JOURNAL OF MATERIALS SCIENCE 22 (1987) 1618–1622

Electrical resistivity, nucleation and crystal growth in amorphous Se_{100-x}–Sb_x

M. M. EL-ZAIDIA, A. EL-SHAFI, A. A. AMMAR, M. ABO-GHZALA
Department of Physics, Faculty of Science, Menoufia University, Shebin El Koom, Egypt

The process of nucleation and crystal growth has been studied, using the change of the electrical resistance with time, for the system Se_{100-x}–Sb_x where $x = 5$, 10 and 15. The X-ray analysis of different records was also used to investigate the same processes. The results show that the apparent activation energies of nucleation were 17.89, 19.88 and 24.25 kcal mol^{-1} (74.90, 83.23 and 101.53 kJ mol^{-1}) for $x = 5$, 10 and 15, respectively. The values of the apparent activation energy of crystal growth were 39.78, 45.67 and 52.70 kcal mol^{-1} (166.55, 191.21 and 220.64 kJ mol^{-1}) for the same respective samples. The activation energy of conduction and the electrical resistance were found to decrease as the antimony content increases in both amorphous and crystalline states.

1. Introduction

Amorphous selenium is an inorganic polymer and is believed to contain two kinds of molecules, polymeric chains and monomeric rings. During crystallization to a trigonal structure the chains and rings break and become rearranged so that atoms polymerize into long chains occupying the correct crystallographic positions [1]. The dependence of the crystallization kinetics on the temperature and other factors has been reported [2]. Under normal conditions selenium crystallizes spherulitically on account of its chain-like molecules in the amorphous states [3–5]. This strongly suggests that crystallization begins when the process of molecular rearrangement in the initial phase has led to some critical concentration of crystallizing structure species, i.e. crystallization begins after molecular rearrangement has completed [6]. Information about the crystallization of the binary system Se–Sb in the literature is very limited [7].

The aim of this work is to study the crystal growth, diffusion and nucleation of amorphous Se_{100-x}–Sb_x where $x = 5$, 10, and 15, using the change in the electrical resistance and the X-ray diffraction technique. The conduction properties of this system will be reported in both amorphous and crystalline states.

2. Experimental procedure

Glassy samples of the system Se_{100-x}–Sb_x, where $x = 5$, 10, and 15, were prepared by mixing selenium and antimony (purity 99.99%) in an evacuated silica glass ampoule. This ampoule was kept in an electric furnace at 850° C for 8 h.

The molten material was quenched in a water–ice mixture to get the material in the glassy state as confirmed by X-ray diffraction.

The electrical resistance of the sample was measured by a digital multimeter Type MX 727A (error ±2%).

To study the amorphous–crystalline transformation, the tube containing the sample was placed in an oven preheated to the required temperature. The resistance of the sample was recorded as a function of time.

X-ray diffraction was recorded using a Shimadzu XD-3 diffractometer (scanning velocity 20° (2θ) min^{-1}, $\lambda = 0.1540$ nm).

3. Results and discussion

Typical annealing curves for the system Se_{100-x}–Sb_x, where $x = 5$, 10, and 15, were recorded isothermally at 80, 100, 110 and 120° C, as resistance ($\log R$) against time (t) for all samples (Figs 1a and b). The annealing temperatures were chosen to allow for the slow and fast phase transformation as indicated by the value of the glassy temperature (T_g) and the value of the crystallization temperature (T_c) deduced from the DTA thermograms (Fig. 2).

Fig. 1a shows that at a given temperature the electrical resistance ($\log R$) decreases gradually with time, reaching a minimum constant value. This means that the sample changes gradually from amorphous state to crystalline state at the end of the run. These curves also show that the rapid decrease of the electric resistance with time during stage B–C may be due to the nucleation and growth of small crystallites. The slow decrease in the value of the resistance with time during stage C–D may be due to the slowing down in the growth process. The rate of decreasing of the electrical resistance has been calculated. The results show that this rate in stage B–C is greater by two orders of magnitude than in stage C–D.

The previous qualitative study of crystal growth was followed by X-ray diffraction analysis. Fig. 3 shows X-ray diffraction patterns at the points A, B, C and D on each curve of Fig. 1. X-ray records corresponding to point A have no peaks, therefore the samples at this point are mostly amorphous. The rest of the X-ray traces show that crystallization increases as the process proceeds to points B, C and D. These

0022–2461/87 $03.00 + .12

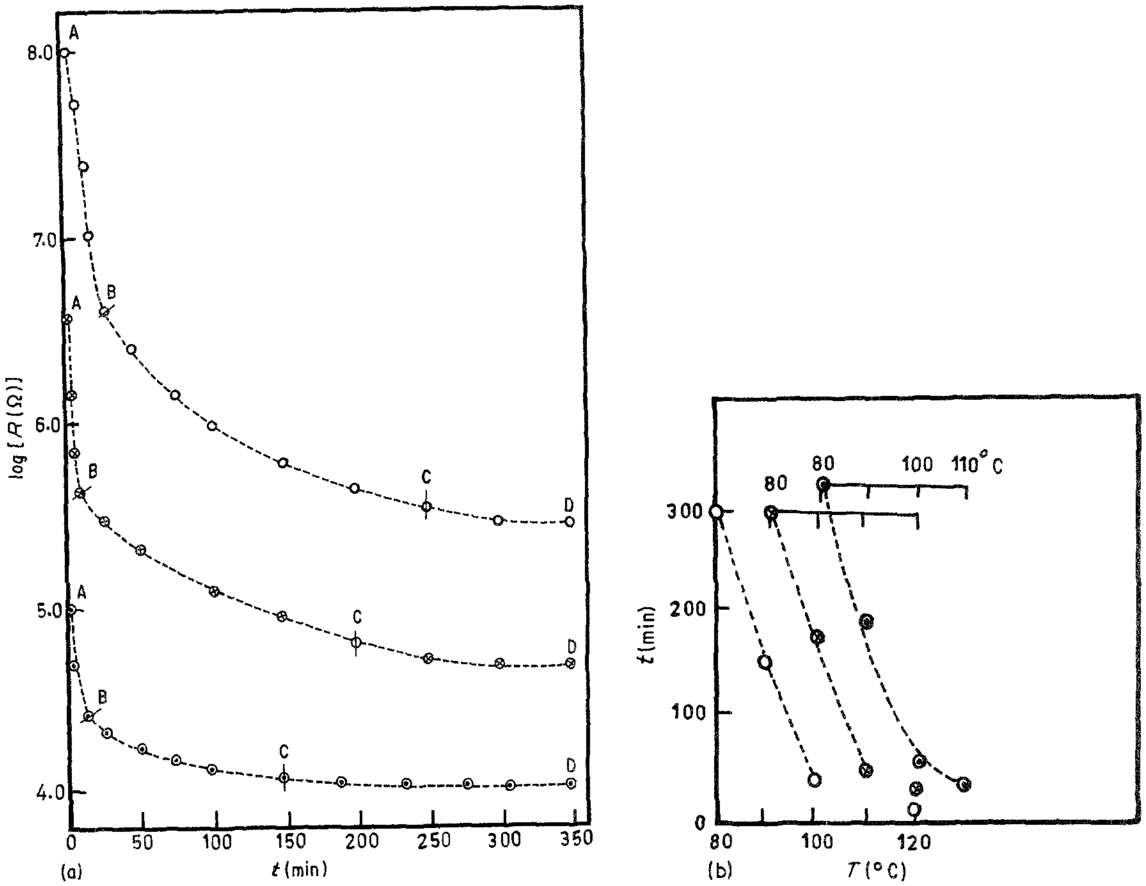

Figure 1 (a) Relation between electrical resistance (log R) and time (t) for x = (○) 5, (⊗) 10 and (⊙) 15 at 80° C. (b) Relation between temperature and time of annealing for x = (○) 5, (⊗) 10 and (⊙) 15.

results show that the growth of peak intensities in stage B–C is greater than their growth in stage C–D. This means that the radial growth of the spherulite crystalline domains in stage B–C is greater than in stage C–D.

The absence of peaks from the X-ray records in stage A–B may be due to the formation of critical nuclei consisting of a number of molecules proceeding via a chain reaction, each step of which is determined by the incorporation of an ambient phase molecule into the growing subcritical complex of the new phase.

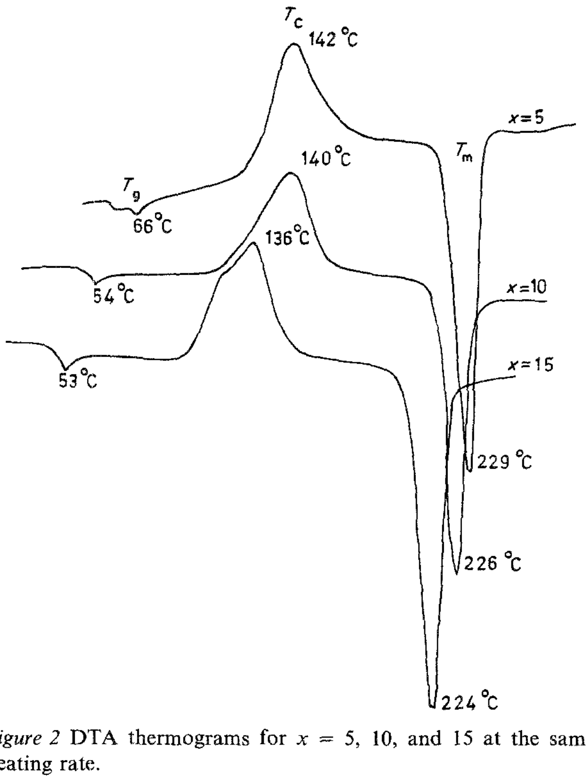

Figure 2 DTA thermograms for x = 5, 10, and 15 at the same heating rate.

The crystallization kinetics are usually described in terms of the Kolomogorov–Avrami equation [8–13]

$$\alpha(t) = 1 - \exp(-kt^n) \qquad (1)$$

where α is the transformed fraction from the old phase to the new phase. The kinetic parameters n and k have been calculated using relations derived [14] from Equation 1, and are given in Table I. These data show that increasing the antimony content leads to a decrease of the fractional values of the reaction order, n. This may be due to a deviation towards unidimensional growth as the antimony atoms increase in the selenium chains.

It has been reported that the crystal of selenium grows as spherulite crystalline domains [3, 15]. This picture could be applied to the alloy system Se_{100-x}–Sb_x. The radius R of the spherulite crystalline domains as a function of time at different temperatures is given by the relation [16]

$$R^2 = 2k(t - t_n) \qquad (2)$$

where t_n is the nucleation time. The linear relation between R and $t^{1/2}$ (Fig. 4) proves that the spherulite crystalline domains grow and propagate with time and temperature as determined from the X-ray traces.

The radial growth rate of such spherulites was governed by the work needed (ΔF) to overcome the surface energy of the two-dimensional nucleus which

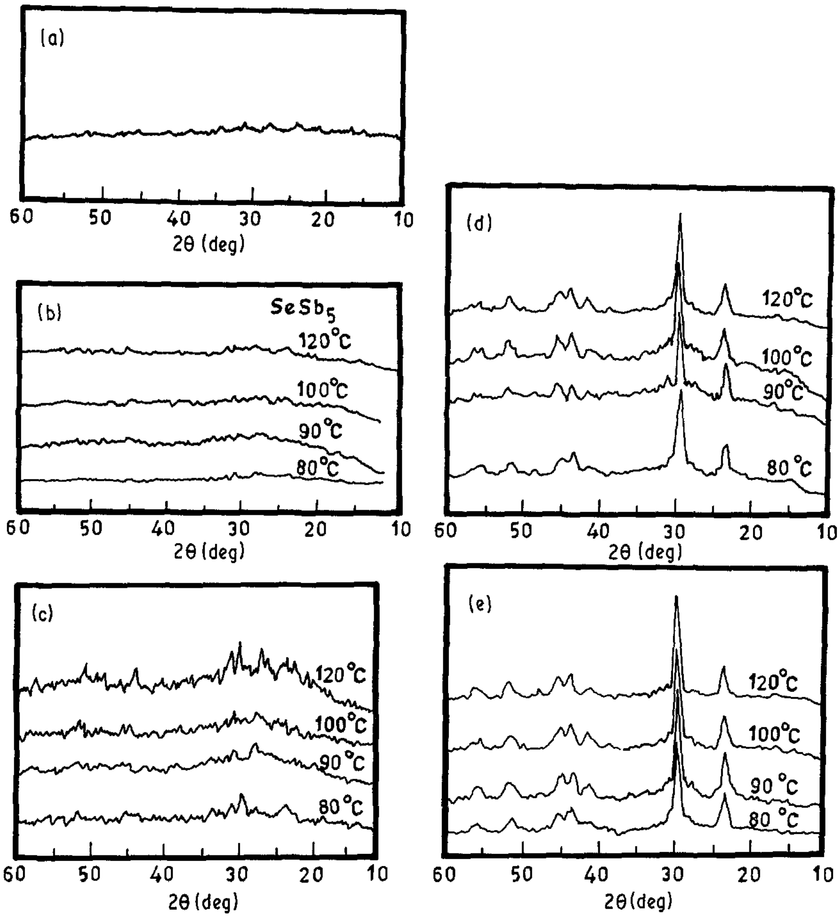

Figure 3 X-ray diffraction records at different annealing times and different temperatures for $x = 5$: (a) at point A in Fig. 1; (b) at point B; (c) at point C; (d) between points C and D; (e) at point D.

was formed on the surface of the crystal, and the energy needed for the transport of molecules to the crystal–amorphous interface from the amorphous phase (E_c). Therefore the radial growth rate k of the spherulite could be described by the equation [16]

$$k = k_0 \exp\left(-\frac{\Delta F}{RT} - \frac{E_c}{RT}\right) \qquad (3)$$

where k_0 is the pre-exponent including the diffusion coefficient of the new phase at the expense of the old phase, R is the universal gas constant, and T is the crystallization temperature (K).

The radial growth rate k of the spherulite may be governed only by the value of E_c/RT because the amorphous medium crystallizes at temperatures well below the melting point (226° C). This reduces the last equation to

$$k = k_0 \exp(-E_c/RT) \qquad (4)$$

The plot of ln$k$ against $(1/T)$ yields the apparent activation energy of crystallization (E_c) of the order of 39.78, 45.76 and 52.70 kcal mol^{-1} (166.55, 191.21 and 220.64 kJ mol^{-1}) for the samples of $x = 5$, 10 and 15, respectively (E_c for pure selenium [15] is 24.9 kcal mol^{-1}).

The increase of the apparent activation energy of

TABLE I Order of reaction (n), rate of crystallization ($\bar{k}$), diffusion coefficient (D) and electric resistance (R)

x	T (° C)	n	$\bar{k}$ (cm sec^{-1})	D (cm^2 sec^{-1})	R (Ω)	
					Initial	Final
0*	85	1.45	13.54 × 10^{-5}	6.09 × 10^{-4}	1.0 × 10^{13}	5.2 × 10^{6}
	100	1.25	71.67 × 10^{-5}	32.25 × 10^{-4}		5.0 × 10^{6}
	120	1.20	200.0 × 10^{-5}	90.00 × 10^{-4}		4.8 × 10^{6}
5	80	1.26	1.90 × 10^{-5}	8.55 × 10^{-5}	1 × 10^{8}	3.16 × 10^{5}
	90	1.20	14.00 × 10^{-5}	6.30 × 10^{-4}		1.90 × 10^{5}
	100	1.15	70.00 × 10^{-5}	31.50 × 10^{-4}		1.50 × 10^{5}
	120	1.05	200.00 × 10^{-5}	90.00 × 10^{-4}		0.70 × 10^{5}
10	80	1.05	1.00 × 10^{-4}	4.50 × 10^{-4}	3.98 × 10^{6}	5.01 × 10^{4}
	90	0.80	9.00 × 10^{-3}	4.05 × 10^{-2}		3.31 × 10^{4}
	100	0.62	24.00 × 10^{-3}	10.80 × 10^{-2}		1.50 × 10^{4}
	110	0.57	34.00 × 10^{-3}	15.30 × 10^{-2}		0.66 × 10^{4}
15	80	0.80	2.35 × 10^{-3}	1.06 × 10^{-2}	1 × 10^{5}	1.00 × 10^{4}
	90	0.68	11.75 × 10^{-3}	5.29 × 10^{-2}		8.70 × 10^{3}
	100	0.60	30.00 × 10^{-3}	13.50 × 10^{-2}		6.61 × 10^{3}
	110	0.50	56.00 × 10^{-3}	25.20 × 10^{-2}		3.16 × 10^{3}

See [17, 18]

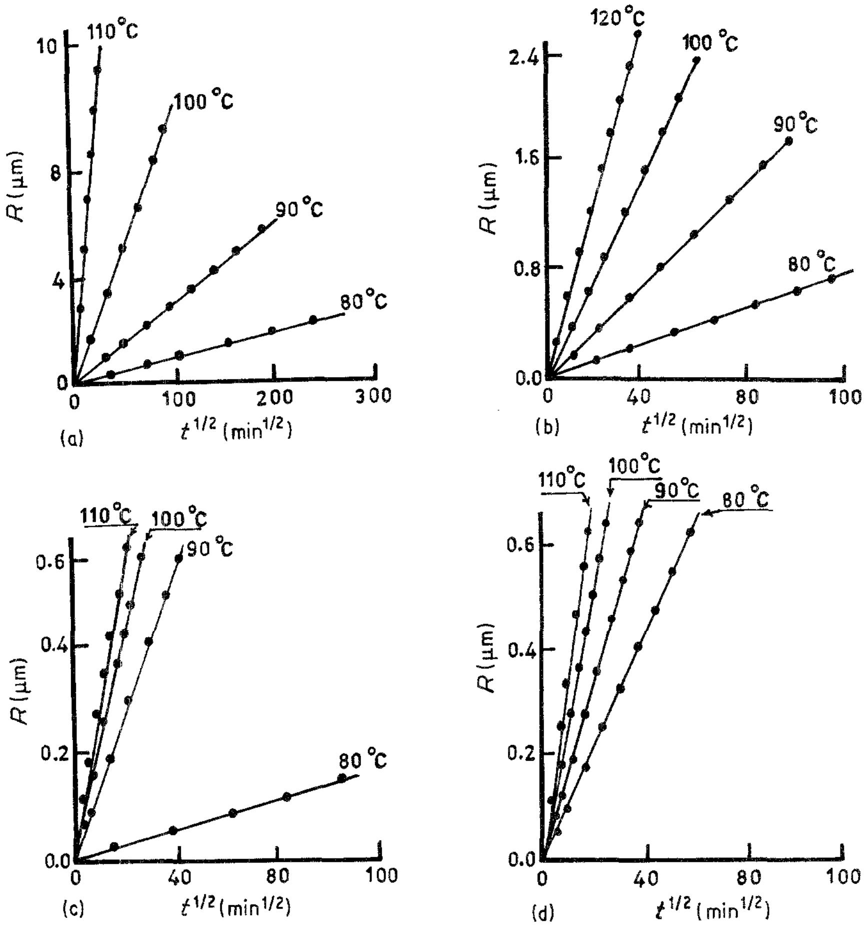

Figure 4 Relation between the radius of spherulite crystalline domains ($\bar{R}$) and time ($t^{1/2}$) for x = (a) ○ [15], (b) 5, (c) 10, (d) 15.

crystallization (E_c) as the antimony content increases may be attributed to the attachment of the antimony atoms on to selenium chains. This attachment leads to an increase of the average length of a selenium chain. Consequently, the mobility of the molecular species decreases, and much energy is required to complete the disorder–order transformation as the antimony content increases.

The growth of the crystalline phase in the old amorphous phase is a diffusion process. The diffusion coefficient (D) of such a process is given by the relation [16]

$$D = 4.5\mathrm{K}$$

The data of Table I show that an increase of antimony atoms leads to an increase of the diffusion coefficient. This may be due to the fact that the diffusion process occurs in a medium free from cilia as the chain length increases.

The effect of the time associated with nucleation (t_n) in stage A–B of Fig. 1a on the radius of the nucleus is not small. Thus the linear relation [16] between lnt_n and the reciprocal of the nucleation temperature yields the apparent activation energy of nucleation process of the order of 17.89, 19.88, and 24.25 Kcal mol^{-1} (74.90, 83.23 and 101.53 kJ mol^{-1}) for the samples of x = 5, 10, and 15, respectively (for pure selenium [17] it is 12.92 kcal mol^{-1}). These values increase as the antimony content increases. This may be due to the non-steady state nature of the nucleation process which requires much energy and time to join the antimony atoms on to the selenium chain.

The values of the electric resistance at initial and

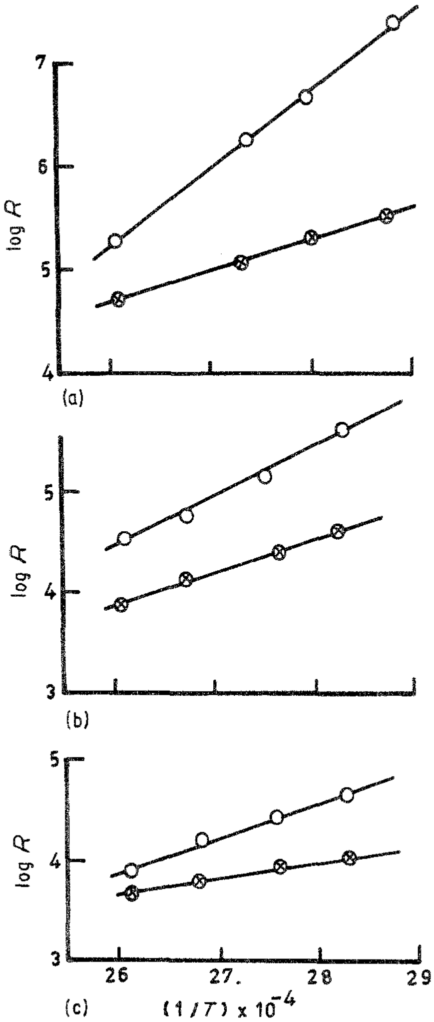

Figure 5 Relation between log R and $1/T$ for x = (a) 5, (b) 10 and (c) 15 in (○) amorphous and (⊗) crystalline states.

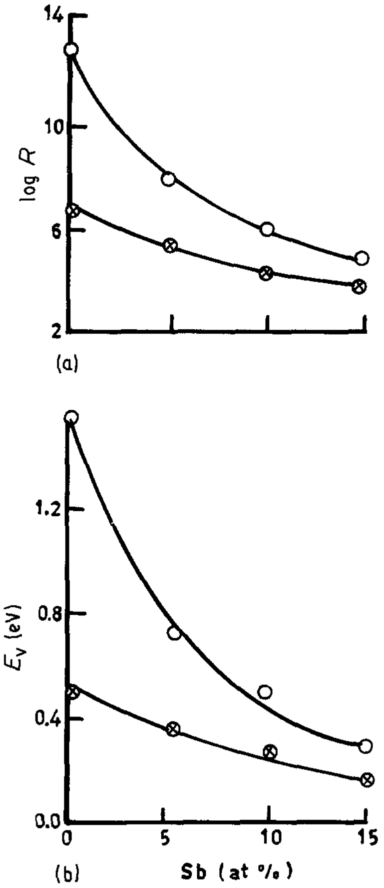

Figure 6 The composition dependence of (a) the resistance and (b) the activation energy of conduction in (○) amorphous and (⊗) crystalline states.

final states for the different compositions at all annealing temperatures, in addition to that of pure selenium [18], are given in Table I. Fig. 5 illustrates the relation between log R and the reciprocal of temperature ($1/T$), for each sample in the amorphous and crystalline states derived from Fig. 1a. The results show that all samples behave as semiconducting material in both amorphous and crystalline states, fitting well the relation $R = R_0 \exp(-E_v/kT)$. Also, the obtained activation energy of conduction (E_v) in the amorphous state is greater than its corresponding value in the crystalline state, for a given material. In addition to this, the obtained results show that increasing the antimony ratio in the binary system Se–Sb leads to a decrease in the electrical resistance as well as the activation energy of conduction in both amorphous and crystalline states (Fig. 6). This may be due to the increase in the selenium chain length, which enhances the conduction process without a metallic transformation.

References

1. A. I. POVOV, *Phys. Chem. Glasses* **19** (1978) 43.
2. I. E. BOLOTOV, S. B. FISHELEVA and S. A. BELAN, *Izv. Vuz. Fiz* **2** (1969) 15.
3. C. H. CHAMPNESS and R. H. HOFFMANN, *J. Non-Cryst. Solids* **4** (1970) 138.
4. C. H. GRIFFITHS and B. FITTON, *J. Appl. Phys.* **39** (1968) 3663.
5. A. J. PENNINGS, *J. Cryst. Growth* **48** (1980) 574.
6. I. GUTZOW, *ibid.* **48** (1979) 589.
7. H. KRIBS, *Angew. Chem. Inst. Ed.* (1966) 544.
8. A. N. KOLOMOGOROV, *Bull. Acad. Sci. URSS (Sci. Math. Nat.)* **3** (1937) 355.
9. M. AVRAMI, *Chem. Phys.* **1** (1939) 1103.
10. *Idem, ibid.* **8** (1940) 212.
11. *Idem, ibid.* **9** (1941) 177.
12. J. N. HAY, *J. Polym. Sci. A* **3** (1965) 433.
13. *Idem, Br. Polym. J.* **3** (1971) 74.
14. M. M. EL-ZAIDIA and A. M. NASSAR, *Phys. Chem. Glasses* **22** (1981) 147.
15. S. HAMADA, T. SATO and T. SHIRAI, *Bull. Chem. Soc. Jpn* **40** (1967) 864.
16. T. MINAMI, N. TOHGE, J. WASHO and M. TANAKA, *Phys. Chem. Glasses* **18** (1977) 112.
17. M. K. EL-MOUSLY, *Proc. Math. Phys. Soc. Egypt* **44** (1977) 189.
18. M. K. EL-MOUSLY and M. M. EL-ZAIDIA, *J. Non-Cryst. Solids* **11** (1973) 519.

Received 13 February
and accepted 21 July 1986