Chapter 6

Conclusions and suggestions for future work

Summary

The thesis presents systematic investigations of the size dependent properties in Titanium dioxide (TiO_2) and Tin dioxide (SnO_2) semiconductor nano oxides. Semiconducting nano-oxides are promising candidates for their diverse applications in science and technology. Our study is mainly focused on the thermodynamic and other surface related properties of SnO_2 and TiO_2 at nano scale. The methodology used to calculate size dependent properties is based on simple thermodynamic model and basic parameters. Our study shows that melting temperature, diffusion coefficients, surface energy, catalytic activation energy and Tolman length of TiO_2 and SnO_2 nanoparticles depend on the particle size. Further these properties are also influenced by different dimensions and shapes of particles. Present thesis also gives direction to synthesize stable and economic TiO_2, SnO_2 and their composites. Silver based oxide (Ag-SnO_2) has been prepared successfully by mechanical alloying to meet the requirements of electric contact materials.

Starting from the fundamental theory of Lindemann's criteria analytical model has been developed to calculate size dependent melting temperature in nanoparticles. Later, the model has been extended to investigate effect of dimension on size variation. Size dependency of melting temperature of tin dioxide nanostructures has been reported for 0, 1 and 2 dimensions. This variation is similar in relatively large nanoparticles irrespective of their dimensions but there is a considerable difference for nanoparticles below the range of 5 nm. We performed calculations of the glass transition and Kauzmann temperatures for SnO_2 nanoparticles using Arrhenius theory and Lindemann criterion. It shows glass transition (T_g) and Kauzmann temperature (T_K) decrease with decrease in particles size. It is observed that

there is a rapid drop of glass transition temperature below 10 nm. Similar nature is found in case of the melting temperature T_m. The Kauzmann temperature lies below the glass transition temperature for the SnO_2 nanoparticles for all sizes consistent with the observations.

We have also studied size and dimension dependences of diffusion coefficient in SnO_2 nanoparticles using Arrhenius relation and Lindemann's criteria. Effect of nitrogen doping has been investigated for SnO_2 nanoparticles with different sizes ranging from 1nm to 20nm. We observed that as the size of nanoparticles decreases, the diffusion activation energy of atoms decreases and results in the increase of diffusion coefficient. The dimension dependence has also been calculated for 0-, 1- and 2 dimensions. We have investigated that diffusion coefficients of SnO_2 nanoparticles in the case of self diffusion and nitrogen diffused nanoparticles are strongly influenced by size and dimensions. Furthermore, higher value of diffusion coefficient is found in the case of spherical nanoparticles which indicates faster diffusion mechanism for zero dimension than one and two dimensional nanostructures.

In the framework of thermodynamic analytical model, we report size dependent surface energy and Tolman length of semiconductor oxides TiO_2 and SnO_2 in present thesis. In these calculations parameters for corresponding bulk systems are obtained from computer simulations using Density Functional Theory (DFT) based data. The surface energy of the TiO_2 and SnO_2 nanoparticles decreases with the decrease in their size. In the case of TiO_2 for which data is available, we observe reasonably good agreement between the present and available data. Size variation in surface energy has been investigated for different planes/facets of TiO_2 and SnO_2 nano-crystals. The energy for different facets of TiO2 and

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SnO2 nanoparticles which saturates around 20nm shows a drastic change below 5 nm. The surface energy for the (110) facet of TiO_2 nanoparticles is minimum in all considered facets indicating lowest energy for this facet and therefore it can be concluded that it is the most stable facet of TiO_2 nanoparticles. The surface energy for (110) facet of rutile TiO_2 is lower than the (110) facet of anataseTiO_2. In the case of SnO_2 nanoparticles, surface energy for (112) and (110) facets has maximum and minimum value respectively suggesting (110) as the most stable phase for the considered size range. Our study also focuses on the important parameter to study surface tension of small droplets known as "Tolman length". The calculated results of size dependent Tolman length in TiO_2 and SnO_2 nanoparticles support an established fact of thermodynamic theory of Tolman length that it can be related to the size dependency of the surface tension. The Tolman length which is positive shows a drastic change below 5nm and saturates faster than the surface energy. The behaviour of Tolman length with size is opposite to the size variation of the surface energy. The results show a clear effect of the size on the surface energy and Tolman length and there is a significant decrease and increase respectively in these quantities with decreasing size.

Catalytic property of nanoparticles is a major subject of research in nanotechnology. Our study gives insight into catalytic activation energy of three oxide nanomaterials i.e. Titanium dioxide (TiO_2), Tin dioxide (SnO_2) and Cerium dioxide (CeO_2). The effect of size and dimension on catalytic activation energy (E_C) of these dioxide nano structured materials is reported. The catalytic activation energy decreases as the size of these nanoparticles decreases and is minimum for zero dimensional structure of all considered materials. We show that the nano sized TiO_2 has the minimum value of catalytic activation energy indicating its better catalytic activity than other nanostructures. The shape dependence of

catalytic activation energy has also been discussed. When compared to cubic and octahedral, minimum E_C is found for tetrahedral shaped nanoparticles indicating their maximum efficiency for catalysis.

Titanium dioxide nanoparticles (TiO_2) were synthesized using reflux method. The XRD confirms anatase structure of TiO_2. Tin dioxide (SnO_2) has been prepared using sol gel method. We found cassiterite structure of SnO_2 from XRD results. Average crystallite size of prepared SnO_2 has been calculated from both Scherrer formula and Williamson-Hall method. At room temperature, prepared sample shows amorphous nature and by increasing annealing temperature crystals grows and we observe decrease in the broadening of diffraction peaks in XRD pattern. Morphology and chemical composition of the sample have been investigated by SEM and EDS characterizations. DSC analysis was performed to study phase transformation in SnO_2. Phase formation of SnO2 nanocrystal is indicated by exothermic peak at 730 K. Efforts have been made to synthesize Fe doped SnO_2. SEM shows particles are agglomerated and having irregular shape. EDS analysis reveals atomic% and weight % of Fe in SnO_2.

Mechanical alloying is an alternative to produce highly homogeneous mixture of nanomaterials. Ag-SnO_2 nanocomposites have been prepared by powder metallurgy method. We have used planetary ball mill and tungsten carbide balls as grinding media. To form bulk solid sample (pellets), after milling Ag-SnO2 nanocomposites powder was pressed on a hydraulic press in single action die compaction mode. We have calculated theoretical density of pellets and to examine effect of sintering it was again calculated after sintering. The XRD results of Ag-SnO_2 powder samples after 1, 2 and 3 hours of milling show diffraction peaks

corresponding to pure silver and SnO_2 phases. Density is derived from dimensions and mass of pellets. After sintering and repressing value of density increases which is obvious because of the integrity and close binding of constituent atoms. We have obtained micro hardness measurement on surface of Ag-SnO_2 pellet is 124 HV 0.05.

Following are the important conclusions of present thesis:

- The thermodynamic properties like melting temperature, glass transition temperature and Kauzmann temperature depend on the particle size and dimension of nanostructures.
- Diffusion coefficient of self diffusion and nitrogen diffusion in SnO_2 nanoparticles are strongly influenced by size and dimension of nanoparticles.
- Surface energy and Tolman length are important parameters to find stability of nanostructures and hence their applications in sensors.
- Catalytic activation energy varies with size, dimension and shape of semiconducting nano oxides and determines their efficiency as catalysts.
- The TiO_2 , SnO_2 and Fe doped SnO_2 nanoparticles are synthesized by varying annealing temperature. Detailed structural analyses of prepared samples are studied by XRD. Particle sizes obtained from Scherrer equation are less than those of obtained from Williamson-Hall method because of the strain of synthesized material. Phase transformation in nano SnO_2 has been studied using DSC analysis.
- Silver based metal oxide Ag-SnO_2 has been prepared by mechanical alloying. XRD analysis performed to confirm structure of nanocomposites. Density and micro

hardness measured of Ag-SnO_2 pellets and considerable increase is observed in theoretical density after sintering repressing of pellets.

Future direction based on present thesis work

The theoretical thermodynamic model to calculate size dependent properties in nanoparticles will be extended to investigate size variation in nanocomposites and doped nanomaterials. Thermodynamic properties can be studied as a function of pressure and temperature at nano scale. Tin dioxide (SnO_2) nanoparticles of different size and with different synthesis conditions can be prepared which will be further fulfilling requirement of gas sensor fabrication. Magnetic properties of Fe doped SnO_2 (Dilute Magnetic Semiconductor (DMS)) will be studied in detail and Fe can be replaced by other transition metals i.e. Co and Ni in order to study variation in different properties at nano scale. Antimony (Sb) doped SnO_2 (ATO) is also an interesting material to use as transparent conductive oxides for future research. Effect of sintering will be studied for different temperature and its consequences in density and hardness of material. Improvement in conductivity and hardness of metal oxide nanocomposites can be fruitful for their application in electric contact material.