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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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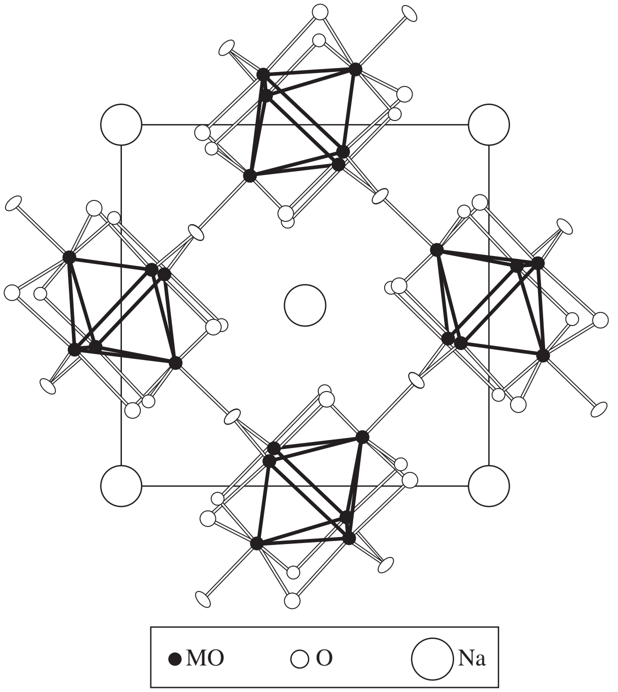

FIGURE 1.1 Structure of $NaMo_4O_6$ (From Ref. 8, Torardi et al., *J. Am. Chem. Soc.*, **101** (1979) 3963. © 1979, American Chemical Society).

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.

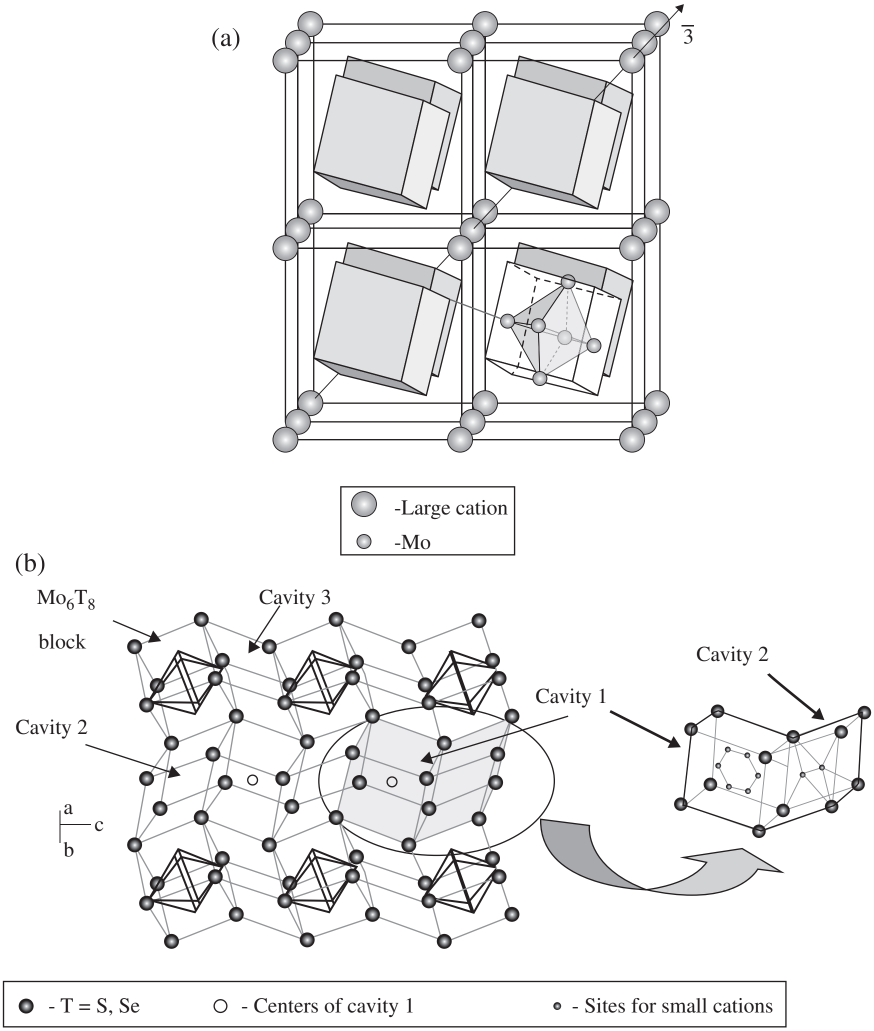

FIGURE 1.2 Crystal structure of Chevrel phases. (a) Type I with large cation in the origin (eight rhombohedral unit cells): each cation is surrounded by eight Mo_6T_8 blocks. The internal structure is shown for one of the blocks. Intercluster Mo–T_1 bond is marked in blue. (b) Three types of pseudocubic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

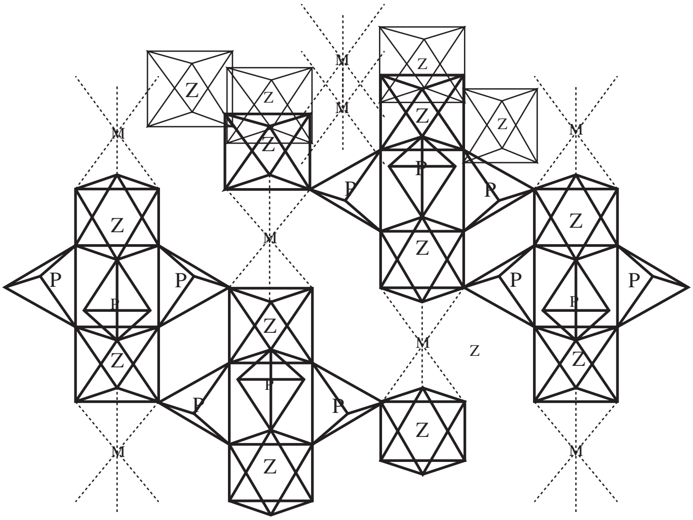

FIGURE 1.3 Structure of NaZr$_2$(PO$_4$)$_3$ which provided the design for NASICON: vacant trigonal–prismatic sites, p; octahedral Zr^{4+} sites, Z; and octahedral sites available for Na$^+$, M. For each M, there are three Mo sites forming hcp layers perpendicular to the *c*-axis.

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.

REFERENCES

[1] P. Hagenmuller (ed), *Preparative Methods in Solid State Chemistry*. Academic Press, New York, 1972.

[2] C.N.R. Rao and J. Gopalakrishnan, *New Directions in Solid State Chemistry*, Cambridge University Press, Cambridge, 1986, paperback ed. 1989, Second Edition 1997.

[3] A.R. West, *Solid State Chemistry and Applications*. John Wiley & Sons, Chichester, 1984.

[4] F.J. Di Salvo, *Science*, **247** (1990) 647.

[5] A.K. Cheetham and P. Day (eds), *Solid State Chemistry – Techniques and Compounds*, Clarendon Press, Oxford, 1987 and 1992.

[6] C.N.R. Rao (ed), *Chemistry of Advanced Materials* (IUPAC 21st Century Monograph Series), Blackwell, Oxford, 1992.

[7] R. Roy, *Solid State Ionics*, **32–33** (1989) 3.

[8] C. Torardi and R.E. McCarley, *J. Am. Chem. Soc.*, **101** (1979) 3963.

[9] J.P. Giroult, M. Goreaud, P.H. Labbe and B. Raveau, *Acta Cryst.*, **B36** (1980) 2570.

[10] K. Yvon, *Current Topics in Materials Science*, Vol. 3 (E. Kaldis, ed), North-Holland, Amsterdam, 1979.

[11] K.H. Jack, *Mater. Res. Bull.*, **13** (1973) 1327.

[12] J.B. Goodenough, H.Y.P. Hong and J.A. Kafalas, *Mater. Res. Bull.*, **11** (1976) 203.

[13] J.M. Newsam, in *Solid State Chemistry-Compounds* (A.K. Cheetham and P. Day, eds), Clarendon Press, Oxford, 1992.

[14] R.C. Haushalter, K.G. Storhmaeu and F.W. Lai, *Science*, **246** (1989) 1289.