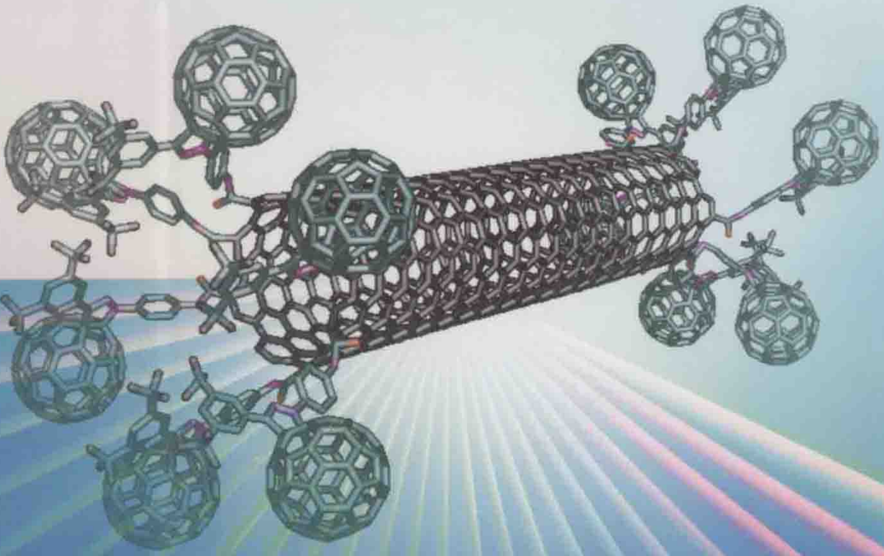
Inorganic Materials Series



Low-Dimensional Solids

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WILEY

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Inorganic Materials Series

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Series Titles

Functional Oxides
Molecular Materials
Porous Materials
Low-Dimensional Solids
Energy Materials

Low-Dimensional Solids

Inorganic Materials Series Preface

Back in 1992, two of us (DWB and DO'H) edited the first edition of *Inorganic Materials* in response to the growing emphasis and interest in materials chemistry. The second edition, which contained updated chapters, appeared in 1996 and was reprinted in paperback. The aim had always been to provide the reader with chapters that while not necessarily comprehensive, nonetheless gave a first-rate and well-referenced introduction to the subject for the first-time reader. As such, the target audience was from first-year postgraduate student upwards. Authors were carefully selected who were experts in their field and actively researching their topic, so were able to provide an up-to-date review of key aspects of a particular subject, whilst providing some historical perspective. In these two editions, we believe our authors achieved this admirably.

In the intervening years, materials chemistry has grown hugely and now finds itself central to many of the major challenges that face global society. We felt, therefore, that there was a need for more extensive coverage of the area and so Richard Walton joined the team and, with Wiley, we set about a new and larger project. The *Inorganic Materials Series* is the result and our aim is to provide chapters with a similar pedagogical flavour but now with much wider subject coverage. As such, the work will be contained in several themed volumes. Many of the early volumes concentrate on materials derived from continuous inorganic solids, but later volumes will also emphasise molecular and soft matter systems as we aim for a much more comprehensive coverage of the area than was possible with *Inorganic Materials*.

We approached a completely new set of authors for the new project with the same philosophy in choosing actively researching experts, but also with the aim of providing an international perspective, so to reflect the diversity and interdisciplinarity of the now very broad area of inorganic materials chemistry. We are delighted with the calibre of authors who have agreed to write for us and we thank them all for their efforts and cooperation. We believe they have done a splendid job and that their work will make these volumes a valuable reference and teaching resource.

DWB, York
DO'H, Oxford
RIW, Warwick
July 2010

Preface

The late Professor Jean Rouxel once wrote that 'solids bring to mind the idea of volume, and it may therefore seem paradoxical to discuss solids of *low dimensionality*'. Nonetheless, the concept has remained useful and is still widely used by both chemists and physicists but perhaps not to describe the same thing!

To a chemist a *low-dimensional solid* may refer to a structure or compound in which there is a high degree of anisotropy in the spatial distribution of the chemical bonds, which may lead to nanoparticulate (0D), fibrous (1D), or lamellar (2D) morphologies. On the other hand a physicist may take advantage of the anisotropy of a certain physical property such as electrical conductivity, optical response or magnetisation. In fact the physical properties of *low-dimensional solids* cannot be fully described by simply transposing in 2 or 1 dimension the physical laws that hold for 3D space. *Low-dimensional solids* can exhibit new phenomena, for example the well-known case of charge density waves that were observed in the layered, transition-metal dichalogenides.

In this book we would like to introduce you to new, relevant, contemporary topics, which deal with the synthesis and properties of *low-dimensional solids*. The five chapters describe structures, applications or phenomena not known when *Inorganic Materials* was produced. Our line-up of distinguished international authors have written on topics ranging from the chemistry and physics of inorganic nanotubes and sheets, quantum effects in nanoparticles, novel layered superconductors to inorganic-DNA delivery systems.

We are delighted by their efforts and trust you find what they have written both fascinating and exciting.

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Metal Oxide Nanoparticles

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1.1 INTRODUCTION

Systems that contain particles with one dimension in the nanometre regime are now referred to as *nanomaterials*. Over the last decade there has been a growing interest from biologists, chemists, physicists and engineers in the applications of these materials, so-called *nanotechnology*, which is often referred to as '*the next industrial revolution*'.[1,2] The reasons for this interest are the unusual properties, with potential technological applications, that are exhibited by these materials when compared with their bulk counterparts.[3–11] Amongst the vast array of chemical compounds that have been prepared as nanomaterials there has been a particular attention on polar oxides, where the bonding is ionic or semi-ionic, and these systems will be the focus of this chapter. There are several reasons for the interest in these materials. First, these materials were amongst the earliest nanomaterials subjected to detailed investigation and there is now a sound background in their preparation and characterisation. For over twenty years there has been continuous research in this area following the pioneering work of Gleiter.[3,4,8] Secondly, the interatomic interactions are often predominantly Coulomb forces, or if not can be modelled quite well with an empirical ionic potential,[12–15] and therefore are an

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ideal test-bed for models of nanocrystalline properties. Finally, these oxides are used in a vast array of important commercial applications. These applications are wide ranging; from electronics and optoelectronics (*e.g.* sensors), to energy storage and production (fuel cells and batteries), and to usage in the chemical industry (catalysts and supports).

The origins of the unusual properties of nanomaterials can be considered as twofold; (i) the fact that the dimensions of the particles approach, or become smaller than, the critical length for certain phenomena (*e.g.* the de Broglie wavelength for the electron, the mean free path of excitons, the distance required to form a Frank–Reed dislocation loop, thickness of the space-charge layer, *etc.*) and (ii) surface effects dominate the thermodynamics and energetics of the particles (*e.g.* crystal structure, surface morphology, reactivity, *etc.*). In nanostructured semiconductors it is the first of these which leads to special electrical, magnetic and optical properties and the possibility of *quantum dot* devices. It is also an explanation of unusual hardness, sometimes referred to as *super-hardness*, of nanocrystals.[16] The second factor can lead to nanocrystals adopting different morphologies to bulk crystals with different exposed lattice planes leading to an extraordinary surface chemistry and catalytic activity.[17] The importance of surfaces and boundaries in nanocrystalline systems is demonstrated in Figure 1.1, which shows the fraction of atoms in these regions as a function of grain size.

Many of the unusual features of nanocrystalline oxides, such as *superplasticity* – the observation of higher strain rates of nanocrystalline

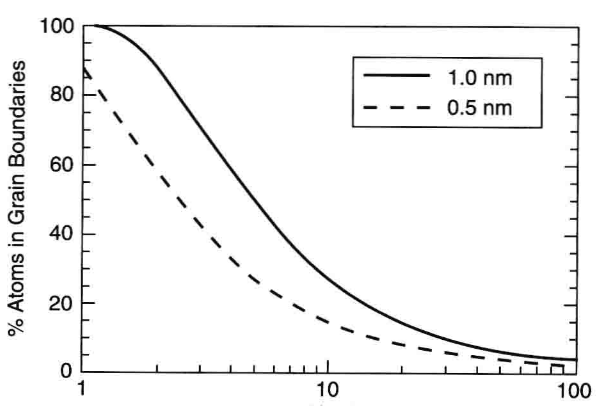

Figure 1.1 Percentage of atoms in grain boundaries as a function of grain size assuming boundary widths of 0.5 and 1 nm (after[9])

ceramics than for their microcrystalline counterparts[16] – are due to unusually high atomic transport, which has been assigned to the special nature of the interfaces between the crystallites. The earliest experimental studies of self-diffusion in nanocrystalline metals yielded diffusion coefficients many orders of magnitude higher than the values found for bulk diffusion in single crystals[4,18,19] and even higher than the values found for grain boundary diffusion, which is usually regarded as the fastest diffusion process in a solid. The phenomenon has been regarded as generic to nanocrystals independent of the interatomic bonding. An early explanation of the origin of this unusually fast atomic transport was that the interfaces between the grains in a nanocrystalline compact were highly disordered in comparison with the normal grain boundaries found in normal solids. The two types of interface are illustrated in Figure 1.2. The model assumed for a nanocrystalline sample is drawn schematically in Figure 1.2a, with extensive disorder in the interface that is several atoms in width. In this figure the black circles represent atoms in the grains and the open circles are the atoms in the interfaces. In some of the early work on nanocrystals this was intuitively assumed to be the case and the interfaces were referred to as 'gas-like' or 'liquid-like'. This structure would clearly account for rapid diffusion in nanocrystalline samples. More recently an alternative view has emerged in which the nanocrystalline interface is similar to a grain boundary in normal bulk materials, as shown in Figure 1.2b. In this case the interfaces would exhibit usual behaviour, although they would be present in unusually large number, and therefore the compacted nanocrystalline sample would show higher diffusivity than a coarse-grained counterpart. Since many of the applications of ionic materials are due to their transport of

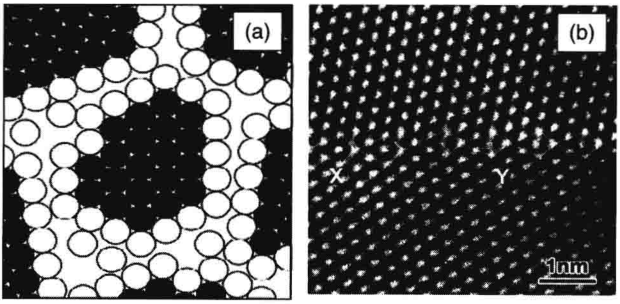

Figure 1.2 Two possible models for the interface between nanocrystalline grains: (a) disordered interface;[3] (b) a 'normal' grain boundary', a boundary in a ZnO bicrystal[19]

charge by the ions the use of nanocrystalline samples offers an obvious means of improved performance.

The aim of this contribution is to review nanocrystalline oxides, including the current state of understanding of the nature of the materials and their applications. Our interest is mainly at the fundamental level and although a number of unusual architectures have recently been developed for ionic and semi-ionic systems (for example, nanowires,[20] nanobelts,[21] nanotubes,[22] *etc.*, and a range of nanocomposites) we will restrict the focus to simple nanocrystals. The contribution has been divided into a number of sections. In order to achieve our aim we will set the scene in the next section by presenting a survey of the types of oxides and their bonding. This will be followed by sections on experimental techniques used to prepare and characterise the materials. The properties and potential applications of the materials, particularly in sensors, batteries and fuel cells, will then be discussed. The final section will give an overview of the current state of knowledge and attempt to foresee future developments in this field.

1.2 OXIDE TYPES; POINT DEFECTS AND ELECTRICAL CONDUCTIVITY

The binary oxides have a range of electronic structures and can be purely ionic, n-type or p-type electrical conductors. Metals to the left of the periodic table tend to produce stoichiometric oxides which are purely ionic in their bulk form (*e.g.* alkali and alkaline earth oxides, TiO_2, ZrO_2, CeO_2, *etc.*). Metals to the right of the periodic table tend to form oxides that are not stoichiometric under normal atmospheric condition and are semiconductors (*e.g.* SnO_2, NiO, *etc.*). It is important here to briefly review the defect chemistry of the different types of oxide as it is this feature which will govern the charge transport in the material and be affected by moving to the nanometre regime. Details of the defect chemistry of oxides can be found in several standard texts and reviews.[23–27]

The defect chemistry of the ionic metal oxides is generally well understood. The interatomic forces are predominantly Coulombic and are well represented by a simple potential (*e.g.* the Born–Mayer equation), hence the defect energies can be obtained with good accuracy from computer modelling.[15] In an ionic crystal the point defects formed must maintain electroneutrality and therefore will occur in pairs or multiplets.[23,28,29] The basic point defects are either *Schottky defects* – cation vacancies and anion vacancies (*e.g.* MgO), or *cation-Frenkel defects* – cation vacancies and interstitial cations (*e.g.* Li_2O), or *anion-Frenkel defects* – anion vacancies and interstitial anions (*e.g.* the fluorite-structured oxides, such as ZrO_2 and CeO_2). Using the Kröger–Vink notation the equilibrium for the formation of a Schottky pair in an oxide can be written as

$$M_M + \mathrm{O_O} \Leftrightarrow M\mathrm{O} + V''_M + V^{\bullet\bullet}_\mathrm{O} \tag{1.1}$$

The Schottky equilibrium constant for this reaction, K_S, is given by a simple mass-action relationship of the form

$$K_\mathrm{S} = [V''_M][V^{\bullet\bullet}_\mathrm{O}] = \exp\left(\frac{-g_\mathrm{S}}{kT}\right) \tag{1.2}$$

Here the square brackets represent concentrations (site fractions) of the defects and g_S is the Gibbs free energy to form the defect pair. In fact g_S is the sum of the Gibbs free energies of the individual defects in the pair and these will be different. In the bulk of a pure crystal there must be equal concentrations of the two types of defect to maintain electroneutrality, hence

$$[V''_M] = [V^{\bullet\bullet}_\mathrm{O}] = K_\mathrm{S}^{1/2} = \exp\left(\frac{-g_\mathrm{S}}{2kT}\right) \tag{1.3}$$

Similar equations can be written for the formation of anion-Frenkel pairs, *i.e.*

$$\mathrm{O_O} + V_i \Leftrightarrow V^{\bullet\bullet}_\mathrm{O} + \mathrm{O}''_i \tag{1.4}$$

and the defect concentration in the pure crystal will be given by

$$[\mathrm{O}''_i] = [V^{\bullet\bullet}_\mathrm{O}] = K_\mathrm{aF}^{1/2} = \exp\left(\frac{-g_\mathrm{aF}}{2kT}\right) \tag{1.5}$$

Here K_aF and g_aF are the anion-Frenkel equilibrium constants and Gibbs free energy of formation of the pairs, respectively.

The defect concentrations in a pure ionic crystal are usually low. Typically the site fractions are the order of 10^{-3} at the melting point of the crystal. However, it is possible to increase the concentration of one of the defects in the pair by selectively adding an aliovalent impurity, a process referred to as doping. In the context of the systems considered in this chapter is the doping of the fluorite-structured oxides with lower valency cations, *e.g.* divalent alkaline earth or trivalent rare earths cations. A good example is the doping of ZrO_2 with Y_2O_3, for which the reaction can be written as

$$\mathrm{Y_2O_3} \overset{\mathrm{ZrO_2}}{\rightarrow} 2\mathrm{Y}'_\mathrm{Zr} + V^{\bullet\bullet}_\mathrm{O} + 3\mathrm{O}^x_\mathrm{O} \tag{1.6}$$