CHAPTER 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

6.1 SUMMARY

The size and shapes of structures formed at the nanoscale, lead to uniqueness. An introduction to nanoscience and nanotechnology on the melting properties of the materials in nanodimensions has been presented. Nanostructured materials may occur at several different geometric configurations including wires, tubes, horns, shells and pores. The special configuration with the cylindrical shape is considered with present investigation. They possess unique properties and are being developed for specific applications. Some of these interesting and emerging trends in nanostructures have been discussed.

A detailed study has been carried out on the nanostructured particles with spherical and cylindrical and with varying sizes. There is a causal relationship between structure and properties. At the nanoscale, shape plays a vital role in determining the properties. The large surface area to volume ratio also reduces the incipient melting temperature of nanoparticles. Nanoscale materials have far larger surface areas than similar masses of larger-scale materials. As surface area per mass of a material increases, a greater amount of the material can come into contact with surrounding materials, thus affecting reactivity.
We have developed a new thermodynamical model to predict the melting point variations with respect to size and shape of the nanoparticles. The radius of curvature varies with respect to the shape of the nanoparticles. The radius of curvature of cylindrical shape which mentions the size of the nanoparticle is obtained by Helix method (Section 2.4.3). To describe and to find the effect of particle size and melting temperature of the nanoparticle quantitatively, the Gibbs-Thomson equation (1928) has widely been used. From the thermodynamic point of view, there is a decrease of the melting temperature on changing from infinite crystal sizes to finite ones. Small crystals are less stable, due to dominance of surface energy, which reduces the cohesion energy of the molecules and shifts the temperature of breakdown of the lattice to lower values. Gibbs and Thomson derived their formula considering the phase in question as homogeneous and isotropic with a spherical boundary. They compared the transition temperature of a ‘bulky’ phase with that after crushing it to a fine powder with a lot of surface. The effects of size and confinement at the nanometre size scale on both the melting temperature \( T_m \) and the glass transition temperature \( T_g \), are reviewed. Although there is an accepted thermodynamic model (Gibbs et al 1928) for explaining the shift in the first-order transition \( T_m \) and the depression of the melting point for the nanomaterials.

The melting temperature of the nanoparticles will be different in different shapes when considering the radius of curvature of nanoparticles; especially when the particle size is mentioned with respect to its radius of curvature. Therefore an indispensable course of action is necessary to consider the particle size when developing the models for the melting temperature of nanoparticles. In the present work, the radius of curvature is considered to account for the particle shape difference, and develop the model for the cylindrical nanoparticles. According to the relation between the melting temperature and radius of curvature of the nanoparticles, an expression for the size and shape dependent melting temperature of
nanoparticles is obtained. The theoretical prediction of this expression for the melting temperature of B₄C nanoparticles is compared between spherical and cylindrical shapes. The present analyses shows that, the melting temperature of B₄C (2450K) decreases significantly when the particle dimensions are reduced to the nanoscale and at ~6nm radius of B₄C spherical shaped nanoparticle melts at temperature ~764K range but the same particle with ~3nm diameter melts at the temperature ~495 K range, since the particle shape is considered in cylindrical shape.

The same investigation has been carried out on gallium nitride, which results that, the melting temperature of GaN (2770K) decreases when the particle dimensions are reduced to the nanoscale. It was obtained that at ~6nm radius of GaN spherical shaped particle melts at temperature ~1747K range but the same size of particle with cylindrical shape melts at the temperature ~1553K range. This same property of GaN nanowires with triangular cross section has been studied using molecular dynamics simulation, and it was reported that the melting temperature of the GaN nanowires increases with increasing cross-sectional area to a saturation value (Zhiguo wang et al 2009). It is stressed, different shape of the nanoparticle may have different radius of curvature which decides the particle size. The present calculation highlights that the present radius of curvature expression is enough for predicting the shape dependent size effect on the temperature of nanoparticle.

The theoretical prediction of the expression for the melting temperature of Au, Ag nanoparticles is compared between spherical and cylindrical shapes. The calculated values of melting point with respect to particle size have been tabulated. The melting temperature of Au (1064K) decreases significantly when particle dimensions are reduced to the nanoscale. Therefore at ~ 6nm radius of Au spherical shaped nanoparticle melts at
temperature ~500K (Buffat and Borel 1976, Erolessi et al 1991, Levis et al 1997), but the same phenomenon occurs at temperature ~ 390K range, since it is considered in cylindrical shape. The melting temperature of Ag (962K) melts at 450K and 340K when it is in spherical and cylindrical shapes respectively. It could be found that, compared to the melting point of spherical nanoparticle, the cylindrical nanoparticle has low melting point.

The surface area of cylindrical nanoparticle (169.56nm² at ~3nm radius range) is larger than the spherical nanoparticle (113.04 nm² at ~3nm radius range). The number of atoms present on the surface will have only fewer neighbouring atoms. Hence, on the larger surface, more number of atoms will have fewer neighbouring atoms in close proximity compared to atoms in the bulk of the nanomaterial. Each chemical bond of an atom sharing with a neighbouring atom provides cohesive energy. So atom with fewer bonds and neighbouring atoms have lower cohesive energy. They require less energy to free from the solid phase. Hence melting point depression of cylindrical shaped nanoparticle with high surface is reduced than the spherical shaped nanoparticles with lower surface. The present work describes the melting temperature effect on the shape difference between the spherical nanoparticles and cylindrical nanoparticles.

6.2 CONCLUSION

We conclude that, the size and shape dependent temperature of B₄C, GaN, Au, Ag nanoparticles are determined using the numerical thermodynamical model, where spherical and cylindrical shapes of the nanoparticle are considered with respect to its radius of curvature. The present results of the melting temperature of B₄C, GaN, Au, Ag nanoparticles consistently decrease with the size of the nanoparticle. The cylindrical B₄C, GaN, Au, Ag nanoparticles whose melting point decreases with decreasing particle radius, become larger than spherical shaped nanoparticle. Further it is
found that, the particle shape can affect the melting temperature of nanoparticles, and this effect on the melting temperature becomes larger with decreasing particle size.

6.3 SUGGESTIONS FOR FUTURE WORK

The uniqueness and distinctiveness of nanoscience and nanotechnology especially with regard to its pervasiveness into virtually all spheres of human life, explain why their potential impacts will exceed those of all other conventional technologies hitherto developed. The convergence of the newly emerging technologies of the 21st Century have the potential to revolutionize social and economic development and may offer innovative and variable solutions for the most pressing problems of the world communities and their habitat. Unlike other technologies, nanotechnology offers a unique chance to bridge the technological gap between the industrialized and the developing world.

The melting property of the materials in nanodimensions with special configuration of the cylindrical shape is considered in the present investigation. The radius of curvature varies according to the shapes of the nanoparticles. The radius of curvature of cylindrical shape nanoparticle is obtained by Helix methods (Section 2.4.3). A new thermodynamical model is developed to derive the particle size with respect to radius of curvature and the temperature of the nanoparticle. In observing the calculated data yielded by the model, when compared to the melting point of spherical nanoparticle, the cylindrical nanoparticle has low melting point. Melting temperature is a very important parameter; the model developed in the present investigation may have potential applications in the temperature related phenomena of nanoparticles.