Low-Dimensional Solids

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Low-Dimensional Solids
Inorganic Materials Series

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Series Titles
Functional Oxides
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Low-Dimensional Solids

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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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1

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’.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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,\textsuperscript{[12–15]} and therefore are an
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. 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. 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](image)

**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\cite{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\cite{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\cite{3} (b) a ‘normal’ grain boundary’, a boundary in a ZnO bicrystal\cite{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$_2$O), 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

$$M_M + O_O \rightleftharpoons MO + V'_M + V''_O$$

(1.1)

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

$$K_S = [V'_M][V''_O] = \exp\left(\frac{-g_S}{kT}\right)$$

(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

$$[V'_M] = [V''_O] = K_S^{1/2} = \exp\left(\frac{-g_S}{2kT}\right)$$

(1.3)

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

$$O_O + V_i \rightleftharpoons V''_O + O''_i$$

(1.4)

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

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

(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$_2$O$_3$, for which the reaction can be written as

$$Y_2O_3 \xrightarrow{\text{ZrO}_2} 2Y'_Zr + V''_O + 3O''_O$$

(1.6)
The open nature of the fluorite structure allows considerably high levels of doping, tens of mole per cent, which is not common in most ionic systems. Thus in doped ZrO$_2$ the concentration of oxide ion vacancies is directly proportional to the dopant concentration, \( i.e. \)

\[
[V_{O}^{\bullet\bullet}] = 1/2[Y_{Zr}']
\]

or for CaO doped ZrO$_2$

\[
[V_{O}^{\bullet\bullet}] = [Ca''_{Zr}]
\]

Although the concentrations of an individual defect in a pair can be increased by doping, these defects may not be ‘free’ to be involved in transport processes. The dopant and the point defect it creates will have opposite effective charges in the lattice and there will be an electrostatic interaction which will lead to the formation of defect pairs and higher order clusters, a process referred to as defect association. In the case of Y$_2$O$_3$ doped ZrO$_2$ the simplest pair would be a yttrium ion adjacent to an oxygen ion vacancy and the defect reaction can be written as

\[
Y_{Zr}' + V_{O}^{\bullet\bullet} \leftrightarrow (Y_{Zr}' V_{O}^{\bullet\bullet})^\cdot
\]

The equilibrium constant for this association reaction, \( K_{ass} \), can be written as

\[
K_{ass} = \frac{[(Y_{Zr}' V_{O}^{\bullet\bullet})^\cdot]}{[Y_{Zr}'][V_{O}^{\bullet\bullet}]} = z \cdot \exp \left( \frac{-g_{ass}}{kT} \right)
\]

Here \( z \) is the number of possible orientations of the pair and \( g_{ass} \) is the Gibbs free energy of the association reaction. Combining Equations 1.5 and 1.10, along with the condition of electroneutrality, the concentration of the free oxide ion vacancies, \( [V_{O}^{\bullet\bullet}] \), can be calculated as a function of temperature and dopant concentration.\[30\]

The diffusion of the ions in an ionic crystal is a classical jump process \( via \) the point defects.\[23,28,29\] Taking ZrO$_2$ as an example, the mobile species is the oxide ion which jumps \( via \) the oxygen ion vacancies. The tracer diffusion coefficient, \( D^t \), of the oxide ion can be written as

\[
D^t = \frac{z'}{6} f [V_{O}^{\bullet\bullet}]a^2 v \exp \left( \frac{-\Delta g_m}{kT} \right)
\]

Here \( z' \) is the number of sites to which the ion can jump, \( a \) is the jump length, \( v \) is a characteristic vibrational frequency and \( \Delta g_m \) is the Gibbs free energy of migration. \( f \) is the correlation factor allowing for nonrandomness.
of the jumps, \textit{i.e.} having made a jump the next most likely jump of the tracer is back to the original site as there is a vacancy there to accept it.

The contribution to the ionic conductivity, \( \sigma_i \), of a particular charge carrier, \( i \), is given by the standard expression

\[
\sigma_i = n_i |q_i| \mu_i
\]

Here \( n_i \) is the density of charge carriers, \( q_i \) is the charge on the carrier and \( \mu_i \) is the mobility of the carriers. Continuing with ZrO\(_2\) as the example, the density of charge carriers is given by

\[
n_i = N[V_0^*]
\]

where \( N \) is number of oxide ion sites per unit volume. The diffusion coefficient and the mobility are related; applying an electric field biases the jumps of the defect. Thus \( \sigma_i \) and \( D_i \), are related by the Nernst–Einstein equation, namely

\[
D_i = \frac{H_R \sigma_i kT}{N_i q_i^2}
\]

\( H_R \) is the Haven ratio, the ratio of the correlation factors for diffusion and conduction.\textsuperscript{[23,28]}

Usually only one of the defects in the pair is the more mobile species and this will dominate the ionic conductivity, \textit{e.g.} the oxide ion vacancies in ZrO\(_2\). The diffusion coefficients or conductivity measurements are plotted in Arrhenius form, \textit{i.e.} \( \log D^i \) or \( \log \sigma \) versus \( 1/T \),

\[
D^i = D_0^i \exp \left( -\frac{Q^*}{kT} \right)
\]

\[
\sigma = \sigma_0 \exp \left( -\frac{Q^*}{kT} \right)
\]

The activation energies, \( Q^* \), from the slopes of these plots are related to the defect energies. In a pure ZrO\(_2\) crystal with no impurity the slopes will yield

\[
Q^* = \frac{h_{dF}}{2} + \Delta h_m
\]

Here \( h \) is the defect enthalpy associated with the corresponding Gibbs free energy. In a doped crystal with no association then the slopes will yield

\[
Q^* = \Delta h_m
\]
In this case \([V_0^+]\) is fixed by the dopant concentration and is independent of temperature.

The condition of electroneutrality will not apply at the surface of a crystal and since Gibbs free energy of each defect in the pair is not equal there will be an excess of one of the defects. This effect, referred to in the early literature as the Frenkel–Lehovec space charge layer, results in an electric potential at the surface of the crystal.\(^\text{[29,31,32]}\) In this instance ‘surface’ will not simply be the external surface but includes internal surfaces such as grain boundaries and dislocations. The effect decays away in moving from the surface to the bulk and can be treated by classical Debye–Hückel theory.\(^\text{[33–36]}\) This leads to a Debye screening length, \(L_D\), given by:

\[
L_D = \left( \frac{\varepsilon_r \varepsilon_0 k T}{2 q^2 c_b} \right)^{1/2}
\]

Here \(\varepsilon_0\) and \(\varepsilon_r\) are the permittivities of free space and the sample, respectively, \(c_b\) is the concentration of the bulk majority carrier with charge \(q\). For a solid with \(\varepsilon \sim 10\) and \(c_b \sim 10^{22}\) m\(^{-3}\) and \(T\sim 600\) K, this leads to a Debye length of \(\sim 50\) nm and a space charge width of approximately two times that value. The qualitative effect on the relative concentrations of the two defects of the pair, \(\zeta_o\), is shown schematically in Figure 1.3 as a function of grain size. Clearly, this increased defect concentration will translate into enhanced ionic diffusion and conductivity in the space-charge region, which is in the plane of the interface. If the grains are sufficiently small this can dominate the ionic transport in the sample and far outweigh the transport in the bulk of the grains.

---

**Figure 1.3** Defect profiles in structures with dimension, \(d\). The bulk defect concentration is not reached when \(d \ll 4L_D\), where \(L_D\) is the Debye length (after\(^\text{[33]}\))
The space-charge layer region described above applies to a sample made purely of small grains of one ionic compound. There will also be space-charge layers at the interfaces between ionic crystals and other materials, such as other ionic crystals, insulators, semiconductors and metals. The theoretical treatments of the effects in these systems can be found in an extensive review. There is a difference in the details for each situation, however; essentially across all the interfaces there will be a difference in the electrochemical potential of the ions leading to an imbalance in the relative defect concentrations in the surface of the ionic crystal and the generation of a space-charge layer. The approach was particularly successful in explaining the high ionic conductivity of materials known as ‘composite electrolytes’ or ‘heterogeneous electrolytes’ or ‘dispersed second phase electrolytes’. These materials consist of an ionic conductor mixed intimately with a fine powdered insulator, such as alumina, silica, titania, etc. The ionic conductivity can be increased by up to two orders of magnitude compared with that found in the pure ionic material. The increased conductivity is due to the enhanced conductivity in the interfacial region, arising from the increase in charge carrying defects in the ionic component. A combination of the space-charge layer approach and percolation theory has provided quantitative models of the dependence of the conductivity on composition, grain size of the insulator and temperature. Clearly, a similar approach can be applied to thin films of an ionic conductor laid down on an insulating surface where an enhanced conductivity is possible due to the space-charge layer at the interface.

The semiconductivity in the metal oxides is a result of nonstoichiometry, an excess or deficiency of oxygen. The oxygen deficient oxides are n-type semiconductors and a good example is tin oxide. This material is usually written as SnO\textsubscript{2} but is better described as SnO\textsubscript{2-x}. The loss of oxygen can be written in the form of a defect reaction

\[
\text{O}_\text{O} \leftrightarrow 1/2\text{O}_2 + V_{\text{O}}^{\ast \ast} + 2e' \tag{1.19}
\]

It follows that in a pure crystal

\[
2[V_{\text{O}}^{\ast \ast}] = [e'] \tag{1.20}
\]

The conductivity will be dominated by the electrons due to their higher mobility. The conductivity will clearly depend on the oxygen partial pressure, \(P_{\text{O}_2}\), and the exponent of a log \(\sigma\) versus log \(P_{\text{O}_2}\) will be \(-1/6\).
usually contains lower valency (acceptor) impurities such as Fe$^{3+}$. To maintain electroneutrality oxide ion vacancies will be created, namely

$$[\text{Fe}'_\text{Sn}] = 2[V^*]$$  \hspace{1cm} (1.21)

This results in the suppression of the electron concentration below the impurity level and the exponent of the pressure dependence is now $-1/4$. The concentration of electrons can be further lowered by deliberately doping with acceptor impurities. Similarly doping SnO$_2$ with donor impurities (such as Sb$^{5+}$) will increase the concentration of electrons and the n-type conductivity.

The effect of exposing n-type semiconductors, like tin oxide to an oxygen atmosphere is the chemisorption of oxygen as oxide ions by removal of the electrons in the surface region. The effect is to lower the conductivity of the material. At moderate temperatures the effect of reducing gases in the atmosphere, such as hydrogen, carbon monoxide or methane, is to react with the chemisorbed oxygen, releasing the electrons and increasing the conductivity. This is the basis of the gas sensors for flammable gases.$^{[38]}$

Analogous treatments to those outlined above can be presented for n-type semiconducting oxides in which the compensating defects are interstitial cations (e.g. ZnO) and for p-type semiconductors. In the latter case parallel equations can be derived for the hole concentrations, $[h^+]$, and they will not be presented here.

Space-charge layer effects need also to be considered for the semiconducting oxides; however, in this case the additional factor of quantum-mechanical effects has to be included when the crystallite size becomes very small.

### 1.3 PREPARATION OF NANOIONIC MATERIALS

A wide variety of methods have been used to prepare nanoionic materials; however, only the most widely used methods will be discussed. The use of mechanical attrition, in particular, high-energy ball milling, has been widely applied to produce all forms of nanocrystals. This method relies on the reduction of the grain size of a given bulk material and means that virtually every material is accessible.$^{[39–42]}$ A further advantage is that careful choice of the milling time means that some control of the final grain size can be achieved. In addition, large amounts of material can readily be produced and use of double decomposition reactions$^{[43,44]}$ means it is possible to produce materials in situ. However, contamination through abrasion of the milling media means that careful choice of the milling vial and balls is
required, while a significant disadvantage is production of significant quantities of amorphous debris during the milling, for example in recent work on ball milled Al$_2$O$_3$, it was found that the sample consisted of nanocrystalline grains embedded in amorphous material.$^{[45]}$

Inert gas condensation (IGC) has been used to prepare both nanocrystalline metallic and metal oxide materials. The general arrangement of the apparatus is shown in Figure 1.4. The required metal is evaporated inside an ultrahigh vacuum chamber, filled with a low pressure of inert

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**Figure 1.4** Inert gas condensation facility for the synthesis of nanocrystalline particles (after $^{[3]}$)
gas. Migration of the vapours from the hot source into a cooler gas leads to nucleation of a large number of clusters that grow via coalescence and agglomeration. These clusters, entrained in the cooling gas, are transported to a liquid nitrogen finger where they can be scraped off and compacted. It has been shown that this technique produces powders with a well-defined, narrow size distribution; however, a disadvantage is that only a limited amount of material is produced leading to several modifications being developed to increase the yield. In contrast, spray pyrolysis has been widely used to prepare a range of nanocrystalline metal oxides including Al₂O₃, ZnO and ZrO₂. A solution of a chemical precursor is dispersed as an aerosol and the droplets are transported to a hot zone where they decompose to form the required nanocrystalline oxide particles.

An alternative method which offers control over both the composition at the molecular level and the structure of the final material is the sol-gel method. Typically, a metal alkoxide, M(OR)ₓ undergoes controlled hydrolysis reactions replacing an OR group by OH resulting in the formation of very small colloidal particles, the sol, which then undergoes condensation reaction to form a gel. The gel is then dried to produce an oxide (as in the case of silicon tetraethylorthosilicate), a hydroxide (zirconium isopropoxide) or a mixed methoxy-hydroxide (magnesium methoxide) before calcination at high temperatures to produce the oxide. It is this final step which presents two major problems since it is difficult to control. The first is that the surface energy of nanocrystals is such that grain growth can occur at relatively modest temperatures (approximately 400 °C in the case of most nanocrystalline oxides, where measurable grain growth is observed after a few minutes). This can be overcome by using a suitably low temperature for calcinations; however, this can lead to the second issue in that a significantly high calcination temperature is required to ensure that all of the residual OH groups are removed from the material, as illustrated by work on ZrO₂. A method of restricting grain growth during calcination at higher temperatures is Zener pinning. This pinning effect is based on the introduction of a dispersion of very small particles of a second phase (in the case of oxides an inert oxide such as silica or alumina) which act to stabilise the highly curved surface of a nanoparticles. The second phase can be introduced at the sol-gel stage by adding the corresponding alkoxide of the inert material. This method has proved very successful for a wide range of oxides; for example it has been shown that 8 nm nanocrystalline tin oxide ‘pinned’ with approximately 15 wt% SiO₂ was obtained after calcination at 1000 °C compared with 56 nm in the unpinned material. An additional advantage is that the pinning particles also act to retard phase
transformations of the nanocrystalline oxide. For example, nanocrystalline tetragonal zirconia, 10 nm in size, was obtained after calcination at 1000 °C when ‘pinned’ with approximately 15 wt% SiO$_2$ compared with 48 nm monoclinic zirconia in unpinned material.\textsuperscript{[57]} However, in some cases the pinning particles may react with the nanocrystalline oxide phase, this has been observed in the case of nanocrystalline MgO pinned with approximately 15 wt% SiO$_2$ after calcination at 1000 °C where the pinning phase was shown to be magnesium silicate. The particle size of the nanocrystalline MgO was found to be 11 nm compared with 61 nm for the unpinned material, indicating that the pinning phase was still very effective.\textsuperscript{[60]}

Other soft chemistry techniques that have been used to produce nanocrystalline powders including hydrothermal methods\textsuperscript{[61,62]} and some of these have been reviewed in a recent paper with particular reference to one-dimensional nanostructures.\textsuperscript{[63]}

In general, the above methods are used for the production of nanocrystalline powders which may be further compacted \textit{via} techniques such as hot-pressing\textsuperscript{[64,65]} or magnetic pulsed compaction\textsuperscript{[66,67]} or spark plasma sintering.\textsuperscript{[68,69]}

In addition, other types of nanoionic materials maybe prepared such as nanometre thin films, using techniques including molecular beam epitaxy,\textsuperscript{[70]} pulsed laser deposition\textsuperscript{[71]} or spin-coating methods,\textsuperscript{[72]} while the preparation of novel structures such as \textit{core-shell}\textsuperscript{[73–75]} and \textit{multilayered}\textsuperscript{[76,77]} (so-called \textit{onion structures}) materials has led to further advances in preparation methods. For example, core-shell composites consisting of a gold core surrounded by a zinc oxide shell (referred to as Au@ZnO core-shell composite) have been prepared by mixing a solution containing the gold seeds with an ethanolic solution of CTAB and zinc nitrate.\textsuperscript{[74]} A suspension of the Au@ZnO nanocomposites was obtained on adding a solution of sodium hydroxide in ethanol; this was then centrifuged to obtain the nanocomposites. In contrast, RuO$_2$/TiO$_2$ core-shell nanowires were prepared by first growing RuO$_2$ nanowires by reactive sputtering, followed by sputtering of the TiO$_2$ layer onto the surface of the RuO$_2$ nanowire.\textsuperscript{[78]}

\section*{1.4 CHARACTERISATION}

\subsection*{1.4.1 Determination of Particle Size and Dispersion}

The most important measurement, and after synthesis usually the first characterisation procedure undertaken, for any nanocrystalline compound
is the determination of the grain (crystallite) size as it is fundamental to understanding the properties of the material. A variety of techniques have been employed to determine characterisation of nanocrystallite size and shape, including optical absorption spectroscopy, dynamical light scattering (DLS), small angle X-ray scattering (SAXS), dark field electron microscopy, low frequency inelastic Raman scattering, proton induced X-ray emission (PIXE), X-ray diffraction (XRD), transmission electron microscopy (TEM) and gas adsorption surface area measurement. It is the last three of these methods that will be treated here as (i) they are the most commonly used, (ii) are readily available in most laboratories, and (iii) are relatively simple measurements to perform and analyse. Each of the methods has its advantages and disadvantages; and there are some well-known problems and artefacts that can be encountered. These will be highlighted along with the results of some recent works which have attempted to compare different methods and assess the techniques.

TEM images result from the direct observation of the particles and provide information on the shape of the particles as well as the size. In addition, high resolution (HR) images will reveal the degree of crystallinity of the particles and the presence of amorphous material in the sample. A good example of this is the study of nanocrystalline ball-milled lithium niobate which shows an amorphous region on the surface of the crystallites.\[79]\ The main disadvantage of the technique is that to obtain a statistical average and the dispersion of the particle size can be very time-consuming as typically the dimensions of several hundred particles has to be determined. In addition, in some cases the lack of contrast or particle overlap can blur the boundaries between particles and often an elaborate sample preparation procedure is required.

The X-ray based methods, SAXS and XRD, are indirect methods but offer the advantage of providing reliable statistical information on the particle size. XRD is particularly attractive as it can be performed on a very basic laboratory-based powder diffractometer and is the most commonly used method. The method involves measuring the peak broadening of the diffraction lines. For perfect crystals the diffraction lines would be sharp, except for a very small inherent broadening due to the uncertainty principle, \textit{i.e.} there is not an infinite number of diffracting planes, but in practice they are broadened due to the instrumental optics and the crystallite size. The most common approach to the determination of the crystallite is to use the Scherrer relation:\[80–82]\n
\[
d_V = \frac{k \lambda}{\beta \cdot \cos \theta}
\]  

(1.22)