CHAPTER 2

Experimental techniques

2.1 Introduction

The synthesis of materials comprises a fundamental activity in materials science research. The synthesis of metal oxides differs from the synthesis of, for example, organic and organometallic compounds. There are two main methods for the preparation of such materials, i.e., the classical solid-state chemistry method, and the soft chemistry method (*la chemie douce).* The syntheses of organic and organometallic compounds typically involves the formation or cleavage of covalent bonds. On the other hand, with inorganic materials (such as the metal oxides), the original structure can be completely disrupted and a new one formed in its place. To probe the structure and properties of the newly-formed materials, a variety of instrumental techniques have to be used. This chapter summarises some synthetic strategies for the materials and the experimental techniques used in their characterisation.

2.2 Methods of synthesis of oxide materials

The solid-state reaction (Rao, 1997; West, 1987) and the soft chemistry route (Segal, 1997; Brinker, 1990) are discussed below.

2.2.1 Solid-state reaction

This method involves heating the starting reagents, which have been intimately mixed by grinding in a furnace for a pre-determined time. The mixture can be heated as a powder, or it can be compressed into a pellet. Examples of materials prepared by this method include vanadium tin oxide and lithium tin oxide. As this method is governed by the rate of the diffusion of atoms or ions between two starting reagents, the particles of both reactants must be sufficiently small so that there is good contact between their crystallite faces.

Increasing the temperature of the reaction leads to a decrease in the reaction time. In general, the reactions require high temperatures close to the melting points of the mixed system, because the rate of diffusion of ions increases with increasing temperature. On completion of the reaction, the product is removed from the furnace; the product must be cooled carefully so that the desired product can be obtained in a pure form. As other phases exist at the same composition, a knowledge of phase diagrams is required. The method suffers from some drawbacks; for example, the final phase can be contaminated with some starting materials, the amount of impurities being somewhat dependent on the method for grinding the mixture. Furthermore, because of the need to maintain a higher temperature, the stoichiometry of the product can be affected by loss of one component owing to sublimation. Only the stable phase with a defined microstructure is obtained; metastable phases can not be obtained by this method.

2.2.2 Soft chemistry method

Soft chemistry techniques comprise all methods that use low temperatures in the preparation. Different methods exist. Among them are sol-gel, precipitation, precursor, ion-exchange and hydrothermal methods (Segal, 1997; Brinker, 1990).

The procedure as schematised in Fig. (2.1) refers to the sol-gel method in which the reacting solution transforms to a gel (Brinker, 1990). A typical example is the preparation of vanadium oxide xerogel $V_2O_5.2H_2O$ (Znaidi et al, 1989; Aldebert et al 1981). A solution of sodium metavanadate is passed through an ion-exchange column to give an acidic solution that forms the gel after 48 hours.

The precipitation method involves the use of a precipitating agent; this reagent when added to the solution gives rise to an immediate precipitate. Examples can be found in literature (Touboul et al, 1994).

The precursor method is used to generate a finely-divided and reactive reactant oxide. Such precursors include metal carbonates, hydroxide and nitrates that decompose at moderate temperatures.

Hydrothermal techniques are widely used in the preparation of vanadates or oxide having an open structure. The reacting solution is heated in a sealed vessel above the boiling point of the solvent, temperatures between 100°C and 200°C are typically required.

The material obtained from the sol-gel and precursor methods is an amorphous or semi-amorphous material that, upon further heating, is transformed into a crystalline material. A metastable phase can be obtained, as exemplified by the amorphous phase shown in Fig. (2.2). A metastable phase is a phase that exists only at some temperature range above which temperature a structural transformation or decomposition occurs. The metastable phase does not have a minimum free energy, Fig. (2.2) but it exists because of the kinetic factor.

Metastable phases with interesting physical properties and ultra-pure materials that are prepared by the sol-gel and precursor methods have been reported (Wu et al, 1996; Touboul et al, 1994; Vallet-Regi et al 1993).

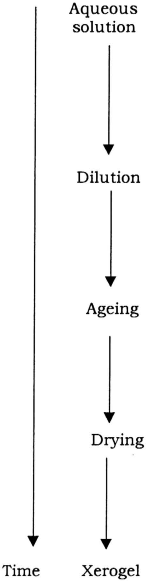
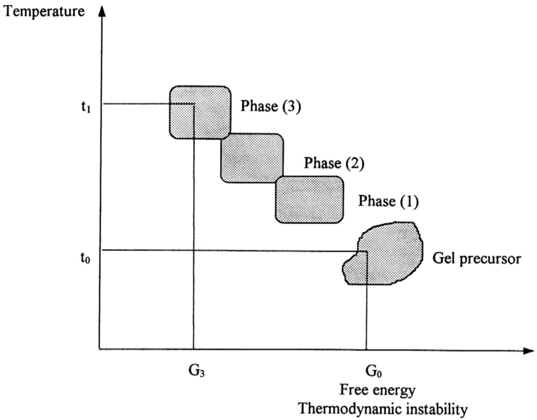


Fig. (2.1): Sol-gel process



$$\text{Gel precursor} \xrightarrow{t_1} \underset{\text{metastable}}{\text{phase (1)}} \xrightarrow{t_2} \underset{\text{metastable}}{\text{phase (2)}} \xrightarrow{t_3} \underset{\text{stable}}{\text{phase (3)}}$$

$G_3 > G_o$ $t_3 > t_2 > t_1$

Fig (2.2): Different phases from a sol-gel reaction

2.3 Techniques for the characterisation of metal oxides

2.3.1 Introduction

Once the compounds have been prepared, it is only logical to determine that it is the desired compound without any impurity. Hence the materials prepared have to be characterised. The characterisation techniques that will be need in this study include X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Thermogravimetry Analysis (TGA), Fourier Transform Infrared (FTIR), and Scanning Electron Microscopy (SEM).

2.3.2 X-ray diffraction and the powder diffractometer

Among the many experimental techniques for the characterisation of materials, the most important technique, one that has expanded the limits of materials science, is X-ray diffraction. The diffraction of X-rays was discovered in 1895 by the German physicist Roentgen. X-ray methods are used in research, development and quality control in the metallurgical, ceramics, minerals, chemical and pharmaceutical industries. X-ray interacts with the atoms that constitute matter. A beam of X-rays is scattered in various directions by these electrons. If the distance between the atoms are comparable with the wavelength of the X-rays, the diffracted X-ray can give information on the spatial arrangement of the atoms (Weller et al, 1994).

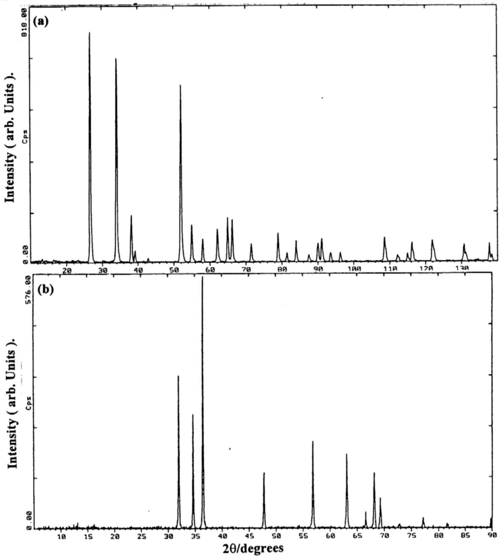


Fig. (2.3): Typical of XRD spectra. (a) Tin(IV) Oxide (b) Zinc(II) Oxide

In a powder diffractogram, diffraction peaks are observed when Bragg's law $\lambda = \mathbf{2d\sin\theta}$ is satisfied. Fig. (2.3) shows typical X-ray diffraction spectra for tin(IV) oxide and zinc(II) oxide. From the position (i.e., the theta angles) of diffraction peaks the cell parameters, the crystal class and the lattice type assigned can be calculated. As the peak intensities are related to atoms and their arrangement in the unit cell, the powder diffractogram can further be examined in order to determine the crystal structure of the material under study.

determine the crystal structure of the material under study.

However, such calculations are generally complex and are not often carried out. The X-ray powder diffraction method is better suited to the identification of impurities in materials and the nature of the phases.

The Simens D-5000 and Philips PW 1840 powder diffractometers equiped with copper radiation (λ = 1.54178 Å) were needed for this purpose.

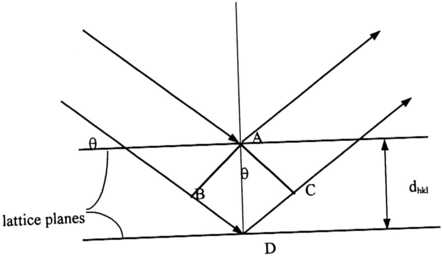


Fig. (2.4): Bragg's law in reciprocal space

2.3.3 Thermal techniques

Thermal analysis usually characterises the nature, purity, and structure of the sample under investigation. Thermal analysis is becoming a more exact science and greatest progress has been made in elucidating the fundamental behaviour and structure of materials. The analysis of materials systems continues to be a rapidly developing field of research as many new materials become available. Thermal analysis include a number of different techniques, each of which can provide certain useful information of the materials under specific conditions.

The following table (Gan, 1997; Smallman and Bishop, 1995) shows the various thermal techniques that have been endorsed by the International Council of Thermal Analysis.

Abbrivation	Property	Principle of technique
TGA	mass	Change of mass with temperature
EGA	mass	Analysis of liberated gas
EGD	mass	Detection of liberated gas
DTA	temperature	Measurement of temperature changes
DSC	enthalpy	Measurement of heat liberated
TMA	modulus	Thermal Mechanical Analysis
DMTA	modulus	Dynamic Thermal Mechanical Analysis

2.3.3.1 Thermogravimetric Analysis (TGA)

This technique is based on the measurement of the weight change of a sample as it is being heated. Isothermal TGA records the change in weight as a function of time at constant temperature whereas dynamic (or non-isothermal) TGA records the change in the weight as a function of both temperature and time at a pre-determined heating rate. Both variations can be used for studying any system that involves weight changes with heating under a nitrogen or oxygen atmosphere. The Rheometric Scientific 1000 thermogravimetric analyser (TGA) equipment was needed for this experiment.

2.3.3.2 Differential Scanning Calorimetry (DSC)

From chemical thermodynamic considerations, DSC is a more useful method because the technique involves the measurement of the chemical and physical changes associated with a change in enthalpy, which is a thermodynamic state function. Furthermore, the method also yields information on the change in heat capacity C_p as a function of temperature. The method is sensitive to small changes in C_p; a large change in the value can be interpreted as some change in the physical state, e.g., melting of the solid.

Other thermodynamic parameters that can be obtained by this technique include glass-transition temperatures, heats of crystallisation, rates of crystallisation at isothermal and non-isothermal conditions, heats of fusion, and rates of degradation and oxidation. The DSC Rheometric Scientific LN instrument was needed for this purpose.

2.3.3.3 Differential Thermal Analysis (DTA)

Differential thermal analysis is a technique for studying the behaviour of materials as they undergo chemical or physical changes while being heated or cooled at some specified rates; the method is particularly useful for studies of fast reactions. Calorimetric parameters under extreme conditions have been obtained with this method (Gan, 1997; Smallman and Bishop, 1995; Cotton, 1986).The Perkin Elmer

DTA 7 instrument was used in this work.

2.3.4 Fourier Transform Infrared spectroscopy (FTIR)

Analysis of Materials

In FTIR spectroscopy, the electronic transitions between the different vibrational modes of a molecule result in absorption of infrared energy. The frequency ν (and wavelength λ) for a given transition is related to the energy difference between the different states ΔE, as given in the following equation:

$$\nu = \Delta \mathbf{E}/\mathbf{h} = \mathbf{c}/\lambda$$

where **h** = Planck constant and **c** = speed of light.

For a simple molecule (one with few atoms only), the peaks in its IR spectrum can be assigned to each vibrational mode. Larger molecules give rise to more complex spectra; FTIR is particularly suited for the analysis of spectrum as the method is much more sensitive than continuous-wave IR spectroscopy (Ocaña et al 1993; Banwell and McCash, 1994). The ATI Mattson Genesis FTIR Spectrometer Recorded the srectra.

2.3.5 Electron Microscopy

Scanning Electron Microscopy (SEM) probes the external (surface structure) of a solid whereas Transmission Electron Microscopy (TEM) probes the internal structure of solids. The first SEM was built in 1965;

commercial SEMs generally operate at a magnification 10 to 300,000 (Raju, 1997). The first TEM was built much earlier, in 1931; the resolution of this instrument is only 0.1 nm. From SEM studies the particul size can be estimated. A Philips 515 Scanning Electron Microscope was needed for this pupose.

The characterisation of materials is summarised in the following table (Ranganathan, 1997).

Characterisation

Structure characterisation	**X-ray diffraction** **FTIR**
Phase identification	**Thermal analysis DTA, DSC, TG** **Morphology SEM, TEM**

Physical properties

Transport measurement	**Conductivity**