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CRYSTALLIZATION KINETICS OF AMORPHOUS $Ge_{20}Se_5Te_{75}$

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ABSTRACT

The effect of heat treatment on the structural transformation and electrical conductivity σ of the amorphous alloy $Ge_{20}Se_5Te_{75}$ was studied. X-ray diffraction experiments on annealed samples, at temperatures higher than the glass transition temperature, showed the presence of Te and TeGe crystalline phases. On heating the amorphous sample above the glass transition temperature irreversible electrical conductivity changes were observed. The temporal changes in the σ values of the $Ge_{20}Se_5Te_{75}$ samples at various isothermal annealing temperatures were used to determine the transformation ratios from the amorphous to crystalline state. The kinetic parameters were also calculated. The crystallization is a two-dimensional process. A value of 1.02 ± 0.12 eV was obtained for the activation energy of the crystal growth in the temperature range 230–270 °C.

INTRODUCTION

The physical properties of glassy alloys have received a great deal of attention in recent years for many technical and scientific purposes [1–7]. Conduction in amorphous and crystalline materials, particularly those containing chalcogen elements, is attracting more interest. This is due to the unusual physical properties of the various states formed on heating or irradiation. The mechanism of conduction between these states is of much interest [5–7].

In this work the effect of heating on the glassy alloy $Ge_{20}Se_5Te_{75}$ was studied in order to obtain information on its electrical transport properties, the type of phases formed on heating and the kinetics of crystallization. Differential thermal analysis (DTA) and X-ray techniques were used to determine the type and number of phases formed on heating. The temporal

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changes in electrical conductivity were used to determine the kinetic parameters of the phase transition from the amorphous to the crystalline state.

EXPERIMENTAL

AnalaR grade elements were used to prepare the sample. A bulk amorphous sample of the composition $Ge_{20}Se_5Te_{75}$ was prepared by mixing the appropriate amounts of Ge, Se and Te elements in powdered form. The mixture was heated in a vacuum-sealed fused silica tube at 950 °C for 25 h, during which time the molten solution was occasionally shaken vigorously. The tube was then removed and quenched in an ice bath.

Differential thermal analysis (DTA) was performed using a MOM Derivatograph System No. 975136 at a rate of 5 K min^{-1}. Sample (50 mg) used for DTA was pulverized in an agate mortar.

The amorphous nature of the annealed and unannealed samples was examined using a Phillips unit, type PW 2103/00 diffractometer. A nickel-filtered, copper target source was used.

For the conductivity measurements, specimens (6 mm × 4 mm × 1 mm) were shaped from the ingot pieces and their surfaces were polished. Two graphite electrodes were positioned on a pair of parallel surfaces and these were connected with an electric source of known voltage and a vibrating reed electrometer type VAJ-51.

RESULTS AND DISCUSSION

The results of the differential thermal analysis of the amorphous $Ge_{20}Se_5Te_{75}$ sample are shown in Fig. 1. A small endothermic peak (softening temperature T_g), several exothermic crystallization peaks (T_1, T_2, T_3 and T_4) and an endothermic peak due to the melting of the crystalline phase formed (T_m) can be seen. The values of T_g, T_1, T_2, T_3, T_4 and T_m are listed in Table 1.

In order to determine the significance of the various peaks observed in the DTA curve (Fig. 1) X-ray examination was carried out. Several samples of $Ge_{20}Se_5Te_{75}$ were annealed, before X-ray examination, for 1 h at temperatures slightly higher than each observed exothermic peak. The X-ray diffraction patterns of the annealed specimens are shown in Fig. 2. The results are summarized in Table 2.

According to the DTA results, the crystallization process occurs in the temperature range 219–328 °C; consequently, the crystallization kinetics of the sample were studied at 230, 240, 250, 260 and 270 °C. At each of these annealing temperatures T_a the σ values were found to change with annealing time t_a. Figure 3 shows a typical plot of lg σ_{t_a} vs. t_a at $T_a = 230$ °C. This

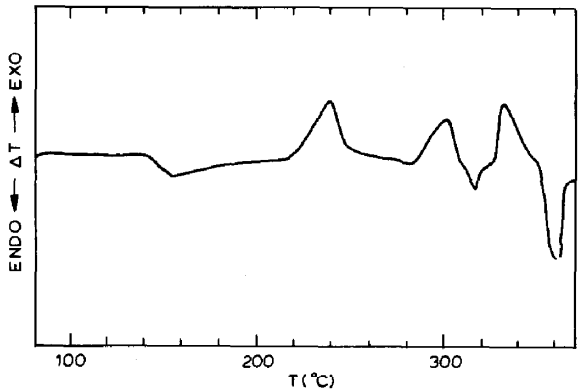

Fig. 1. DTA curve of amorphous $Ge_{20}Se_5Te_{75}$ (heating rate, 5 K min^{-1}).

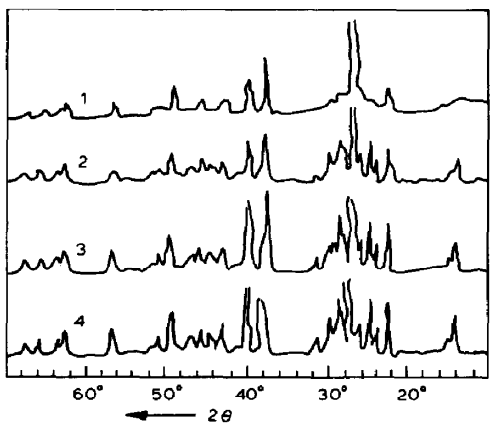

Fig. 2. X-ray diffraction patterns of $Ge_{20}Se_5Te_{75}$ annealed at various temperatures for 1 h: (1) annealed at 240 °C; (2) annealed at 300 °C; (3) annealed at 325 °C; (4) annealed at 335 °C.

temporal change in the conductivity was used to determine the rate of crystallization in the amorphous sample. In Fig. 3 two time-dependent conductivity stages can be distinguished. Part AB represents a gradual increase in σ as a result of the normal heating of the sample. The second stage (BC) shows a small increase in σ relative to the first stage. The second stage attains a limiting value (point C) after a time τ, the time necessary to

TABLE 1

DTA results of the glassy alloy $Ge_{20}Se_5Te_{75}$

T_g (°C)	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	T_m (°C)
143	219	283	318	328	350

TABLE 2

Crystalline phases formed on annealing the glassy alloy $Ge_{20}Se_5Te_{75}$

Sample	Annealing temperature (°C)	Crystallization temperature (°C)	Crystalline phases
1	240	219	Te
2	300	283	Te + GeTe
3	325	318	Te + GeTe
4	335	328	Te + GeTe

complete the crystallization process. From the conductivity results obtained at the other annealing temperatures, it was found that the total time τ decreases as the annealing temperature increases (Fig. 3).

The DTA results and the X-ray examination (see above) indicate that the increase in the conductivity values with increasing annealing time can be attributed to the increase in the number of crystallites per cubic centimetre

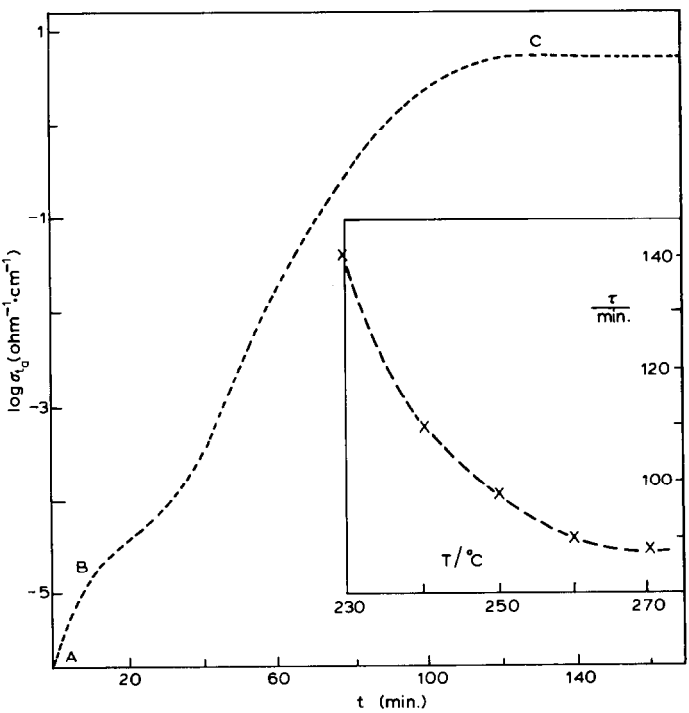

Fig. 3. Dependence of lg σ_{t_a} on annealing time during the transformation of $Ge_{20}Se_5Te_{75}$ from the amorphous to the crystalline state at 230 °C. The inset shows the temperature dependence of the total time of transformation τ.

TABLE 3

Values of the Avrami parameter n and ln K as a function of annealing temperature

Annealing temperature (°C)	n	$-\ln K$
230	2.41	10.01
240	2.35	9.58
250	2.30	9.11
260	2.24	8.72
270	2.21	8.30

in the amorphous $Ge_{20}Se_5Te_{75}$. The transformed fractions α at the various annealing times can be evaluated using the Avrami equation [8]

$$\theta = 1 - \alpha = \frac{\lg \sigma_c - \lg \sigma_{t_a}}{\lg \sigma_c - \lg \sigma_a} = \exp(-Kt_a^n)$$

where θ is the fraction which is uncrystallized at a time t_a and σ_c, σ_{t_a} and σ_a are the conductivity values at the end, at annealing time t_a and at the beginning of the crystallization process respectively. The parameter K is the temperature-dependent rate constant and n is a parameter which depends on the nucleation and growth mode. The value of n can be determined by plotting $\ln(-\ln \theta)$ against $\ln t_a$, according to the equation

$$\ln(-\ln \theta) = \ln K + n \ln t_a$$

At every crystallization temperature, the plot of $\ln(-\ln \theta)$ vs. $\ln t_a$ gives a straight line, whose slope is equal to n. The values of n and K at the various

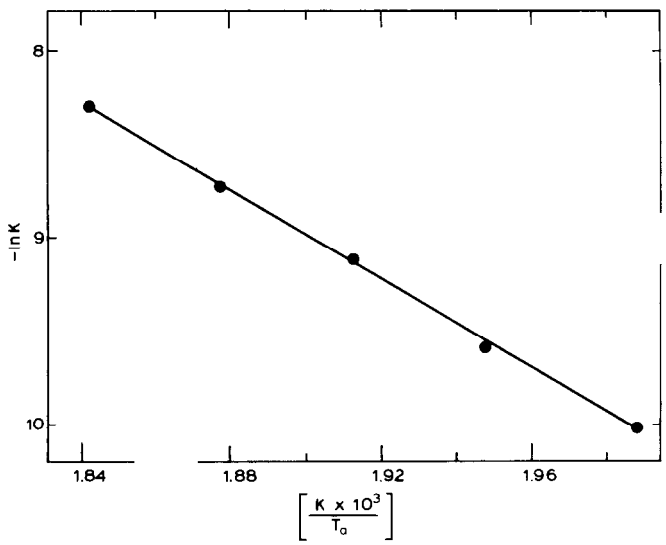

Fig. 4. Ln K vs. $1/T_a$ for the crystallization process.

annealing temperatures are given in Table 3. There is a slight decrease in n value with increasing annealing temperature. This indicates that the crystallization process gradually changes from sporadic to regular, which leads to a progressive reduction in n. The mean value of n is almost 2, which means that the crystallization in the annealed glassy alloy $Ge_{20}Se_5Te_{75}$ is a two-dimensional process.

The activation energy for the crystal growth can be calculated from the temperature rate constant, using the equation [1]

$$K = K_0 \exp\left(-\frac{E_a}{RT_a}\right)$$

where K_0 is a constant. The plot of ln K vs. $1/T_a$ (Fig. 4) gives a straight line and from its slope an activation energy of 1.02 ± 0.12 eV is obtained.

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