Solid State Chemistry
Techniques

Edited by

A. K. Cheetham

and

P. Day

Solid State Chemistry

Techniques

Edited by

A. K. Cheetham

University Lecturer in Chemical Crystallography
University of Oxford

and

P. Day

University Lecturer in Inorganic Chemistry
University of Oxford

List of contributors

D. M. ADAMS
Department of Chemistry, The University, Leicester LE1 7RH, UK

C. R. A. CATLOW
Department of Chemistry, University College, 20 Gordon Street, London WC1, UK

A. K. CHEETHAM
Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, UK

J. D. CORBETT
Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA. (Ames Laboratory is operated for US Department of Energy by Iowa State University under contract No. W-7405-Eng-82.)

R. G. DENNING
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

C. A. FYFE
Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Ontario N1G 2W1, Canada

A. HAMNETT
Inorganic University Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

W. E. HATFIELD
Department of Chemistry, The University of North Carolina at Chapel Hill, Venable and Kenan Laboratories 045 A, Chapel Hill, North Carolina NC 27514, USA

A. NAVROTSKY
Department of Geological and Geophysical Sciences, Princeton University, Guyot Hall, Princeton, New Jersey 08544, USA.

R. E. WASYLISHEN
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4H6, Canada

G. K. WERTHEIM
Bell Laboratories, Murray Hill, New Jersey NJ 07974, USA

Preface

The continuing worldwide search for new and useful materials has ensured that the solid state is one of the major growth areas of chemistry and there is a widely perceived need for good, up-to-date textbooks in the area. This book, like the previous volume which dealt with Techniques, is aimed at final-year honours and postgraduate students who may be planning a career in the field. As with Volume 1, we chose a multiauthor approach in order that our account should be more authoritative, and we are delighted and encouraged by the very positive response from colleagues who were invited to contribute. The book deals first with bonding in solids, and then focuses on several classes of important inorganic materials. Whilst we have been able to cover many key areas, including superconductors and zeolite catalysts, our coverage is not as comprehensive as this wide-ranging subject deserves. Significant omissions that we hope to fill in a subsequent edition include optoelectronic and magnetic materials and solid electrolytes. Nevertheless, we hope that readers will find this a useful and interesting book, and that it will be perceived as a valuable complement to Volume 1.

Oxford
December 1991

A.K.C.
P.D.

Contents

10 Thermodynamic aspects of inorganic solid-state chemistry

1 Synthesis of solid-state materials†

J. D. Corbett

1.1 Introduction

The fields of solid-state chemistry and physics are important because the chemical and physical properties of infinite non-molecular solids are so different from those associated with discrete molecules in solids or, as more frequently studied, molecules or small ions in solution. Likewise, the first requirement for a solid-state study, the synthesis and some characterization of the material of interest, usually involves techniques and concepts that are very different from those conventionally applied in molecular studies. The preparation of 'pure' and well-defined, and perhaps even novel, inorganic phases is the subject of this chapter. Some of the needs and opportunities in solid state synthesis have been outlined by Warren and Geballe.[1]

Our approach will be to describe the classes of reactions possible, the difficulties which are characteristically associated with each (and the means for avoiding some of these), and some bases for the selection of a synthetic method; although clearly we cannot go further than to categorize compounds and reactions with a few examples. Many properties of solid materials will be important in these considerations, but none will be more significant than the rate of diffusion or mass transfer within, and between, solid particles. Solid-state reactions and the successful synthesis of single-phase, homogeneous products are often very much at the mercy of these intrinsically slow (but still highly variable) processes. The use of high temperatures in synthesis is a common means of improving these rates, but a consequence of this is that much solid-state chemistry at lower temperatures is lost. One may to some extent alleviate these restrictions on reactivity through the use of liquid- or gas-phase materials with their intrinsically much higher mobilities and shorter effective path lengths, but sometimes only with some sacrifices. Vaporization equilibria which allow the transfer of solid phases through the vapour state will be especially useful here. Other means of

achieving reactivity as well as factors in the choice of reactants will also be considered.

Some mechanistic aspects of reactions between real solids are important for understanding later considerations. For more details the reader should see Steele (Vol. 2),[2] or the more extensive Hannay[3] or Schmalzried[4] volumes. The relevant process is the so-called chemical diffusion, that of a substitutional component under composition gradient which takes place via vacant lattice and interstitial sites. As a reaction this is strictly only pertinent to solid solutions, in exchange reactions, for example. A simple but informative description by which a third phase is formed by diffusion can be visualized as follows. For a reaction of the type $M_2Y(s) + LY(s) \rightarrow M_2LY_2(s)$, presume that the diffusion of M and L are responsible for the mass transfer, the common anion serving as a fixed reference matrix. An interface between M_2Y and LY would be transformed to the intervening product M_2LY_2 by the scheme

M_2Y	M_2LY_2	LY

$$\xrightarrow{2M^{n+}}$$
$$\xleftarrow{L^{2n+}}$$
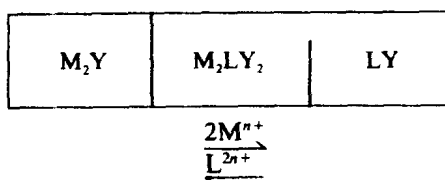
the indicated fluxes being fixed by electroneutrality. This reaction now includes the transfer of M and L across the phase boundaries together with the chemical diffusion of M and L as shown through the product phase to the opposite boundary. Unfortunately *real* synthetic reactions of this character are even more complicated, and consequently are less well studied and understood, so that making new phases in all-solid reactions is in practice more empirical. Because material transfer is facilitated by large areas of interphase contact, small diffusion pathlengths and minimum pore volume, it is customary to employ powdered reactants, usually in a compressed form. But real systems also involve the generally much more rapid diffusion on surfaces and along dislocations, and both of these also become more important in powdered samples. Of course the product is also apt to be defect-laden, which will increase reactant mobilities therein, and changes in grain boundary area and free volume usually also occur during the reaction. On the other hand, some products may form a compact and cohesive layer through which there is negligible reactant diffusion so the reaction virtually stops (tarnishing or surface blockage).

Nucleation of the new phase in most systems is not at all well understood. Nucleation in simple decomposition reactions is well known to be favoured at dislocation and defect sites. But in some oxide systems, anion defects are highly organized into crystallographic shear planes, and oxidation or reduc-

tion by H_2/H_2O mixtures occur by motion of these planes, with the reactant and product phases growing in fixed orientation (topotaxy).[5]

1.1.1 Reaction types

Our discussion of the many aspects of synthesis will be helped if we first identify classes of possible reactions and their individual advantages and problems. One common group of reactions involve gases except for one solid reactant and the desired product D(s). The most common is the metathetical or exchange reaction (1.1)

$$A(g) + B(s) \rightarrow C(g) + D(s) \qquad [\text{e.g. } CO + MnO_2 \rightarrow CO_2 + MnO] \quad (1.1)$$
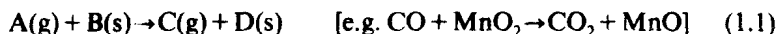
while the related combination and decomposition reactions (1.2) and (1.3), which lack C or A, are also useful,

$$A(g) + B(s) \rightarrow D(s) \tag{1.2}$$

$$B(s) \rightarrow C(g) + D(s). \tag{1.3}$$

The use of gaseous reactants naturally facilitates the conversions, while problems may arise with these routes from the dynamic (non-equilibrium) nature of processes (as usually carried out) as well as diffusion limitations as D forms on the surface of particles of B. Some mechanistic details of nucleation and growth of D have received substantial attention in reaction (1.2) for the oxidation of metals and for (1.3), in decomposition reactions.[3]

Synthesis with condensed phases may sometimes be conveniently performed 'neat' (i.e. on stoichiometry to yield a single phase) if one reactant is liquid,

$$A(l) + B(s,l) \rightarrow D(s) \qquad [\text{e.g. } 2NdCl_3 + Nd \rightarrow 3NdCl_2]. \tag{1.4}$$

Not only does liquid A provide greater contact and mobility but it may also dissolve some D and prevent blockage. A particularly facile reaction occurs if the reaction can be run above the congruent melting point of D (see Section 1.2.3). Otherwise, diffusion limitations may again appear when the amount of A(l) becomes small or an intermediate solid forms, particularly if it occurs along the B→D or A→D pathway.

A more conventional solvent may also be employed to give a different version of (1.4), namely

$$A(l,s) + B(l,s) \xrightarrow{\text{solvent}} D(s). \tag{1.5}$$
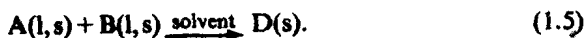
Use of a molecular or melt solvent, sometimes at elevated temperatures, speeds the reaction by bringing A and B together, presuming the solvent can be removed subsequently. Solvent-assisted reactions that are run very much below the melting point of the product will often yield a very finely divided, even amorphous material, which may be an advantage or a disadvantage depending on the intended use.

A few possibilities remain if the above reaction types are not feasible or suffer from incomplete conversions, side reactions, or contamination. Obviously, volatility of the product allows a simple separation from the contaminants. Thus the complex and incomplete reaction

$$Al_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 3CO(g) \qquad (1.6)$$

and its various analogues present few complications because the product $AlCl_3$ is volatile at the reaction temperature (and much below), and re-sublimation if necessary gives a very pure product. On the other hand, an all-solid reaction

$$A(s) + B(s) \rightarrow C(s), \qquad [\text{e.g. } CaO + TiO_2 \rightarrow CaTiO_3] \qquad (1.7)$$
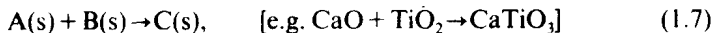
will in the absence of any volatility probably be orders of magnitude slower and thence will present greater difficulty in achieving a respectable yield and purity. Reactions of this character are avoided whenever possible and (if not avoided) may utilize some combination of intimate mixing, even on the atomic scale, high temperature or high pressure or an added flux. Of course the flux remains as an impurity if not later dissolved or volatilized.

A second means of facilitating both a reaction as well as phase separation and purification amounts to the use of 'gaseous solvent', a reagent that reversibly converts a non-volatile reactant or product to a gaseous species. This process goes under the general name *chemical* or *vapour phase transport (VPT)* (see Section 1.3). Thus an all-solid reaction would be facilitated by any reagent X which carries otherwise non-volatile A to B or vice versa, that is

$$A(s) + X(g) \rightleftarrows AX(g) \qquad (1.8)$$

followed by

$$AX(g) + B(s) \rightarrow C(s) + X(g). \qquad (1.9)$$
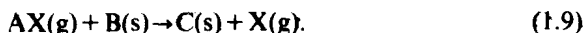
An example is the formation of the spinel $MgCr_2O_4$ according to

$$MgO(s) + Cr_2O_3(s) \xrightarrow{O_2} MgCr_2O_4(s) \qquad (1.10)$$
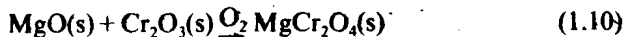
where added O_2 literally carries Cr_2O_3 to MgO through the reversible formation of gaseous CrO_3. Diffusion of this Cr_2O_3 into the MgO and nucleation of the product are still required. Obviously this process provides a means for purifying Cr_2O_3 alone by taking advantage of the temperature dependence of the last reaction, a process which would probably provide excellent single crystals of Cr_2O_3 as well.

The foregoing presentation implies that only reactions that give single-phase products, or nearly so, are found or need be considered. Though this is desired for most subsequent characterization measurements it is unfortunately often far from practice. The investigator sometimes must settle for a product that is far from ideal. Although some needs can probably be met