

Pressure-induced polymorphous crystallization in bulk $\text{Si}_{20}\text{Te}_{80}$ glass

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The effect of pressure on the electrical resistivity of bulk $\text{Si}_{20}\text{Te}_{80}$ glass has been studied up to a pressure of 8 GPa. A discontinuous transition occurs at a pressure of 7 GPa. The X-ray diffraction studies on the pressure quenched sample show that the high pressure phase is crystalline with hexagonal structure ($c/a = 1.5$). On heating, the high pressure hexagonal phase has an exothermic decomposition at $T = 586$ K into two crystalline phases, which are the stable phases tellurium and SiTe_2 obtained by simple heating of the glass.

1. Introduction

Glasses are considered to be supercooled liquids which are thermodynamically metastable. Usually glasses undergo a glass-crystal transformation with thermal treatment [1]. Pressure is a less used thermodynamic variable in the study of crystallization of glasses. Studies of pressure-induced glass-crystal transitions in covalent inorganic glasses are playing an important role in furthering the understanding the local molecular structure. A difference between the free energy of the low pressure glassy phase and that of the high pressure crystalline phase leads to a pressure-induced transition, which can be a sharp discontinuous or a continuous transition.

In general, chalcogenide glassy semiconductors transform to the corresponding crystalline metal under high pressure with a continuous change in the resistivity [2]. However, some chalcogenide glasses transform into crystalline phases with a discontinuous change in the electrical resistivity under high pressure [3-6]. In this paper we describe a pressure-induced amorphous to crystalline transformation in bulk $\text{Si}_{20}\text{Te}_{80}$ glass.

2. Sample preparation and experimental techniques

Bulk glasses of $\text{Si}_{20}\text{Te}_{80}$ were prepared by quenching the melts in an ice-water mixture. Appropriate amounts of the starting materials (99.999% pure silicon and tellurium) were vacuum sealed (10^{-6} torr) in fused silica tubes and heated to 1100 K in a horizontal furnace. The molten alloy was continuously and thoroughly agitated by using a motor, which rotated the ampoules at a speed of 10 r.p.m. When thorough mixing had been ensured by rotating the system for about 36 h, the molten alloy was quenched into an ice-water mixture. The composition regions of glass formation in the Si-Te system is reported to be

$0.10 < x < 0.27$ [7]. The glassy nature of the sample was confirmed by X-ray and electron diffraction studies. The calorimetric measurements were carried out in a Perkin-Elmer DSC-2 differential scanning calorimeter over a temperature range 300 to 800 K, at a rate of 20 K min^{-1} . The observation of a double T_g effect and double stage crystallization in this alloy has been described elsewhere [8].

The high pressure electrical resistivity measurements were carried out with a Bridgman anvil apparatus as described elsewhere [9, 10]. The sample was embedded in the steatite or sodium chloride pressure-transmitting medium and surrounded by a heat-treated pyrophyllite gasket. The conventional four-probe method was used for electrical resistivity measurements, with a Keithley constant current source and a Keithley electrometer as the measuring instruments. The measurements were found to be reproducible within the experimental errors. For recovering the samples subjected to high pressures, sodium chloride was used as the pressure-transmitting medium instead of steatite. The resistivity of the sample at room temperature and atmospheric pressure (ρ_0) was measured by the Van der Pauw technique. The changes in the dimensions of the sample under pressure were not taken into account in calculating the resistivity of the sample under pressure. The value of ρ_0 is $1.39 \times 10^6 \Omega \text{ cm}$, which is in good agreement with the reported value in the literature, namely $1.86 \times 10^6 \Omega \text{ cm}$ [7].

3. Results

The variation of electrical resistivity as a function of pressure is shown in Fig. 1. The room temperature atmospheric resistivity value is $1.39 \times 10^6 \Omega \text{ cm}$. Initially the resistivity decreases almost exponentially with pressure and there is a small change in the slope of the log (resistivity) against pressure curve at 3 GPa.

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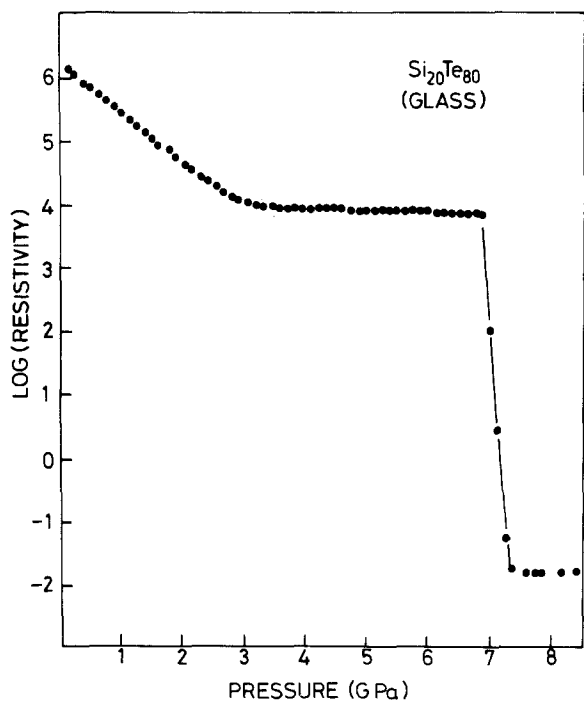


Figure 1 Pressure dependence of the electrical resistivity of bulk $\text{Si}_{20}\text{Te}_{80}$ glass at $T = 300$ K.

Then at 7 GPa the resistivity abruptly drops by about six orders of magnitude. Beyond 7 GPa the change in the resistivity with pressure is very small.

Fig. 2a shows the X-ray diffraction pattern of the as-prepared sample, indicating the glassy nature of the material. The X-ray diffraction pattern for the sample recovered at a pressure of 3 GPa is shown in Fig. 2b; at this pressure the plot of the electrical resistivity

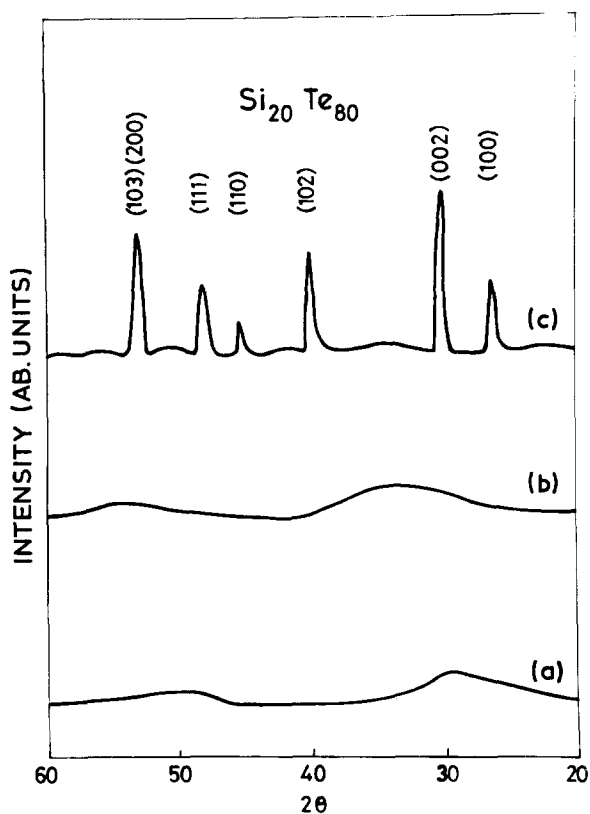


Figure 2 Curve (a) shows the X-ray diffraction pattern of the sample indicating amorphous nature. Curves (b) and (c) show the X-ray diffraction patterns of the samples recovered from pressures of 3 and 7 GPa, respectively.

TABLE I The X-ray spacings for the pressure quenched $\text{Si}_{20}\text{Te}_{80}$ sample

d_{hkl} (nm)	(hkl)
0.347	(100)
0.2999	(002)
0.2267	(102)
0.2000	(110)
0.1898	(111)
0.1732	(103)
0.1732	(200)

against pressure shows a change in slope. Fig. 2b indicates that the sample is amorphous at 3 GPa and there is no structural change. Fig. 2c gives the X-ray diffraction pattern for the sample recovered at a pressure of 8 GPa. It is seen from Fig. 2c that the $\text{Si}_{20}\text{Te}_{80}$ glass had undergone crystallization at 7 GPa.

Fig. 3 indicates the differential scanning calorimeter (DSC) trace for the sample previously recovered at a pressure of 8 GPa. It shows an exothermic peak at $T = 586$ K, indicating a transformation. Fig. 4 gives the X-ray diffraction pattern for the pressure-recovered sample (at 8 GPa), heated to melting and cooled to ambient temperature. It indicates the eutectic crystallization of the pressure-recovered sample into two phases, identified as tellurium and SiTe_2 , by the method below.

In order to study the nature of the crystallization, the X-ray data have been analysed. Table I gives the observed and calculated d -spacings for the high pressure crystalline phase of $\text{Si}_{20}\text{Te}_{80}$. The d -spacings are calculated by assuming a single crystalline phase having a hexagonal structure with $c = 0.6$ nm and $a = 0.4$ nm. Table II gives the d -spacings of the crystalline phases obtained by heating the pressure-recovered sample to its melting point and then cooling it. The data are compared with the d -values, calculated by assuming $c = 0.5915$ nm and $a = 0.4447$ nm for tellurium and $c = 0.578$ nm and $a = 0.408$ nm for SiTe_2 crystalline hexagonal phases. The comparison in Table II shows that there is an excellent agreement between the observed and the calculated d -values.

4. Discussion

Glasses regain their original volume only during the initial stages of compressions. At higher pressures all

TABLE II X-ray d -spacings for the sample recovered from a pressure of 8 GPa and then annealed at 600 K

Observed spacing (nm)	Calculated spacing (nm)	Phase	(hkl)
0.50108	0.50063	SiTe_2	(100)
0.37385	0.38513	Te	(100)
0.31644	0.32274	Te	(101)
0.31644	0.31628	SiTe_2	(101)
0.28938	0.28904	SiTe_2	(110)
0.23559	0.23585	SiTe_2	(111)
0.23209	0.23457	Te	(102)
0.22116	0.22235	Te	(110)
0.20579	0.20813	Te	(111)
0.19490	0.19717	Te	(003)
0.19028	0.19256	Te	(200)
0.18879	0.18892	SiTe_2	(102)

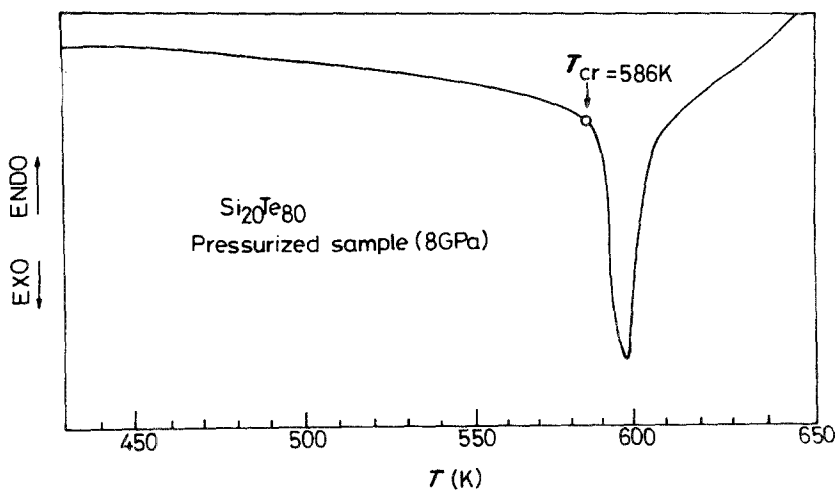


Figure 3 DSC trace of the sample recovered from the pressure cell after the application of 8 GPa pressure. This indicates an exothermal (crystallization) peak at $T_{cr} = 586$ K.

glasses show an increase in density and refractive index after pressurization [11]. Studies on some vapour-deposited amorphous materials like selenium, germanium, arsenic, etc. [12] reveal that the densities of these amorphous materials increase monotonically with pressure and crystallization occurs when a certain pressure level is reached. Initially the material becomes more and more compacted under pressure, and after a certain level of compaction further increase in pressure causes rearrangement of atoms, bonds, etc., within the material itself, which finally leads to crystallization. Bulk glasses usually crystallize at much higher pressures than amorphous thin films. Pressure induced crystallization has been observed in semiconducting binary chalcogenide glasses including $Ge_{20}Te_{80}$ [4, 6], $GeSe_2$ [5], $Al_{23}Te_{77}$ [13], $Se_{100-x}Te_x$ [3] and ionic glasses like $PbO-PbX_2$ ($X = F, Cl$) glasses [14].

The phenomenon of pressure-induced crystallization is not very straightforward. Atomic migration rates in solids are controlled by the repulsive forces an atom meets as it moves from one equilibrium position to another. The magnitude of these repulsive forces increases rapidly with decreasing interatomic distance and consequently the atomic migrations are slowed down by the application of high pressures. Diffusion measurements on crystalline materials under pressure [15–20] indicate a considerable decrease in the diffusion rate under pressure, with the diffusion coef-

ficient decreasing exponentially with pressure. The activation enthalpy increases and the activation volume decreases with increase in pressure. The diffusion of atoms and molecules in glasses should also be retarded under pressure. If the crystallization of the glass under pressure is to occur by nucleation and growth, the diffusion of atoms must take place at high pressures. Normally we cannot expect such a process to occur because of the retardation of diffusion under pressure. Nevertheless, under certain circumstances enhancement of diffusion under pressure may be favoured. For example, in the case of polycrystalline silver and γ -uranium, it has been observed that diffusion rates increase with pressure at moderately high pressures [21], the phenomenon being attributed to an enhancement in postulated grain-boundary diffusion under pressure. Similar effects have been observed in polycrystals of iron and Fe-Ti alloys [22]. It is also interesting to note that the application of hydrostatic pressure to LiF near its melting point causes dislocations to anneal out more quickly [23]. Thermal annealing of radiation damage in chemical compounds has shown that pressure actually accelerates recovery [24]. Hence it is possible for the crystallization of glasses to take place at high pressures, the decrease in diffusion constant under pressure being compensated by a possible decrease in the activation barriers involved.

If the crystallization of the glass under pressure does not involve nucleation and growth, the other possible

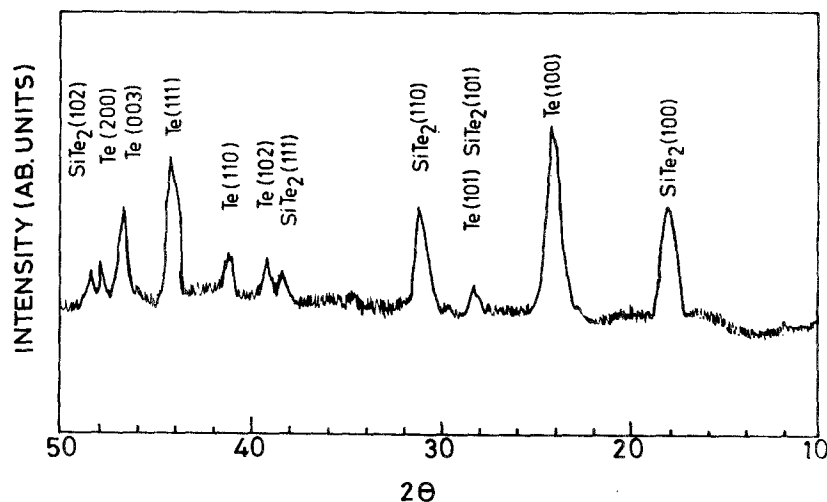


Figure 4 The X-ray diffraction pattern for the sample recovered from a pressure of 8 GPa and then annealed at 600 K.

mechanism by which it can occur is a diffusionless, martensitic transformation. Pressure-induced martensitic transformations are quite common and have been observed in many crystalline materials [25, 26]. These transformations may be sharp or may occur over a range of pressures. The martensitic transformation in pure iron, between α and ϵ phases, occurs over a pressure range of 30 kbars [25]. In the case of potassium, the transformation is sharp and occurs at around 360 kbar of pressure at 77 K [26]. Pressure-induced crystallization may be a sharp martensitic transformation, involving regimented movement of atoms. In the case of crystalline materials the transformation is reversible under pressure, with hysteresis. The pressure-induced crystallization of glasses is irreversible and can be understood on the basis that the transformation is from a metastable glassy state to the stable crystalline state. Crystallization of glasses under pressure need not necessarily be sharp. In glasses like As_2Te_3 [2], $\text{In}_{20}\text{Te}_{80}$, Cu-In-Te [27], $\text{Se}_{100-x}\text{Te}_x$ ($x > 8$) [3], the crystallization occurs as a continuous transformation. It is also interesting to observe that in some glasses a time-dependent crystallization under pressure is observed [28, 29]. In martensitic transitions, the degree of transformation is virtually independent of time. At a constant temperature a fraction of the original phase transforms very rapidly, after which there is usually no further change. Though this is a primary characteristic of martensitic transformations, in some reactions there is a small amount of isothermal transformation to the martensitic phase and in a few cases the change is almost completely isothermal [30]. However in $\text{Si}_{20}\text{Te}_{80}$ glass and some other glasses like $\text{Ge}_{20}\text{Te}_{80}$ [4, 6] GeSe_2 [5] etc., the pressure-induced crystallization is sharp at a particular pressure and occurs within a period of 30 sec, the lower limit of our present experiments. There is no appreciable time dependence over prolonged periods of time.

At present, it is not possible to infer whether the nucleation and growth mechanism or martensitic-like transformation leads to pressure-induced crystallization. The occurrence of crystallization continuously with pressure in some glasses indicates that the pressure-induced crystallization may not be martensitic.

High pressure electrical resistivity measurements on $\text{Si}_{20}\text{Te}_{80}$ glass reveal that the resistivity initially decreases almost exponentially with pressure and at 7 GPa (P_T), there is a sharp semiconductor-metal transition (Fig. 1). X-ray diffraction studies on the pressure-recovered sample indicate that the material undergoes a polymorphous crystallization at 7 GPa, going into a hexagonal structure with $c/a = 1.5$ (Fig. 2). In order to understand the nature of crystallization, whether it occurs abruptly or continuously, samples are recovered at 3 GPa, the pressure at which the curve of resistivity against pressure shows a change in slope. X-ray diffraction studies on the samples recovered at 3 GPa indicate the absence of crystallization (Fig. 2).

Raman spectroscopic studies on silicon chalcogenide glasses reveal that in these glasses heteropolar bonds are strongly favoured at all compositions of

glass formation and chemically ordered glassy compounds exist [31]. Comparing the silicon and germanium chalcogenides, some interesting differences can be noted. Although the basic molecular unit of the crystalline compounds is tetrahedral in both cases, the packing of the tetrahedra is considerably different. Silicon is comparatively more covalent than germanium and has a lesser tendency to have more than four nearest neighbours and to exist in the divalent state. These factors result in the higher molecular character and lesser metallic nature of silicon chalcogenide glasses. Consequently in $\text{Si}_{20}\text{Te}_{80}$ glass the magnitude of the pressure coefficient of resistivity (for the pressure region $P < P_T$, the transition pressure) is less than that in the case of glassy $\text{Ge}_{20}\text{Te}_{80}$. The value of the transition pressure (P_T) is also higher in the case of $\text{Si}_{20}\text{Te}_{80}$ glass, when compared to glassy $\text{Ge}_{20}\text{Te}_{80}$ [4, 6].

It has been observed that $\text{Si}_{20}\text{Te}_{80}$ glass shows the phenomenon of double glass transition and double stage crystallization [8]. On heating the $\text{Si}_{20}\text{Te}_{80}$ glass, excess tellurium crystallizes first at a temperature T_{c_1} , with the remainder staying as an amorphous phase. The remaining amorphous matrix then crystallizes as SiTe_2 with hexagonal structure ($c/a = 1.558$). This corresponds to the primary crystallization of a glass with one of the components crystallizing first. During this reaction the amorphous phase becomes rich in the other component, until further crystallization is stopped by reaching a metastable equilibrium. The remaining amorphous matrix then transforms later or at higher temperatures [32]. The dispersed primary crystallized phase may act as the preferred nucleation site for the following crystallization. Electron microscope photographs taken of $\text{Si}_{20}\text{Te}_{80}$ glass after the first crystallization show a pattern consistent with a dendritic structure. The phenomena of double glass transition and double stage crystallization are also observed in $\text{Al}_{23}\text{Te}_{77}$ [13], $\text{Ge}_{20}\text{Te}_{80}$ [33] glasses.

It is extremely interesting to note that under pressure $\text{Si}_{20}\text{Te}_{80}$ glass undergoes a polymorphous or congruent crystallization. This corresponds to the crystallization of the amorphous alloy without any change in concentration into a supersaturated alloy of a metastable or stable crystalline compound. This reaction normally occurs in concentration ranges near the pure elements or compounds. As far as supersaturated phases crystallize during this reaction they decompose by subsequent precipitation reactions; a metastable crystalline compound will undergo a phase transformation into the stable equilibrium phases [32]. Here, it is observed that under pressure $\text{Si}_{20}\text{Te}_{80}$ glass undergoes a polymorphous crystallization into SiTe_4 crystal, with hexagonal structure ($c/a = 1.50$) (Fig. 2). It is to be noted that $\text{Si}_{20}\text{Te}_{80}$ glass which undergoes polymorphous crystallization corresponds to a composition far away from the equilibrium stable compounds Si_2Te_3 , SiTe and SiTe_2 . DSC studies on the pressure-recovered sample, after the polymorphous crystallization, indicate that on heating it undergoes a phase transformation (exothermic peak on DSC curve) at 586 K (Fig. 3). X-ray diffraction studies on the pressure-recovered samples heated to melting and

cooled back indicate the presence of two crystalline phases, tellurium crystals and a new crystalline phase with hexagonal structure ($c/a = 1.416$) (Fig. 4). This new phase may be identified with SiTe_2 with a hexagonal structure, having a slightly higher c/a value ($c/a = 1.558$). The reason for this difference is not clear. Perhaps the material crystallized under pressure is disturbed by defect structures. In the crystals obtained by the thermal cycle, particles have greater mobility and hence the defect states may be annealed out.

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