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Short communication

Effect of doping on binary Se-In chalcogenide glasses

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This paper presents a comparative study of the results available from the kinematical studies of glass transition and crystallization in glassy Se-In, Se-In-Te, Se- In- Pb and Se- In- Bi semi conducting glasses. Glass transition region has been investigated in terms of activation energy, and dependence of (T_c-T_g) on coordination number was evaluated. Further more, the growth kinetics and dimensionality are looked in to. It has been found that the Pb doped Se-In system is the most stable glass composite compared to those doped with Bi and Te.

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Chalcogenide glasses are band gap semiconductors and are infrared transmitting [1]. Selenium has been found to have tremendous potential in device technology [2] since it exhibits a unique property of reversible transformation. These properties make these glasses very useful in memory devices. However the shortcoming of pure glassy selenium for practical applications include its short lifetime, low sensitivity and thermal instability. To over come these difficulties certain additives like Te, In, Pb, Sb etc are routinely used [3]. Efforts [4,5] to study and understand binary and ternary Se based glassy alloys have been intensifying for the last few years. These binary and ternary alloys have advantages like greater hardness, higher sensitivity, higher crystallization temperature, higher conductivity and smaller ageing effects as compared to pure amorphous selenium [6]. The addition of a third element to binary [7] system expand the glass forming area and also create compositional and configurational, disorder in the system. Kinetics of glasses is associated with the study of parameters like glass transition temperature, crystallization temperature, and peak temperature of crystallization and activation energy of crystallization. In the crystallization phenomenon of glasses this activation energy is connected with nucleation and growth process that are responsible for most of the devitrification of glassy solids. Mehta et al. [8] studied the effect of metallic additives on the kinetics of glass transition in $Se_{80}Te_{20}$ glassy alloy.

This study reports the effects of addition of different elements as a dopant to $Se_{80}In_{20}$ at the expense of In using differential scanning calorimetry (DSC).

Se_{80} In_{20} binary system has been doped with equal amount of Pb, Te and Bi respectively and four compositions, Se_{80} In_{20}, Se_{80} $In_{10}Pb_{10}$, Se_{80} $In_{10}Te_{10}$, Se_{80} In_{10} Bi_{10} are scanned in a DSC at the heating rate of 20 K/min. Glass transition temperature (T_g) and Peak Crystallization temperature (T_p) are thus evaluated and the values of T_g,T_c, (T_c-T_g) are calculated. The change in crystallization activation energy ΔEc, nucleation parameters n and m are evaluated using the usual methods of Kissinger and Matusita [7,9,10]. The evaluated parameters are given in Table 1. When In is added to Se, structural changes takes place in selenium. The generally accepted structural model [11] of amorphous Se includes two molecular species; meandering chains, which contain helical chains, of trigonal Se& Se_8 ring molecules of monoclinic Se.

As In atoms are incorporated to Se they probably get dissolved in the Se chains increasing relatively the number of Se_8 rings while the number of long chain Se-Se decreases. Further it has been experimentally confirmed by X-ray studies [12] of Se-In glasses that at higher percentage In enters into the Se_8 rings. For $Se_{80}In_{20}$ glass system the value for n is found to be1.67, which given m=1. This shows a one-dimensional growth for the Se-In sample.

Table. 1.

Composition	T_g	T_c	T_c-T_g	E_c kJ/mol	n	m	z
$Se_{80}In_{20}$	322	398	76	12.14	1.67	1	2.6
Se_{80} $In_{10}Pb_{10}$	320	407	87	17.14	2.74	2	2.7
$Se_{80}In_{10}Bi_{10}$	320	379	59	322	2.94	2	2.4
Se_{80} $In_{10}Te_{10}$	335	375	40	108.2	2.93	2	2.3

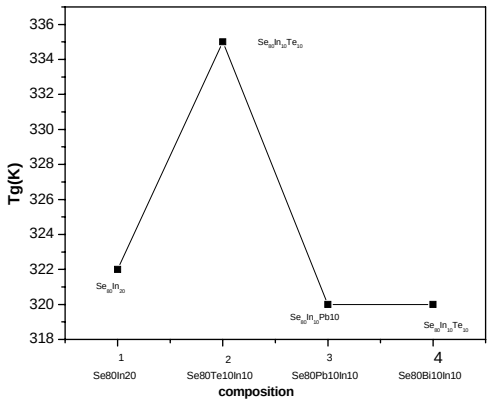

Fig. 1. Variation of T_g with composition.

When Pb is added into Se_{80} In_{20} at the cost of In and at a heating rate 20 K/minute there are two well defined crystallization exotherms, whose characteristics features are as follows. The glass composition may crystallize into two phases; Se-In and Se-Pb [7], and T_g decreases with the addition of Pb. This is because when Pb content is in cooperated they are dissolved in the Se chains increasing relatively the number of Se_8 ring while the number of long chain Se-Se gets decreased [3]. It is known [13] that the glass transition temperature T_g should decrease with increasing ring concentration. The value of n for this system is found to be 2.74. Therefore m = 2 which shows a two dimensional growth for ternary Se-In-Pb system. When Bi is incorporated into Se_{80} In_{20} at the cost of In, glass transition temperature is same as that of Se_{80} In_{10} $Pb_{!0}$. But the activation energy is greater than Se_{80} In_{10} Pb_{10}. In the case of chalcogenide glasses containing Pb and Bi (x >8) it is observed that [10] a charge reversal from usual p- type to n- type conduction. Se_{80} In_{10} Bi_{10} also shows a two dimensional growth.

However the addition of Te to Se_{80} In_{20} at the cost of In, increases the glass transition temperature. When Te is added to Se_{80} In_{20}, Se-Te polymeric chains are formed. T_g increases with increase in chain length. Se_{80} In_{10} Te_{10} also shows a two dimensional growth [8].

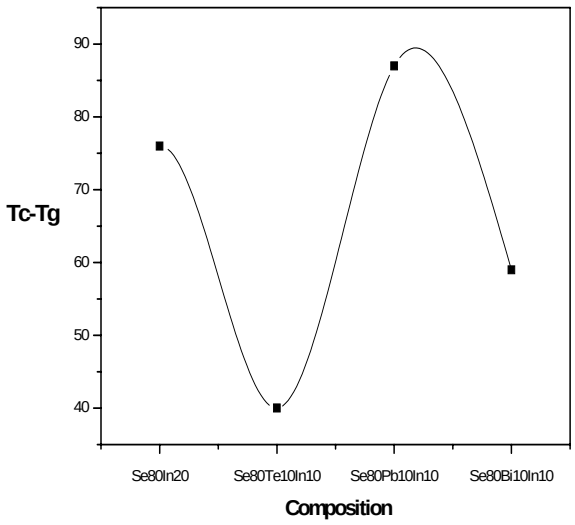

Fig. 2. Variation of (T_c-T_g) with composition.

The T_g of a multicomponent glasses are known to be dependent on several independent parameters such as band gap, coordination numbers, bond energy, effective molecular weight, and the type and fraction of various structural units formed [7]. It is observed that Se_{80} In_{10} $Pb_{!0}$ is the most stable glass in this system, since the value of (T_c-T_g) is maximum for Se_{80} In_{10} $Pb_{!0}$. This is confirmed by considering the activation energy of crystallization. The activation energy of crystallization is minimum for Se_{80} In_{10} $Pb_{!0}$, which is an indication that this glass has higher thermal stability. The average coordination number is also maximum for the system Se_{80} In_{10} $Pb_{!0}$ which has maximum value for (T_c-T_g). This again confirms the stability of this system. The values of activation energies of crystallization are given in Table 1.

The effect of three dopants in equal atomic proportions to Se_{80} In_{20} glass system is investigated using the Differential Scanning Calorimetry and it is found that the Pb doped glass composition possessed maximum stability among Bi and Te doped ones. While all the three dopants produce the same dimensionality of growth, the Te doped composition showed a different T_g value compared to other two compositions

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