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Behaviour of ultrasonic velocities in amorphous $Se_{90}Ge_{10}$ and $Se_{85}Ge_{15}$ alloys near their glass transition

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Abstract. Precise measurements of 10 MHz frequency longitudinal and shear wave velocities are reported in amorphous SeGe alloys near their glass transition temperature T_g. There is a sharp decrease of the velocities near T_g, but the reduction in velocities appears smaller than expected.

Keywords. Chalcogenides; glass transition; ultrasonic velocities.

1. Introduction

Many amorphous materials undergo a transition from a solid-like behaviour to liquid-like state, the so-called glass transition. This takes place in a relatively narrow range ($\sim$ 1-2°C) of temperature around T_g. As the system is cooled from above T_g, the viscosity η increases from a few poise in the liquid to $\sim 10^{10}$-10^{14} poise in the solid within this narrow range of temperature. It seems to obey an equation of the form $\eta = A \exp [B/(T - T_0)]$ around T_g. The free volume model (Chen and Turnbull 1959; Cohen and Grest 1979) and entropy model (Gibbs and DeMarzio 1958) are generally used to understand the behaviour of transport properties, especially viscosity near the glass transition.

In liquids, the longitudinal ultrasonic velocities are roughly half the values characteristic of the solids, while shear waves are damped out and have zero velocity. Then across the glass transition from the solid state, one expects the longitudinal velocity to decrease to about half its value in the solid state. The shear velocity should decrease from the value in the solid state to a zero value as one goes past T_g.

There have been very few measurements of ultrasonic velocities near glass transition. Kittinger (1977, 1978) and Etienne *et al* (1979) have reported measurement of ultrasonic velocities in amorphous selenium near T_g. We reported measurement of ultrasonic velocities both longitudinal and transverse near T_g in amorphous Se-P (Padaki *et al* 1980) and Se-Te (Lakshmikumar *et al* 1981) systems.

2. Experiments and results

The amorphous alloys of the GeSe system have been chosen because the Se-rich alloys of the system can be produced as large samples ($\approx$ 8 mm dia $\times$ 8 mm length)

without too much of difficulty. The samples also have very little of internal voids, which helps in the ultrasonic measurements. Moreover earlier work (Ota *et al* 1978) has shown that the glass transition temperature T_g is reasonably low, being about 102°C for $Se_{85}Ge_{15}$ and about 87°C for $Se_{90}Ge_{10}$ samples.

Longitudinal and transverse velocities in amorphous $Se_{90}Ge_{10}$ and $Se_{85}Ge_{15}$ samples have been measured using a pulse echo interferometer (Srinivasan *et al* 1975) Kartha *et al* 1980) based on McSkimin pulse super position technique (McSkimin 1961; Papadakis 1976). The measurements are made while the sample is slowly heated at an average rate of 5-6 K/hour. The results of the ultrasonic measurements near the glass transition are shown in figures 1 to 4 where longitudinal and transverse

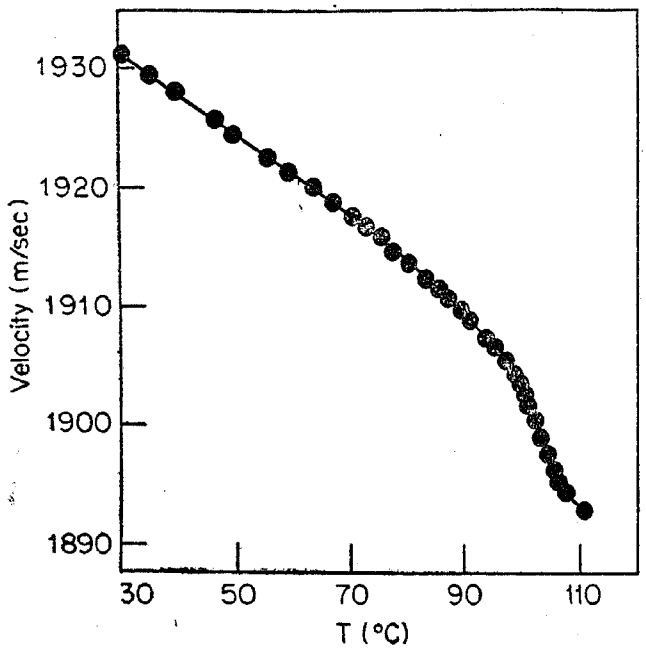

Figure 1. Longitudinal wave velocity in amorphous $Ge_{15}Se_{85}$ sample plotted against temperature.

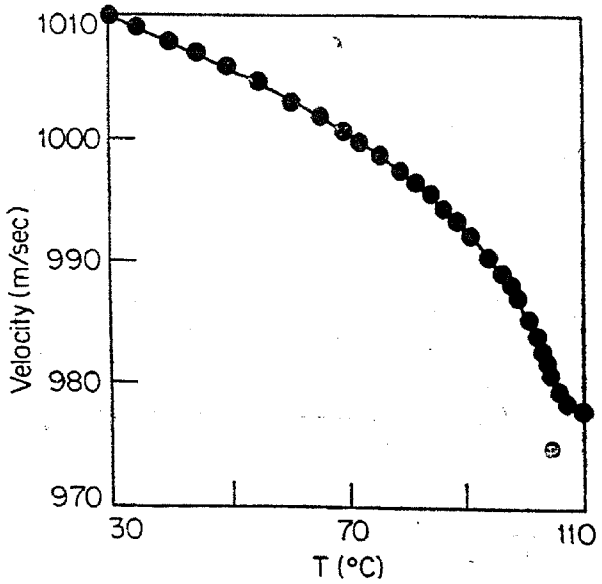

Figure 2. Transverse wave velocity in amorphous $Ge_{15}Se_{85}$ sample plotted against temperature.

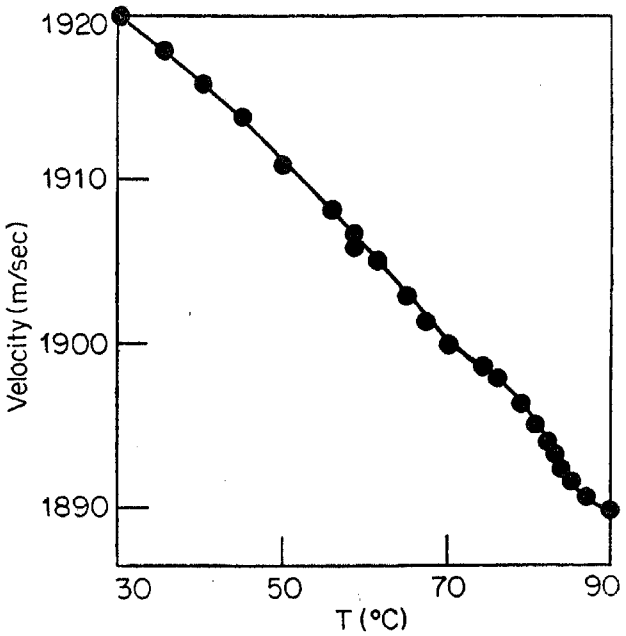

Figure 3. Longitudinal wave velocity in amorphous $Ge_{10}Se_{90}$ sample plotted against temperature.

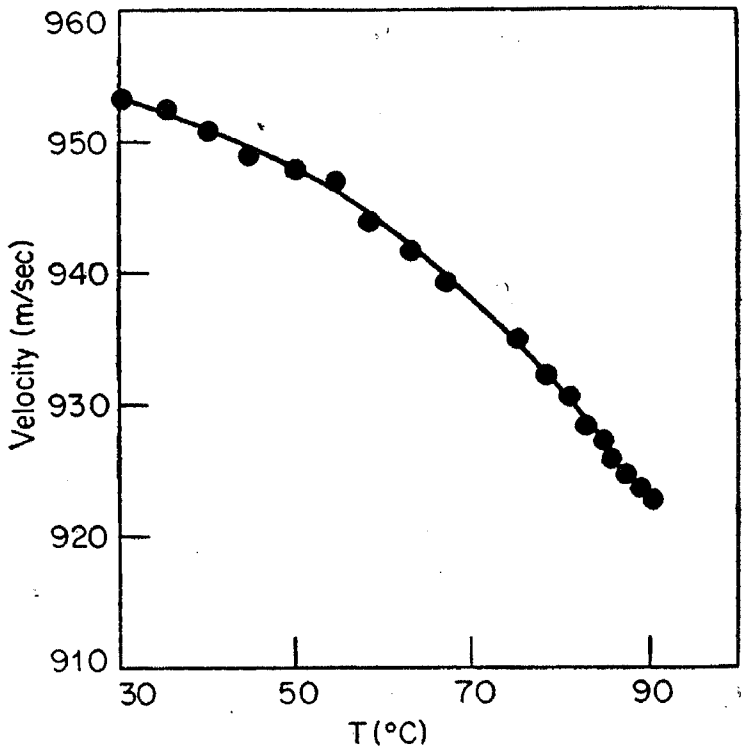

Figure 4. Transverse wave velocity in amorphous $Ge_{10}Se_{90}$ sample plotted against temperature.

velocities in Se_{85} Ge_{15} and Se_{90} Ge_{10} alloys are presented. The longitudinal velocities are around 1900 m/sec and the shear velocities around 900 m/sec. These are roughly 50% of the values typical of crystalline solids. Figures 5 and 6 show the variation of $(1/v)$ (dv/dt) as a function of temperature.

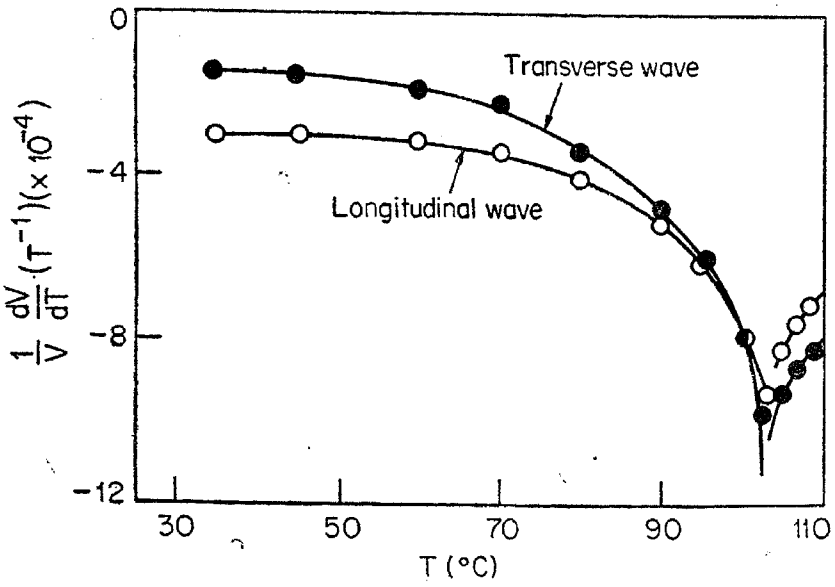

Figure 5. Normalized temperature coefficient of longitudinal and transverse wave velocities in amorphous $Ge_{15}Se_{85}$ sample plotted against temperature.

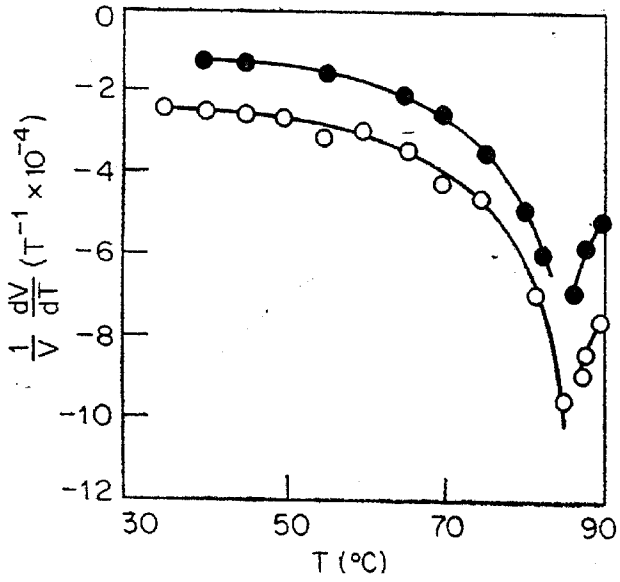

Figure 6. Normalized temperature coefficient of longitudinal and transverse wave velocities in amorphous $Ge_{10}Se_{90}$ sample plotted against temperature.

3. Discussion of results

As discussed earlier one should expect the velocity to decrease above T_g, from the definition of glass transition which represents the transition from liquid to a glass. The basic ideas of propagation of acoustic waves in viscoelastic material have been discussed by many workers and are summarized by Landau and Lifshitz, (1958). According to this picture, when a highly viscous liquid is deformed, the mechanical deformations exist for a time τ after the deformation force is removed. If ω is the frequency of mechanical disturbance (the acoustic waves in the present case) then for

$\omega \tau > 1$, the material behaves as a solid and for $\omega \tau < 1$, it behaves like a liquid. τ is related to η and the modulus of rigidity μ by $\eta \propto \tau \mu$.

On this basis one can start explaining the behaviour of the ultrasonic velocities in the present samples. As one goes above T_g, it is known that η decreases exponentially. Gradually the rigidity disappears and shear waves would propagate only if $\omega \tau > 1$. Thus one expects the ultrasonic velocities to decrease rapidly above the glass transition. For the transverse waves, the velocity should go to zero, well above the T_g and the longitudinal velocity should asymptotically attain the value in the liquid near T_m.

The velocity of transverse wave is about 1000 m/sec and that of longitudinal wave is about 1900 m/sec in the present glasses. If one expects the longitudinal and transverse velocities to be substantially smaller in the liquid phase, then the slow decrease in the velocities above T_g is not clear. The total change in the velocities from room temperature to T_g is quite small (30 to 40 m/sec). One expects that the velocities should start decreasing well away from T_g. Further the decrease in velocity is pronounced at T_g and then levels off as shown in figures 5 and 6. It should be mentioned that a similar behaviour of $(1/v)\,(dv/dt)$ is reported for amorphous selenium (Kittinger 1978) and other chalcogenide systems (Padaki *et al* 1980; Lakshmikumar *et al* 1981).

An attempt to measure velocities well above T_g has not been possible because of the failure of the bonding material. The bond used was CIBA araldite. It seems that soon after the transition takes place to liquid phase, the changes in the mechanical properties of the sample affect the seal and the echoes disappear. This is observed both in longitudinal and transverse velocity measurements in both the compositions.

Another factor is also to be considered, namely the deformation of the viscoelastic material above T_g under its own weight and the small spring loading provided on the sample to keep the sample transducer assembly in position. This would introduce a contraction in the sample after the transition. Since the velocity calculations are done taking the room temperature length of the sample (in the absence of thermal expansion data) the actual changes in velocity are probably slightly obscured by the changes in the length due to sample contraction.

The temperature at which the minimum in $(1/v)\,(dv/dt)$ is observed coincides reasonably for both longitudinal and shear waves as seen in figures 5 and 6. The T_g observed in the velocity measurements are very close to the values reported earlier (Ota *et al* 1978) and obtained by us from DSC plots. The T_g values obtained in the experiments are 86°C and 104°C for amorphous $Se_{90}Ge_{10}$ and $Se_{85}Ge_{15}$ samples respectively.

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