"CRYSTALLIZATION KINETICS AND PHASE CHANGE STUDIES IN AMORPHOUS SEMICONDUCTING ALLOYS"

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In the present thesis, the results of the crystallization kinetics by means of isothermal conductivity, non-isothermal DSC measurement and effect of optical band gap during thermal annealing between glass transition and crystallization temperature on some amorphous systems have been given.

The following glassy alloys have been investigated in the present work. $Se_{80}In_{20-x}Pb_x$ (x = 0, 2, 6 and 10), $Bi_{0.5}Se_{99.5-x}Zn_x$ (x = 0, 0.1, 0.2, 0.5 and 1), $Ga_5Se_{95-x}Sb_x$ (x = 0, 1, 5 and 10), $Se_{80}Te_{20-x}Pb_x$ (x = 0, 2, 6 and 10) and $Ge_5Se_{95-x}Te_x$ (x = 0, 2, 5 and 10).

Quenching technique was adopted to prepare these glassy alloys. The amorphous nature of the glassy alloys was verified by X-ray diffraction. Isothermal measurements were made using electrical conductivity method. Non-isothermal measurements were performed by using Differential Scanning Calorimeter through continuous heating rate of 5,10, 15 and 20 K/min.

Amorphous thin films were prepared by the vacuum evaporation technique. Thin films of glassy alloys were crystallized in a specially designed sample holder under a vacuum of 10^{-4} Torr at different temperatures, which are below the crystallization temperature of the samples. A JASCO, V-500, UV/VIS/NIR computerized spectrophotometer is used for measuring optical absorption, reflection and transmission.

Crystallization studied by an isothermal technique using conductivity measurements:
Crystallization kinetics of amorphous $Se_{80}In_{20-x}Pb_x$, $Bi_{0.5}Se_{99.5-x}Zn_x$ and $Ga_5Se_{95-x}Sb_x$ chalcogenide glasses [1-3] has been studied by annealing the sample at certain fixed temperatures above the glass transition temperature and measured the dc conductivity with time during crystallization. These results fit well with the Avrami equation of isothermal transformation. During isothermal annealing at temperature in between the glass transition and crystallization temperatures, the electrical conductivity is found to vary with time. The kinetic parameters D E_c and n have been calculated.

In $Se_{80}In_{20-x}Pb_x$ glasses, it has been found that order parameter n increases with increasing annealing temperatures and on Pb concentration. A discontinuity in ΔE_c with Pb concentration at x > 2 can be understood in terms of the formation of stable phases at higher concentration of Pb. In $Bi_{0.5}Se_{99.5-x}Zn_x$ chalcogenide glasses the study of order parameter represents one-dimensional growth of crystallites in the present glassy system. In $Ga_5Se_{95-x}Sb_x$ sample, it was found that the order parameter (n) decreases with increasing temperature while ΔE_c decreases with increasing Sb content in the present system.

Crystallization studied by non-isothermal DSC technique:

The thermal crystallization behavior of bulk amorphous semiconducting $Se_{80}In_{20-x}Pb_x$, $Bi_{0.5}Se_{99.5-x}Zn_x$, $Ga_5Se_{95-x}Sb_x$ and $Se_{80}Te_{20-x}Pb_x$ glasses [4-6] has been studied using non-isothermal measurement with different heating rates of 5, 10 , 15 and 20 K/min. The results indicate that the glass transition and crystallization temperatures depend on the heating rate. The results of crystallization kinetics indicate that the degree of crystallization (α) under non-isothermal conditions fit well with the theory of Matusita, Sakka and Kissinger. A multiple scanning technique was used to calculate ΔE_c and it was found that the value of ΔE_c by both techniques is in agreement with each other.

In $Se_{80}In_{20-x}Pb_x$ sample the activation energy is found to vary with compositions indicating a structural change due to the addition of lead. The temperature difference ($T_c - T_g$) is highest for the composition of 6% of Pb. Hence the glass with 6% of Pb is most stable and the enthalpy released are found to be minimum for 6% of Pb which further indicates the maximum stability of the glass. The activation energy of structural relaxation (ΔE_t) increases with increasing Pb content in the present system. In $Bi_{0.5}Se_{99.5-x}Zn_x$ the activation energy is found to vary with compositions indicating a structural change due to the addition of Zinc. The rate of crystallization is found to be minimum for $Bi_{0.5}Se_{99.5}$ glass and hence it is most stable in comparison with other glasses in the present system. The values of order parameter (n) increases with increasing temperature for all the samples $Bi_{0.5}Se_{99.5-x}Zn_x$. The temperature difference [$T_c - T_g$] and the enthalpy released are found to be minimum and maximum respectively for $Bi_{0.5}Se_{99}Zn_{0.5}$ glass, which indicates that this glass is the least stable one. In $Ga_5Se_{95-x}Sb_x$ the value of order parameter (n) increases with increasing temperature. The activation energy of structural relaxation (ΔE_t) has also been calculated. It was found that ΔE_t decreases up to 5% of Sb content and at higher concentration of Sb it increases. In $Se_{80}Te_{20-x}Pb_x$ glasses the activation energy is found to vary with compositions indicating a structural change due to the addition of Lead. The activation energy of structural relaxation (ΔE_t) increases with increasing Pb content in the present system.

Effect of thermal annealing and laser induced crystallization on optical properties:

The optical absorption measurements of a-$Ge_5Se_{95-x}Te_x$ and a-$Ga_5Se_{95-x}Sb_x$ films [7-8] during crystallization indicate that the absorption occurs due to indirect transition. Crystallization of chalcogenide films is accompanied by a change in the optical band gap. In $Ge_5Se_{95-x}Te_x$ films the optical band gap increases on increasing annealing temperature and on Te concentration. This change in the optical band gap may be due to the increase in the grain size and the reduction in the disordered of the system. From the reflectance studies of as-prepared films of $Ge_5Se_{95-x}Te_x$, it may be concluded that the refractive index decreases, while the value of the extinction coefficient increases with photon energy. In a-$Ga_5Se_{95-x}Sb_x$, it has been found that the optical band gap increases on increasing annealing temperature This may be due to the increase in the grain size, the reduction in the disorderedness of the system. This may also be due to the decrease in the density of defect states, which results in the reduction of tailing of bands. The refractive index n decreases, while the value of the extinction coefficient k increases with photon energy for as-prepared films.

With large absorption coefficients and compositional dependence of reflection, these materials may be suitable for optical disk applications.

References:

[1] **Shamshad A. Khan**, M. Zulfequar, M. Husain, J. of Mat. Science Latter, 21(2002) 1085.

[2] **Shamshad A. Khan**, M. Zulfequar, M. Husain, Current Appl. Phy., USA (In Press)(2003)

[3] **Shamshad A. Khan**, M. Zulfequar, M. Husain, J. Phy. & Chem. of Solids, 63 (2002)1787.

[4] **Shamshad A. Khan**, M. Zulfequar, M. Husain, Solid State Comm., 123 (2002) 463.

[5] **Shamshad A. Khan**, M. Zulfequar, M. Husain, J. of Mat. Science and Tech., 18(2002) 924.

[6] **Shamshad A. Khan**, M. Zulfequar, M. Husain, Comm. J. of Non-Crystalline Solids, USA

[7] **Shamshad A. Khan**, M. Zulfequar, M. Husain, Physica B, Netherland 324 (2002) 336.

[8] **Shamshad A. Khan**, M. Zulfequar, Zishan H. Khan, M. Husain, J. of Modern Optics, 50(2003) 51.