REVIEW ARTICLE ON THERMAL CHARACTERIZATION OF NANOPARTICLES

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ABSTRACT

Materials with nanometer size have unusual structural properties. Nanopowders, controlled to nanocrystalline size **(**< 100 nm), can show atom like behaviours which result from higher surface energy due to their large surface area and wider band gap when they are divided to near atomic size. Success in devising and assembling systems on the scale of nanometers requires a deeper understanding of the basic processes and phenomena involved. Hence, one of the current key objectives is to adapt and develop a range of techniques that can characterize the thermal properties of nanostructured systems. Techniques, that provide local information on the nanometer scale, are important in obtaining a complete picture of material properties. Due to extreme selectivity of size of nanomaterials, the physical properties of nanomaterials are much different.

INTRODUCTION

Research in nanomaterials opens many new challenges both in fundamental science and technology. There are three key steps in the development of nanoscience and nanotechnology: materials preparation, property characterization and device fabrication. Preparation of nanomaterials has been advanced by numerous physical and chemical techniques as described in section. The purification and size selection techniques can produce nanocrystals with well defined structure and morphology. The current most challenging tasks are property characterization and device fabrication. Characterization contains two main categories: structure analysis and property measurements. Structure analysis is carried out using a variety of microscopy and spectroscopy techniques, while the property characterization is rather challenging. Recent development of low dimensional materials including nano-sized particles, nanometer thick thin films, nano wires, nano tubes, and nano grained polycrystalline solids, presented many novel properties and performance that are attractive to technological applications. At the same time, these advanced materials provide us new venues for studying melting of solids because they all possess numerous amounts of surfaces or interfaces. Especially these low dimensional materials brought unique opportunities to examine the role of surfaces and interfaces in melting as well as the size effect on melting kinetics. To maintain and utilize the basic and technological advantages offered by the size specificity and selectivity of nanomaterials, it is imperative to understand the principles and methodologies for characterizing the physical properties of individual nanoparticles. The properties of nanostructures depend strongly on their size and shape [1]. Therefore, an essential task in nanoscience is property characterization [2] of individual nanoparticles with well-defined atomic structures. Characterizing the properties of individual nanoparticles is a challenge to many existing testing and measuring techniques because of the following constrain. First, the size (diameter and length) is rather small; prohibiting the applications of the well established testing techniques. Secondly, the small size of the nanostructures makes their manipulation rather difficult, and hence special techniques are needed for picking up and installing individual nanostructures. Finally, new methods and technologies must be developed to quantify the properties of individual nanostructures. The very high surface-to-volume ratio of nanometer sized particles can lead to novel and unexpected atomic arrangements, and may also have dramatic effects on other physical or chemical attributes. Because of this, the precise determination of nanoparticles structure is a fundamental issue. Nanomatenals are a bridge that links single elements with single crystalline bulk structures. Quantum mechanics has successfully described the electronic structures of single elements and single crystalline bulks. The well-established bondings, such as ionic, covalent and metallic are the basis of solid-state structures. Thus, a thorough understanding of the structure of nanocrystals can provide deep insight in the structural evolution from single atoms to crystalline solids. The finite size of the particles confines the spatial distribution of electrons, leading to quantised energy levels.

Many authors observed new phases and additional exothermic and endothermic peaks in nanostructured materials, which were not present in their bulk counterparts. The new peaks and phases are explained on the basis of grain growth process and their microstructure and atonuc configuration changes when exposed to high temperature. A large fraction of atoms in nanoparticles are surface atoms and these atoms have significant influence on the thermal properties of nanostructured materials. Structural changes can be expected in small particles because of the large amount of free energy [3] associated with their grain boundaries. The energy associated with the interface regions becomes substantial when the size of the crystallites is in nanosized regime and it may influence phase transitions in nanophase materials. Other types of lattice imperfections may also exist due to small size of the particles. Hence the phase transitions in nanoparticles are expected to exhibit modified behaviour from that of the bulk materials.

WORKING OF THERMAL ANALYZER

The sample should be powdered where possible and should be spread in a thin and uniform layer in the sample container. Thermobalance is normally housed in a glass or metal systems to control the pressure and the atmosphere inside it. A regular gaseous flow may be maintained in order to remove the evolved gases from the thermobalance with the care that these the flow gases don not disturb the balance [4]. Temperature sensors are either platinum resistance thermometers or thermocouples. The temperature controller attached to the instrument offer heating rates from a fraction of a degree per minute to nearly 100 °C min^{-1} with additional characteristic of isothermal heating.

The beam is displaced by change in weight loss with temperature on sample side. This displacement is detected optically and the drive coil current is changed to return the displacement to zero. The detected drive coil current change is proportional to the amount of weight change in sample and is output as the TG signal. The DTA detects the temperature difference between the sample holder and the reference holder using electromotive force of thermocouples, attached to the holders. The differential is output as the DTA signal.

Thermogravimetric analysis involves the determination of the mass of a specimen as a function of temperature, or time of heating, or both, and when properly applied, provides more useful information than does loss on drying at fixed temperature, often for a fixed time and in what is usually gas atmosphere. Usually, loss of surface absorbed solvent can be distinguished from solvent in the sample and from degradation losses. The measurements can be carried out in atmospheres having controlled humidity and oxygen concentration to reveal interactions with the drug substance, between drug substances, and between active substances and excipients or packaging materials. While the details depend on the manufacturer, the essential features of the equipment are a recording balance and a programmable heat source. Equipment differs in the ability to handle specimens of various sizes, the means of sensing specimen temperature, and the range of atmosphere control. Calibration is required with all systems, i.e., the mass scale is calibrated by the use of standard weights; calibration of the temperature scale, which is more difficult, involving either variations in positioning of thermocouples and their calibration; or in other systems, calibration involves the use of standard materials because it is assumed that the specimen temperature is the furnace temperature.

Procedural details are specified in order to provide for valid interlaboratory comparison of results. The specimen weight, source, and thermal history are noted. The equipment description covers dimensions and geometry, the materials of the test specimen holder, and the location of the temperature transducer. Alternatively, the make and model number of commercial equipment are specified. In all cases, the calibration record is specified. Data on the temperature environment include the initial and final temperatures and the rate of change or other details if nonlinear. The test atmosphere is critical; the volume, pressure, composition, whether static or dynamic, and if the latter, the flow rate and temperature are specified.

Table 1. Classification of Thermoanalytical Techniques.

Physical Property	**Derived Technique**
Mass	Thermogravimetry (TG)
	Isobaric mass change determination
	Evolved gas detection (EGD)
	Evolved gas analysis (EGA)
	Emanation thermal analysis
Temperature	Heating or cooling curve determination
	Differential thermal analysis (DTA)
Enthalpy	Differential scanning calorimetry (DSC)
Dimensions	Thermodiliatometry
Mechanical characteristics	Thermochemical measurements
	Dynamic Thermochemical measurements
Acoustic characteristic	Thermosonimetry
	Thermoacoustimetry
Optical characteristic	Thermoptometry
Electrical characteristic	Thermoelectrometry
Magnetic characteristic	Thermomagnetometry

THERMOGRAVIMETRY

Thermogravimetric analysis covers a wide spectrum of thermo analytical techniques, which monitor one or more physical properties of a substance that is undergoing a temperature programmed heating as a function of time and temperature. It provides a quantative measurement of any weight changes associated with thermally associated changes. Thermogravimetric analysers can be called as a thermo balance which is a combination of a suitable electronic microbalance with a furnace, which is operated with a computer controlled heating programme. It allows the sample to be weighed and heated or cooled in a temperature controlled manner and the mass, time and temperature data to be recorded under specific atmosphere. The thermogravimetry analyzer (TGA) system, which combines thermogravimetry (TG) and differential thermal analyzer (DTA), is widely used in the fields of gas– solid interactions, fuels, catalysis, polymers and chemical synthesis. Thermogravimetric analysis is used to determine the material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated. This is explained later in detail. The measurement is normally carried out in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of temperature. In addition to weight changes, some instruments also record the temperature difference between the specimen and the reference pan (differential thermal analysis, or DTA) or the heat flow into the specimen crucible compared to that of the reference crucible (differential scanning calorimetry, or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process.

A DTA apparatus consists of a sample holder comprising thermocouples, sample containers and a ceramic or metallic block; a furnace; a temperature programmer; and a recording system. The key feature is the existence of two thermocouples connected to a voltmeter. One thermocouple measures the temperature of an inert material such as Al_2O_3, while the other is used for measurement for the sample temperature under study. As the temperature is increased, there will be a deflection of the voltmeter if the sample is undergoing a phase transition. This occurs because the input of heat will raise the temperature of the inert substance, but be incorporated as latent heat in the material changing phase. In DTA, the differential temperature is plotted against the time, or against the temperature (DTA curve or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is related to the enthalpy change of the sample. Generally a sharp endothermic (negative peak) DTA peak at particular temperature indicates the melting point of the sample as the temperature of the sample at this particular temperature would lag behind the temperature of reference substance where as an exothermic peak indicate the onset of decomposition process.

THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermal properties like heat capacities, the glass transition temperature, melting and degradation of macromolecules can be analyzed using thermogravimetry and differential thermal analysis along with differential scanning calorimetry (DSC). Thermal measurements are based on the measurement of dynamic relationship between temperature and some property of a system such as mass, heat of reaction or volume when the material is subjected to a controlled temperature programme. In thermogravimetric analysis, the mass of the sample is recorded continiously as a function of temperature as it is heated or cooled at a controlled rate. A plot of mass as a function of temperature is known as thermogram. The apparatus required for thermo-gravimetric analysis include a sensitive recording analytical balance, a furnace, a temperature controller, and a programmer that provides a plot of the mass as a function of temperature. Often an auxiliary equipment to provide an inert atmosphere for the sample is also needed. Changes in the mass of the sample occurs as a result of rapture and/or formation of various physical and chemical bonds at elevated temperature that led to the evolution of volatile products or formation of reaction products. Thus TGA curve provides information regarding the thermodynamics and kinetics of various chemical reactions, reaction mechanisms, and intermediate and final reaction products.

DIFFERENTIAL THERMAL ANALYSIS (DTA)

A technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to the same controlled temperature programme. The record is the differential thermal or DTA curve; the temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards and temperature or time on the abscissa increasing from left to right. The term quantitative differential thermal analysis i.e. Quantitative DTA, cover those uses of DTA where the equipment is designed to produce quantitative results in terms of energy and / or any other physical parameter.

THERMAL ANALYSIS FOR PHYSICAL SIGNIFICANCE

Thermal analysis refers to a group of techniques in which the properties of a substance under study is monitored with respect to time and temperature in a specified atmosphere. This is often done by heating the precursors (starting materials) in an evaporator isothermally. Volatization of solid in a broad sense includes any process which result in conversion of matter from the solid state to the vapor phase. Volatization process can be accomplished by two ways.

1. Sublimation process in which the gaseous phase composed of the same type of atoms or molecules supplied by the solid phase i.e. the composition of the gaseous phase and the solid phase remain the same - a true vaporization process.
2. A chemical reaction between the solid phase and another species to form gaseous products. The additional species may be environmental gases, adsorbed water, or some some solid like container material. In both cases the composition of the gaseous phase is always different from the solid phase. This is often termed as decomposition or pyrolysis.

As solid is heated, the extent of lattice vibrations within the solid are increased and a temperature would be reached during heating where following changes can occur

1. Melting: the forces of attraction between the constituents decrease which maintain an orderly arrangement of the solid and comes down to a more disordered system called liquid state.
2. Phase transition: a new arrangement of the lattice structure.
3. Sublimation: direct transformation from the solid state to the gas phase occurs.

4. Decomposition: sometimes the molecular rearrangements of bonds within the solid during heating also result in formation products chemically different from the solid. These products can be a solid or gasses. This occurs over a range of temperature.

Thus by obtaining gravimetric data of heating a solid sample with time or temperature in a specified atmosphere, one would easily predict about the volatility, thermal stability and physical state of the sample at a particular temperature.

Precisely determined thermodynamic events, such as a change of state, can indicate the identity and purity of drugs. Compendia standards have long been established for the melting or boiling temperatures of substances. These transitions occur at characteristic temperatures, and the compendia standards therefore contribute to the identification of the substances. Because impurities affect these changes in predictable ways, the same compendial standards contribute to the control of the purity of the substances.

Thermal analysis in the broadest sense is the measurement of physical-chemical properties of materials as a function of temperature. Instrumental methods have largely supplanted older methods dependent on visual inspection and on measurements under fixed or arbitrary conditions, because they are objective, they provide more information, they afford permanent records, and they are generally more sensitive, more precise, and more accurate. Furthermore, they may provide information on crystal perfection, polymorphism, melting temperature, sublimation, glass transitions, dehydration, evaporation, pyrolysis, solid solid interactions, and purity. Such data are useful in the characterization of substances with respect to compatibility, stability, packaging, and quality control. The measurements used most often in thermal analysis, i.e., transition temperature, thermogravimetry, and impurity analysis, are described here.

Transition Temperature - As a specimen is heated, its uptake (or evolution) of heat can be measured [differential scanning calorimetry (DSC)] or the resulting difference in temperature from that of an inert reference heated identically [differential thermal analysis (DTA)] can be measured. Either technique provides a record of the temperature at which phase changes, glass transitions, or chemical reactions occur. In the case of melting, both an “onset” and a “peak” temperature can be determined objectively and reproducibly, often to within a few tenths of a degree. While these temperatures are useful for characterizing substances, and the difference between the two temperatures is indicative of purity, the values cannot be correlated with subjective, visual “melting range” values or with constants such as the triple point of the pure material.

PARTICLE SIZE DEPENDANT THERMAL PROPERTIES

Melting, a phase transformation from a crystalline solid state (rigid and topologically long range ordered) into a liquid state (fluid and topologically long-range-disordered), is a common phenomenon in nature. Investigations on melting of solids have dated back to beginning of the last century for its scientific and technological importance. Melting is born to be a key subject in condensed matter physics. As one of the most important phase transformations in processing and applications of materials, melting is also a vital process in materials science and engineering. In addition, melting of solids is closely related to nature environment, biology, and many other fields [5]. Therefore, investigations on the nature of melting are of interdisciplinary interests covering a broad range of sampling from tiny clusters containing several tens of atoms to the inner core of the earth. In the framework of classic thermodynamics, melting of a solid is known as a first - order discontinuous phase transformation occurring at a critical temperature at which Gibbs free energies of the solid and the liquid states are equal, i.e. T_0 of the solid. The melting process of a solid involves an abrupt change in latent heat and volume at T_0. Numerous experimental observations verified that melting is normally initiated at solid surfaces because of the vanishing nucleation barrier there [6]. In addition, investigations revealed that various kinds of defects in solids, such as interfaces, grain boundaries, voids, impurities and other defects also facilitate melting. Indeed, understanding of the melting process has been greatly improved after extensive and intensive studies in the past century and several models for melting of solids have been developed. Nevertheless, many aspects of melting are to be understood and the intrinsic mechanism of melting in solids is still a mystery.

Thermal kinetics behaviour of low dimensional materials, in which surfaces and/ or interfaces play a dominant role, is much deviated from that for the conventional bulk solids. For example, the melting point of free-standing nanometer sized particles is remarkably depressed relative to T_0 [7]. It is also observed that when the nanoparticles are properly coated by (or embedded in) a high melting point matrix, the melting point of the particles can be elevated above T_0 [7], that rarely happens in bulk solids. These interesting phenomena make melting of low-dimensional solids to be an attractive topic which has drawn increasing attentions in both fields of condense matter physics and materials science in recent years. With the increasing technological applications of low dimensional materials in industries, thermal stability of the materials becomes one of the crucial issues to concern for their practical performance. Melting becomes one of the failure modes at elevated temperatures for low dimensional materials. For example, owing to the size effect, catalysts of nano sized metallic particles might melt and agglomerate at temperatures far below T_0, thus losing their functionality. Clearly, investigations on melting of low dimensional materials, on the other hand, are of significance for the technological applications of this new materials family. It is known that melting is normally nucleated at solid surfaces or interfaces. Once the heterogeneous nucleation of melt is somehow suppressed at the solid surfaces or interfaces, one may expect that the solid phase persists in its metastable solid form above T_0, which is known as superheating, or overheating [8]**.**

Pioneering exploration of superheating in metals was performed by Daeges et al. [9] in 1986 and they successfully achieved superheated Ag micro-sized particles coated by Au. Since then, numerous investigations on superheating of metallic particles in various systems have been reported and several models accounting for the superheating phenomenon have been proposed. Superheating of solids provides an interesting subject and a new territory for studies of melting. On one hand, studying superheating of solids greatly facilitates understanding of the nature of melting and the ultimate stability limit of crystalline solids. On the other hand, achieving superheated solids may provide effective approach for stabilization of low dimensional materials exposed to elevated temperatures, which is of technological significance for materials. In recent years, extensive experimental and theoretical investigations as well as computer simulations on melting and superheating of crystalline solids (especially on low dimensional materials) have been carried out. Significant progresses have been made on this fascinating subject with a large body of publications appeared in the literature, including several review articles related to some aspects of melting [10 - 20]. Emphasis had been made on melting and superheating of nanostructured solids including thermodynamic and kinetic analyses of the size effect and the interfacial structure effect on melting processes.

Melting of solids is a common phenomenon in nature. It is also one of the most important phase transformations in materials science and engineering. In recent years, extensive experimental and theoretical investigations in conjunction with computer simulations on melting of solids, with various geometries ranging from bulk forms to nanometer- sized clusters, have greatly enhanced our understanding of the nature of melting. This paper reviewed the up to date research results on this classical and cutting edge topic. Emphasis was made on melting and superheating of nano sized particles and thin films including thermodynamic and kinetic analyses of the size effect and the interfacial structure effect on melting processes.

Conclusion

Here author describes about working mechanism as well as up to date research carried out on general physical significance regarding different thermal parameter. It leads / helpful to other researchers towards the thermal characterization of synthesized nanoparticles.

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