

**THERMODYNAMIC AND THERMOKINETIC CHARACTERIZATION  
OF VITREOUS EUTECTIC GERMANIUM-TELLURIUM ALLOY  
BY DIFFERENTIAL SCANNING CALORIMETRY**

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For germanium-tellurium binary glass of eutectic composition heat capacities have been measured using differential scanning calorimetry. From these values enthalpy, entropy and corresponding configurational terms have been deduced, which agree closely with the "hole-theory". Below the glass transition temperature, differences have been observed for the thermodynamic characteristics of vitreous and crystalline forms.

For closely-related glasses kinetic parameters are more suitable for characterization than the above thermodynamic parameters. For germanium-tellurium alloys with small amounts of gold added, kinetics of devitrification have been expressed in terms of the crystallinity ratio. Values of Kgl parameters of glass-formation ability are also given ( $K_{gl} = 0.478$  for the eutectic composition alloy without gold).

Semiconducting glassy materials are studied mostly via their mechanical, optical and electronic properties, but as these properties are often dependent upon the preparation mode and the previous thermal history of such materials, it is frequently difficult to obtain reproducible characteristics. Exhaustive characterization thus requires the use of thermal methods, too; and in this field differential scanning calorimetry (DSC) is a very useful tool for establishing thermodynamic and thermokinetic characteristics [1, 2]. Before the application of thermal methods to glassy samples, a novel treatment of the curves obtained by DSC is proposed for heat capacity determination, from which many other thermodynamic parameters can be deduced.

To illustrate these points, binary germanium-tellurium eutectic alloy, interesting for its opto-electronic properties and its ability to form vitreous alloys, was chosen [3]. For the devitrification characteristics, the same material with small amounts of gold added was used. The structural stabilities of these alloys are interesting because of the well-known critical diffusion problems which commonly appear at Ge/Te/Au connections.

### **Materials and methods**

All experiments were carried out using a Perkin-Elmers DSC 1 B differential scanning calorimeter, which was calibrated against standards of known melting points and known heat capacity samples (sapphire discs). Experiments were

conducted with samples encapsulated in sealed aluminium pans, in the size range 5 to 20 mg.

Bulk vitreous germanium-tellurium alloys were obtained by melting powder of germanium and tellurium, in the required composition, in a quartz vessel under vacuum, followed by air quenching.

Compositions of samples were checked by atomic absorption spectrometry on tellurium using a Perkin-Elmer spectrometer model 360 fitted with a tellurium intensitron hollow cathode lamp. A mixture of hydrofluoric and concentrated nitric acids was used to dissolve samples in a teflon beaker. For alloys near the eutectic composition, results of analysis, which agree closely with the composition as calculated from the weight of the mixture of pure species, indicate that the bulk ingot is homogeneous. In the case of samples close to the eutectic composition, phase separation occurs, and it becomes very difficult to achieve homogeneous vitrification throughout the sample. All the vitreous amorphous germanium-tellurium alloy compositions studied were very close to the atomic eutectic composition  $\text{Ge}_{1.8}\text{T}_{82}$ .

#### *Heat capacity determination by DSC*

In a small temperature range, heat capacities are relatively simple to obtain with DSC, using the classical "specific heat mode" first described by Wunderlich [4] and recently by O'Neill [5]. Results so obtained can, moreover, be improved by using the methods developed by Richardson [6], Vucelic [7] or Flynn [8]. However, in a large temperature range this method implies some restrictions in the matter of the alignment of the base lines before and after the heating period; these cannot easily be satisfied, and they restrict its field of application [5].

We recently proposed [9] a new graphical treatment of DSC curves which eliminates such restrictions. This method was developed in order to allow the obtaining of a large number of thermodynamic data in a short period of time.

As the detailed principle and checks used in this method have already been described, we need only summarize the proposed graphical treatment here.

Experiments started with the calorimeter temperature,  $T_1$ , constant, in order to define an isothermal base line (line *EA* in Fig. 1). By working the scanning at a linear heating rate ( $16$  or  $32 \text{ K min}^{-1}$ ) from  $T_1$  to  $T_2$ , a deflection was obtained which depends on the heat capacity difference between the two pans, but which could not be used owing to the difficulty encountered in defining a true base line from such curves. If we stop, simultaneously, the heating program and the scanning of the recorder, we obtain, when the thermal equilibrium is reached, point *B* of Fig. 2, which can be used, as we explain below, to define a pseudo base line that makes heat capacity determination possible.

If we consider the curves so obtained respectively for a sample (here a sapphire disc) and the blank (sample-pan empty) in the temperature range 310 to 570 K, we observe that the curves are bent and it can be shown, by stopping scanning (and recording) from time to time that the real corresponding base lines, from

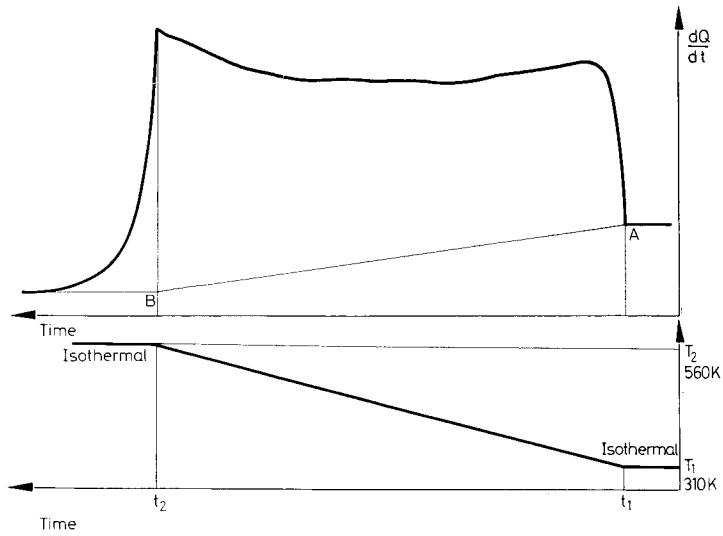


Fig. 1. DSC curve for heat capacity determination

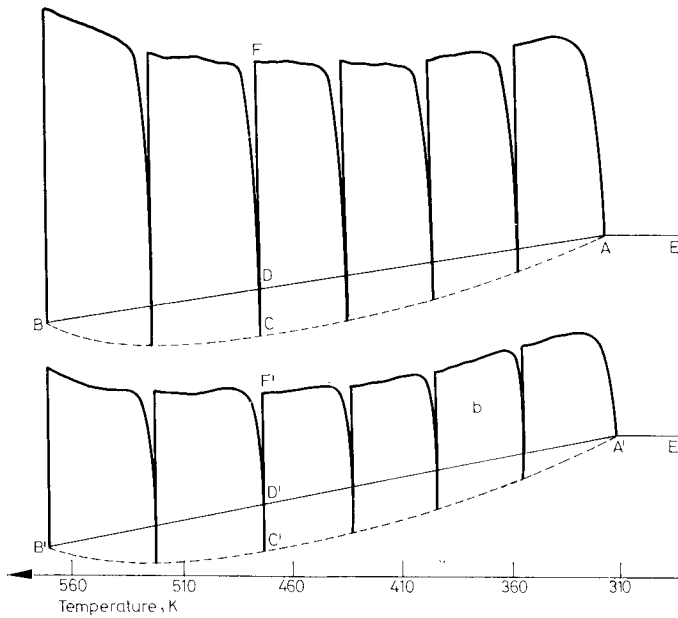


Fig. 2. Heat capacity determination over a large temperature range. a) Sample (sapphire); b) Blank (empty sample-pan); Slope 5.80. Scanning rate  $32\text{ K min}^{-1}$

which heat capacities can be calculated by the classical method ( $C_p = k(\overline{FC} - \overline{F'C})$ ) are also bent (dotted curves  $AB$  and  $A'B'$ ). In fact, such "real base line" plotting was not necessary for heat capacity measurements, because, by direct joining of points  $A$  and  $B$  (or  $A'$  and  $B'$ ) we obtained two straight lines which could be used directly as "pseudo base lines". It was proved experimentally that if the lengths of segments  $DC$  and  $D'C'$  of Fig. (2) are identical, we obtain:

$$C_p = k(\overline{FC} - \overline{F'C}) = k(\overline{FD} - \overline{F'D'}) \quad (1)$$

so that:

$$C_{p_s} = \frac{(FC - F'C)_s}{(FC - F'C)_r} \times \frac{m_r}{m_s} C_{p_r} \quad (2)$$

$$C_{p_s} = \frac{(FD - F'D')_s}{(FD - F'D')_r} \times \frac{m_r}{m_s} C_{p_r} \quad (3)$$

Subscript  $s$  or  $r$  refers, respectively, to sample and to reference;  $C_{p_r}$  is the heat capacity of the sample used as reference, here discs of synthetic sapphire;  $m_r$  and  $m_s$  are the weights of reference and sample. The above procedure was completely confirmed experimentally by extensive testing of aluminium and nitrate samples; results agree closely with those obtained by other static calorimetric methods. The accuracy was about 1% for a scanning temperature range of less than 30 degrees and 2% for a larger range of about 100 degrees. For example, with aluminium samples in the temperature range 350 to 650 K the mean variation coefficient was 0.9%.

### Thermodynamic characterization of amorphous eutectic germanium-tellurium alloy

Heat capacity measurement of eutectic germanium-tellurium alloys was performed using the thermal curve treatment described in the previous section. The crystalline form was obtained by heating of the amorphous form to above its devitrification temperature, followed by slow cooling. The values of these heat capacities are given in Fig. 3. Our results are consistent with those of de Neufville [10]; however, below the glass transition temperature, the heat capacities for the crystalline and amorphous forms are not exactly the same, these two structures having vibrational modes that are slightly different.

With temperatures above 480 K, after a time the sample was partly crystallized. At such temperatures the samples are mixtures of crystals and undercooled liquid. At a higher temperature (600 K), reaction may occur between sample and aluminium sample-pan.

For thermodynamic characterization of vitreous samples with no change of their properties, measurement of heat capacity must be carried out over a limited temperature range. Although differential scanning calorimetry over a large temper-

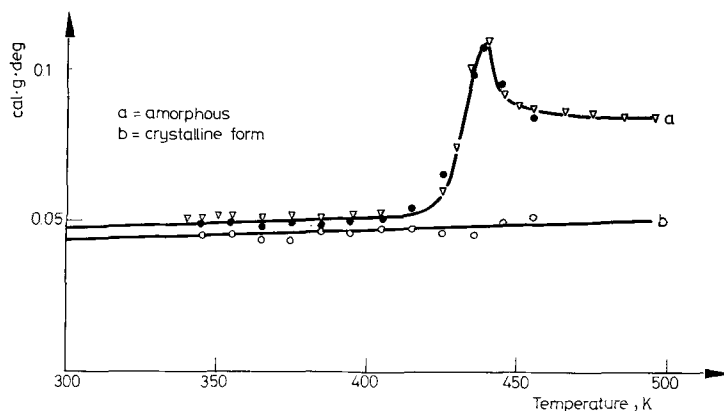


Fig. 3. Heat capacity determination for eutectic germanium-tellurium alloy. a) Vitreous sample; b) Crystalline sample

ature range can yield further significant information (such as enthalpy and entropy variation, transition temperature), it must be remembered that this test can be a destructive one, causing crystallization, phase separation, etc.

Specific enthalpy and entropy values for such materials can easily be deduced from specific heat capacity determination (Figs 3 and 4).

For enthalpy,

$$H_T = H_0 + \int_{T_0}^T C_p dT \quad (4)$$

where the reference value  $H_0$  was arbitrarily chosen equal to zero at  $T_0 = 298$  K. Moreover, for a small temperature range  $C_p$  can be assumed to be constant from  $T_0$  to  $T$ . Similarly, for entropy we have

$$\{S_T = S_0 + \int_{T_0}^T \frac{C_p}{T} dT \quad (5)$$

Entropy values  $S_0$  for crystalline eutectic germanium-tellurium alloy at  $T_0$  can be calculated from the entropy values of pure tellurium and the alloy of composition GeTe

$$\{S_{\text{Te}}^{\circ} (298 \text{ K}) = 11.88 \text{ cal (atg deg)}^{-1}$$

$$S_{\text{GeTe}}^{\circ} (298 \text{ K}) = 11 \text{ cal (atg deg)}^{-1}$$

$$S_0 = S_{\text{Ge}_{18}\text{Te}_{22}}^{\circ} (298 \text{ K}) = 11.58 \text{ cal (atg deg)}^{-1} = 0.98 \text{ cal} \cdot \text{g}^{-1} \text{deg}^{-1}$$

For each temperature  $T$  the difference of entropy between the crystalline and vitreous forms represents the configurational entropy  $\Delta S_0$ . A theoretical calculation

of such an entropy was possible using the Gutzow [11] model. This model, based upon the hole theory of liquids, gives the expression

$$\frac{\Delta S_c}{\Delta S_m} T = \begin{cases} \frac{a_0 T}{T_m} + 1 - a_0 & \text{for } T_0 \leq T \leq T_m \\ 0 & \text{for } 0 \leq T \leq T_0 \end{cases} \quad (6)$$

where  $\Delta S_m$  is the entropy of melting at  $T_m$  and  $T_0 = \left(1 - \frac{1}{a_0}\right) T_m$  is the temperature below which it can be sufficiently assumed confidently that the free relative volume of the liquid is nil. From this equation, at the glass transition temperature  $T_g$ ,  $a_0$  can be determined directly by the expression:

$$a_0 = \left( \frac{1}{1 - \frac{T_g}{T_m}} \right) \left( 1 - \frac{\Delta S_g}{\Delta S_m} \right) \quad (7)$$

For eutectic germanium-tellurium alloy the empirical rule between the absolute temperature of melting and  $T_g$ , established by Kauzmann [12]:

$\frac{T_g}{T_m} \approx \frac{2}{3} = 0.667$  holds very well, as we obtained experimentally a value of  $\frac{T_g}{T_m}$  equal to 0.64:

$$\frac{T_g}{T_m} = \frac{421}{662} = 0.64$$

Therefore, assuming that  $\frac{\Delta S_g}{\Delta S_m} = \frac{1}{3}$ , as is the case for many vitreous substances,

we have  $a_0 = 1.85$

and  $T_0 = 0.46 T_m = 304 \text{ K}$

An experimental value of  $T_0 = 300 \text{ K}$  can be deduced graphically from the temperature-dependence of  $H_T$  (Fig. 4).

This agreement between the calculated and the experimental values of  $T_0$  shows that the "hole theory" can be used for this vitreous chalcogenide alloy. For such substances  $T_0$  is an interesting characteristic parameter. Heat capacity measurement and related parameters are useful for thermodynamic characterization of amorphous materials, but they give no information about devitrification characteristics. This structural transformation, which is of great importance in switching and memory devices, will be studied, via kinetic studies of devitrification (crystallization) of eutectic germanium-tellurium glass with a small amount of gold added.

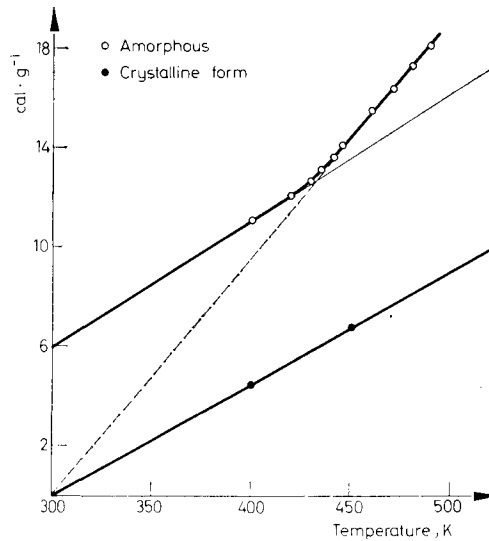


Fig. 4. Enthalpy variation for eutectic germanium-tellurium alloy

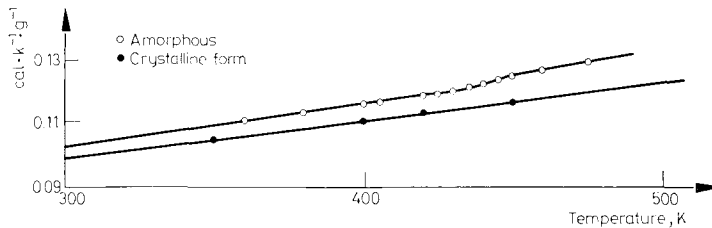


Fig. 5. Entropy variation for eutectic germanium-tellurium alloy

### Crystallinity ratio – Reference states

At every moment the state of a glassy material can be clearly defined by its crystallinity ratio  $X$ :

$$X = \frac{M_a - M_s}{M_a - M_c} \quad (8)$$

$M_i$  being a characteristic parameter, such as microhardness, density, heat capacity for the studied sample,  $M_s$ , the same sample entirely amorphous,  $M_a$ , and entirely crystalline,  $M_c$ . Obtaining  $M_c$  is very easy, but direct obtaining of  $M_a$  is very difficult. For determination of  $M_a$ , two methods can be considered:

a) One is based upon the line sharpness of the X-ray diffraction pattern. This is only a qualitative method.

b) The other is based upon the evolution of a characteristic value, directly connected to the crystallinity ratio, with the cooling rate of the sample. If this characteristic value becomes constant beyond a given cooling rate (critical cooling rate), it is reasonable to think that for a faster cooling rate the sample will be entirely vitreous. This method will be valid only if no phase separation occurs. Such a phase separation can be detected in the DSC curve by a splitting of the melting peak.

If we choose  $M_i$  as the characteristic, the devitrification enthalpy  $\Delta H_c$  and (8) become:

$$X = \frac{(\Delta H_c)_a - (\Delta H_c)_s}{(\Delta H_c)_a}$$

$(\Delta H_c)_a$  obviously being nil.

Figure 6 shows the variations of the devitrification enthalpy  $(\Delta H_c)_s$  with the cooling rate for the eutectic germanium-tellurium alloy and the same alloy with 0.05% of gold added, respectively. For such a sample the critical cooling rate is about  $30^\circ \text{ min}^{-1}$  for the eutectic alloy, and  $60^\circ \text{ min}^{-1}$  for the alloy with 0.05% of gold added. For greater amounts of gold added, phase separations occur for such alloys, as appears in the DSC curves (Fig. 7). As vitrification of such samples requires a cooling rate greater than  $60^\circ \text{ min}^{-1}$ , the DSC 1 B is not suitable for such measurements.

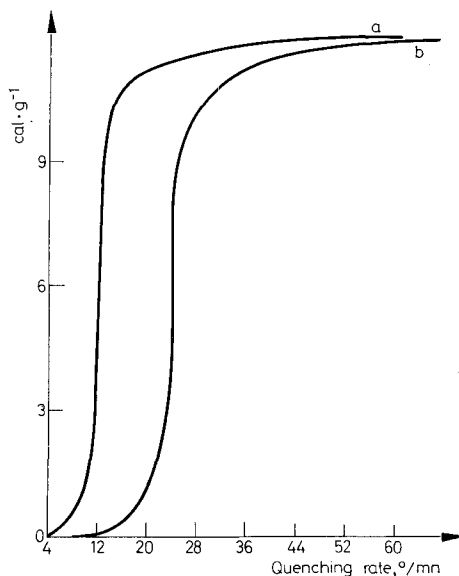


Fig. 6. Devitrification heat  $\Delta H_c$  for various quenching rates. a)  $\text{Ge}_{18}\text{Te}_{82}$ ; b)  $\text{Ge}_{18}\text{Te}_{82} + 0.05\%$  gold



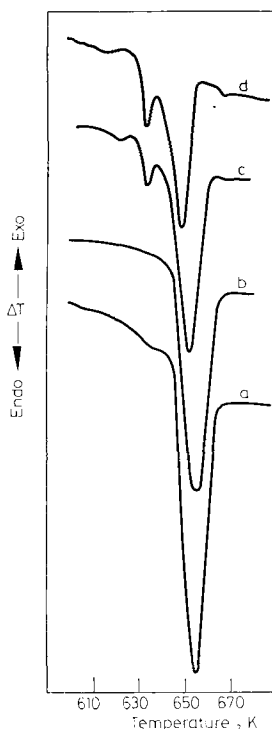


Fig. 7. Melting enthalpy for germanium-tellurium alloy with small amount of gold added. a)  $\text{Ge}_{18}\text{Te}_{82}$ ; b)  $\text{Ge}_{18}\text{Te}_{82} + 0.05\%$  gold; c)  $\text{Ge}_{18}\text{Te}_{82} + 0.5\%$  gold; d)  $\text{Ge}_{18}\text{Te}_{82} + 1\%$  gold

Curves like those of Fig. 6 can be useful for kinetic characterization of amorphous materials, but determination of  $(\Delta H_0)_a$  is not always possible. In such a case we propose a useful relative method of kinetic characterization. For each sample the heat given off during crystallization is measured on the curve continuously and then compared with the heat given off when the sample is entirely devitrified,

$(\Delta H_c)_{\max}$ . Plotting  $\frac{\Delta H_c}{\Delta H_{c\max}}$ , as a function of time gives a useful picture for a representation of the kinetics of devitrification at a given temperature.

The corresponding experimental work mode is extremely simple to carry out by keeping the sample at a given temperature below the crystallization temperature, where the devitrification proceeds very slowly, and by successive graphical integration of  $\Delta H_c$ .

Our results are summarized in Fig. 8. Addition of gold shows clearly a decrease in incubation time and a quicker devitrification process. From such curves the kinetics are of the order of 1. For a crystallinity ratio of 0.5, the rate constants  $k$  are given in Table 1. For alloys with 1% of gold added, values of  $k$  are too high and cannot be measured with the DSC 1 B.

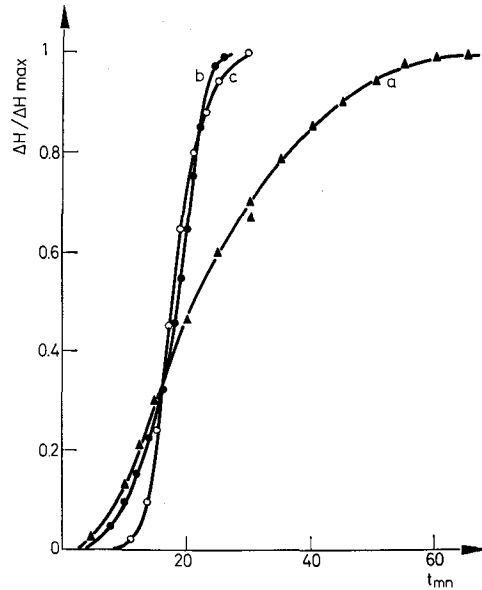


Fig. 8. Devitrification kinetics of: a)  $\text{Ge}_{18}\text{Te}_{82}$  at 470 K; b)  $\text{Ge}_{18}\text{Te}_{82}$  + 0.05% gold at 470 K; c)  $\text{Ge}_{18}\text{Te}_{82}$  + 0.5% gold at 455 K

Table 1

Values of rate constant  $k$  for devitrification of  $\text{Ge}_{18}\text{Te}_{82}$  alloys with added gold

Amount of gold added in atomic per cent	$T$ , K	$\log k$ in $\text{s}^{-1}$
0	470	3.52
0.05	470	3.56
0.5	455	3.60

For the alloy with 0.5% of gold added, determination of  $k$  is not possible at 470 K with the DSC 1 B, devitrification occurring too fast at such a temperature.

### Kgl parameter for glass-formation ability

As previously shown, using the DSC 1 B it is impossible to get a heating or cooling rate exceeding  $64 \text{ K min}^{-1}$ . However, for materials which exhibit too fast a rate of transformation it is possible to use a glass-formation ability constant  $K_{gl}$  which does not involve any kinetic consideration.

This parameter  $K_{gl} = \frac{T_c - T_g}{T_m - T_g}$ , introduced by Hruby [13], although scanning rate-dependent, gives a relative measure of vitrification facility. Values of transition temperatures for eutectic germanium-tellurium alloy with small amounts of gold added are given by the curves shown in Fig. 9.

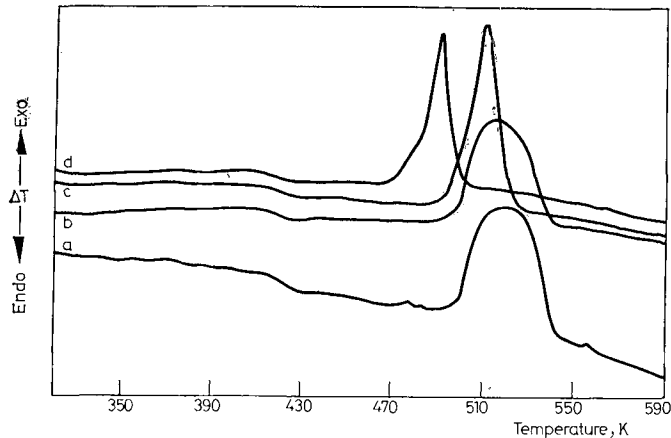


Fig. 9. DSC curves showing devitrification for germanium-tellurium alloys. a)  $\text{Ge}_{18}\text{Te}_{82}$ ; b)  $\text{Ge}_{18}\text{Te}_{82} + 0.05\%$  gold; c)  $\text{Ge}_{18}\text{Te}_{82} + 0.5\%$  gold; d)  $\text{Ge}_{18}\text{Te}_{82} + 1\%$  gold

The values of  $K_{gl}$  given in Table 2 clearly show the influence of gold, especially with concentrations exceeding 0.5 atomic per cent, on the ability of germanium-tellurium alloy to crystallize. Such gold concentrations can easily be obtained accidentally by diffusion of gold, with GeTe/Au soldering, for a working temperature around  $100^\circ$ .

Table 2

Values of parameter  $K_{gl}$  for glass-formation ability

Amount of gold added in %	Glass transition temperature $T_g$ , K	Devitrification temperature $T_c$ , K	Melting point $T_m$ , K	$T_g/T_f$	$K_{gl}$
0	421	499	662	0.636	0.478
0.05	421	498	661	0.637	0.474
0.5	420	495	657	0.640	0.463
1	419	475	653	0.641	0.314

According to Lasocka [14] the devitrification onset temperature  $T_0$  and the glass transition temperature are to a considerable degree dependent upon the scanning rate; consequently, these values of Kgl are significant only for a given scanning rate, here  $32 \text{ K min}^{-1}$ . The Kgl value for the glass of composition  $\text{Ge}_{18}\text{Te}_{82}$  is consistent with the value obtained by Lasocka [14] for the same scanning rate on the same material (Kgl = 0.41), the observed difference probably resulting from a slight difference in the material composition ( $\text{Ge}_{15}\text{Te}_{85}$  instead of  $\text{Ge}_{18}\text{Te}_{82}$ ). For glasses obtained by splat-quenching, this author found a Kgl value of 0.28. This illustrates the absolute necessity, when comparing two glassy samples, to detail carefully all the exact conditions of preparation and treatment of samples.

In conclusion, for thermokinetic characterization of glassy samples, two classes of parameters are useful to compare the abilities of vitreous material samples to crystallize:

a) Parameters, such as critical cooling rate and incubation time, which involve isothermal measurement during phase transformation.

b) Parameters, such as Kgl, which involve phase transformation temperatures of the glasses, obtained from temperature scanning thermograms at a definite scanning rate.

These two kinds of parameter appear to be useful for thermokinetic characterization of glasses.

### Conclusion

For thermodynamic characterization of vitreous materials, heat capacity, which is directly connected with the structure and configuration of a glass, is a very important parameter, from which the main thermodynamic functions such as enthalpy and entropy can be deduced.

The treatment of the DSC curves that we have proposed, though very simple and swift, seems to be very convenient for such determinations, especially for small samples like those used for glassy material study (10 mg). On the other hand, heat capacity is not very sensitive to impurities and moreover appears not to be very suitable for crystallinity ratio determination from which thermokinetic parameters of glassy materials can be estimated. For such determination, devitrification enthalpy appears to be a much more valuable criterion, as shown by our measurements.

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### References

1. M. LASOCKA and H. MATYJA, *J. non Cryst. Solids*, 14 (1974) 41.
2. J. A. SAVAGE, *J. non Cryst. Solids*, 11 (1972) 121.
3. J. CORNET, *Ann. Chim.*, 10 (1975) 239.
4. B. WUNDERLICH, *J. Phys. Chem.*, 69 (1965) 2078.
5. M. J. O'NEILL, *An. Chem.*, 38 (1966) 1331.
6. M. J. RICHARDSON and P. BURRINGTON, *J. Thermal Anal.*, 6 (1974) 345.
7. D. VUCELIC, V. VUCELIC and N. JURANIC, *J. Thermal Anal.*, 5 (1973) 459.
8. J. H. FLYNN, *Thermochim. Acta*, 8 (1974) 69.
9. P. CLECHET, C. MARTELET and NGUYEN DINH CAU, *Symposium on Thermal Analysis, Plymouth, Sept. 77 Analysis*, 6 (1978) 220.
10. J. P. DE NEUFVILLE, *J. non Cryst. Solids*, 8 (1972) 85.
11. I. GUTZOW, *Amorphous materials*, J. Wiley (1972) p. 159.
12. W. KAUFMANN, *Chem. Rev.*, 43 (1948) 213.
13. A. HRUBY, *Czech. J. Phys., Ser. B*, 22 (1972) 1187.
14. M. LASOCKA, *J. Mat. Sci. Lett.*, 11 (1976) 1770.

RÉSUMÉ — Les capacités calorifiques de verres formés à partir d'alliages binaires germanium-tellure de composition eutectique ont été déterminées par analyse calorimétrique différentielle à compensation de puissance (D. S. C.) de même que les valeurs d'enthalpie, d'entropie et des termes configurationnels correspondants. Ces résultats sont en accord avec la théorie de Gutzow. En dessous de la température de transition vitreuse des différences ont été observées entre les caractéristiques thermodynamiques de la forme vitreuse et celles de la forme cristalline.

Pour de tels verres les paramètres cinétiques sont mieux adaptés que les grandeurs thermodynamiques précédentes pour les problèmes de caractérisation. Dans le cas d'alliages germanium-tellure additionnés de faible quantité d'or la cinétique de dévitrification a été exprimée en termes de taux de cristallinité. Les valeurs des paramètres Kgl caractérisant l'aptitude à la vitrification ont été déterminées ( $Kgl = 0.478$  pour l'alliage germanium-tellure de composition eutectique).

ZUSAMMENFASSUNG — Die Wärmekapazitäten von binären Germanium-Tellur Gläsern eutektischer Zusammensetzung wurden durch Differential-Abtastkalorimetrie gemessen. Aus diesen Ergebnissen wurden Enthalpie, Entropie und die entsprechenden Konfigurationsparameter abgeleitet, welche in guter Übereinstimmung mit der »Loch-Theorie« sind. Unterhalb der Glas-Übergangstemperatur wurden Unterschiede der thermodynamischen Charakteristika zwischen dem Glas- und der kristallinen Form festgestellt.

Zur Charakterisierung nahe verwandter Glas-Arten eignen sich kinetische Parameter besser als die obigen thermodynamischen Parameter. Für Germanium-Tellur-Legierungen mit geringen Goldanteilen wurde die Entglasungskinetik durch das Kristallinitätsverhältnis ausgedrückt. Die Werte der Kgl Parameter der Glasbildungsfähigkeit werden ebenfalls angegeben ( $Kgl = 0.478$  für die eutektische Zusammensetzung der Legierung ohne Gold).

Резюме — Используя дифференциальную сканирующую calorimetрию, были измерены теплоемкости германий-теллур бинарных стекол эвтектического состава. Из этих значений были определены энтальпия, энтропия и конфигурационные термы, которые хорошо согласуются с «теорией дырок». Ниже температуры остеклования наблюдали различия между термодинамическими характеристиками стеклообразной и кристаллической форм. Для характеристики родственных стекол кинетические параметры являются более приемлемыми, чем термодинамические. Для германий-теллурических сплавов с небольшими добавками золота, кинетика расстекловывания может быть выражена на основе соотношения кристалличности. Приведены параметры Kgl, характеризующие способность к стеклообразованию ( $Kgl = 0.478$  для эвтектического состава сплава без золота).