Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 393–404

NON-ISOTHERMAL CRYSTALLIZATION KINETICS OF V_2O_5–MoO_3–Bi_2O_3 GLASSES[*]

R. Iordanova[1], *E. Lefterova*[2], *I. Uzunov*[1], *Y. Dimitriev*[3**] *and D. Klissurski*[1]

[1]Insitute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, blvd. 'Acad. G. Bonchev' 11, Sofia 1113, Bulgaria
[2]Central Laboratory for Electrochemical Power Sources – BAS, Sofia 1113, Bulgaria
[3]University of Chemical Technology and Metallurgy, Sofia 1756, Bulgaria

(Received May 5, 2001; in revised form May 22, 2002)

Abstract

Characteristic temperatures, such as T_g (glass transition), T_x (crystallization temperature) and T_l (liquidus temperature) of glasses from the V_2O_5–MoO_3–Bi_2O_3 system were determined by means of differential thermal analysis (DTA). The higher content of MoO_3 improved the thermal stability of the glasses as well as the glass forming ability. The non-isothermal crystallization was investigated and following energies of the crystal growth were obtained: glass #1 ($80V_2O_5 \cdot 20Bi_2O_3$) E_G=280 kJ mol^{-1}, glass #2 ($40V_2O_5 \cdot 30MoO_3 \cdot 30Bi_2O_3$) E_G=422 kJ mol^{-1} and glass #3 ($80MoO_3 \cdot 10V_2O_5 \cdot 10Bi_2O_3$) E_G=305 kJ mol^{-1}. The crystallization mechanism of glass #1 (n=3) is bulk, of glass #3 (n=1) is surface. Bulk and surface crystallization was supposed in glass #2. The presence of high content of a vanadium oxide acts as a nucleation agent and facilitates bulk crystallization.

Keywords: glass forming ability, non-conventional glasses, non-isothermal crystallization kinetic, thermal stability

Introduction

It is well known that V_2O_5, MoO_3 and Bi_2O_3 oxides belong to non-conventional network formers. Due to their high crystallization tendency it is difficult to vitrify them individually by standard methods of cooling. However, V_2O_5 and MoO_3 have been claimed to form glasses by the use of special experimental technique [1]. Many binary and multicomponent non-conventional glasses with a large amount of V_2O_5, MoO_3 or Bi_2O_3 can be obtained by introducing modifiers or other glass formers [2–6]. The glass forming regions in the V_2O_5–MoO_3–Bi_2O_3 [7] and Fe_2O_3–MoO_3–Bi_2O_3 [8] systems have been established and the structure of these glasses has been investi-

---

[*] Paper was presented at "Solid State Chemistry 2000' in Prague

[**] Author for correspondence: E-mail: yanko@uctm.edu

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

gated. It has been proved that VO_4, MoO_4 and BiO_6 groups participate in the formation of the glass network.

The present study is an extension of these investigations. It is aimed at clarifying, by DTA, the competing effect of the components for the thermal stability and crystallization tendency of the glasses under non-isothermal conditions. Three glass compositions have been selected. V_2O_5 prevails in the first one, the three components are approximately in equal amounts, in the second composition, and MoO_3, prevails in the last one.

Theoretical basis

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are very suitable for determination of the kinetic parameters of glass crystallization under non-isothermal conditions [9–11]. At isothermal conditions the crystallization is described by the well-known Johanson–Mehl–Avrami–Kolmogorow–Erofeev (JMAKE) equation:

$$-\ln(1-\alpha) = (kt)^{\mathrm{n}} \tag{1}$$

where α is the volume fraction crystallized after time t, k is the rate constant for the whole transformation process, the dimensionless quantity n is the Avrami exponent, which depends on the crystallization mechanism and $n=\beta+m$ [9, 10]. The dimensionality of crystal growth is described by m [13], where $m=3$ for three- dimensional growth, $m=2$ for two-dimensional growth, $m=1$ for one-dimensional growth or surface crystallization (Table 1). The value of β is related to the nucleation process: $\beta=0$ for fixed number of nuclei and $\beta=1$ when nucleation rate is constant.

Table 1 The values *n* and *m* for various crystallization mechanisms [13]

Mechanism	*n*	*m*
Bulk crystallization		
Three-dimensional growth	4	3
Two-dimensional growth	3	2
One-dimensional growth	2	1
Surface crystallization	1	1

The temperature dependence of k in a small temperature range can be presented by an Arrhenius type equation:

$$k=A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where E is the effective (apparent) activation energy of the crystallization process, and A is a frequency factor. The overall effective activation energy E is expressed by [10]:

$$E\approx\frac{\beta E_N+mE_G}{n} \tag{3}$$

where E_N and E_G are the effective activation energies for nucleation and crystal growth, respectively. If E_N is negligible over the temperature range investigated, then

$$E\approx\frac{m}{n}E_G \tag{4}$$

When the sample is heated with a constant rate b, the temperature in a certain moment t is given by:

$$T=T_o+bt \tag{5}$$

where T_o is the initial temperature. In this case, k is a function of time, and the mechanism of the crystallization process is given by the equation [9–11]:

$$[-\ln(1-\alpha)]^{1/n}=g(\alpha)=\int_{t_0}^{t}kT(t)\mathrm{d}t=\frac{A}{b}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{6}$$

After solving this exponential integral, using the Doyle approximation [12] the following equation is obtained [9]:

$$\ln[-\ln(1-\alpha)]=-n\ln(b)-1.052\frac{nE}{RT}+\text{const.} \tag{7}$$

In the case of a large number of existing nuclei in the glass (β=0), when it is possible to neglect the nucleation rate, $n=m$. Then $E=E_G$ and Eq. (7) can be used in this form to determine the activation energy of crystal growth. When the nucleation proceeds with constant rate (β=1), $n=m+1$ and taking into account Eq. 4 (E_N is negligible), the Eq. (7) can be written as:

$$\ln[-\ln(1-\alpha)]=-n\ln b-1.052\frac{mE_G}{RT}+\text{const.} \tag{8}$$

which is the well-known Matusita–Sakka relationship [13, 14]. It allows simple determination of E_G and n:

$$\left.\frac{\mathrm{d}\ln[-\ln(1-\alpha)]}{\mathrm{d}(\ln b)}\right|_T=-n \quad \text{(Ozawa method [15, 16]),} \tag{9}$$

$$\left.\frac{\mathrm{d}(\ln b)]}{\mathrm{d}(1/T)}\right|_\alpha=-1.052\frac{m}{n}\frac{E_G}{R} \quad \text{(modified Ozawa–Chen method [16, 17]),} \tag{10}$$

$$\left.\frac{\mathrm{d}\ln[-\ln(1-\alpha)]}{\mathrm{d}(1/T)}\right|_b=-1.052\frac{mE_G}{R} \quad \text{(Šatava method [18]).} \tag{11}$$

Another opportunities for E_G and n estimation are the equations:

$$\ln\Delta y \cong -\frac{mE_{\mathrm{G}}}{RT} + \mathrm{const.} \quad \text{(Piloyan method [19]),} \tag{12}$$

$$\ln b = -\frac{m}{n}\frac{E_{\mathrm{G}}}{RT_{\mathrm{p}}} + \mathrm{const.} \quad \text{(modified Marotta–Buri method [9, 20, 21]),} \tag{13}$$

$$\ln\left(\frac{b^{\mathrm{n}}}{T_{\mathrm{p}}^{2}}\right) = -1.052m\frac{E_{\mathrm{G}}}{RT_{\mathrm{p}}} + \mathrm{const.} \quad \text{(modified Kissinger method [14, 22]),} \tag{14}$$

where Δy is the deflection from the base line and T_{p} is the peak temperature of devitrification.

These are linear dependencies from which slopes E_{G} and n can be easily determined. The values of n can be calculated by the Ozawa method from the Eq. (9) or by comparing mE_{G} (Eqs (11), (12)) with $(m/n)E_{\mathrm{G}}$ (Eqs (10) and (13)).

By means of DTA and DSC it is also possible to determine the glass characteristic temperatures, such as glass transition temperature T_{g}, crystallization temperature T_{x}, melting temperature T_{m} (and/or liquidus temperature T_{l}). These thermal parameters are suitable for a qualitative estimation of the thermal stability of glasses and the glass forming ability of the compositions.

By Kauzmann, the relationship is proposed for typical single component glass forming melts, at normal cooling rate [23]:

$$T_{\mathrm{rg}} = \frac{T_{\mathrm{g}}}{T_{\mathrm{m}}} \approx \frac{2}{3} = 0.67 \tag{15}$$

This rule was confirmed for a number of compositions, and generalized for multicomponent systems by Sakka and Mackenzie [24], replacing T_{m} with liquidus temperature (T_{l}). According to Turnbull [25], for metallic glasses T_{rg} should be considerably lower than 0.67, which later was confirmed by Donald and Davies [26]. Using the lattice-hole model, Gutzow [27–29] obtained a more common formula for glass forming systems:

$$T_{\mathrm{rg}} = \frac{T_{\mathrm{g}}}{T_{\mathrm{m}}} \approx \frac{1}{2} + F, \qquad (F = 0.1 \div 0.2) \tag{16}$$

James and Zanoto [30, 31] have established a relation between the type of crystallization and T_{rg}. In glasses with $T_{\mathrm{rg}}<0.58$, bulk crystallization occurs, while for values of $T_{\mathrm{rg}}>0.58$, surface crystallization is typical. This dependency was confirmed by Wakasugi *et al.* [32].

There are two other criteria based on temperature differences. One of them is the so-called Hruby coefficient [33]:

$$k_{\mathrm{gl}} = \frac{T_{\mathrm{x}} - T_{\mathrm{g}}}{T_{\mathrm{l}} - T_{\mathrm{x}}} \tag{17}$$

The bigger difference $\Delta T=T_x-T_g$ and the smaller temperature interval T_l-T_x make difficult the processes of crystallization, and hence facilitate glass formation. A second one [34] interprets the glass forming ability as the difference $\Delta T=T_x-T_g$ only.

Experimental

The compounds V_2O_5, MoO_3 and Bi_2O_3 were used as initial raw materials. After homogenization, the batches were melted in the temperature range of 800–1200°C. The glasses were obtained at high cooling rates, using roller technique (cooling rate of 10^4–10^5 K s^{-1}). The amorphous state of the samples was established by X-ray diffraction (Dron-3, CoK_α radiation). DTA measurements (Paulik–Paulik–Erdey derivatograph) were performed at different heating rates (2.5, 5 and 10 K min^{-1}).

Results

Table 2 shows the thermal characteristics of the investigated glasses as well as some of the glass forming ability criteria. According to the present DTA data, T_g varies between 240 and 270°C, while the temperature of crystallization lies in the range 275–325°C. The glass #1, with the highest V_2O_5 content possesses the lowest crystallization temperature. The DTA curve of the glass #3 shows two crystallization peaks as a result of the formation of two crystalline phases [7]. Both the Hrubi coefficient and ΔT increase with the MoO_3 content. T_{rg} for the sample #1 is 0.58, in the case of sample #2 is 0.66 and for the glass #3 this value is a bit smaller –0.63.

Table 2 Composition, glass transition temperature T_g, crystallization temperature T_x, liquidus temperature T_l, and glass forming ability parameters ΔT, T_{rg}, k_{gl}

No.	Composition	T_g/°C	T_x/°C	T_l/°C	T_{rg}	ΔT/°C	k_{gl}
#1	$80V_2O_5\cdot 20Bi_2O_3$	240	275	610	0.58	35	0.104
#2	$40V_2O_5\cdot 30MoO_3\cdot 30Bi_2O_3$	270	310	550	0.66	40	0.167
#3	$80MoO_3\cdot 10V_2O_5\cdot 10Bi_2O_3$	260	325 405	570	0.63	65	0.265

Figures 1–6 presents the plots from which the kinetic parameters of crystallization of the glasses are calculated using the methods mentioned above. Table 3 summarizes the values of the kinetic parameters of crystallization of the sample #2. The calculations of $E=(m/n)E_G$, are made using Ozawa–Chen method (Eq. (10)), (Fig. 1), at given value of α (0.3÷0.6), obtained at different heating rates (column 1). By applying the method of Šatava (Eq. (11)), (Fig. 2) is determined mE_G, and comparing E and mE_G, the value of Avrami exponent $n\approx 2$ is obtained. The value of E_G, is calculated accepting that nucleation rate is constant ($n=m+1$), (column 4). In the col-

Table 3 Kinetic parameters of crystallization of glass #2 ($40V_2O_5\cdot30MoO_3\cdot30Bi_2O_3$), calculated by different methods

$E=(m/n)E_G$/ kJ mol^{-1}	mE_G/ kJ mol^{-1}	n	E_G/ kJ mol^{-1}	$E=(m/n)E_G$/ kJ mol^{-1}	mE_G/ kJ mol^{-1}	n	E_G/ kJ mol^{-1}	n	mE_G/ kJ mol^{-1}	E_G/ kJ mol^{-1}
Eq. (10)	Eq. (11)			Eq. (13)	Eq. (12)			Eq. (9)	Eq. (14)	
	437±1		437	227±23	–	1.99	454	2.19±0.2	436±34	436
196±18 (α=0.3)		2.23	392	–	451±25	–	451	–	–	–
200±25 (α=0.4)		2.18	400	–	–	–	–	–	–	–
217±22 (α=0.5)		2.01	434	–	–	–	–	–	–	–
203±15 (α=0.6)		2.15	406	–	–	–	–	–	–	–

[*] The calculation of E_G was made using the nearest theoretical value of n, i.e. $n=2$ and $m=1$ (Table 1)

umns 5÷8 are presented the data for the same parameters calculated according to (Eqs (13) and (12)) (Figs 3, 4). The last data (columns 9÷11) are obtained using Ozawa method for determination of n and Eq. (14) for estimation of mE_G (Figs 5, 6). Analyses of the obtained data show that activation energy of crystal growth and geometrical factor n of glass #2 calculated by different methods are compatible. That is why in Table 4 are presented only the generalized results of the kinetic parameters of crystallization for all investigated glasses.

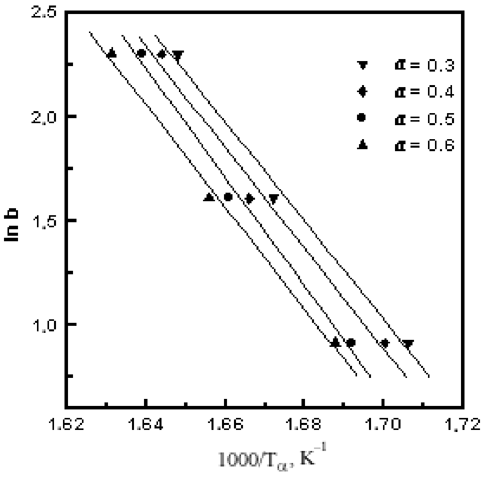

Fig. 1 Ozawa–Chen plot (ln$b$ *vs*. $1/T_\alpha$) for determination of $E=(m/n)E_G$ at different values of α for glass #2

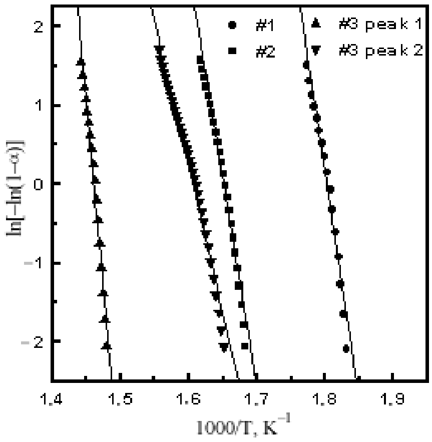

Fig. 2 Determination of mE_G according to the Šatava method by plotting ln[–ln(1–α)] *vs*. $1/T$ at a heating rate b=5 K min^{-1}

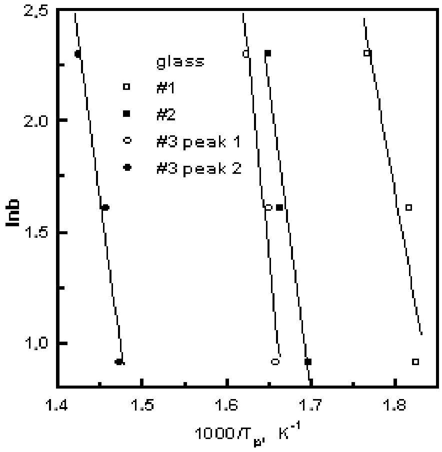

Fig. 3 ln$b$ *vs.* $1/T_p$ (Marrota–Buri method) for determination of $E=(m/n)E_G$

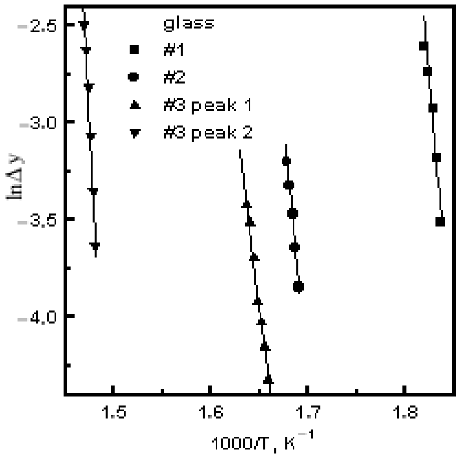

Fig. 4 lnΔy *vs.* $1/T$ (Piloyan method) for determination of mE_G at heating rate b=5 K min^{-1}

Table 4 Kinetic parameters of glasses from the V_2O_5–MoO_3–Bi_2O_3 system. The present parameters are average of the values obtained by different methods

No.	Composition	$E=(m/n)E_G$/ kJ mol^{-1}	E_G/ kJ mol^{-1}	n
#1	$80V_2O_5\cdot 20Bi_2O_3$	187±9	280±7	2.9±02
#2	$40V_2O_5\cdot 30MoO_3\cdot 30Bi_2O_3$	208±12	422±22	2.1±0.2
#3	$80MoO_3\cdot 10V_2O_5\cdot 10Bi_2O_3$	305±15	305±15	1.1±0.1
		243±8	324±11	3.9±0.2

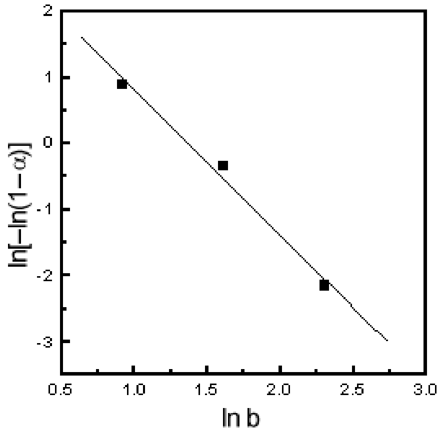

Fig. 5 Determination of *n* by plotting ln[–ln(1–α)] *vs.* ln*b* (Ozawa method) for glass #2 at a temperature of 330°C

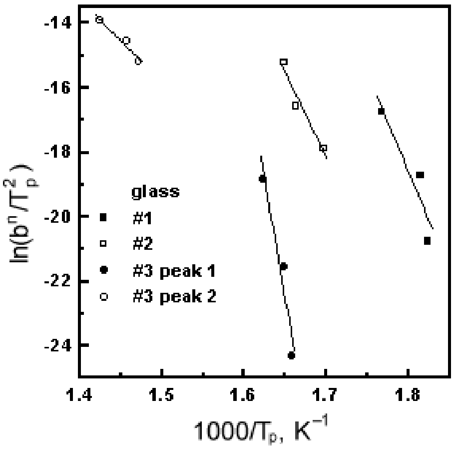

Fig. 6 Determination of mE_G according a modified Kissinger method by plotting $\ln(b^n/T_p^2)$ *vs.* $1/T_p$

Discussion

From the obtained data for the kinetic criteria ΔT, k_{gl} (Table 2) and the activation energies (Table 4) it is possible to make some conclusions for the competitive role of V_2O_5, MoO_3 and Bi_2O_3 as a conditional network formers. It can be seen (Table 2) that an increase in amount of MoO_3 leads to an increase in glass forming ability. The apparent activation energy have the highest value with glass #3 (Table 4). It is useful to compare the obtained activation energies with the data known for other glasses. For pure TeO_2 glass, E=184 kJ mol^{-1}. obtained by the Kissinger method has been reported [35]. For $2TeO_2 \cdot V_2O_5$ E_G=203 kJ mol^{-1} [36], and for $30Li_2O \cdot 70TeO_2$ E_G=429 kJ mol^{-1} [37] have been found from the equation of Matusita–Sakka. The activation energy values for Bi-base glasses, calculated by different methods, vary between 200 and 500 kJ mol^{-1} [38–44]. For alkali-silicate glasses these values are between 180–400 kJ mol^{-1} [13, 14, 20, 21, 45–47]. The data for CaO–P_2O_5 glasses [48, 49] are of the same order. The highest activation energy values ($E \approx 600 \div 800$ kJ mol^{-1}) are reported for $2CaO \cdot Al_2O_3 \cdot SiO_2$ glass [50]. The data obtained in our experiments tend to the lower values (Table 4) in comparison with the data of traditional glasses. This is in accordance with their lower glass forming ability. Of course it is necessary to be careful at such comparison of the data because the experimental details affect the mechanism of nucleation and crystal growth, even for glasses of the same composition [51]. A suggestion about the probable crystallization mechanism can be made from the values of n, m and T_{rg} presented in Tables 1, 2 and 4. Following this scheme, the crystallization of glass #1 is bulk, and the crystal growth is controlled by two-dimensional growth (n=3, T_{rg}=0.58). The crystallization mechanism for sample #2, corresponds to one-dimensional growth. On the other hand, T_{rg} for this glass is 0.66 and following James–Zanotto criteria, surface crystallization should occur. Hence, the possibility of simultaneous bulk and surface crystallization should be discussed. For glass #3, where T_{rg}=0.63 and n=1, surface crystallization should take place. The second exo-effect of this glass corresponds to the three dimensional crystal growth.

A more detailed discussion of the problem about the n values, depending on the crystallization mechanism is given in [52, 53]. However, direct microscopy observations on nucleation and crystal growth are needed for more precise interpretation.

Conclusions

The glass forming ability (thermal stability) was investigated by non-isothermal crystallization of model compositions of glasses from the V_2O_5–MoO_3–Bi_2O_3 system. Generally, all glasses crystallize easily at low temperatures ($T_x \leq 325^{\circ}C$). A higher MoO_3 content improves the thermal stability of the glasses and the glass forming ability. The presence of a high concentration of vanadium oxide acts as a nucleation agent and facilitates bulk crystallization.

* * *

Thanks are due to the Ministry of Science and Education for financial support under Contract #X831/1998.

References

1 P. T. Sarjent and R. Roy, J. Am. Ceram. Soc., 50 (1967) 500.
2 Y. Dimitriev, Proc. First Balkan Conf. Glass Sci. & Technology, Volos Greese, 9–10 Oct. 2000, Eds G. Kordas and N. S. Vlachos, p. 34.
3 Y. Dimitriev, Y. Jordanova and E. Gateff, J. Non-Cryst. Solids, 45 (1981) 297.
4 W. H. Dumbaugh and J. C. Lapp, J. Am. Ceram. Soc., 75 (1992) 2315.
5 Y. Dimitriev and V. Mihailova, J. Mat. Sci. Lett., 9 (1990) 1251.

6 R. G. Gossink, PhD Thesis, Eindhoven Technical University, 1971.
7 R. Iordanova, V. Dimitrov, Y. Dimitriev and D. Klissurski, J. Non-Cryst. Solids, 180 (1994) 58.
8 R. Iordanova, Y. Dimitriev, V. Dimitrov, S. Kassabov and D. Klissurski, J. Non-Cryst. Solids, 231 (1998) 227.
9 T. Kemény and J. Šesták, Thermochim. Acta, 110 (1987) 113.
10 H. Yinnon and D. R. Uhlmann, J. Non-Cryst. Solids, 54 (1983) 253.
11 N. Afify, J. Non-Cryst. Solids, 142 (1992) 247.
12 C. D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285, 6 (1962) 639.
13 K. Matusita and S. Sakka, Phys. Chem. Glasses, 20 (1979) 81.
14 K. Matusita, T. Komatsu and R. Yokota, J. Mat. Sci., 19 (1984) 291.
15 T. Ozawa, Polymer, 12 (1971) 150.
16 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
17 H. S. Chen, J. Non-Cryst. Solids, 27 (1978) 257.
18 V. Šatava, Thermochim. Acta, 2 (1971) 423.
19 G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, Nature, 212 (1966) 1229.
20 A. Marotta, A. Buri and P. Pernice, Phys. Chem. Glasses, 21 (1980) 94.
21 F. Branda, A. Buri and A. Marotta, Verres Réfract., 33 (1979) 201.
22 H. E. Kissinger, Analyt. Chem., 29 (1957) 1702.
23 W. Kauzmann, Chem. Rev., 43 (1948) 219.
24 S. Sakka and J. D. Mackenzie, J. Non-Cryst. Solids, 6 (1971) 145.
25 D. Turnbull, Contemporary Phys., 10 (1969) 473.
26 I. Donald and H. A. Davies, J. Non-Cryst. Solids, 30 (1978) 77.
27 I. Gutzow, Amorphous Materials, Proc. Third International Conference on the Physics of Non-Cryst. Solids, Eds R.W. Douglas and B. Ellis, Sheffield, 1970, Wiley, London 1972, p. 159.
28 I. Gutzow, Fiz. i Khim. Stekla, 1 (1975) 431.
29 I. Gutzow and A. Dobreva, J. Non-Cryst. Solids, 129 (1991) 266.
30 P. F. James, J. Non-Cryst. Solids, 73 (1985) 517.
31 E. D. Zanotto, J. Non-Cryst. Solids, 89 (1987) 361.
32 T. Wakasugi, L. L. Burgner and M. C. Weinberg, J. Non-Cryst. Solids, 244 (1999) 63.
33 A. Hruby, Czech. J. Phys., B22 (1972) 1187, B23 (1973) 1623.
34 C. A. Angell, Proc. 2nd Int. Symp. on Halide Glasses, Rensselaer Polytechnic Institute, Troy, NY, 1983, paper No. 8
35 R. El-Mallawany, J. Mat. Sci.: Mat. Electr., 6 (1995) 1.
36 E. Lefterova, P. Angelov and Y. Dimitriev, to be published.
37 P. Balaya and C. S. Sunandana, J. Non-Cryst. Solids, 162 (1993) 253.
38 M. Tatsumisago, C. A. Angell, Y. Akamatsu, S. Tsuboi, N. Tohge and T. Minami, Appl. Phys. Lett., 55 (1989) 600.
39 M. R. De Guire, N. P. Bansal and C. J. Kim, J. Am. Ceram. Soc., 73 (1990) 1165.
40 N. P. Bansal, J. Appl. Phys., 68 (1990) 1143.
41 H. Zheng and J. D. Mackenzie, Phys. Rev., B 43 (1991) 3048.
42 G. Fuxi and L.I. Guangming, The Physics of Non-Crystalline Solids, Eds L.D. Pye, W.C. LaCourse and H.J. Stevens, Taylor & Francis, London 1992, p. 406.
43 T. Komatsu, R. Sato, Y. Kuken and K. Matusika, J. Am. Ceram. Soc., 76 (1993) 2795.
44 N. C. de Souza, R. Lebullenger, M. C. Custódio and A.C. Hernandes, J. Non-Cryst. Solids, 273 (2000) 94.

45 A. Marotta, P. Pernice, A. Aronne and A. Buri, J. Non-Cryst. Solids, 127 (1991) 159.

46 C. S. Ray, D. E. Day, W. Huang, K. Lakshmi Narayan, T. S. Cull and K. F. Kelton, J. Non-Cryst. Solids, 204 (1996) 1.

47 C. S. Ray, W. Huang and D. E. Day, J. Am. Ceram. Soc., 74 (1991) 60.

48 J. C. Perng, J. S. Lee, T. J. Lin and C. W. Huang, Thermochim. Acta, 177 (1991) 1.

49 J. S. Lee, J. C. Perng, C. W. Huang and W. P. Pan, Thermochim. Acta, 192 (1991) 29.

50 A.Małecki, R. Gajerski, S. Łabuś, B. Prochowska-Klisch and J. Obłakowski, J. Non-Cryst. Solids, 212 (1997) 55.

51 Y. Hu and C. L. Huang, J. Non-Cryst. Solids, 278 (2000) 170.

52 J. Šesták, Thermophysical Properties in Solids, Their Measurement and Theoretical Analysis, Elsevier, Amsterdam, 1984; Mir, Moscow 1987, p. 204.

53 I. Cutzow and J. Schmelzer, The Vitreous State-Thermodynamics, Structure, Rheology and Crystallization, Springer-Verlag Berlin Heidelberg 1995, p. 391.