular to the c-axis.

Chapter 02

Figure 2.1 Stability diagrams for (a) Co_{1-x}O and (b) Fe_{1-x}O in long $f(\text{O}_2)$ -temperature representation. Upper solid line gives the oxidation limit and lower solid line the reduction limit. Dashed lines, CO/CO_2 gas mixtures with percentage of CO_2 shown in number (i.e., $100\text{CO}_2/\text{C} + \text{CO}_2$).

Figure 2.2 Mechanism of formation of metastable TiO_2 (B) from $\text{K}_2\text{Ti}_4\text{O}_9$.

Figure 2.3 Preparation of $\text{Ti}_2\text{Nb}_2\text{O}_8$ (b) from KTiNbO_5 (a).

Figure 2.4 Preparation of layered double hydroxides (LDH). The thickness of the $\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ slab varies with the oxidation state of nickel and cobalt.

Chapter 03

Figure 3.1 Experimental set-up for synthesis of oxide nanowires.

Figure 3.2 SEM images of (a) Si_3N_4 and (b) $\text{Si}_2\text{N}_2\text{O}$ nanowires prepared by carbothermal reaction.

Chapter 04

Figure 4.1 Distribution of two different cations (closed and open dirks) in reactant particles and the diffusion distances in (a) the ceramic procedure and (b) in precursor compounds or precursor solid solutions.

Figure 4.2 Plot of the rhombohedral lattice parameters, a_R , of a variety of binary and ternary carbonates of calcite structure (e.g. Ca-M, Ca-M-M, Mg-M, M-M' where M, M' = Mn, Fe, Co, Cd etc.) against the mean cation radius.

Figure 4.3 Structures of (a) $\text{Ca}_2\text{Fe}_2\text{O}_5$ (brownmillerite) and (b) $\text{Ca}_2\text{Mn}_2\text{O}_5$, oxygen vacancy-ordering in the a - b plane is also shown.

Figure 4.4 $\text{Ca}_3\text{Fe}_2\text{MnO}_{7.5}$ obtained by the topotactic reduction of $\text{Ca}_3\text{Fe}_2\text{MnO}_8$. The latter is prepared by decomposition of the precursor carbonate, $\text{Ca}_2\text{Fe}_{4/3}\text{Mn}_{2/3}(\text{CO}_3)_4$.

Figure 4.5 Some of the complex oxides prepared by the decomposition of carbonate precursors.

Chapter 05

Figure 5.1 Combustion reaction during the preparation of a cuprate.

Figure 5.2 $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder resulting from the combustion reaction.

Chapter 06

Figure 6.1 DC arc furnace.

Chapter 07

Figure 7.1 Piston-cylinder apparatus.

Figure 7.2 Different anvil design. (a) Simple opposite face anvil, (b) tetrahedral anvil and (c) cubic anvil.

Figure 7.3 Belt apparatus.

Chapter 08

Figure 8.1 (a) Expected MOF of [Zn₂(ta)₂(dabco)] assembly. (b) MOF isomers. Red O, gray C, blue N, purple Zn.

Figure 8.2 Schematic representation of mechanochemical synthesis of COFs through Schiff base reaction performed via grinding using mortar and pestle.

Figure 8.3 (a) Schematic illustration of the sonochemical preparation of single-walled carbon nanotubes on silica powders. (b) Scanning electron microscope (SEM) image of carbon nanotube bundles on polycarbonate filter membrane. (c) High-resolution transmission electron microscopy (HRTEM) images of single-walled carbon nanotubes within the bundles.

Chapter 09

Figure 9.1 Schematic representation of microwave heating procedure.

Chapter 10

Figure 10.1.1 Dehydration of MoO₃·2H₂O to MoO₃·H₂O.

Figure 10.1.2 X-ray diffraction patterns of 20 mol% V₂O₅ dispersed in TiO₂ support: (a) at 625 K in air; (b) after exposure to liquefied petroleum gas (LPG) at 625 K (note the VO₂ (B') peaks); (c) further exposure of (b) at 675 K (note the V₂O₃ peaks); (d) after

exposure of (c) to air at 625 K (the process is fully reversible).

Figure 10.1.3 Schematic representation of $\text{MoO}_3 \cdot \text{H}_2\text{O}$. MoO_3 in ReO_3 -like structure and the layered structure of MoO_3 : (a) along $[010]$; (b) along $[001]$.

Figure 10.1.4 Different WO_3 phases obtained by the dehydration of $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ at different temperatures.

Figure 10.1.5 Schematic arrangement of MnO_6 octahedra and MnO_5 square-pyramids in $\text{CaMnO}_{2.8}$.

Figure 10.1.6 Structures of YBa_2CuO_7 and YBa_2CuO_6 .

Figure 10.2.1 Staging in intercalation compounds (schematic). Guest molecules are represented by circles in between the layers (shown by lines).

Figure 10.2.2 (a, b) TEM images of MoS_2 layers. (c) High-resolution TEM image of layered MoS_2 . (d, e) Images of WS_2 layers. The bends in the layers may arise from defects.

Figure 10.2.3 Transmission electron micrographs of colloidal $\text{TBA}_x\text{H}_{1-x}\text{Ca}_2\text{Nb}_3\text{O}_{10}$ sheets.

Figure 10.3.1 The twist of the 12-coordinate cavity in ReO_3 to form two octahedra sharing faces, as found in LiReO_3 and Li_2ReO_3 .

Figure 10.3.2 (a) Part of the layer framework of $\text{K}_{1.9}\text{Mn}_{0.95}\text{Sn}_{2.05}\text{S}_6$ (KMS-1) viewed down the c -axis. The Mn-Sn and S atoms are represented by blue and yellow balls, respectively. (b) View of the structure, with a polyhedral representation of the layers, along

the *c*-axis. (c) X-ray powder diffraction patterns for the pristine $K_{2x}Mn_xSn_{3-x}S_6$ ($x = 0.5-0.95$) and Sr^{2+} -exchanged materials.

Figure 10.4.1 Phase diagram of K_2S/S system.

Figure 10.4.2 Structure of $Rb_4Sn_5P_4Se_{20}$ viewed down the *b*-axis. All atoms are labelled. Disordered atoms are omitted for clarity. Rb blue, Sn yellow, P black, Se red.

Figure 10.5.1 Photographs of films produced by the hydrolysis and condensation of sol-gel precursors before pyrolysis.

Figure 10.6.1 Schematic diagrams of (a) the electrochemical cell and (b) the rotating disc electrode.

Figure 10.7.1 Hydrothermal reactors: (a) typical reactor, (b) Morey-type reactor and (c) Teflon-lined stainless-steel autoclave.

Figure 10.7.2 TEM image of GaN nanocrystals. Inset shows the image of a single nanocrystal (scale bare, 2 nm). Photoluminescence spectrum of the 2.5 nm GaN nanocrystals is shown as an inset.

Chapter 11

Figure 11.1 Apparatus employed for preparing films by nebulized spray pyrolysis.

Figure 11.2 (a) and (b) SEM images; (c) and (d) TEM images of MWNTs obtained by nebulized spray pyrolysis of metallocene.

Chapter 12

Figure 12.1 Schematic representation of ALD using self-limiting surface chemistry and an AB binary.

reaction sequence.

Chapter 13

Figure 13.1 (a) The overall scheme for the ultra-large-scale synthesis of monodisperse NPs and TEM of magnetite. (b) TEM image, high-resolution transmission electron microscopy (HRTEM) image and electron diffraction pattern of monodisperse MnO nanocrystals.

Figure 13.2 (a) TEM image of size-selected Cu_{2-x}Se NPs grown for 15 min at 300°C , having an average size of 16 nm (the size estimated by X-ray diffraction (XRD) was 18 nm). The inset shows a sketch of the hexagonal projection of a cuboctahedron shape. (b) HRTEM image of Cu_{2-x}Se NPs. Most of the displayed NPs are seen under their [30] zone axis. The inset shows their two-dimensional fast Fourier transform. (c) Scanning electron microscopy (SEM) image of Cu_{2-x}Se NPs drop-casted from solution onto a glass substrate. (d) Elastic-filtered (ZL) image of several NPs. (e, f) Cu and Se elemental maps from the same group obtained by filtering the Cu L edge (at 931 eV) and the Se L edge (at 1436 eV). (g) Elemental quantification of a group of NPs by EDS.

Figure 13.3 TEM image of a relatively dense arrangement of CdSe NPs showing a tendency to close-packing in the plane (bar = 50 nm). The inset shows a histogram of particle sizes.

Figure 13.4 Schematic showing the thermomorphic nature of fluoros and hydrocarbon solvents.

Figure 13.5 TEM images of fluoros thiol-capped (a) 4 nm CdSe and (b) 3.5 nm CdS NPs with HRTEM images as insets. Photographs of the dispersions of

the NPs in perfluorocarbon (PFC) are also given as insets.

Figure 13.6 TEM images of (a) Au, (b) Ag, (c) CdS, and (d) CuS NPs formed at liquid-liquid interface.

Figure 13.7 (a, b) SEM and TEM images of the overall morphology of Au-Pd nanocubes self-assembled on the Si wafer and Cu grid, respectively. The dashed frames indicate the core area of particles. (c) Scanning transmission electron microscopy (STEM) images of the octahedral Au seed within a cubic Pd shell and cross-sectional compositional line profiles of a Au-Pd nanocube along the diagonal (indicated by a red line). (d) TEM image of an Au-Pd nanocube at high magnification. The inset is the SAED pattern taken from individual nanocubes.

Figure 13.8 TEM images of core-shell nanoparticles of (a) ReO_3 -Au formed with a 5 nm ReO_3 particle. Inset shows ReO_3 -Au formed over an 8 nm ReO_3 particle. (b) ReO_3 - TiO_2 core-shell nanoparticle formed over a 32 nm ReO_3 particle with the inset showing a core-shell nanoparticle formed over a 12 nm ReO_3 nanoparticle. UV-visible absorption spectra of (c) ReO_3 -Au core-shell nanoparticles (1:2 and 1:4). (d) ReO_3 - TiO_2 core-shell nanoparticles (1:2 and 1:4) with a 12 nm ReO_3 particle.

Figure 13.9 (a) Schematic representation of VLS nanowire growth mechanism including three stages: (I) alloying, (II) nucleation and (III) axial growth. The three stages are projected onto (b) the conventional Au-Ge binary phase diagram to show the compositional and phase evolution during the nanowire growth.

Figure 13.10 In situ TEM images recorded during nanowire growth: (a) Au nanoclusters in the solid state at 500°C; (b) alloying initiated at 800°C, where Au exists mostly in the solid state; (c) liquid Au-Ge alloy; (d) nucleation of the Ge nanocrystal on the alloy surface; (e) elongation of the Ge nanocrystal with further Ge condensation, eventually forming (f) a wire.

Figure 13.11 TEM image of gold nanorods with aspect ratio ~25 obtained by solution-based reduction method making use of nanoparticle seeds.

Figure 13.12 (a, b) SEM images of zinc and cadmium nanowires obtained by the pyrolysis of the corresponding metal acetates at 1173 K. (c) TEM image of zinc nanowires and (d) TEM image of ZnO nanotubes obtained by the oxidation of Zn nanowires at 723 K.

Figure 13.13 (a) Crystal structure of *t*-Se showing a unit cell with helical chains of covalently bonded Se atoms extended along the *c*-axis. The growth direction of the one-dimensional nanostructures is shown along with an atomic model of a rod. (b) XRD patterns of the *t*-Se nanorods and bulk selenium powder used as the starting reagent. (c) SEM image of the Se nanorods obtained after 4 days by reacting 0.025 g of Se with 0.03 g of NaBH₄ in 20 ml water. (d) High-resolution electron microscopy (HREM) image of nanorods (arrow indicates the growth direction of the nanorods). (e) SEM image of *t*-Se scrolls obtained under hydrothermal conditions.

Figure 13.14 (a) Typical low-magnification TEM image of a ZnO nanohelix, showing its structural uniformity. (b) Low-magnification TEM image of a ZnO nanohelix with a larger pitch to diameter ratio.

The selected-area ED pattern (SAED, inset) is from a full turn of the helix. (c) Dark-field TEM image from a segment of a nanohelix. The edge at the right-hand side is the edge of the nanobelt. (d, e) High-magnification TEM image and the corresponding SAED pattern of a ZnO nanohelix with the incident beam perpendicular to the surface of the nanobelt, respectively, showing the lattice structure of the two alternating stripes. (f) Enlarged HRTEM image showing the interface between the two adjacent stripes.

Figure 13.15 (a, b) SEM images of the three-dimensional PbS nanowire array with an observable cubic seed (c) SEM image of units of the nanowire arrays prepared under a larger gas flow rate.

Figure 13.16 XRD patterns of (a) AlN, (b) GaN and (c) InN nanowires (asterisk indicates peaks arising due to substrate or gold). SEM images of (d) AlN, (e) GaN, (f) InN nanowires.

Figure 13.17 (a) Star-shaped PbSe nanocrystals and (b, c) radially branched nanowires. (d) TEM image of the (100) view of the branched nanowire and the corresponding selected-area electron diffraction pattern. (e) TEM image of the (110) view of the branched nanowire and the corresponding selected-area electron diffraction pattern.

Figure 13.18 (a) Schematic cross-sectional image of InP/InAs/InP core-multishell nanowire. (b) SEM image of periodically aligned InP/InAs/InP core-multishell nanowire array. (c) SEM image showing highly dense ordered arrays of core-multishell nanowires. Schematic illustration and high-resolution SEM cross-sectional image of a typical core-multishell nanowire observed after anisotropic dry.

etching and stain etching. Inset shows the top view of a single nanowire.

Figure 13.19 TEM images of (a) MoS₂ and (b) WS₂ nanotubes obtained by the decomposition of precursor ammonium salts.

Figure 13.20 (a) TEM image of few-layer Bi₂Se₃ nanostructure. (b) HRTEM image of bent edges of nanostructure, upper inset is a magnified image of indicated region and the lower inset is a TEM image of a hexagonal nanodisc. (c) HRTEM lattice image of hexagonal nanodisc shown in the lower inset of (b). Right inset in (c) shows an edge of the same nanodisc. The left inset in (c) is the corresponding SAED pattern projecting [0001] zone axis view. (d) AFM image of few-layer Bi₂Se₃ nanostructure.

Chapter 14

Figure 14.2.1 (a) Scanning electron microscopy (SEM) image of GaSe scrolls. Inset shows nanoflowers. (b) Transmission electron microscopy (TEM) image of GaSe nanotubes obtained by thermal treatment. (c, d) High-resolution transmission electron microscopy (HRTEM) images of GaSe nanotubes.

Figure 14.2.2 Sections of the incommensurately modulated structure of Te₄[Bi_{0.74}Cl₄]. Left: Projection along the *c*-axis. Right: Sequence of chloridobismuthate anions and stacks of tellurium polycations.

Figure 14.4.1 (a) Schematic illustration of the experimental set-up for the synthesis of uniformly sized transition metal phosphide nanorods. (b)

Transmission electron microscopy (TEM) images of various transition metal phosphide nanorods

Figure 14.5.1 Different types of intergrowth structures formed by the Aurivillius family of bismuth oxides. Notice the intergrowth of (1, 2), (2, 3) and (3, 4) layered units.

Figure 14.5.2 HRTEM of (3, 4) intergrowth structures: (a) $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$ involving the Aurivillius phases $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n = 3$) and $\text{Bi}_5\text{Ti}_3\text{CrO}_{15}$ ($n = 4$) and (b) $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$. Computer-simulated images and unit cell lengths are shown.

Figure 14.5.3 Schematic drawing of (1, 4), (1, 5) and (1, 6) ITB. Hexagonal tunnels of HTB strips separate the WO_3 slabs shown in the polyhedral unit.

Figure 14.5.4 HRTEM of Bi_xWO_3 intergrowth bronze. The dark circles between the WO_3 slabs represent Bi atoms.

Figure 14.5.5 HRTEM of MYMY₆ intergrowth in barium ferrite: $\text{M} = \text{BaFe}_{12}\text{O}_{19}$; $\text{Y} = \text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ ($\text{Me} = \text{Zn}, \text{Ni}$ or Mg).

Figure 14.5.6 Schematic representation of (a) the structure of the $(\text{MX})_{1+y}(\text{TX}_2)$ misfit compound, (b) the structure of the $(\text{MX})_{1+y}(\text{TX}_2)$ misfit compound at initiation of the bending, and (c) formation of the tubular structure.

Figure 14.7.1 Superconducting $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ and $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$.

Figure 14.7.2 Schematic structures of 123, 124 and 247 cuprates.

Figure 14.7.3 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4(\text{T}')$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4(\text{T})$.

Figure 14.7.4 Schematic structures of (a) $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_4\text{Cu}_2(\text{SO}_4)\text{O}_y$ and (b) $\text{YCaBa}_4(\text{Ba}_2\text{Sr}_2)\text{Cu}_5[\text{CO}_3]_{1-x}[\text{NO}_3]_x\text{O}_y \cdot \text{SO}_4$ units are shown as tetrahedra while CO_3 and NO_3 units are shown by triangles.

Figure 14.7.5 Six different structures of the FeAs-based materials, which contain the FeAs planes. The formulas given here represent the typical ones. RE, rare earth.

Figure 14.7.6 Structure of the BaFe_2As_2 .

Figure 14.8.1 Powder X-ray diffraction pattern of (a) cubic SBA-11 and (b) hexagonal SBA-15.

Figure 14.8.2 Phase transition in mesoporous solids: (a-d) lamellar-hexagonal; (e-f) hexagonal-cubic. The circular objects around the surfactant assemblies are the metal-oxo species.

Figure 14.8.3 (a) XRD patterns of as-synthesized and calcined (600°C) forms of an MSU-H silica molecular sieve assembled from sodium silicate and Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) under neutral pH conditions at 60°C . TEM images of the calcined MSU-H silica: (b) low and (c) high magnification.

Figure 14.8.4 Schematic structures of AlPO_4 -5 and VPI-5.

Figure 14.8.5 Single-crystal X-ray structures of MOF-5. On each of the corners is a cluster $[\text{OZn}_4(\text{CO}_2)_6]$ of an oxygen-centered Zn_4 tetrahedron that is bridged by six carboxylates of an organic linker. The large spheres represent the largest sphere that would fit in

the cavities without touching the van der Waals atoms of the frameworks.

Figure 14.8.6 (a) Fusion of butlerite-type chains to form the layered structure in $M_2F_2(SO_4)_2(H_2O)_2]_n^{2n-}$, (M = Fe, Mn). (b) Layered in $[Fe_2^{III}Fe_3^{II}F_{12}(SO_4)_2(H_2O)_2]^{4-}$ with symmetrical capping of the sulfate tetrahedra in the triangular lattice and the 10-membered aperture within it, redrawn from Ref. 33. (c) Polyhedral view of the kagome layer in $[HN(CH_2)_6NH][Fe^{III}Fe_2^{II}F_6(SO_4)_2][H_3O]$.

ESSENTIALS OF INORGANIC MATERIALS SYNTHESIS

C.N.R. RAO

KANISHKA BISWAS

International Center for Materials Science & New

Chemistry Unit

Jawaharlal Nehru Centre for Advanced Scientific Research

Bangalore, India

WILEY

Copyright © 2015 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey

Published simultaneously in Canada

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permissions>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Rao, C.N.R. (Chintamani Nagesa Ramachandra), 1934- author.

Essentials of inorganic materials synthesis / C.N.R. Rao, Kanishka Biswas.
pages cm

Includes bibliographical references and index.

ISBN 978-1-118-83254-7 (hardback)

1. Inorganic compounds--Synthesis. I. Biswas, Kanishka, author. II. Title. QD156.R36 2014 541'.39-dc23

2014035381

AUTHOR BIOGRAPHIES



C.N.R. Rao obtained his Ph.D. degree from Purdue University (1958) and D.Sc. degree from the University of Mysore (1961). He is the National Research Professor and Linus Pauling Research Professor at the Jawaharlal Nehru Centre for Advanced Scientific Research and Honorary Professor at the Indian Institute of Science (both at Bangalore). His research interests are mainly in the chemistry of materials. He is a fellow of the Royal Society, London, a foreign associate of the US National Academy of

Sciences and a member of many other science academies. He is the recipient of the Einstein Gold Medal of UNESCO, the Hughes and Royal Medals of the Royal Society, the August Wilhelm von Hofmann medal of the German Chemical Society, the Dan David Prize and the Illy Trieste Science prize for materials research and the first India Science Prize.



Kanishka Biswas obtained his Ph.D. degree from Solid State Structural Chemistry Unit, Indian Institute of Science, India (2009), and did his postdoctoral research from Department of Chemistry, Northwestern University, USA (2009–2012). He is now a Assistant Professor (Faculty Fellow) in the New Chemistry Unit of Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India. He is an Associate of Indian Academy of Sciences,

Bangalore. He is pursuing research in solid-state chemistry of metal chalcogenides and thermoelectric 'waste heat to electrical energy conversion'.

PREFACE

Chemical methods of synthesis play a crucial role in designing and discovering novel materials, especially metastable ones which cannot be prepared otherwise. They often provide better and less cumbersome methods for preparing known materials. There is a tendency nowadays to avoid brute-force methods and instead employ methods involving mild reaction conditions. Soft-chemistry routes are indeed becoming popular and will continue to be pursued greatly in the future. In view of the increasing importance of materials synthesis, we considered it appropriate to provide a proper account of the chemical methods of synthesis of inorganic materials in a book.

John Wiley had published a small monograph written by the first author of this book entitled *Chemical Approaches to the Synthesis of Inorganic Materials* some years ago (1994). We felt the need for a book which was more complete and yet handy, covering most of the synthetic methods employed by chemists and materials scientists. We believe that the present work answers such a need.

In this book, we briefly examine the different types of reactions and methods employed in the synthesis of inorganic solid materials. Besides the traditional ceramic procedures, we discuss precursor methods, combustion method, topochemical reactions, intercalation reactions, ion-exchange reactions, alkali-flux method, sol-gel method, mechanochemical synthesis, microwave synthesis, electrochemical methods, pyrosol process, arc and skull methods and high-pressure methods. Hydrothermal and solvothermal syntheses are discussed separately and also in sections dealing with specific materials.

Superconducting cuprates and intergrowth structures are

discussed in separate sections. Synthesis of nanomaterials is dealt with in some detail. Synthetic methods for metal borides, carbides, nitrides, fluorides, silicides, phosphides and chalcogenides are also outlined.

While this book is not expected to serve as a laboratory guide, it is our hope that it provides an up-to-date account of the varied aspects of chemical synthesis of inorganic materials and serves as a ready reckoner as well as a guide to students, teachers and practitioners. The key references cited in the monograph would help to obtain greater details of preparative procedures and related aspects.

Bangalore
2015

C.N.R. Rao
Kanishka Biswas

1

INTRODUCTION

Much chemical ingenuity is involved in the synthesis of solid materials [1–6] and this aspect of material science is getting increasingly recognized as a crucial component of the subject. Tailor-making materials of the desired structure and properties is the main goal of material science and solid-state chemistry, but it may not always be possible to do so. While one can evolve a rational approach to the synthesis of solid materials [7], there is always an element of serendipity, encountered not so uncommonly. A good example of an oxide discovered in this manner is NaMo_4O_6 ([Fig. 1.1](#)) containing condensed Mo_6 octahedral metal clusters [8]. This was discovered by Torardi and McCarley in their effort to prepare the lithium analogue of $\text{NaZn}_2\text{Mo}_3\text{O}_8$. Another chance discovery is that of the phosphorus-tungsten bronze, $\text{Rb}_x\text{P}_9\text{W}_{32}\text{O}_{112}$, formed by the reaction of phosphorus present in the silica of the ampoule, during the preparation of the Rb-WO_3 bronze [9]. Since the material could not be prepared in a platinum crucible, it was suspected that a constituent of the silica ampoule must have got incorporated. This discovery led to the synthesis of the family of phosphorus-tungsten bronzes of the type $\text{A}_x\text{P}_4\text{O}_8(\text{WO}_3)_{2m}$. Chevrel compounds of the type $\text{A}_x\text{MO}_6\text{S}_8$ ($\text{A} = \text{Cu}, \text{Pb}, \text{La}$ etc.) shown in [Figure 1.2](#) were also discovered accidentally [10].

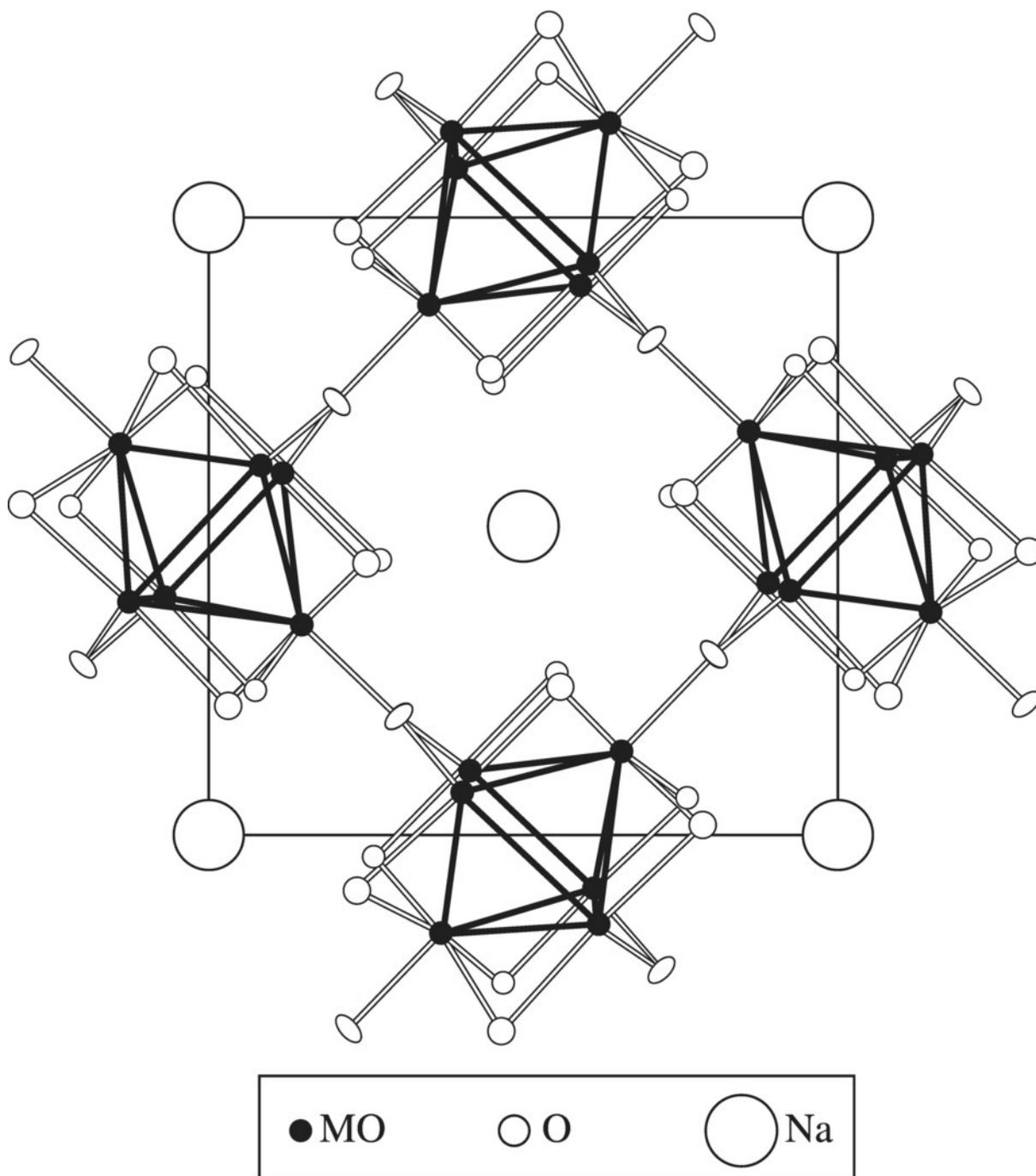


Figure 1.1 Structure of NaMo₄O₆.

(From Ref. 8, Torardi et al., *J. Am. Chem. Soc.*, **101** (1979) 3963. © 1979, American Chemical Society)

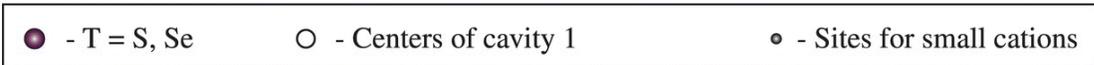
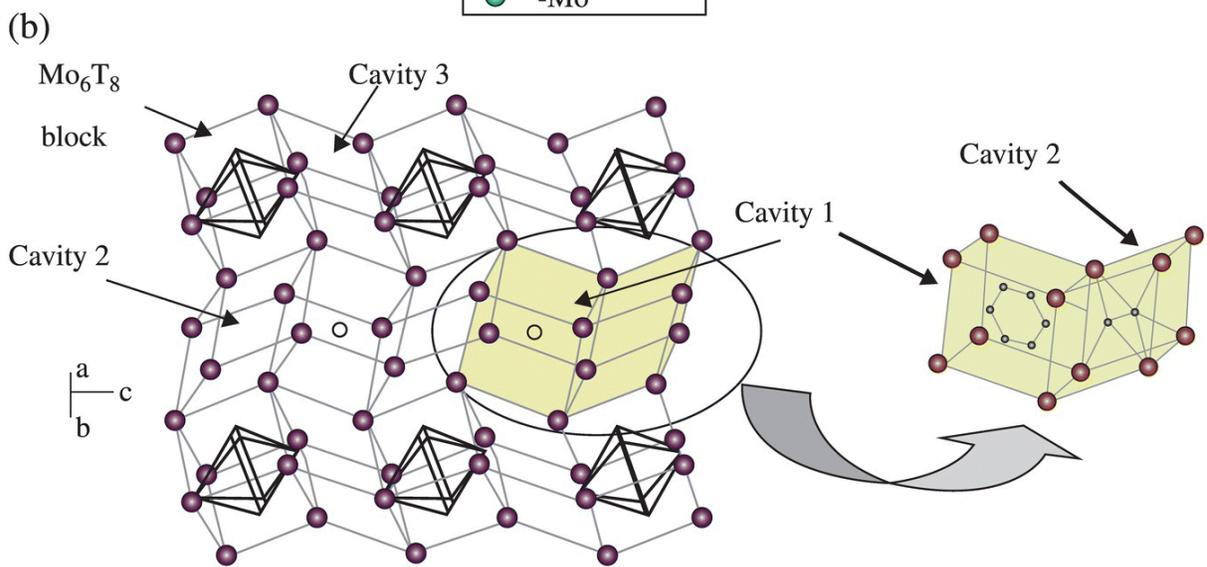
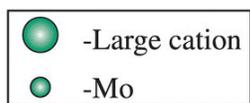
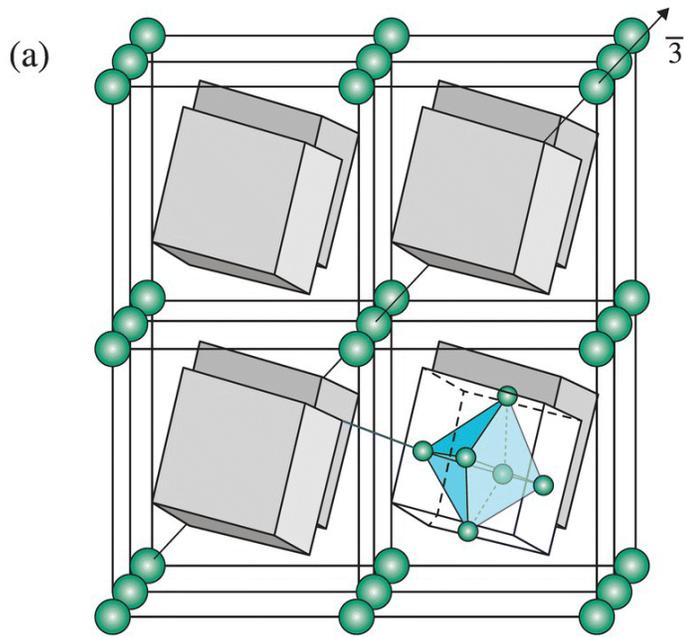


Figure 1.2 Crystal structure of Chevrel phases. (a) Type I with large cation in the origin (eight rhombohedral unit cells): each cation is surrounded by eight Mo_6T_8 blocks. The internal structure is shown for one of the blocks. Intercluster Mo-T₁ bond is marked in blue. (b) Three types of pseudocubic cavities between the Mo_6T_8 blocks. Cavities 1 and 2 form the diffusion channels in three directions (a channel in one of the directions is shown here). Sites for small cations in cavities 1 and 2 are presented separately on the right.

Rational synthesis of materials requires knowledge of crystal chemistry besides thermodynamics, phase equilibria and reaction kinetics. There are several examples of rational synthesis. A good example is SIALON [11], where Al and oxygen were partly substituted for Si and nitrogen in Si_3N_4 . The fast Na^+ ion conductor NASICON, $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$ (Fig. 1.3), was synthesized with a clear understanding of the coordination preferences of the cations and the nature of the oxide networks formed by them [12]. The zero-expansion ceramic $\text{Ca}_{0.5}\text{Ti}_2\text{P}_3\text{O}_{12}$ possessing the NASICON framework was later synthesized based on the idea that the property of zero-expansion would be exhibited by two or three coordination polyhedra linked in such a manner as to leave substantial empty space in the network [7]. Synthesis of silicate-based porous materials, making use of organic templates to predetermine the pore or cage geometries, is well known [13]. A microporous phosphate of the formula $(\text{Me}_4\text{N})_{1.3}(\text{H}_3\text{O})_{0.7} \text{Mo}_4\text{O}_8(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, where the tetramethyl-ammonium ions fill the voids in the 3-dimensional structure made up of Mo_4O_8 cubes and PO_4 tetrahedra, has been prepared in this manner [14].

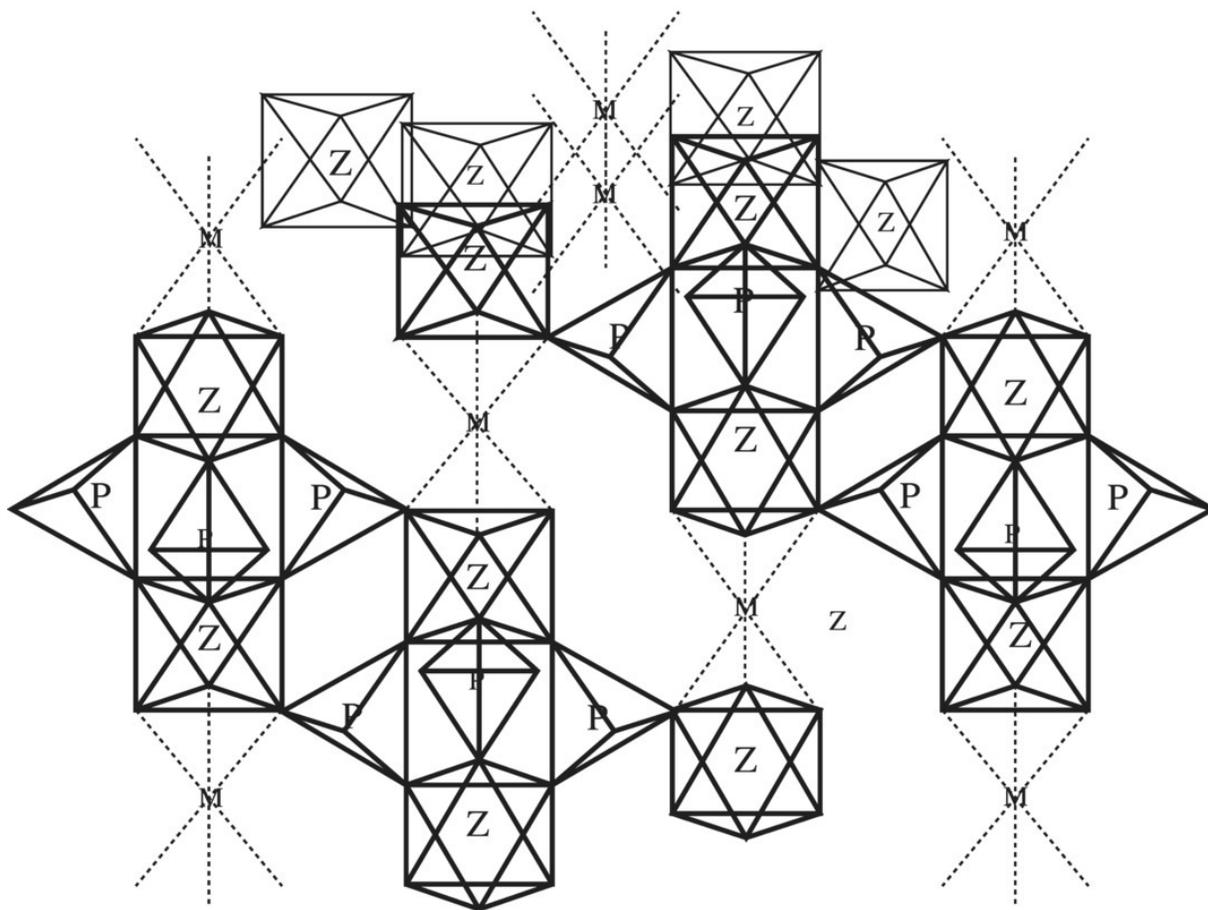


Figure 1.3 Structure of NaZr₂(PO₄)₃ which provided the design for NASICON: vacant trigonal-prismatic sites, p; octahedral Zr⁴⁺ sites, Z; and octahedral sites available for Na⁺, M. For each M, there are three Mo sites forming hcp layers perpendicular to the *c*-axis.

A variety of inorganic solids have been prepared in the past several years by the traditional ceramic method, which involves mixing and grinding powders of the constituent oxides, carbonates and such compounds, and heating them at high temperatures with intermediate grinding when necessary. A wide range of conditions, often bordering on the extreme, such as high temperatures and pressures, very low oxygen fugacities and rapid quenching, have been employed in material synthesis. Low-temperature chemical routes and methods involving mild reaction conditions are,