Chapter 6 CONCLUSION AND SCOPE FOR THE FUTURE WORK

6.1 Conclusion

The thesis entitled "*THERMODYNAMIC INVESTIGATIONS OF PHASE TRANSFORMATIONS IN AMORPHOUS ALLOYS AND POLYMERS"* embodies theoretical and experimental investigations on amorphous metallic systems.

The thesis covers two parts:

(**A)** The theoretical investigations on the thermodynamic aspects of glass forming ability of metallic alloys. This mainly includes the derivation of an analytical expression for Gibbs free energy difference (ΔG), which is the driving force for crystallization.

(**B**) The experimental study contains two cases: (i) understanding the kinetics of crystallization for two metallic glasses namely Co65Si15B14Fe4Ni2 and (ii) understanding the kinetics of crystallization for ZBLN glass.

(**A**)The Gibbs free energy change for crystallization of an undercooled liquid (ΔG) is an important parameter in the nucleation theory and also in predicting the glass forming ability of metallic alloys. At the theoretical front different thermodynamic parameters i.e. Gibbs free energy difference ΔG, Entropy difference ΔS and Enthalpy difference ΔH are evaluated for different metallic glassy systems. Gibbs free energy change for crystallization of an undercooled liquid exponentially depends on nucleation rate. Gibbs free energy difference is the driving force for the crystallization; therefore The lower the value of ΔG higher is the glass forming ability of the alloy. Hence an accurate estimation of ΔG will be very much useful in designing new bulk amorphous alloys. The ΔG values can be estimated if one knows the experimental specific heat difference (ΔCp). But, due to metastable nature of the undercooled liquid the experimental data for ΔCp is not easily available. Hence, in deriving expression for ΔG, a linear or hyperbolic assumption for ΔCp is assumed. As explained in Chapter 3, for a particular metallic glass if values of $\alpha 1$ and $\alpha 2$ are nearly equal then ΔCp can be taken as constant for that particular system and if two α values are different then ΔCp is not constant and it is varying with temperature in the undercooled region for that system. This assumption gives two main limitations. i) The exact nature of variation of ΔCp in case of bulk metallic glasses cannot be predicted. It is observed that in most of the case ΔCp remains constant while in few systems it increases with undercooling. Therefore, in deriving expression for ΔG, linear and hyperbolic variations of ΔCp are assumed. ii) If exact temperature dependence of ΔCp is taken into consideration than the ΔG values can be

estimated only if the Kauzmann temperature *TK* is known. But it is difficult to estimate *TK* since it lies much below the melting temperature, *Tm*. These expressions excellently account for ΔG in multi component metallic glass forming alloys and polymers in the entire undercooled region. Glass forming ability (GFA) of metallic glassy systems is very much important from theoretical and practical point of view. There are so many different criteria available in literature for the estimation of glass forming ability. *ΔG* has played an important role in predicting the GFA of multicomponent metallic alloys. Lesser the value of *ΔG*, easier is the formation of BMGs. From the results, *ΔG* emerges out as the best GFA criterion. The GFA of Ti-Cu-Ni-Hf-Zr based metallic alloys is investigated through *ΔG* and different GFA parameters. *ΔG* is the best GFA criterion Also GFA of ZBLAN glass is studied through *ΔG* and different GFA parameters. Different expressions of *ΔG* were derived. On comparing the theoretically obtained values of *ΔG* with the experimental data for Ti-Cu-Ni-Hf-Zr metallic glasses and glass forming polymeric melts,the expression of *ΔG* derived on the basis of hyperbolic variation of *ΔCp* was found to explain the variation of *ΔG* with temperature, in its entire undercooled region, excellently well.

(**B**) Crystallization Kinetics of and technologically important soft magnetic amorphous alloy system namely Co65Si15B14Fe4Ni2 another potential candidates for optical telecommunication devices namely ZBLAN glass explores the possibility of their wide range of applications. Crystallization kinetics is the way to determine the activation energy and other kinetic parameters of the metallic glass. Thus, we can predict glass forming ability and thermal stability of glassy alloy. Crystallization of metallic glasses involves nucleation and growth processes. DSC technique is used to study crystallization kinetics Metallic glasses can be transformed to crystalline state by continuous heating in DSC. The transformation from amorphous to fully crystalline state can proceed in one step (polymorphous and eutectic crystallization) or in several steps (primary crystallization). Crystallization of metallic glasses involves nucleation and growth processes. The activation energy of crystallization is calculated for various degree of conversions by linear integral iso-conversional methods i.e., Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS), The term that is expected to cause non-linearity, i.e., $(AT\omega/2\beta)2$ is almost constant for all heating rates. Thus, the non-linear heating rate does not change the nature of different linear iso-conversional methods. The linear behavior of the various expressions remain intact.DSC technique is used to study crystallization kinetics of Co65Si15B14Fe4Ni2 and ZBLAN glasses. The activation energies have been found using and isoconvertional approaches**.**

6.2 Scope for future work

From an overview of the results, it is evident that, there is a scope for future work on metallic systems, polymers and ZBLAN glass. In future, the research work carried out for this thesis can be extended by the utilizing the knowledge of Gibbs free energy difference (ΔG) in the undercooled region to plot Time-Temperature-Transformation (TTT) diagram. The value of critical cooling rate (Rc) can be obtained from the values of nose time (tn) and temperature (Tn) of TTT diagram. Also the oxidative stability and corrosion resistance of metallic glasses can be studied. This in turn will provide us the insight to properly utilize the properties of different metallic glasses in various spheres of life. The research on metallic glasses can further be extended by studying their electrical properties. Four probe method can be used to measure electrical conductivity of metallic glass samples. Further, studies can be extended to the formation of nano-crystallites in the amorphous matrix of a metallic glass. . It will be interesting to see their properties in their nano phase. These microstructures tend to improve their hard and soft magnetic properties. Hence, these studies will contribute towards improvement and utilization of the properties of metallic glasses in a more effective way. Hence, accurate measurements of ΔCp is important which can be done using a modulated DSC with good sensitivity can be used.

Kinetics of glass transition can be studied for ZBLAN glass. One can explore new methods to find out the glass transition activation energies of metallic glasses as well as ZBLAN glasses. Further study can be done for the optical constants for the ZBLAN samples were then characterized using a combination of refractive index matching liquids, ellipsometer data and an analysis approach.

Comparative study of crystallization kinetics through DSC and MDSC can be carried out for polymer samples and how the sinusoidal heating rate effects the kinetic parameters of polymers. One can study the connection between the pronounced slowing down of glassy dynamics on cooling toward the glass transition temperature (Tg) and the thermodynamics of glass forming polymers. Thermal analysis and testing of polymers can be done by DSC. It will be useful to measure physical properties, transitions, ageing processes, the effect of additives and the influence of diverse production conditions on materials. Further, one can use Capillary Rheometry to study the thermal stability, onset of unstable flow, and wall slip measurements. Hence, these studies will contribute towards improvement and utilization of the properties of polymer in a more effective way.