JOURNAL OF MATERIALS SCIENCE: MATERIALS IN ELECTRONICS 6 (1995) 404–408

Non-isothermal kinetic studies for binary TeO_2–P_2O_5 glass system

M. M. ELKHOLY
Physics Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

A study of TeO_2–P_2O_5 glass system has been carried out by Differential Thermal Analysis (DTA) to elucidate the kinetics of crystallization for these glassy samples. The results of DTA performed at different heating rates are discussed. The values of the glass transition temperature, T_g, as well as the glass crystallization temperature, T_c, are found to be dependent upon the heating rate. From this dependence, the values of activation energy for both the glass transition and crystallization are evaluated and discussed

1. Introduction

The TeO_2–P_2O_5 glass system has the ability to form glasses from 0 up to 100% TeO_2 content. This ability seems to be connected with chemical ordering in the liquid states [1], and the ability of TeO_2 and P_2O_5 to form glasses on their own.

Many workers [2–6] have studied the different physical properties of oxide glasses, but little work has been done on the crystallization kinetics of these glasses.

Kinetic studies are mostly connected with the concept of activation energy. Two separate phenomena are associated with the glass crystallization, both of which need some kind of activation energy. These phenomena are the nucleation and growth processes that dominate the devitrification of most glassy solids. The nucleation and growth are separate steps in the transformation, although they have been combined into an activation energy representative of the overall crystallization process [7–9].

In the present work, the dependencies of the glass transition temperature, T_g, and the glass crystallization temperature, T_c, upon the composition and heating rate have been studied. From the heating rate dependence of T_g and T_c, the activation energy of the glass transition and the activation energy of crystallization have been evaluated.

Crystallization studies have been made under non-isothermal conditions with the samples heated at several uniform rates. Valuable information about the crystallization process has been obtained for the binary TeO_2–P_2O_5 glass system using a recent analysis developed for non-isothermal crystallization studies.

2. Experimental procedure

2.1. Glass preparation

For each binary TeO_2–P_2O_5 glass system in the present study, the thermal history (i.e. melting temperature, melting time, annealing temperature and time, and all other preparation conditions were as similar as possible.

The binary TeO_2–P_2O_5 glasses were prepared by melting appropriate mixtures of Analar phosphorus pentoxide P_2O_5, 99.99% purity, and Analar tellurium oxide TeO_2, 99.99% purity, using open alumina crucibles heated in an electric furnace open to the atmosphere. The mixture was heated first at 300 °C for one hour and then transferred to a second furnace held at 800 °C for 45 min. The glass melts were stirred occasionally with an alumina rod, to ensure homogeneous melts. The highly viscous melt was cast into a cylindrically shaped split-mould of mild steel. The produced glass was annealed at 300 °C in a second furnace for one hour. Finally, the furnace was switched off and the glass allowed to cool *in situ* for 24 h.

2.2. Differential Thermal Analysis (DTA)

The characteristic of the prepared glasses (such as the transition temperature, T_g, melting temperature, T_m, chemical transformations, etc.) were studied using the Shimadzu Differential Thermal Analysis system. This is a sensitive instrument for the ready evaluation of thermal behaviour over the temperature range of ambient to 1575 K. When the sample and reference substance are heated at a constant rate, their temperatures rises. The temperature of the reference substance, which is thermally inactive, rises uniformly, while the temperature of the sample stops rising when an endothermic reaction (e.g. fusion) occurs, because the heat supplied from outside is consumed by the reaction. When the reaction is over, the sample temperature is very much less than ambient. Initially, its temperature rises rapidly, then more uniformly. The temperature difference ΔT is detected, amplified and recorded, as a peak. The temperature in the sample holder is measured by a thermocouple, the signal of which is compensated for the ambient temperature and fed to the temperature controller. This signal is compared with program signal and the voltage applied to the furnace is adjusted. Thus the sample and reference substance are heated or cooled at the desired rate.

3. Results and discussion

A small amount of powdered sample ($\sim$ 0.1 g) and a thermally inert standard sample of γ-alumina were placed in the furnace. Fig. 1 shows typical DTA traces for the TeO_2–P_2O_5 glass samples with different TeO_2 content heated at different heating rates. It is evident from the figure that at the glass transition temperature, T_g, there is a drop in output due to the change in the heat capacity and also an increase in the specific heat of the glass samples. Before and after T_g, the structure remains unchanged, softening of the originally hard material only occurring at T_g. On further heating the DTA curves show an exothermic peak representing devitrification. This temperature corresponds to a change in the glassy material to a crystalline structure. Since the glass structure exhibits higher energy state than the corresponding crystal phase, this is indicated by the evolution of heat. On further heating, a drop in the output (an endothermic peak) is observed. In this region the crystal absorbs the latent heat on changing to the liquid state.

The glass transition temperature, or the softening temperature, T_g, as well as the crystallization temperature, T_c, which have been obtained using the DTA charts of Fig. 1 are tabulated in Tables I and II. It was noted that both T_g and T_c are increased with increasing TeO_2 content at different heating rates. The glass transition temperature, T_g, plotted in Fig. 2 is found to vary linearly with TeO_2 content. The changes in T_g with TeO_2 are due to the closeness of the network structure of these glasses and correspond to the increase in density [2]. Also, the increase of T_g with TeO_2 may be due to the fact that, as TeO_2 increases, the fraction of phosphorus atoms participating in terminal charged PO_4 units increases and therefore the chains become shorter. Also, with increasing TeO_2 mole %, the ratio of tellurite to phosphate increases and therefore the crosslink density increases. Both the increase in the fraction of shorter, stiffer chains and the increase in strong ionic crosslinks serve to increase

TABLE I Composition, T_g, density and number of bonds per unit volume for binary TeO_2–P_2O_5 glass system

Glass type	TeO_2 (mole %) chemically analysed	T_g (°C)	Density (g cm^{-3})	$n_b \times 10^{-22}$
Pure P_2O_5	–	290	2.52	6.42
T_1	28.18	312	3.13	6.89
T_2	32.38	314	3.17	6.92
T_3	36.15	317	3.30	7.08
T_4	40.16	319	3.34	7.01
T_5	45.72	322	3.47	7.14
T_6	52.55	327	3.65	7.19
T_7	59.42	333	3.80	7.22
T_8	62.80	336	3.91	7.30
T_9	64.28	337	3.95	7.32
T_{10}	68.40	340	4.06	7.36
T_{11}	73.51	346	4.34	7.65
T_{12}	76.49	350	4.47	7.78
T_{13}	81.09	355	4.82	8.14
Pure TeO_2	98.40	320	5.13	7.74

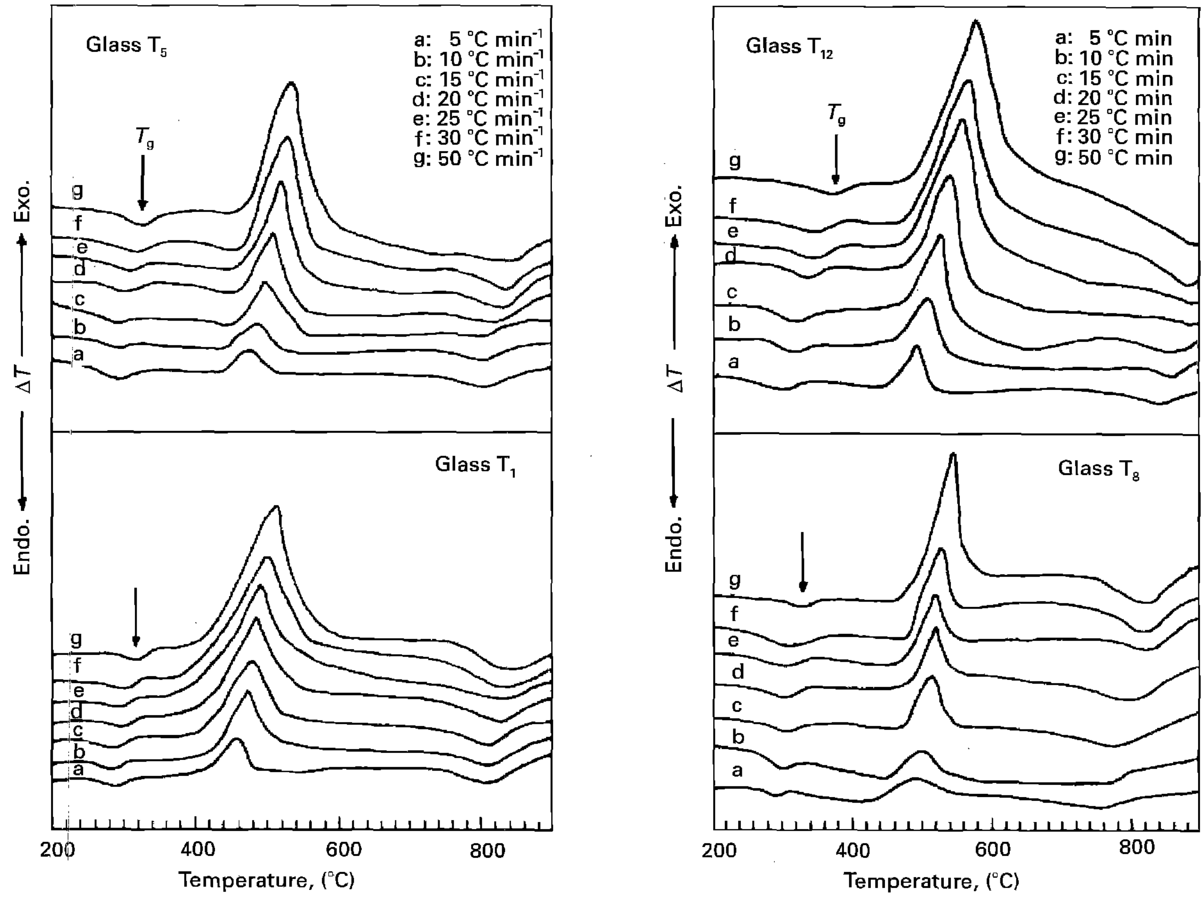

Figure 1 Typical DTA traces of TeO_2–P_2O_5 glass system recorded at different heating rates.

TABLE II Glass transition temperatures, T_g, and crystallization temperatures, T_c, recorded at different heating rates for TeO_2–P_2O_5 glass system

Glass type	Glass transition temperature, T_g, recorded at different heating rates						
	5 °C min^{-1}	10 °C min^{-1}	15 °C min^{-1}	20 °C min^{-1}	25 °C min^{-1}	30 °C min^{-1}	50 °C min^{-1}
T_1	305	309	312	314	316	318	322
T_3	307	313	317	320	323	325	332
T_5	309	317	322	325	329	332	340
T_6	311	321	327	331	335	338	346
T_8	314	326	333	338	342	345	356
T_{10}	316	330	340	346	350	355	367
T_{12}	320	340	350	360	365	370	385

Glass type	Glass crystallization temperature, T_c, recorded at different heating rates						
	5 °C min^{-1}	10 °C min^{-1}	15 °C min^{-1}	20 °C min^{-1}	25 °C min^{-1}	30 °C min^{-1}	50 °C min^{-1}
T_1	460	472	476	484	492	500	508
T_5	480	492	503	516	528	532	540
T_8	500	510	520	524	530	540	556
T_{12}	502	516	528	544	562	570	580

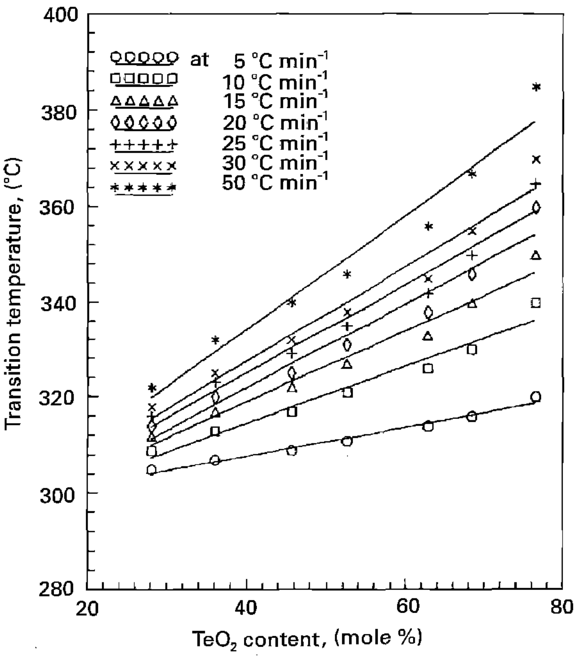

Figure 2 Glass transition temperature as a function of TeO_2 content for TeO_2–P_2O_5 glass system.

the transition temperature of the TeO_2–P_2O_5 glass system with increasing TeO_2 content.

The glass transition temperature can be taken as a measure of the onset of diffusion motion and thus it corresponds to the fixed value of viscosity (or of reciprocal fluidity). In such a case, the T_g can be connected with

(i) the average number of bonds per atom (N) which must be broken to obtain fluidity;

(ii) the bond strength, which can be related to the optical gap.

Based on this idea, attempts are made to calculate the number of bonds per unit volume (n_b) for each glass sample using the following expression:

$$n_b = n_f N_A \rho / M_g \qquad (1)$$

where n_f is the co-ordination number, N_A is Avogadro's number, ρ is density and M_g is the molecular mass of the glass sample, which is given by

$$M_g = x M_1 + (1 - x) M_2 \qquad (2)$$

where M_1 and M_2 are the atomic masses, and x and $1 - x$ the fractional atomic concentrations, of the oxides used. The calculated number of bonds per unit volume using the above equations are presented in Table I. From Table I it was found that the number of bonds per unit volume increases with increasing TeO_2 content and thus the average crosslink density also increases leading to compactness of this binary glass system, confirming the increase in density and T_g for the same glass system.

Since T_c depends upon the heating rate, crystallization must be a kinetic rather than an equilibrium thermodynamic process for the glasses. Thermodynamically, the metastable condition of glass differs from the stable condition of the crystal by virtue of its higher free energy. The transition (vitreous–crystalline) takes place via two kinds of reaction: nucleation and crystal growth. The first is an endothermic process, while the latter is exothermic. As early as 1993, Tammann [10] established that these processes are based on different rate-controlling mechanisms.

It must be added that according to the Tammann interpretation of devitrification at a constant temperature below T_m, nuclei can be formed at a constant rate. Tuszyhski [11], on the other hand, explains the phenomenon of crystallization in glasses in such a manner that an endless number of nuclei of the phase to be formed can be assumed. The maximum crystal nucleation occurs either next to or just above T_g. This can be theoretically substantiated by the impediment of nucleation as a result of elastic deformation below T_g [12], as well as on an atomistic basis in terms of resonance of thermal vibrations at the point of conversion T_g or in its immediate vicinity (up to about 15 degrees above T_g).

Three approaches are used to discuss the dependence of T_g and T_c on the heating rate α. One of them is the empirical relationship

$$T_g = A + B \log \alpha \qquad (3)$$

where A and B are constants for a given glass composition [13]. Fig. 3 shows the variation of T_g as a function of log α and indicates the validity of this relationship for the present glass system.

The second approach is the so-called Kissinger formula [14] for the evaluation of the activation energy of the glass transition. It has been shown [15, 16] that the dependence of T_c upon α is given by

$$\log (T_c^2/\alpha) + \text{constant} = E/(RT_c) \qquad (4)$$

where E is the effective activation energy and R is the universal gas constant. It was found that this expression is valid for the glass transition [17] and has been used to calculate values of the glass transition activation energy [15–18]. Kissinger assumed that the temperature of maximum deflection in DTA is also the temperature at which the reaction rate is maximal. Plots of both log (T_g^2/α) versus $1/(T_g)$ and (T_c^2/α) versus $1(T_c)$ for these glasses are shown in Figs 4 and 5, respectively; these indicate linearity with heating rate and yield values for the glass transition activation energy and the activation energy of crystallization. The glass transition activation energy was found to decrease with increasing TeO_2 content, from 345 kJ mol^{-1} to 104 kJ mol^{-1}. When the TeO_2 content increased from 28.18 to 76.49 mole %. The activation energy of crystallization was found to be higher than the activation energy of glass transition and shows anomalous behaviour with TeO_2 content. The third approach uses the Ozawa relationship [19] which is based on the shift in the peaks as the heating rate is changed, as indicated from the following equation:

$$\log \alpha = E/4.57 \times 1/T_g + \text{constant} \qquad (5)$$

Plotting log α versus $1/T_g$ and $1/T_c$ gives straight lines (see Figs 6 and 7), the gradients of which give values for the glass transition activation energy and the activation energy of crystallization. By inspection of Figs 4–7, one can see that the glass transition

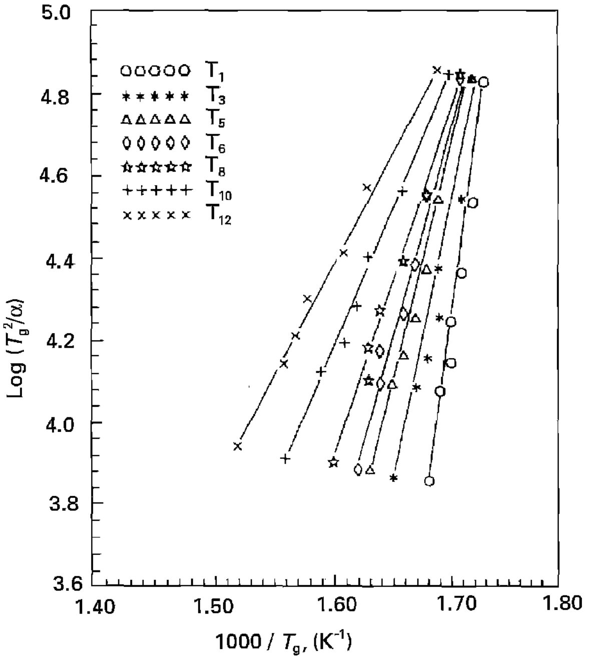

Figure 4 Log (T_g^2/α) versus $1000/T_g$ obtained from DTA traces for TeO_2–P_2O_5 glass system.

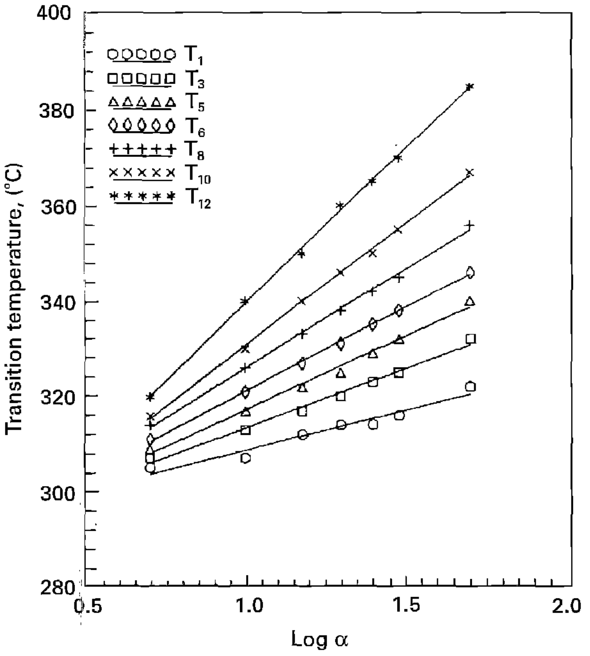

Figure 3 Glass transition temperature as a function of heating rate, α, for TeO_2–P_2O_5 glass system.

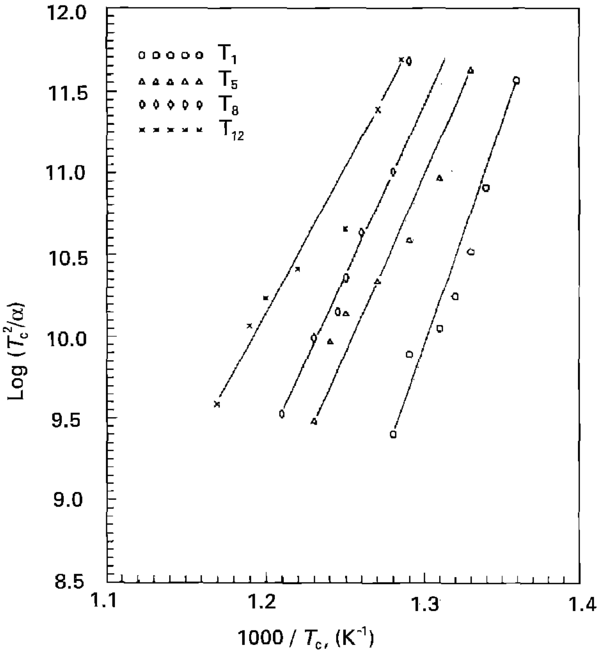

Figure 5 Log (T_c^2/α) versus $1000/T_c$ obtained from DTA traces for TeO_2–P_2O_5 glass system.

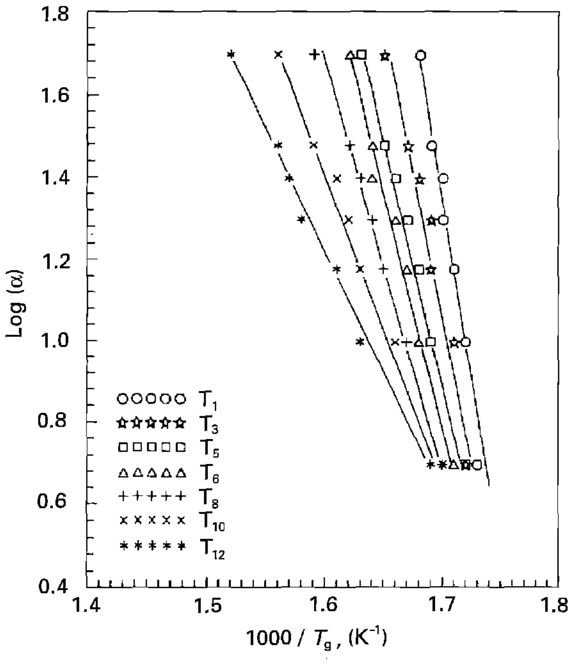

Figure 6 Log α versus $1000/T_g$ obtained from DTA traces for TeO_2–P_2O_5 glass system.

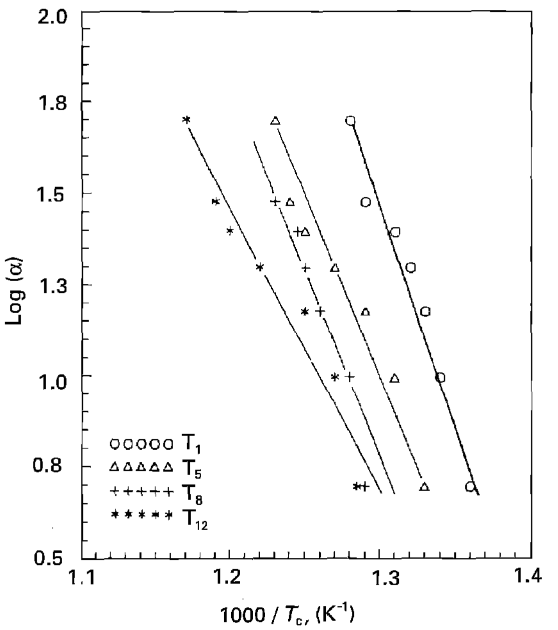

Figure 7 Log α versus $1000/T_c$ obtained from DTA traces for TeO_2–P_2O_5 glass system.

activation energy and the activation energy of crystallization (which are summarized in Table III) calculated by the Kissinger and Ozawa relationships are in agreement.

4. Conclusion

The general trend for the P_2O_5–TeO_2 glass system is that both the glass transition temperature and the glass crystallization temperature T_c increase with increasing TeO_2 content. It seems that as the heating rate, α, increases, the glass transition temperature and the activation energy of crystallization shift to higher temperatures for all compositions. Also, we noted that as α increased, the area under the crystallization and melting peaks of the DTA traces increased. Smaller areas mean that only small amounts of the sample material have been crystallized and may be increased at higher heating rates. The activation energies calculated by either the Kissinger or Ozawa methods are in good agreement and their values decrease with increasing TeO_2 content.

TABLE III Glass transition activation energy, E_g, and crystallization activation energy, E_c, calculated using Kissinger and Ozawa methods for TeO_2–P_2O_5 glass system

Glass type	Glass activation energies, kJ/mol			
	Kissinger method		Ozawa method	
	E_g	E_c	E_g	E_c
T_1	82.40	113.84	86.14	121.65
T_3	58.36	–	65.44	–
T_5	48.90	84.04	51.28	91.13
T_6	46.30	–	48.76	–
T_8	38.60	114.71	42.41	122.93
T_{10}	31.10	–	32.81	–
T_{12}	24.76	77.00	27.28	78.42

References

1. S. SURIÑACH, M. D. BARO, M. T. CLAVAGUERA-MORA and N. CLAVAGUERA, *Fluid phase Equilibria* **20** (1985) 341.
2. S. NEOV, I. GERASSINOVA, V. I. KOZHUKAROV and M. J. MARINOV, *Mater. Sci.* **15** (1980) 1153.
3. V. KOZHUKHAROV, H. J. OEL and B. CAMARA, *Glastechn. Ber.* **54** (1981) 292.
4. E. F. LAMBSON, G. A. SOWNDER, B. BRIDGE and R. A. EL-MALLAWANY, *J. Non-Cryst. Solids* **69** (1984) 117.
5. A. ABDEL-KADER, A. A. HIGAZY and M. M. ELKHOLY, *J. Mater. Sci.* **26** (1991) 4298.
6. A. ABDEL-KADER, A. A. HIGAZY and M. M.. EL-KHOLY, *J. Mater. Sci. Mater. Elec.* **2** (1991) 157.
7. H. G. KISSINGER, *Anal. Chem.* **29** (1957) 1702.
8. S. MAHADEVAN, A. GIRIDHAR and A. K. SINGH, *J. Non-Cryst. Solids* **88** (1986) 11.
9. N. RYSAVA, T. SPASOV and L. J. TICHY, *Therm. Anal.* **32** (1987) 1015.
10. G. TAMMANN, Der Glaszustand, Leiizing (1933).
11. W. TUSZYHSKI, *Phys. Chem. Glasses* **15** (1974) 95.
12. A. M. KALININA, and V. N. FILIPOVIC, 10th International Congress on Glasses, Kyōto, Japan, 1974, Vol. 14, p. 56.
13. M. LASOCKA, *Mater. Sci. Eng.* **23** (1976) 173.
14. H. G. KISSINGER, *J. Res. Nat. Bur. Stand.* **57** (1956) 217.
15. H. S. CHEN, *J. Non-Cryst. Solids* 27 (1978) 257.
16. J. E. SHELBY, *ibid.* **34** (1979) 111.
17. J. COLEMENERO and J. M. BARANDIARAN, *ibid.* **30** (1978) 263.
18. J. A. MACMILLAN, *J. Phys. Chem.* **42** (1965) 3497.
19. T. OZAWA, *Polymer* **12** (1971) 150

Received 24 November 1992
and accepted 19 April 1993