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APPLICATION OF PILOYAN'S METHOD IN THE STUDY OF THE ENERGETICS OF A GLASS-TO-CRYSTAL TRANSITION

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On the basis of the results obtained for eutectic Te–Ge glass, the application of the simple Piloyan method for study of the energetics of the glass-to-crystal transition was considered. Some new applications of this method to not yet completed transitions were proposed. Limitations of the method and factors exerting an effect on the calculated activation energies were discussed. Piloyan's procedure was compared with Kissinger's method.

The simplest way of determining the activation energy of a solid-state transition seems to be that suggested by Piloyan et al. [1]. It requires only one DTA experiment, at an arbitrarily chosen heating rate (within the range 10–40 deg/min). The basic assumption is that the deviation from the baseline, ΔT, is proportional to the reaction rate $d\alpha/dt$, independently of the fraction reacted, within the α range 0.05–0.8 (α is the extent of reaction). This assumption holds true for zero-order reactions [2].

In the original paper [1] the authors mentioned, in support of their method, reactions of dissociation ($CaCO_3$, $MgCO_3$) and dehydration ($CuSO_4.5\,H_2O$, $CaC_2O_4.H_2O$). In the present work, the suitability of this method for the study of the energetics of a glass-to-crystal transition was considered. Our own earlier data obtained for eutectic Te–Ge glass [3] were re-calculated in order to assess Piloyan's method. Activation energies E given in [3] have been determined according to Kissinger [4].

In the system studied, the glass-to-crystal transition comprises two stages with different mechanisms. Only the first stage is controlled by a diffusional mechanism [3], and that is why the results concerning this stage were taken into further consideration. In Table 1 the experimental data are presented, together with the estimated values of E. The function $\log I$ vs. $1/T$ is plotted in Fig. 1. The results permit the conclusion that, for estimation of E, it suffices to use only one DSC-trace taken at arbitrarily chosen parameters. The error is below 10%. However, some precautions should be taken:

– independently of the shape of the peak, at least four points are needed ($n \geq 4$);

– temperature range ΔT (about 3–10 deg) should correspond to about the half-height of the peak (Fig. 2);

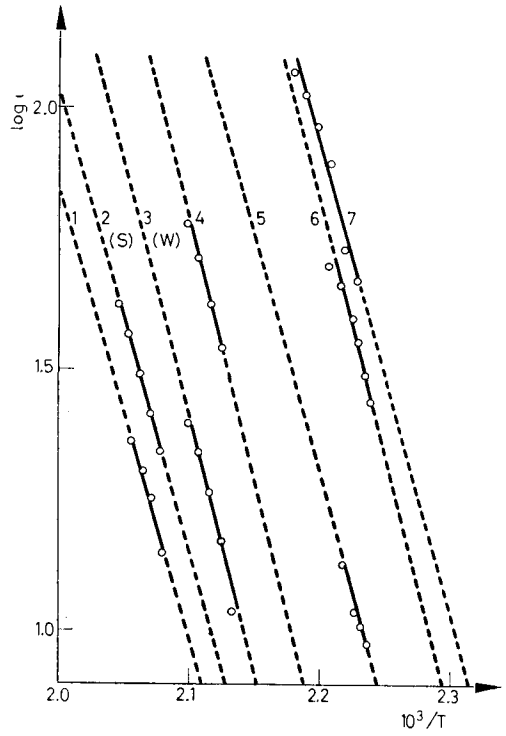

Fig. 1. Plots for determination of activation energy according to Piloyan's method: $E = 2.303\ R\ (\log l_1 - \log l_2)/(1/T_2 - 1/T_1)$. Full description of lines in Table 1

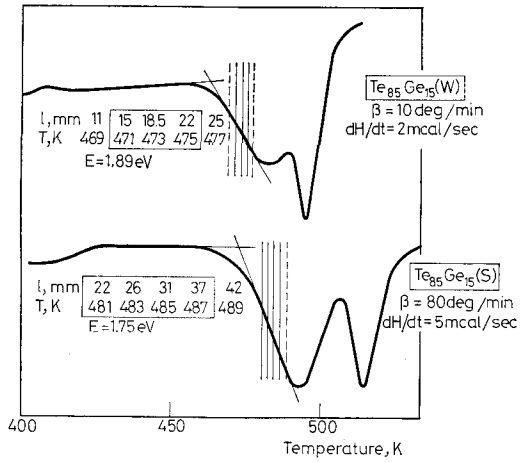

Fig. 2. Examples of selecting data from DSC-traces (Apparatus: Perkin-Elmer DSC-2). Broken lines represent the least correct points of the respective lines in Fig. 1. Straight lines in Fig. 1, corresponding to the two traces in Fig. 2, are denoted as 2(S) and 3(W), respectively

Table 1

Example of application of Piloyan's method for determination of activation energy of glass-to-crystal transition in eutectic Te—Ge glass formed by cooling from the melt

Results of E determination			Parameters of DSC experiments			Data read from DSC-traces necessary for applying Piloyan's method				
Line in Fig. 1	E, eV	Error, %	Scan rate deg/min	Sensitivity mcal/sec	Mass of sample, mg	Number of points	l, mm		T, K	
							l_1	l_n	T_1	T_n
1	1.68	8.69	20	5	10	4	14	23	481	487
2	1.75	4.89	80	5	2	5	22	42	481	489
3	1.89	2.72	10	2	10	5	11	25	469	477
4	1.97	7.06	40	5	6	4	35	60	471	477
5	1.79	2.72	2.5	1	5	4	8	11	446	449
6	1.80	2.17	2.5	1	20	6	23	46.5	445	451
7	1.73	5.98	5	1	20	6	47	118	449	459

Note: The value of E determined by the Kissinger method amounts to 1.84 eV (standard deviation 0.149 [3]). Against this true value the errors (%) of each determination were calculated. The mean value of E obtained by Piloyan's method is 1.80 eV.

– the temperature axis should be extended by increasing the chart speed (for example 40 mm/min for a scanning rate of 20 deg/min);

– points representing the beginning of the transition ($\alpha \leq 0.1$) should be avoided (Fig. 2).

On the other hand, the results are not affected by the following factors:

– mass of sample, within the range 2–20 mg;

– the absolute height of the peak, within the l range of the order of 10–100 mm (Table 1);

– heating rate within the range 2.5–80 deg/min.

Since Piloyan's method allows us to estimate the activation energy of a non-completed transition ($\alpha < 1$), it offers a very convenient and rapid way of studying changes in the activation energy E of the glass-to-crystal transition caused by partial crystallization of the glass (Fig. 3). A glassy sample heated below the temperature of the maximum transition range, cooled and re-heated, shows another E than during the first heating. This tendency observed in some ternary Te-rich glasses is discussed in a separate publication [5].

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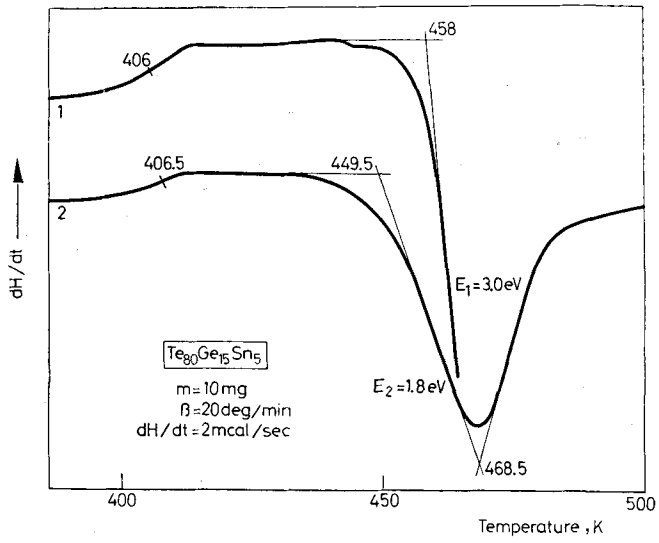

Fig. 3. Example of DSC-traces used for determination of changes in E, caused by partial crystallization. The slope of the left branch of the peak is a measure of activation energy E

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