Chapter 3

Experimental methods and characterization techniques

It is necessary to prepare nanomaterials with required composition and properties to make them suitable for certain applications. Once the material has been prepared its structure as well as electrical, optical, magnetic and other behaviour should be analyzed with proper characterization techniques. Thus, synthesis and characterization of nanomaterials is an important and challenging task. The size and shape controllable process to develop nanoparticles has attracted immense interest to study quantum effect and other properties [3.1]. In this chapter, different synthesis methods of oxide nanoparticles and characterization techniques are discussed in detail. Some of these methods, we have used to prepare nano structured Titanium dioxide (TiO_2) and Tin dioxide (SnO_2) and will be described in chapter 5.

3.1 Synthesis methods for nanoparticles

There are generally two methods for the synthesis of nanomaterials namely (i) Top-down and (ii) Bottom-up approach. As shown in fig. 3.1 in the bottom up approach, starting from the small scale atoms/molecules are assembled to the nano sized particles. While in top-down method, it starts from the bulk system and by breaking the material one can obtain small dimensional material. Table 3.1 lists examples of synthesis methods based on top-down and bottom-up approach. Both the techniques are employed for the preparation of nanomaterials in various fields as per requirements since they have their advantages as well as disadvantages.

(i) Top-down: Materials prepared using this technique contains high surface imperfection. For example, in lithography the structure of crystal may be damaged and also it can have large amount of impurities. In nanotechnology, surface-to-volume ratio of materials has great

Chapter 3

Experimental methods and characterization techniques

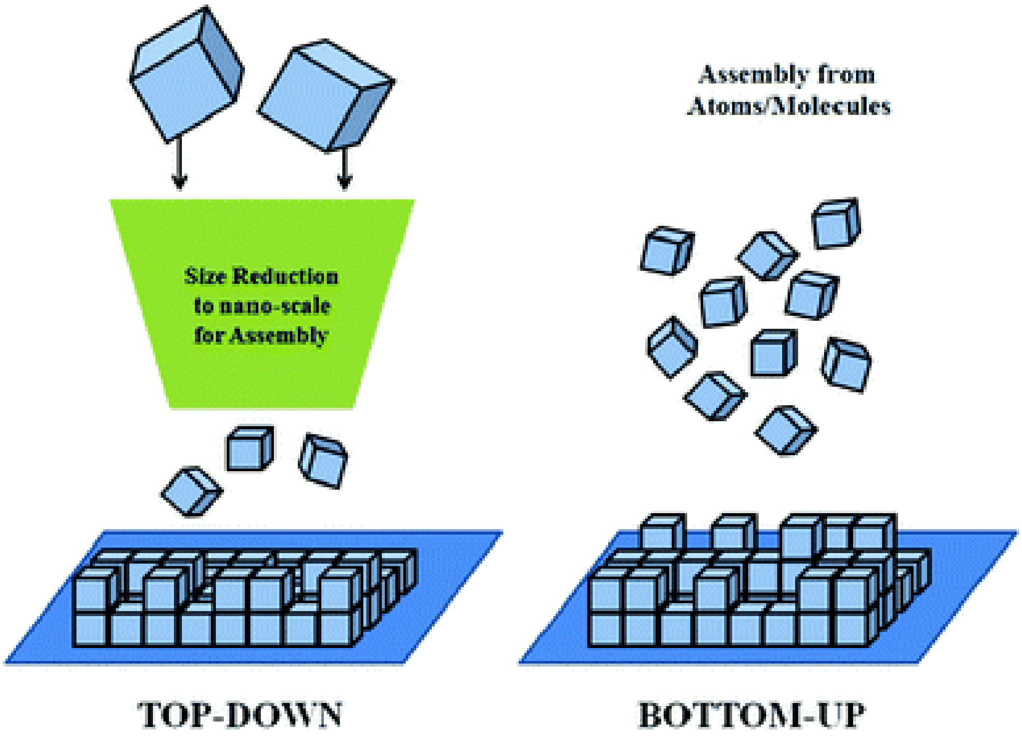

Fig. 3.1 Schematic representation of top-down and bottom-up approach

(Source: http://pubs.rsc.org/en/content/articlelanding/2013/ra/c2ra21810k/unauth#!divAbstract)

[Table 3.1]

Examples of synthesis methods based on top-down and bottom-up approach

Top down methods	Bottom-up methods
High energy ball milling	Sol-gel processing
Lithography	Chemical vapour deposition
Gas condensation	Physical vapour deposition
Severe plastic deformation	Soft lithography

(Source: http://www.slideshare.net/arunpl/nano-technology-5464209) significance. Therefore such kind of surface defects may affect material's efficiency at small scale. Furthermore, particles synthesized by this method do not have uniform size distribution and shape. Generally, nanocomposites used in some applications where accuracy of size and shape is not necessary are prepared by milling method. In such applications impurities of the material can be neglected up to some level. However, process of annealing also reduces these impurities. Another problem related to surface imperfection is that it affects surface scattering and thereby conductivity of material. Despite these disadvantages, this method is frequently used because it is relatively easy and simple to process [3.2].

(ii) Bottom-up: It mainly involves wet chemical synthesis methods in which nucleation and growth of liquid substance takes place. As compared to top-down this technique has advantage of uniform size and shape of particles. There are also fewer chances of surface defects and impurities. In addition, materials prepared by this approach are almost at the thermodynamically equilibrium [3.2].

From above discussion it can be concluded that reduction of the size is not the only task in nanomaterials synthesis but it requires following properties such as [3.2],

- Uniform size distribution of particles
- regular shape and morphology
- proper chemical composition and crystal structure
- defect free surface and entire crystal structure
- prevention from agglomeration

Chapter 3

Experimental methods and characterization techniques

3.1.1 Co-precipitation method

Precipitation method is a kind of liquid phase synthesis route which involves wet chemistry. Precipitates are generally found by chemical reaction of a solid inside solution. When simultaneous precipitation occurs from different ions and large numbers of small particles are formed it is called co-precipitation. These precipitates are generally hydroxides and by annealing/calcinations they can be converted to oxides at high temperature. Here the process of calcination removes organic impurities and also at high temperature it prevents growth of particles so they can be obtained in nano size. The general procedure is shown in figure below.

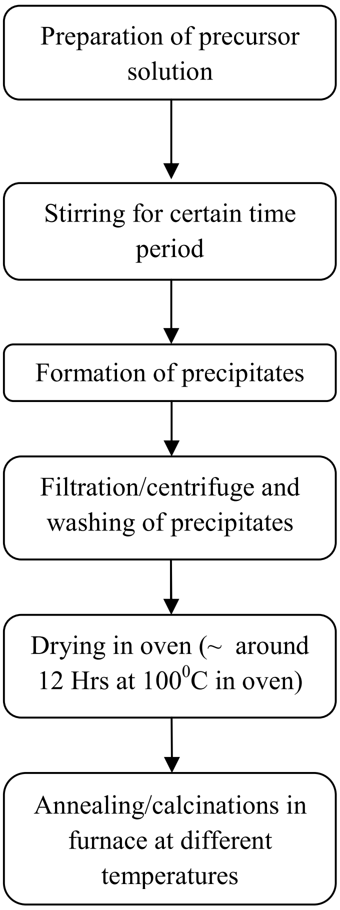

Fig. 3.2 A general synthesis route of nanomaterials by co-precipitation method

This method is comparatively simple, easy and cheap compared to other wet chemical methods for the preparation of nanoparticles. Using this synthesis route material can be prepared in large quantity. But sometimes it is time consuming when precipitates are difficult to filter and wash. Rashad et. al. prepared nano structured SnO_2 using co-precipitation and solvothermal methods. They have found particles size to be around 16.2nm in the prepared sample. In addition, prepared sample also shows homogeneity and tetragonal structure from TEM results [3.3]. Naje et. al. also found another synthesis route based on chemical precipitation to prepare SnO_2 nanoparticles. They have estimated average crystallite in the range to be 8-10 nm from X-ray diffraction (XRD) analysis [3.4]. Generally, stannic chloride pentahydrate ($SnCl_4·5H_2O$) and stannous chloride dihydrate ($SnCl_2·2H_2O$) are used as precursors to prepare nano sized tin dioxide (SnO_2). They form hydroxide precipitates when reacted with ammonia solution under continuous stirring and these precipitates are then treated thermally at high temperature.

3.1.2 Sol-gel synthesis

It is another wet chemical method to synthesize size and shape controlled nanoparticles. Here sols refer to liquid with dispersed colloidal particles. Size of the colloid particles is in the range of 1-100nm. And gel is a porous matrix like structure of sub micrometer dimensions. It is the combination of solid and liquid phases [3.5-3.6]. In the conventional process, sol is formed from starting material (generally metals, chlorides) and then water content of sol is removed by drying process that results in gel like structure. Finally gel is annealed at high temperature to obtain oxide nanoparticles. Fig. 3.3 shows the general synthesis route of sol-gel process to synthesize oxide nanoparticles. Low sintering temperature (~200-600^{0}C) and purity of final product are the main advantages of this route. It is also a simple, economic and effective option to obtain high quality coatings. Though sol-gel method can not be applied to commercial level because of some limitations like weak bonding, low wear-resistance, high permeability and difficult controlling of porosity [3.7].

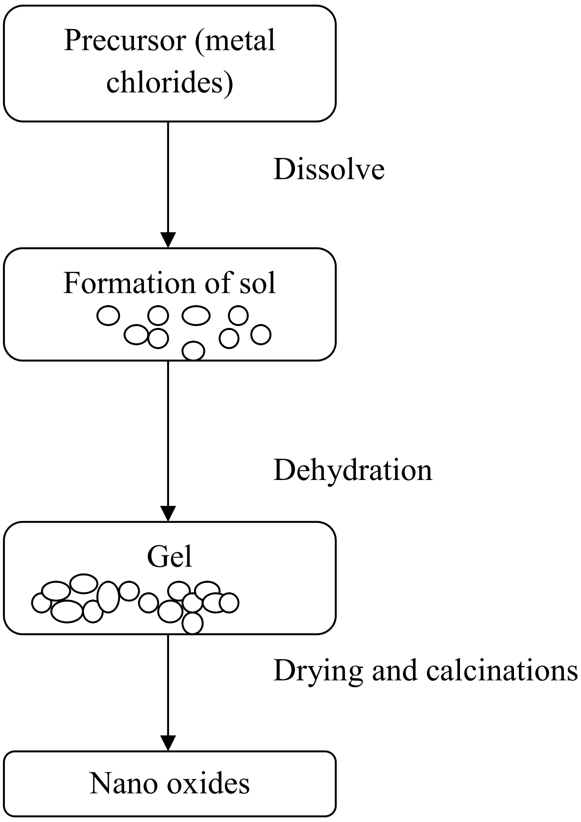

Fig. 3.3 A general synthesis route of nanomaterials by sol-gel method

(Source: http://www.gitam.edu/eresource/nano/nanotechnology/bottamup%20app.html)

Aziz and co-workers have prepared nanoparticles of SnO_2 in the range of 22-31 nm using sol-gel method [3.8]. In other work, SnO_2 nanocrystalline of size 2.8 nm, 4.0 nm and 5.1 nm have been synthesized by sol-gel method at different annealing temperature 300^0C, 400^0C and 500^0C respectively [3.9].

3.1.3 Powder Metallurgy method

The process of ball milling has grown up as powder metallurgy method which follows top-down approach to produce nano or sub micron sized fine dispersed powders [3.10, 3.11]. This mechanical attrition can be milling of elemental powders or dissimilar alloys. The former is mechanical milling and latter known as mechanical alloying. Nanoparticles are a kind of meta-stable materials which can be prepared by process of ball milling. The ball milling is used to shrink the grain size to nano scale in solid elements. There are number of parameters which affect the size reduction including properties of material and type of process. It is reported that in FCC structured metals, minimum grain size achieved by milling scales inversely with their melting temperature [3.12]. Another important factor is milling temperature that affects growth of nanocrystals. In their studies, Shen and Koch reported that as compared to room temperature, samples milled at lower temperature had smaller grain size. For instance, crystallite size of Cu is 26 ± 3 nm when prepared at room temperature while it has size of 17 ± 2 nm when milled at -85^0C [3.13]. Reduction in grain size because of milling at lower temperature has also been found in the intermetallic compound CoZr and elemental Zn [3.14, 3.15]. Fecht et al. in 1990, proposed the process of mechanical attrition to prepare nanocrystals. A typical process can be described in three steps as follow [3.16]:

I. Deformation localization in shear bands which contains high dislocation density.

II. Formation of nano sized grains by dislocation rearrangements

III. In the final stage, high angle grain boundaries replace the low angle grain boundaries by grain boundary rotation.

Klassen and co-workers observed phase formation and microstructure grow during mechanical alloying of dissimilar powders Ti and Al [3.17]. Trudeau et al. reported both low milling energy mechanical alloying of Fe and Ti elements to prepare FeTi nano crystals [3.18].

The main limitation of the ball milling process is contamination due to grinding medium and materials. Contamination is found in most of the milling process from grinding media (generally balls and vial) or atmosphere. For example, iron contamination takes place when steel balls and containers are used. Contamination due to lower energy mills is found quite less than highly energetic mills. This problem can be minimized by using grinding media made up of tungsten carbide or ceramic materials [3.10].

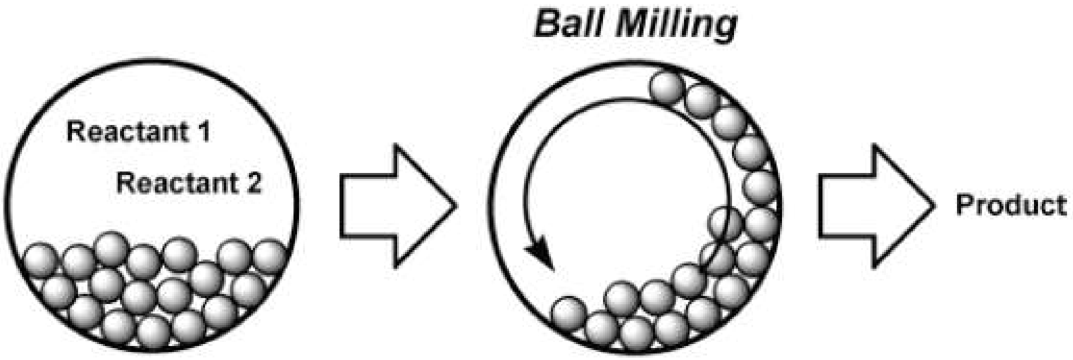

Fig. 3.4 A schematic diagram of milling process [3.19]

(Source: alpha.chem.umb.edu/chemistry/ch471/documents/Ballmilling-Jackie.pdf)

Chapter 3

Experimental methods and characterization techniques

From past few years, ball milling has developed as a solvent free and green synthesis route. Using few basic types of equipment like mortar and pastel one can prepare nano scale materials with this approach. The below figure shows ball mill is a kind of grinder to grind materials into fine powder using balls of tungsten or carbide like materials. As described before grain size of final product depends upon various parameters including temperature, size and number of the balls, material of the ball and speed of rotation [3.19-3.21]. In addition to this, ratio of weight of the balls to powder has great impact in milling process. The time required to achieve final product is less when ball to powder ratio is higher. it is due to fact that when weight proportion of the ball increases the number of collisions between balls per unit time increases and therefore process of making alloys becomes faster [3.22,3.23].

Fig. 3.5 (Source: alpha.chem.umb.edu/chemistry/ch471/documents/Ballmilling-Jackie.pdf) [3.19]

Among different types of mills, planetary ball mill is extensively used for the attrition of alloys at nano scale. Generally, in this type of ball mill few hundred grams of the powder can be processed in one time. As the name suggests in this type of mill, vials (containers) exhibit planet like movement. Vials are placed on a rotating disc and driven to rotate around their centres too. Consequently, there will be two motions of vials one is because of the rotating disc and other will be around their own axes. The centrifugal force produced by these both motions cause material to be ground. Direction of these two rotations are opposite so centrifugal force also applies alternatively in similar and opposite directions. In the previous days it was not possible to independently control the rotational speed of disk and vial of planetary ball mill but now days it is available in latest versions. Commercially grinding balls and vials are made up of eight different materials, i.e. agate, silicon nitride, sintered corundum, zirconia, chrome steel, Cr-Ni steel, tungsten carbide and plastic polyamide [3.23].

3.2 Characterization techniques

The details of the characterization techniques which have been used to confirm structure, chemical composition and morphology of the prepared samples in present thesis are described in the following section.

3.2.1 Powder X-Ray diffraction (XRD)

Based on the atomic arrangement and structure any solid can be categorized in two main classes: i) Amorphous and ii) Crystal. The arrangement of atoms in amorphous material is not uniform and they found in random fashion while in crystal structure atoms are arranged in long-range periodic array. To identify prepared nano material one has to know its crystal structure. Powder X-ray diffraction is a powerful tool to get information about crystal structure, its available phases and crystallite size of the synthesized material. In 1919, W. Hull introduced the concept of certain diffraction pattern in crystalline material [3.24].

According to that each crystalline material has unique pattern that will be remain unchanged. In a compound like material each of the component elements produces its own pattern which is independent from others. Using this method of analysis it is possible to find crystal structure of synthesized material [3.25]. It can be explained by diffraction due to arranged atoms of crystal. The x-ray wavelength is comparable to inter-atomic distance in solids and scattered by periodic array of atoms producing constructive interference at specific angles [3.26]. The required condition for diffraction can be understood by Bragg's law which states,

$$n\lambda = 2d\sin\theta \qquad ...(1)$$

Where, n is integer number

λ is used wavelength of X-ray

θ is scattering angle and

d is inter- planar distance in lattice.

Following figure shows the requirement to obtain diffraction in crystal planes.

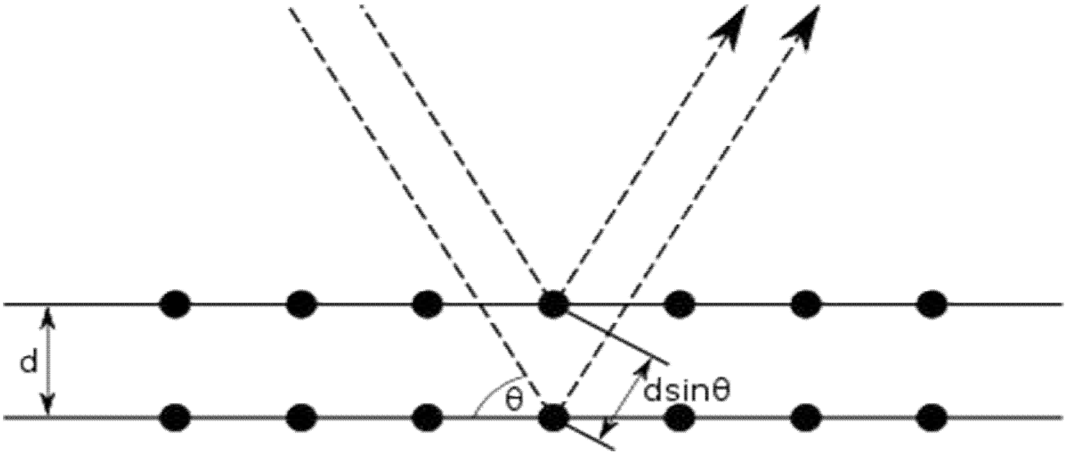

Fig. 3.6 Diffraction of two beams from two different atoms in crystalline solid [3.27]

Eqn. (1) can be experimentally applied to measure spacing (d) between different planes of crystal if wavelength of X-ray (λ) and scattering angle (θ) are known. By re-writing above eqn.,

$$\sin\theta = n\lambda/2d \qquad \dots (2)$$

The unit cell dimensions determine possible values of 2θ where reflection occurs. The intensities of reflections depend on the distribution of electrons in the unit cell. Around the atoms electron density is highest. Therefore intensity depends on the position of atoms in the unit cell. Reflection from the crystal planes where electron density is high is strong and weak for the low density electron planes. The interaction between incident rays produces constructive interference when Bragg's condition is satisfied. These X-rays are then detected and counted by scanning a sample over a range of 2θ angles. During this process, it is important to cover all the possible direction of lattice because of the random orientation of crystal. It can be done by comparing set of d-spacing of that material with standard data [3.28, 3.29]. Fig. 3.7 shows θ-2θ arrangement of X-ray source and sample in which X-ray tube is fixed to its position, sample rotates at θ^0 and detector rotates at $2\theta^0$. In another type of instrument sample is fixed, X-ray tube rotates at θ^0 and detector rotates at θ^0 which is known

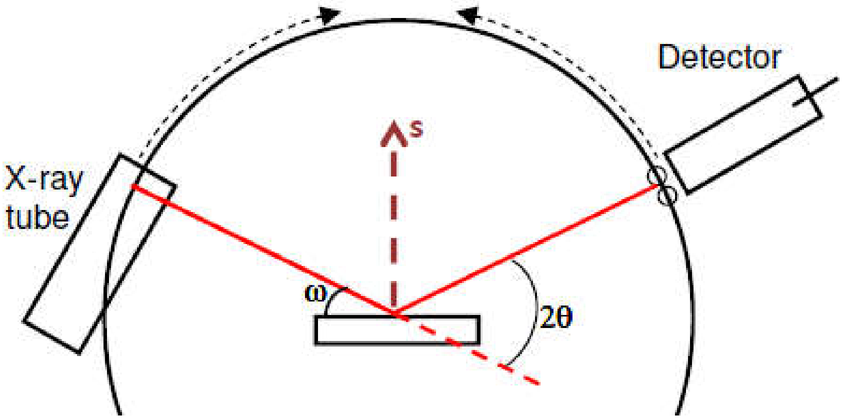

Fig. 3.7 Bragg-Brentano geometry in powder diffractometer [3.26]

as θ-θ geometry [3.26, 3.28]. In the present study, X-ray diffraction of the samples performed on a PANlytical X’pert Pro diffractometer as shown in fig. 3.8. In this diffractometer Cu K-Alpha radiation is used and step size of scanning is 0.0170.

Fig. 3.8 PANlytical X’pert Pro diffractometer [3.30]

3.2.2 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is an essential technique to study surface morphology of nanoparticles. High energy beam of electrons is used to scan sample surface. The electron beam and constituent atoms of the sample interact with each other that produce signal containing information about the sample. This signal is detected and amplified by electronic device. In a further process, signal is displayed as an image on a cathode ray tube in which the scanning is synchronized with that of the microscope and final image displayed on a computer monitor [3.31]. The SEM signal can be made up of either of the three i.e. i) secondary electrons, ii) backscattered electrons, iii) characteristics X-rays and light. It depends on beam of electrons striking the surface and interacting with sample at its surface. In secondary electron imaging, SEM can produce resolution such that details of 1 to 5nm in size can be observed from a sample surface. SEM micrograph of the same explains surface structure of the sample. Characteristic X-rays are another imaging mode for the SEM. Sometimes they are used to detect elemental composition of sample. Back scattered electrons imaging generally used in analytical SEM along with spectra of characteristic X-rays due to the elemental composition of the sample [3.32]. When electron beam strikes the sample, electrons are scattered from the surface atoms and escape from the surface with low energy due to scattering. These electrons are called secondary electrons. But when scattering is elastic, electron do not loose energy during the collision. As a result, they escape from atoms with high energy and their trajectory will be at high angle mostly in the back direction of their source. These electrons are known as back-scattered electrons. Because of the energy difference in secondary electrons and backscattered electrons, they are separated by different detectors and produce different signals and images [3.33].The resolution of SEM is approximately 10nm. The main advantage of SEM is that it can produce three dimensional topographical images. Furthermore, SEM is easy to operate, works fast, generates data in digital form and requires minimal preparation actions [3.34]. In the present work, SEM analysis of prepared samples was carried out on JEOL JSM-5610LV scanning electron microscope at operating voltage of 15 KV. Fig. 3.9 shows this scanning electron microscope.

Fig. 3.9 JEOL JSM-5610LV scanning electron microscope

(Source: https://center.belstu.by/labs-micr)

3.2.3 Energy dispersive spectroscopy (EDS)

As mentioned in above discussion, interaction of electron beam with a sample produce different types of emissions in which characteristic X-rays of different elements are detected by Energy Dispersive X-ray Spectroscopy (EDS). Corresponding energy spectrum is used to get information about chemical composition of materials. Generally, EDS instruments are integrated into Scanning Electron Microscope (SEM). Main components of this system are sensitive X-ray detector, liquid nitrogen for cooling and software to record energy spectrum. The detector is placed in the sample chamber of the main system at the end of a long arm, which is cooled by liquid nitrogen. Typically, detectors are made of Si(Li) crystals that can be operated at low voltages to improve sensitivity. In latest technology "silicon drift detectors" are available which operate at higher count rates without liquid nitrogen cooling. The detector is composed of crystal which absorbs the energy of X-rays by ionization, releasing free electrons in a crystal so it becomes conductive and produces an electrical charge bias. Consequently energy of individual X-rays is converted into electrical voltage corresponds to the characteristic X-rays of the particular element. Therefore EDS is an instrument to quantify chemical composition of the sample. The main limitation arises due to overlap of energy peaks among different elements. For instance, Mn-Kα and Cr-Kβ or Ti- Kα and various L lines in Ba overlap with each other. Mainly at higher energies, a single peak may correspond to different elements. To overcome this, one has to separate peaks by deconvolution methods [3.35].

3.2.4 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermo-analytical technique to measure difference in heat flow to a sample and reference which is monitored as a function of temperature. There are two types of DSC as described below:

i) Power compensated DSC

In this type, sample and reference are heated by separate individual heat sources. The temperature difference between the two (sample and reference) should be close to zero and electric power required to maintain this difference to zero is measured.

ii) Heat-flux DSC

In heat flux DSC, sample and source are heated by same source and temperature difference (ΔT) is measured. And signal is converted to a power difference (ΔP) using calorimetric sensitivity.

The Differential Scanning Calorimeter is used in this work to study phase transformation of prepared nanomaterials. We used heat flux type DSC (Shimadzu DSC-50) and thermal analyzer (TA-50 WSI, Shimadzu, Japan) to record DSC scans which is interfaced to computer. This DSC has detection sensitivity of ~10 µW. The phase transformation can be observed from the thermograms using software provided with the instrument. In this DSC, positive (up-going) peaks are considered as exothermic process and negative peaks as endothermic process.

Fig. 3.10 Shimadzu DSC-50 Differential Scanning Calorimetry

(Source: http://pglab.nolda.co.kr/research/equipments.php)

3.2.5 Micro Hardness Measurement

Micro indentation hardness method measures material’s resistance to plastic deformation usually by indentation. Generally, an indenter is pressed into the surface of the material to be tested under certain load for a specific time interval, and a measurement is made of the size or depth of the indentation .Hardness test is done mostly to examine suitability of a material for the certain application. Once the value of hardness is known other mechanical properties of the material can be derived from the same. There are no absolute standards for this test and so hardness of material can have any arbitrary value. In common testing, applied loads are below 1Kg and testing sample should have dimensions in micrometer [3.36].

References

3.1 P. Saravanan, R. Gopalan, and V. Chandrasekaran, Def. Sci. J. **58,** 504 (2008).

3.2 J. Behari, Ind. J. of Exp. Bio. **48,** 1008 (2010).

3.3 M. M. Rashad, I. A. Ibrahim, I. Osama and A. E. Shalan, Bull. Mater. Sci. **73,** 903 (2014).

3.4 A. N. Naje, A. S. Norry, A. M. Suhail, Int. J. of Inno. Res. in Sci. Engg. and Tech. **2,** 7068 (2013).

3.5 L. L. Hench and J.K. West, Chem. Rev. **90,** 33 (1990).

3.6 J. T. Davis, E. K. Rideal, In Interfacial Phenomena; Academic Press: New York (1963).

3.7 http://www.ceramics.mmat.ubc.ca/introduction.html

3.8 M. Aziz, S. S. Abbas, W.R.W. Baharom, W.Z.W. Mahmud, Mater. Lett. **74,** 62 (2012).

3.9 J. Zhang, L. Gao, J. of Solid State Chem. **177,** 1425 (2004).

3.10 C.C. Koch, Rev. Adv. Mater. Sci. **5,** 91 (2003).

3.11 J.S. Benjamin, Sci. Amer. **234,** 40 (1976).

3.12 J. Eckert, J.C. Holzer, C.E. Krill III and W.L. Johnson, J. Mater. Res.**7,** 1751 (1992).

3.13 T.D. Shen and C. C. Koch, Mater. Sci. Forum, **179-181**, 17 (1995).

3.14 D.K. Pathak, Ph.D. Dissertation, North Carolina State University, 1995.

3.15 X. Zhang, Ph.D. Dissertation, North Carolina State University,2001.

3.16 H.J. Fecht, E, Hellstern, Z. Fu and W.L. Johnson, J. Mater. Res **7,** (1992) 1751.

3.17 T. Klassen, M. Oehring and R. Bormann, J. Mater. Res. **9,** (1994) 47.

3.18 M.L. Trudeau, R. Schultz, , L. Zaluski, S. Hosatte, D.H. Ryan, C.B. Doner, P. Tessier, J.O. Strom-Olsen and A. Van Neste, Mater. Sci. Forum, **88-90, 537** (1992).

3.19 alpha.chem.umb.edu/chemistry/ch471/documents/Ballmilling-Jackie.pdf

3.20 Lance Frazer, Env. health perspectives, **10,** 111 (2003).

3.21 Belen Rodríguez, Adv. Synth. Catal. **349,** 2213 (2007).

3.22 C. Suryanarayana, Prog. in Mater. Sci. **46,** 1 (2001).

3.23 C. Suryanarayana , G. H. Chen, F.H. Froes, Scri. Met. Mater. **26,** 1727 (1992).

3.24 A.W. Hull, J. Am. Chem. Soc. **41,** 1168 (1919).

3.25 http://old.vscht.cz/clab/RTG/dokumenty/thermo/xrd/Introduction.pdf

3.26 http://prism.mit.edu/xray

3.27 https://en.wikipedia.org/wiki/Bragg%27s_law

3.28 B. D. Cullity, Elements of X-ray Diffraction; Addison-Wesley Publishing Company: USA, (1978).

3.29 M. M. Woolfson, An Introduction to X-ray Crystallography; Cambridge University Press Vikas Publishing House Pvt. Ltd: New Delhi, (1970).

3.30 http://www.panalytical.com/XPert3-MRD-XL.htm

3.31 http://www.smtcorp.com/scanning-electron-microscopy

3.32 L. N. Wing, Ph. D. Thesis, City University of Hong Kong; Hong Kong, (2008).

3.33 Scanning Electron Microscopy (SEM) Imaging Modes. Cobham Technical Services Reliability and Failure Analysis.

3.34 http://www.microscopemaster.com/scanning-electron-microscope.html

3.35 http://serc.carleton.edu/research_education/geochemsheets/eds.html

3.36 Hardness Testing, 2nd Edition, 06671G Harry Chandler, Editor.