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Thermal Behavior of Chalcogenide glasses $Te_{90}Se_{10}$ and $Se_{90}Te_{10}$

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ABSTRACT

In the present research work melt quenching method has been adopted to prepare the glassy Te-rich ($Te_{90}Se_{10}$) and Se-rich ($Se_{90}Te_{10}$) Chalcogenide at a pressure of 10^{-2} Torr with constant Temperature at 1000°C for 8 hours. Devitrification characteristics of the pure glassy Chalcogenide $Te_{90}Se_{10}$ and $Se_{90}Te_{90}$ were investigated by using Differential scanning Calorimetry (DSC) 4000 Perkin Elmer. All the measurements carried out at fixed heating rate 10 ^{0}C/min under non-isothermal conditions. The Glass transition temperature (Tg) and other thermal properties were examined by temperature modulated differential scanning Calorimetry at 40 ^{o}C to 445 ^{o}C. Glass transition temperature (Tg) represents the strength or rigidity of the glass structure. Tg affords valuable information on the thermal stability of the glassy state but T_g alone does not give any information on the glass forming tendency. The difference of the Peak crystallization temperature (Tp) and Glass transition temperature (Tg) is a strong indication of the thermal stability. The higher the value of Tc and Tg the greater is the thermal stability. Glass transition temperature ($Tg=216^{0}C$) of Tellurium rich ($Te_{90}Se_{10}$) is more than Glass transition temperature ($Tg=73^{0}C$) of Selenium rich ($Se_{90}Te_{90}$) due to semi metallic nature of Tellurium. The difference of (Tp-Tg) is a strong indicator of both the thermal stability and Glass forming ability (GFA). Higher the value of (Tp-Tg), higher is the thermal stability and GFA because higher values of this difference indicate more kinetic resistance to the crystallization. Glass forming ability (GFA) and thermal stability of $Te_{90}Se_{10}$ is greater than $Se_{90}Te_{90.}$ For memory and switching materials, glass thermal stability and GFA parameters are very important. Intensity of Se-rich ($Se_{90}Te_{10}$) is more than Te-rich ($Te_{90}Se_{10}$) and both samples are polycrystalline in nature.

Keywords: *$Te_{90}Se_{10}$, $Se_{90}Te_{10}$ powder, DSC and XRD.*

1. INTRODUCTION

Chalcogenide are generally considered as ore former elements and belong to group 16. Chalcogenide glasses actually belong to a family of vitreous materials built from sulphur, selenium and tellurium. Transition metal Chalcogenide occur with many stoichiometries and many structures. Te- rich alloys show metallic nature therefore due to semi-metallic nature of Te, limits the glass formation ability where as Se-rich alloys show a semiconducting nature. Pure Te shows high degree of crystallinity. Se based glasses are intrinsically good glass formers but are limited in transparency in long wavelength regions.Te- rich glasses are poor glass formers but possess very large optical windows(1). Se-based chalcogen show high transparency in middle and infrared region and also have nonlinear properties, useful for all optical switching. Since, Se easily forms amorphous phase. Te as additive for alloying Se which gives higher sensitivity, higher crystallization temperature and smaller ageing effect. Due to unstable toward crystallization of Te based chalcogen that have found application as phase change materials for optical storage such as digital

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versatile disk(DVD).Similarly good transparency in the infrared range of Se based chalcogen used for optical fibres, lenses etc. The main difference between Se and Te is the nature of the bonding responsible for the interchain cohesion (1). Amorphous Te-Se alloys are interesting for their great potential for industrial utilization. The Te-Se alloys exhibits higher photo sensitivity, greater hardness, better thermal stability and lower ageing effects (2).These glasses have poor thermo mechanical property. Phonon absorption due to the vibrational modes of the network which is prominent in the IR region is directly related to the relative atomic mass of the elements used to build the glassy framework. Thus, glasses made from heavy chalcogen (Se-Te) will offer a huge advantage for developing materials transparent in the IR. Se-Te glassy alloys are widely used for various applications in many fields as optical recording media because of their excellent laser writer sensitivity, xerography and electro–graphic application such as photoreceptors in photocopying and laser printing, IR spectroscopy etc. The low phonon energy of the Chalcogenide enables an efficient laser transition between closely spaced electronic energy level allowing many IR transition. These light induced changes in Chalcogenide glasses occur due to their structural flexibility and also due to their high-lying lone-pair in their valance bands(3). Due to large atomic mass of these elements, Chalcogenide glasses are known for their large transparency window extending much further than classical silica based glasses. These glasses transparent from the visible region upto the mid infrared depending on the glass composition. Chalcogenide glasses are generally opaque in the visible spectral region where as they exhibit transmission window in the infrared spectral region. The begin of the cut-off appearing beyond 20 micrometer is correlated to the glassy network phonon energy. The main advantage of vitreous materials over single or polycrystalline materials relies on the fact that, above the glass transition temperature, glasses are plastic materials, which can be molded or tapered with high precision. Nevertheless, it is also known that within the plastic regime the risk of crystallites nucleation/ growth could prevent the shaping operation (4).Chalcogenide glasses have their unique technological significance and applications such as in rectifiers, photocells, memory and switching devices due to their unique electrical, thermal and optical properties. The better optical and thermal properties of these materials make them of potentials use in the technological applications such as in photonics and phase change memories because of higher values of refractive index, lower value of phonon energy of these glasses (5). Thermally activated transformations in the solid state can be investigated by isothermal or non-isothermal experiments. In the isothermal method the sample is brought quickly to a temperature above the glass transition temperature (Tg) and the heat evolved during the crystalline process is recorded as a function of time. In the non-isothermal method the sample is heated at a fixed rate and the heat evolved is again recorded as a function of temperature or time. A disadvantage of the isothermal technique is the impossibility of reaching a test temperature instantaneously and, during the time in which the system needs to stabilise, no measurements are possible. A constant heating rate experiment does not have this drawback (6)

2. EXPERIMENTAL PROCEDURE

In the present research work melt quenching method has been adopted to prepare the glassy $Te_{90}Se_{10}$ and $Se_{90}Te_{10}$Chalcogenide. One of the most important features of the melt quenching is the high flexibility of geometry and composition and the advantage of obtaining materials of large size in comparison to other methods. This method can be used for the preparation of silicate, borate, phosphate, oxide or non oxide systems. One of the main disadvantages of this method is the lack of ultra high purity as compared to other chemical methods. In order to avoid contamination the crucibles made of noble metals can be used. Melt quenching techniques is based on the fusion of raw materials into a viscous solid, followed by forming in to a shape and quenching to a glass. Here $Te_{90}Se_{10}$ and $Se_{90}Te_{10}$ Chalcogenide powder is prepared using Se pellets and Te ingots of purity greater than 99.999% purchased from Sigma Aldrich. Melting point of Se and Te is 221^0C and 450°C respectively. The electronic grade (5N purity) constituent elements (Te and Se) are weighed in proportion to 90 and 10% of their atomic weight percentage respectively, were crushed to powder in a mortar and pestle. The powder mixture was filled in a quartz ampoule having 8 mm internal diameter and around 5 cm length, evacuated for half an hour at a pressure of 10^{-2} Torr before sealing the ampoule thermally and then for another half an hour during sealing with oxygen-indane flame torch using rotary pumps. Pre-cleaning and evacuating helps to avoid the presence of impurities. Sealed quartz ampoule was then kept in muffle furnace. Heating was done at a rate of 4^{o}C/min and the temperature was maintained at 1000°C for 8 hours. Frequent rocking was done to ensure homogenization of the melt. Red hot quartz ampoule containing TeSe melt was rapidly quenched in ice cold water. The material turned in a black solid which was recovered from the ampoule and crushed for 1 hour to making fine powder. The filtered chalcogen powder obtained was characterized For DSC studies at Constant heating rate of 10^0C/min for DSC scans. First we recorded a blank run by putting sample and reference aluminium pans empty inside the DSC cell. Then 5-10 mg of the sample was kept inside in the pans and then thermoscans were recorded under almost identical conditions. Characterizations of the $Te_{90}Se_{10}$ and $Se_{90}Te_{10}$ Chalcogenide powder for thermal studies by (DSC) 4000 Perkin Elmer and XRD from NPL Delhi.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction and Structure Determination

The powder diffraction method is the ideally suited for characterization and identification of polycrystalline phases. The crystallite size or grain size of the nanoparticles calculated by Scherrer's equation D=K*ë/â*Cosè, Where D is average crystal or particle size in nm, ë is wavelength of copper Ká line (1.5406A of X-ray), â is FWHM of the peak or broadening of the diffraction peak, è is diffraction angle or the angle between the incident beam and the reflection lattice planes.XRD method measures the property of the crystalline grains and not the size of the aggregated particles .Peak positions tell about the translational symmetry namely what is the size and shape of the unit cell. Peak intensities tell about the electron density inside the unit cell to the location of atoms. The peak widths and shapes give the information on deviations from a perfect crystal (Cubic, Tetragonal, Orthorhombic, Rhombohedral, Hexagonal, Monoclinic, and Triclinic).Both sample shows polycrystalline in nature and Intensity of Se-rich ($Se_{90}Te_{10}$) is more than Te-rich ($Te_{90}Se_{10}$).

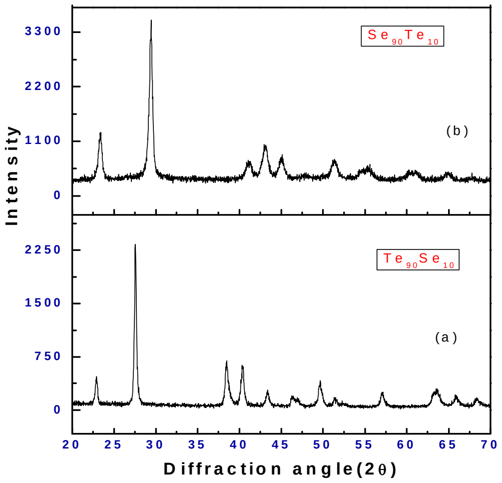

Fig.1 : (a,b): X-ray spectrum of Te-rich ($Te_{90}Se_{10}$) and Se-rich ($Se_{90}Te_{10}$)

3.2 Glass Transition Temperature

The temperature at which the materials undergo a glass transition is known as the glass transition temperature. Glass transition or glass-liquid transition is the reversible transition in amorphous materials or in amorphous regions within semi crystalline materials from a hard and relative brittle state into a molten or rubber-like state. The thermal expansion, heat capacity, shear modulus and many other properties of inorganic glasses show a relatively sudden change at the Tg. Tg is directly proportional to bond strength, it depends on thermodynamic parameters of the bond.(7). Glass transition temperature has no latent heat associated with it and such transitions are referred as to second order transition. Tg is assigned to the midpoint temperature of the range of the temperature during the transition. Tg can vary depending on the rate at which the material is heated or cooled under continuous heating the next step for an amorphous material will be for the material to become crystalline(8).Tg of glass depends on optical gap, connectedness, average coordination number, mean bond energy, heating rate used in measurement and thermal history of the sample. Glass transition causes a baseline shift. The operative definition of glass transition temperature is that at this temperature or within a few degrees, the specific heat, the coefficient of thermal expansion, the free volume, dielectric constant all changes rapidly(10).Tg is also an important characteristic of non crystalline and semi crystalline materials. Generally, Tg point depends on the processing of the materials as well as materials natural characteristics such as structure, bonding, molecular weight. Since it takes energy to break these bonds, Tg appears on a DSC curve as an endothermic process. In DSC, Tg can be found by a permanent decrease in baseline heat flow and Tg is usually taken as the inflection point in the curve (11).Glass transition temperature is proportional to cohesive forces or the rigidity of the network. Physical quantities like melting, magnitude of photo darkening, mean atomic volume, width of the band tails in Chalcogenide glasses are also related to Tg(12).An abrupt change in specific heat at Tg is characteristic of all Chalcogenide glasses(13).Glass transition temperature Tg represents the strength or rigidity of the glass structure. Tg affords valuable information on the thermal stability of the glassy state but Tg alone does not gives any information on the glass forming tendency. The higher the values of Tc, Tg the greater is the thermal stability (14).

3.3 Crystallization Temperature

Crystallization is an exothermic process. When a material is crystallized it becomes ordered. Crystallization is a first order transition and thus a latent heat is associated with the transition. Due to exothermic process thermal energy is released and sample gets hotter and during crystallization the sample heater supplies less energy than the reference heater to maintain the constant set heat rate. At or near the Tc, the material has gained enough energy so that its atoms/molecules could re-arrange into a more stable and ordered state by nature, materials tend toward the lowest energy state (10). Formation of bonds during crystallization is an exothermic process. Generally the Tc is found by finding the onset point of the crystallization curve (13).In a crystallization process three types of activation energy have to be considered such as activation energy for nucleation, activation energy for growth and activation energy for whole crystallization process. Activation energy (Ec) for growth may be taken as equal to the activation energy for the whole crystallization process. Crystallization of Chalcogenide glasses is associated with a nucleation and growth process and rate of crystallization increases with an increase in temperature (6).

3.4 Glass Forming Ability

Glass forming ability and the stability of the glass belong to the basic thermo –physical characteristics of each glassy material. (5)Glass forming ability (GFA) and thermal stability of vitreous materials can be established from the DSC measurement analysis. Hurby described the glass forming ability (GFA) criterion Hr = (Tp-Tg)/(Tm-Tp).Higher value of (Tp-Tg) indicates the delay in the nucleation process and smaller value of (Tm-Tp) shows retardation to the growth process. The difference (Tp-Tg) is a strong indicator of both the thermal stability and GFA. Higher the value of (Tp-Tg), higher is the thermal stability and GFA because higher values of this difference indicate more kinetic resistance to the crystallization which varies with alloy's structural units in compositions. Where Tg , Tp and Tm are glass transition temperature, peak crystallization temperature and melting temperature respectively. For memory and switching materials, glass thermal stability and GFA parameters are very important.(5).

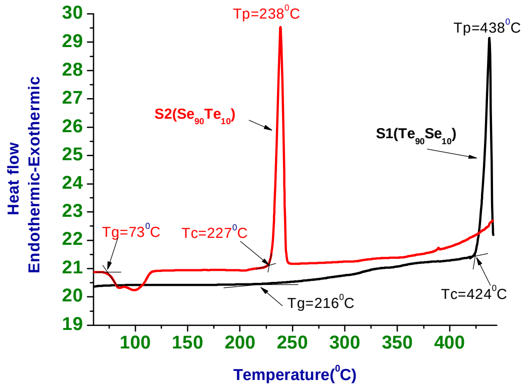

Fig.2: Endothermic-Exothermic graph of of Te-rich (Te$_{90}$Se$_{10}$) and Se-rich (Se$_{90}$Te$_{10}$)

4. CONCLUSION

Glass transition temperature (Tg=216^{0}C) of Tellurium rich Te$_{90}$Se$_{10}$ (S1) is more than (Tg=73^{0}C) of Selenium rich Se$_{90}$Te$_{10}$(S2) due to semi metallic nature of Tellurium. Rigidity of the of Tellurium rich is more than Selenium rich. Crystallization temperature (Tc=424^{0}C) of Te$_{90}$Se$_{10}$ (S1) is more than (Tc=227^{0}C) of Se$_{90}$Te$_{10}$(S2). Thermal stability and glass forming ability of Te-rich Te$_{90}$Se$_{10}$ (S1) is more than Se-rich Te$_{90}$Se$_{10}$ (S1). Both samples are polycrystalline in nature and Intensity of Se-rich (Se$_{90}$Te$_{10}$) is more than Te-rich (Te$_{90}$Se$_{10}$).

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