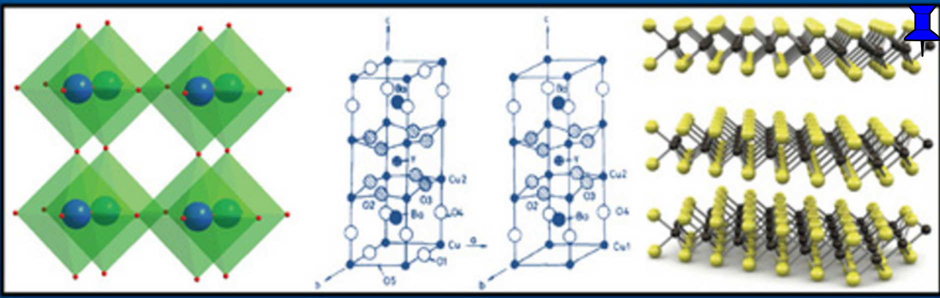
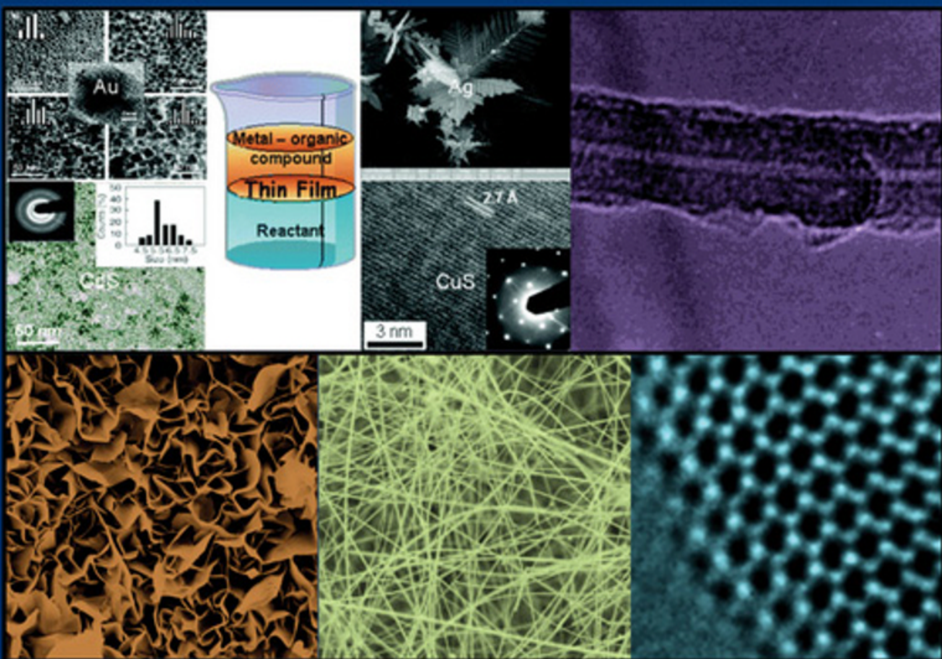


Essentials of

Inorganic Materials Synthesis



C. N. R. Rao • Kanishka Biswas

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ESSENTIALS OF INORGANIC MATERIALS SYNTHESIS

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CONTENTS

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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

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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 $NaZn_2Mo_3O_8$. Another chance discovery is that of the phosphorus–tungsten bronze, $Rb_xP_9W_{32}O_{112}$, 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 $A_xP_4O_8\,(WO_3)_{2m}$. Chevrel compounds of the type $A_xMO_6S_8$ (A = Cu, Pb, La etc.) shown in Figure 1.2 were also discovered accidentally [10].

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, $Na_3Zr_2PSi_2O_{12}$ (Fig. 1.3), was synthesized with a clear understanding of the

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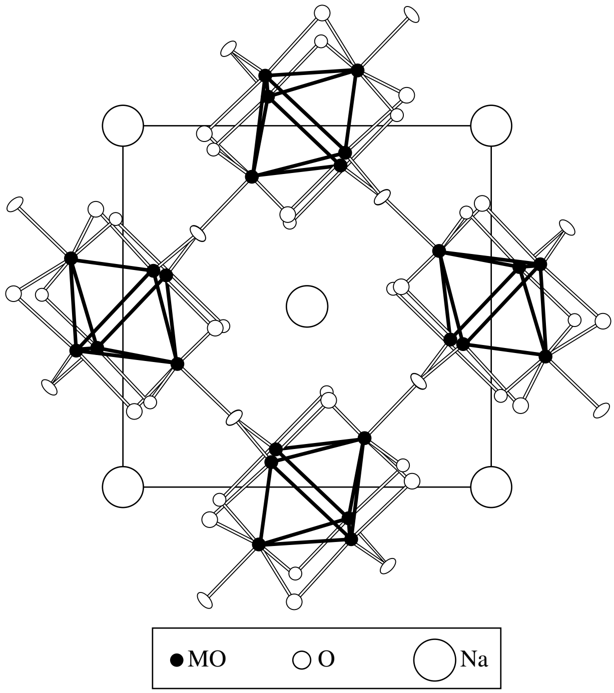

FIGURE 1.1 Structure of $NaMo_4O_6$ (From Ref. 8, Torardi et al., *J. Am. Chem. Soc.*, **101** (1979) 3963. © 1979, American Chemical Society).

coordination preferences of the cations and the nature of the oxide networks formed by them [12]. The zero-expansion ceramic $Ca_{0.5}Ti_2P_3O_{12}$ 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 $(Me_4N)_{1.3}(H_3O)_{0.7}$ $Mo_4O_8(PO_4)_2{\cdot}2H_2O$, where the tretramethyl–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].

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, however, of greater interest. The present-day trend is to avoid brute-force methods in order to get a better control of the structure, stoichiometry and phasic purity.

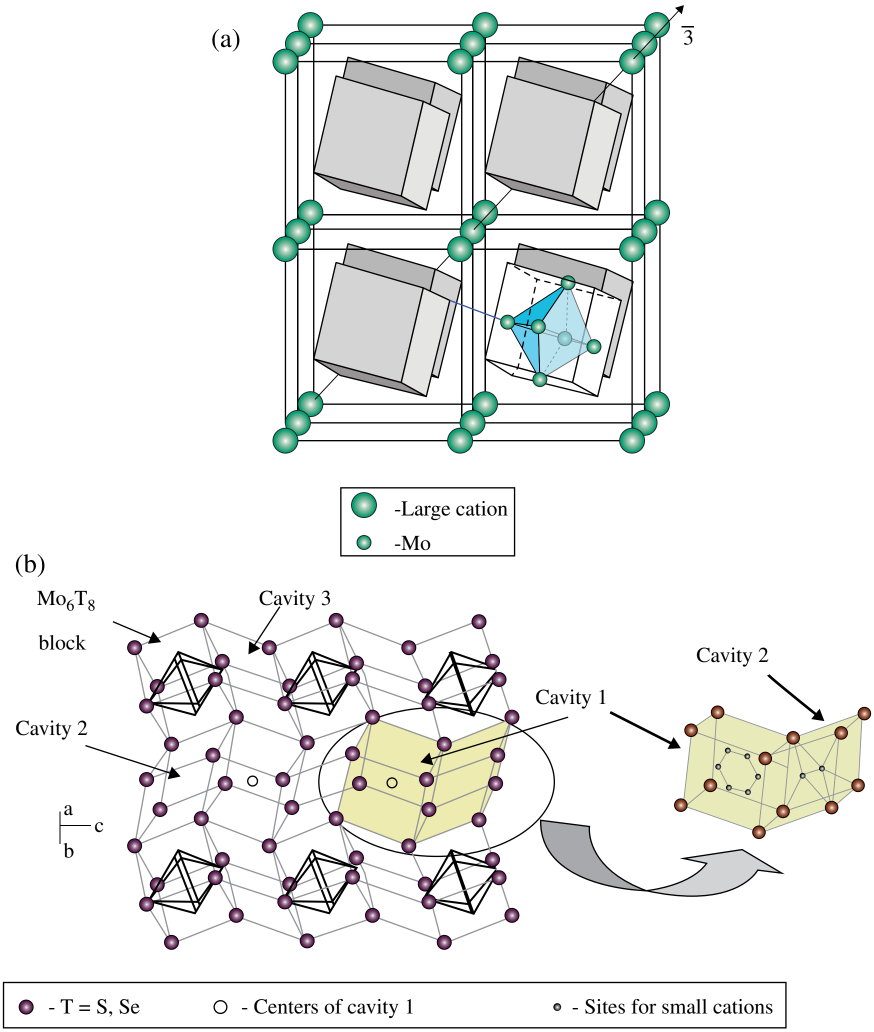

FIGURE 1.2 Crystal structure of Chevrel phases. (a) Type I with large cation in the origin (eight rhombohedral unit cells): each cation is surrounded by eight Mo_6T_8 blocks. The internal structure is shown for one of the blocks. Intercluster Mo–T_1 bond is marked in blue. (b) Three types of pseudocubic 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.

Soft-chemistry routes, which the French call *chimie douce*, are indeed desirable because they lead to novel products, many of which are metastable and cannot otherwise be prepared. Soft-chemistry routes essentially make use of simple reactions such as intercalation, ion exchange, hydrolysis, dehydration and reduction that can be carried out at relatively low temperatures. The topochemical nature of certain

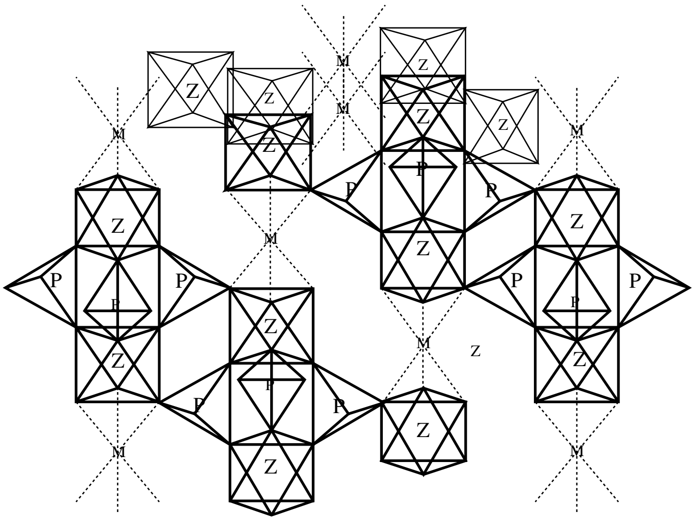

FIGURE 1.3 Structure of $NaZr_2(PO_4)_3$ which provided the design for NASICON: vacant trigonal–prismatic sites, p; octahedral Zr^{4+} sites, Z; and octahedral sites available for Na^+, M. For each M, there are three Mo sites forming hcp layers perpendicular to the *c*-axis.

solid-state reactions is also exploited in synthesis. Ion exchange, intercalation and many other types of reactions are generally topochemical.

Many of the materials that are prepared are metastable. Metastable phases possess higher free energy than the corresponding stable phases of the same composition. Metastability can arise from frozen disorder and/or defects (e.g. glasses, ionic conductors). Topological metastability is found in porous materials including zeolites. Nanocrystals of many materials crystallize in metastable structures due to the excess surface free energy. Kinetics determine the evolution of structures in many instances and the metastable phases are favoured when the system is far from a state of equilibrium. In the case of zeolitic materials or aluminosilicates, the dense phases are thermodynamically stable, but the useful phases are less dense, porous and metastable. Metastable materials are often formed by quenching from high temperature or pressure, or by using soft-chemical routes. Atomic layer deposition or layer-by-layer deposition can be used to prepare metastable structures.

In the sections that follow, we briefly discuss the synthesis of inorganic solids by various methods with several examples, paying attention to the chemical routes. While oxide materials occupy a great part of the monograph, other classes of materials such as chalcogenides, carbides, fluorides and nitrides are also discussed. Superconducting oxides, intermetallics, porous materials and intergrowth structures have been discussed in separate sections. We have added a new section on nanomaterials.

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2

COMMON REACTIONS EMPLOYED IN SYNTHESIS

Various types of chemical reactions are used in the synthesis of inorganic materials [1, 2]. Corbett [1] has written a fine article on the subject. Some of the common reactions employed for the synthesis of inorganic materials are described as follows:

1. **Decomposition**

$$A(s) \rightarrow B(s) + C(g)$$
$$A(g) \rightarrow B(s) + C(g)$$

2. **Addition**

$$A(s) + B(g) \rightarrow C(s)$$
$$A(s) + B(s) \rightarrow C(s)$$
$$A(s) + B(l) \rightarrow C(s)$$
$$A(g) + B(g) \rightarrow C(s)$$

3. **Metathetic reaction (which combines 1 and 2)**

$$A(s) + B(g) \rightarrow C(s) + D(g)$$

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4. Other exchange reactions

$$AX(s) + BY(s) \rightarrow AY(s) + BX(s)$$
$$AX(s) + BY(g) \rightarrow AY(s) + BX(g)$$
$$AX(s) + BY(1) \rightarrow AY(s) + BX(s)$$

Typical examples of these reactions are as follows:

1. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

   $M_mO_n(s) \rightarrow M_mO_{n-\delta}(s) + \frac{\delta}{2}O_2(g) \quad (M = \text{metal})$

   $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$

2. $YBa_2Cu_3O_6(s) + O_2(g) \rightarrow YBa_2Cu_3O_7(s)$

   $ZnO(s) + Fe_2O_3(s) \rightarrow ZnFe_2O_4(s)$

   $BaO(s) + TiO_2(s) \rightarrow BaTiO_3(s)$

   $Cd(s,1) + CdX_2(s,1) \rightarrow Cd_2X_2(s)$

3. $CO(g) + MnO_2(s) \rightarrow CO_2(g) + MnO(s)$

   $Pr_6O_{11}(s) + 2H_2(g) \rightarrow 3Pr_2O_3(s) + 2H_2O(g)$

   $MO_n(s) + nH_2S(g) \rightarrow MS(s) + nH_2O(g) \quad (M = \text{Metal})$

   $SiCl_4(g) + 2H_2(g) \rightarrow Si(g) + 4HCl(g)$

   $3SiCl_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12HCl(g)$

   $GaMe_3(g) + AsH_3(g) \rightarrow GaAs(g) + 3CH_4(g)$

   $MR_x(g) + M'R'_y(g) \rightarrow MM'(s) + R_xR'_y(g) \quad (R = \text{alkyl}, M = \text{Cd, Te etc.})$

   $(NH_4)_2MoS_4(s) + H_2(g) \rightarrow MoS_2(g) + 2NH_3(g) + 2H_2S(g)$

4. $ZnS(s) + CdO(s) \rightarrow CdS(s) + ZnO(s)$

   $MnCl_2(s) + 2HBr \rightarrow MnBr_2(s) + 2HCl$

   $LiFeO_2(s) + CuCl(1) \rightarrow CuFeO_2(s) + LiCl(s)$

Complex reactions involving more than one type of reaction are employed in solid-state synthesis. For example, in the preparation of complex oxides, it is common to carry out thermal decomposition of a compound followed by oxidation (in air or O_2) essentially in one step.

$$2Ca_{0.5}Mn_{0.5}CO_3(s) + \frac{1}{2}O_2(g) \rightarrow CaMnO_3(s) + 2CO_2(g)$$

Vapour phase reactions and liquid–gas reactions yield solid products in many instances. For example, the reaction of $TiCl_4$ and H_2S gives solid TiS_2 and HCl gas. Reaction of metal halides with NH_3 to yield nitrides is another example.

In chemical vapour transport reactions, a gaseous reagent acts as a carrier to transport a solid by transforming it into the vapour state. For example, $MgCr_2O_4$ cannot be readily formed by the reaction of MgO and Cr_2O_3. However, Cr_2O_3 (s) reacts with O_2 giving CrO_3 (g), which then reacts with MgO giving the chromate. The overall reaction is

$$MgO(s) + Cr_2O_3(s) \xrightarrow{O_2} MgCr_2O_4(s)$$

Some of the typical transport reaction equilibria are

$$ZnS(s) + I_2 \rightleftarrows ZnI_2 + \frac{1}{2}S_2$$

$$TaOCl_2(s) + TaCl_5 \rightleftarrows TaOCl_3 + TaCl_4$$

$$Nb_2O_5(s) + 3NbCl_5 \rightleftarrows 5NbOCl_3$$

$$GaAs(s) + HCl \rightleftarrows GaCl + \frac{1}{2}H_2 + As$$

Transport of two substances in opposite directions is possible if the reactions have opposite heats of reaction. For example, Cu_2O and Cu can be separated by using HCl as the transporting agent.

$$Cu_2O(s) + 2HCl(g) \underset{1070\ K}{\overset{770\ K}{\rightleftarrows}} 2CuCl(g) + H_2O(g)$$

$$Cu(s) + HCl(g) \underset{770\ K}{\overset{870\ K}{\rightleftarrows}} CuCl(g) + \frac{1}{2}H_2(g)$$

Another example of this kind is the separation of WO_2 and W by using I_2 (g), involving the formation of WO_2I_2 (g). Volatility of the product also allows its separation from other species. Thus, the reaction of Cl_2 gas with a solid mixture of Al_2O_3 and carbon yields $AlCl_3$ and CO gas.

Vapour transport methods are used in the synthesis of materials as exemplified by the reaction of MgO and Cr_2O_3; another example is the formation of $NiCr_2O_4$ involving the CrO_3 (g) species:

$$Cr_2O_3(s) + \frac{3}{2}O_2(g) \rightleftarrows 2CrO_3(g)$$

$$2CrO_3(g) + NiO(s) \rightarrow NiCr_2O_4(s) + \frac{3}{2}O_2(g)$$

The formation of Ca_2SnO_4 by the reaction of CaO and SnO_2 is facilitated by CO via the formation of gaseous SnO, which then reacts with CaO. $ZnWO_4$ is made by heating ZnO and WO_3 at 1330 K in the presence of Cl_2 gas (volatile chlorides being the intermediates). In the reaction of Al and sulfur to form Al_2S_3 by using I_2, the sulfide is transported through the formation of AlI_3.

$$2Al + 3S \rightarrow Al_2S_3$$

$$Al_2S_3(s) + 3I_2(g) \rightleftarrows 2AlI_3(g) + \frac{3}{2}S_2(g)$$

Cu_3TaSe_4 is formed by the reaction of Cu, Ta and Se in the presence of gaseous I_2. In Table 2.1, we list a few examples of the chemical transport system. Table 2.2 lists some crystals grown by the chemical vapour transport method.

Oxidation of many metals occurs slowly. Thus, oxidation of Cu stops at the stage of Cu_2O at 1270 K in oxygen. In order to promote further oxidation (e.g. to CuO in the case of Cu), an easily oxidizable salt is used (e.g. CuI → CuO at 620 K). Similarly, fluorination of a compound may be easier than that of the native metal (e.g. $CuCl_2 \rightarrow CuF_2$ in the presence of F_2, instead of $Cu + F_2$).

Reduction of oxides is carried out in an atmosphere of (flowing) pure or dilute hydrogen (e.g. N_2–H_2 mixtures) or sometimes in an atmosphere of CO or CO–CO_2 mixtures. Reduction of oxides for the purpose of lowering the oxygen content is also

TABLE 2.1 Examples of Chemical Transport

Solid	Transporting agent	Solid	Transporting agent
Nb_2O_5	Cl_2, $NbCl_5$	CrOCl	Cl_2
TiO_2	$I_2 + S_2$	$FeWO_4$	Cl_2
IrO_2	O_2	$MgFe_2O_4$	HCl
WO_3	H_2O	$CaNb_2O_6$	Cl_2, HCl
NbS_2	S	ZrOS	I_2
TaS_3	S	$LaTe_2$	I_2
$MnGeO_3$	HCl	V_nO_{2n-1}	$TeCl_4$
$MgTiO_3$	Cl_2	NbS_2Cl_2	$NbCl_4$

TABLE 2.2 Examples of Crystals Grown by Chemical Transport

Starting materials	Product (crystal grown)	Transporting agent	*T* (K)
SiO_2	SiO_2	HF	470–770
Fe_3O_4	Fe_3O_4	HCl	1270–1070
Cr_2O_3	Cr_2O_3	$Cl_2 + O_2$	1070–870
$MO + Fe_2O_3$ (M = Mg, Co, Ni)	MFe_2O_4	HCl	–
$Nb + NbO_2$	NbO	Cl_2	–
$NbSe_2$	$NbSe_2$	I_2	1100–1050

achieved by heating oxides in argon or nitrogen or by using other metals as getters (e.g. Ti or Zr sponge, molten Na) to remove some of the oxygen. Thus, the oxygen content of $YBa_2Cu_3O_{7-\delta}$ can be varied by heating in N_2 or in the presence of hot Ti sponge. Application of vacuum at an appropriate temperature (vacuum annealing or decomposition at low pressures) is also used. Exact control of oxygen stoichiometry in oxides such as Fe_3O_4 or V_2O_3 is accomplished by annealing the oxide in CO–CO_2 mixtures of known oxygen fugacity at an appropriate temperature. In preparing oxides of exact stoichiometry, it is necessary to have the fugacity diagrams of the type shown in Figure 2.1. The obvious means of reducing solid compounds is by hydrogen. Hydrogen reduction is employed for reducing not only oxides, but also halides and other compounds. Thermal decomposition of metal halides often yields lower halides.

$$M_2O_3(s) + H_2(g) \rightarrow 2MO(s) + H_2O(g) \quad (\text{e.g. } M = Fe)$$

$$ABO_3(s) + H_2(g) \rightarrow ABO_{2.5}(s) + \frac{1}{2}H_2O(g) \quad (\text{e.g. } LaCoO_3 \text{ and } CaMnO_3)$$

$$MCl_3(s) + H_2(g) \rightarrow MCl_2(s) + HCl(g) \quad (\text{e.g. } M = Fe, Cr)$$

$$MCl_2(s) + H_2(g) \rightarrow M(s) + 2HCl(g) \quad (\text{e.g. } M = Cr)$$

$$MX_3 \xrightarrow{\text{heat}} MX_2 + \frac{1}{2}X_2 \quad (\text{e.g. } M = Cr)$$

Reduction of oxides can be accomplished by reacting with elemental carbon or with a metal. Reduction of halides is also carried out by metals.

$$2MCl_3 + M \rightarrow 3MCl_2 (\text{e.g. } M = Nd, Fe)$$

$$3MCl_4 + M'(s) \rightarrow 3MCl_3(s) + M'Cl_3(g)$$

$$Nb_2O_5 + 3Nb \rightarrow 5NbO$$

$$TiO_2 + Ti \rightarrow 2TiO$$

Metals such as aluminium are used as reducing agents for other metal halides.

$$3HfCl_4 + Al \rightarrow 3HfCl_3 + AlCl_3$$

Metal oxychlorides are obtained by heating oxides with Cl_2 (LaOCl from La_2O_3). Fluorination is generally carried out by using elemental fluorine, HF or other fluorine compounds (see Section 14.3 for details). There are examples where oxides are reacted with a fluoride such as BaF_2 to attain partial fluorination. Sulfidation is generally carried out by heating the metal and sulfur together in a sealed tube (see Section 14.2). Oxides can be sulfided by heating them in a stream of H_2S or CS_2.

Plasma or electrical discharge reactions have been employed for material synthesis. Amorphous silicon is produced by the decomposition of SiH_4 under discharge. Unusual compounds such as $ZrCl_3$ are obtained by rapid quenching of the plasma out