Journal of Non-Crystalline Solids 121 (1990) 279–281
North-Holland

ADIABATIC NUCLEATION AND CRYSTALLIZATION OF GELS

Erich MEYER [a], Edgar D. ZANOTTO [b] and Michel A. AEGERTER [c]

[a] *Instituto de Fisica, Universidade Federal do Rio de Janeiro, 21945 Rio de Janeiro, Brazil*
[b] *Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, 13560 São Carlos, SP, Brazil*
[c] *Instituto de Fisica e Quimica de São Carlos, Universidade de São Paulo, 13560 São Carlos, SP, Brazil*

Adiabatic Nucleation Theory (ANT) has been successfully applied to pure liquid metals, oxide glasses, metallic glasses and polymers. This paper shows that ANT gives an interesting correlation between the crystallization data of gels of both reluctant and good (dense) glass forming systems. For reluctant glass formers, one finds that $T_{ch} < T_{14}^{-}$, whereas for good (dense) glass formers, $T_{ch} > T_{14}^{-}$. T_{14}^{-} is the temperature predicted by ANT at which nucleation starts in cooling experiments or ceases during heating and T_{ch} is the experimental temperature of crystallization on heating. For systems with T_{ch} considerably lower than T_{14}^{-}, as observed for reluctant glass formers, it is doubtful that one can obtain dense glasses by heat treatment of gels. This conclusion is in disagreement with the often advanced idea that the gel route can lead to dense glasses of unusual, reluctant glass forming compositions.

1. Introduction

A recently developed Adiabatic Nucleation Theory (ANT) shows, that pure liquid elements can be supercooled down to

$$T_{14}^{-}/T_M = \left(\Delta h_L/c_p T_M\right)\left[1.67 - 0.26/\sqrt{Q}\right]^{-1} \times \left[\exp\left(\Delta h_L/c_p T_M\right) - 1\right]^{-1}, \quad (1)$$

where T_{14}^{-} and T_M are the absolute maximum supercooling and melting temperatures, respectively, Δh_L is the latent heat of melting, c_p the average specific heat of the liquid and solid at the melting temperature and Q the number of atoms per molecule [1].

This theory has been been used to predict whether oxide glasses, metallic glasses and polymers show homogeneous nucleation or not [2–6]. For those systems where

$$T_g > T_{14}^{-}, \quad (2)$$

where T_g is the normal, slow cooling glass transition temperature, no homogeneous nucleation is expected during cooling. Such materials can be classified as good glass formers.

In those cases where

$$T_g \cong T_{14}^{-}, \quad (3)$$

homogeneous nucleation can be avoided by fast cooling or quenching from the melt, because in this case the effective, fast cooling glass transition temperature T_g^* can be increased above T_{14}^{-} (by quenching). It has also been shown that the relation $T_g \cong T_{14}^{-}$ is, in general, valid for eutectic or nearly eutectic metallic glasses [6]. Systems with $T_g \cong T_{14}^{-}$ may form glasses by quenching. In this paper these materials are classified as glass formers.

When

$$T_g \ll T_{14}^{-}, \quad (4)$$

no glass formation is expected when liquids are cooled or quenched from the melt, because these materials nucleate and crystallize near T_{14}^{-}, before having a chance to freeze in at T_g. In this case T_g cannot be found experimentally due to complete crystallization and, therefore, $T_g < T_{14}^{-}$ has to be postulated. Copolymers (with unequal repetitive units) can be exceptions to this rule [4].

It is the purpose of this paper to investigate whether gel-derived (dense) crystalline or non-

crystalline materials, which form when these materials are heated instead of cooled (as in the cases discussed above), can also be classified by relations (2)–(4).

2. Classification of gel-derived materials

A first attempt to classify gel-derived materials was made by Mackenzie [7], who argued that there are two groups of gel-derived materials:

(A) Oxides with experimentally determined crystallization temperatures on heating, T_{ch}, such that

$$T_{ch} > T_M/2, \tag{5}$$

were called good (dense) glass forming oxides.

(B) Oxides with

$$T_{ch} < T_M/2, \tag{6}$$

were called non-(dense) glass forming oxides or reluctant glass formers.

Table 1 and fig. 1 show these two groups of materials. Reduced crystallization temperatures T_{ch}/T_M (full triangles) and reduced glass transition temperatures T_g/T_M (full circles) of good dense glass formers, and reduced crystallization temperatures (open triangles) of reluctant (dense) glass formers are shown in fig. 1. The dotted lines

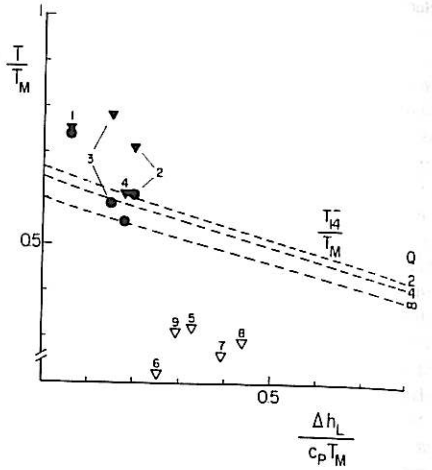

Fig. 1. Reduced crystallization temperatures T_{ch}/T_M (full triangles) and reduced glass transition temperatures T_g/T_M (full circles) of good dense glass formers and reduced crystallization temperatures (open triangles) or reluctant (dense) glass formers are shown. The dotted lines show T_{14}^-/T_M as a function of $\Delta h_L/c_pT_M$ for molecules with 2 and 4 atoms ($Q = 2$ and 4) and for the limiting case of very large molecules ($Q = \infty$). Materials with $T_{ch} \ll T_{14}^-$ do not form dense glasses.

show T_{14}^-/T_M as a function of $\Delta h_L/c_pT_M$ for molecules with 2 and 4 atoms ($Q = 2$ and 4) and for the limiting case of very large molecules ($Q = \infty$). The corresponding numerical values are given in table 1. One sees that for materials of group (A), where eq. (5) is valid, eqs. (2) or (3) are also satisfied. For materials of group (B), where eq. (6) is valid, no T_g has ever been reported. As, in general, it can be assumed that significant crystallization is only detectable above T_g for all materials,

$$T_g \leq T_{ch}, \tag{7}$$

and, therefore, eq. (4) is also satisfied for group (B).

Table 1
Group (A) are good (dense) glass formers. Group (B) are reluctant (dense) glass formers

		T_M (K)	Δh_L (J/mol)	c_p (J/mol K)	$\frac{T_{ch}}{T_M}$	$\frac{T_g}{T_M}$	$\frac{T_{14}^-}{T_M}$	Ref.
Group (A)								
1.	SiO_2	1998	9600	79	0.75	0.74	0.64	[2,8]
2.	$CaO–Al_2O_3–2SiO_2$	1826	135500	376	0.71	0.61	0.57	[2,9]
3.	GeO_2	1387	15100	72.6	0.78	0.59	0.61	[2,10]
4.	$Li_2O–2SiO_2$	1307	57300	243	0.61	0.55	0.58	[2,11]
Group (B)								
5.	Al_2O_3	2323	108700	140.9	0.32		0.54	[12,13]
6.	TiO_2	2143	47650	86.9	0.22		0.58	[12,14]
7.	ZrO_2	2993	86940	74.4	0.26		0.54	[12,15]
8.	Ta_2O_5	2150	200600	213.2	0.29		0.51	[12,16]
9.	Y_2O_3	2693	104500	131.7	0.31		0.55	[12,17]
10.	V_2O_5	2250			0.25			[18]
11.	$BaTiO_3$	1885			0.46			[19]
12.	$PbTiO_3$	1593			0.49			[20]
13.	$LiNbO_3$	1523			0.50			[21]

These new correlations can be understood in the following way: materials of group (A), when heated, densify at $T \cong T_g$. ANT predicts that nucleation only occurs for temperatures smaller than or equal to T_{14}^-. However, since $T_g > T_{14}^-$ in this case, homogeneous nucleation on heating is not detectable experimentally due to slow molecular rearrangement. These materials may crystallize at a temperature T_{ch} above T_g by heterogeneous nucleation, because foreign particles always exist, at least at the surfaces. However, if these materials are cooled immediately after densification, stable glasses are obtained. That is why these materials are called good (dense) glass forming oxides and consequently

$$T_{ch} \geq T_g \geq T_{14}^- \tag{8}$$

is valid.

Materials of group (B), should also densify at $T \cong T_g$. However, in this case $T_g \ll T_{14}^-$ and thus nucleation occurs at high rates and the system can crystallize completely, at an eventually higher temperature T_{ch}. For this class of materials the following equation

$$T_g \cong T_{ch} \ll T_{14}^- \tag{9}$$

is valid.

These two last equations can then be written in a simplified approximate way:

$$T_{ch} > T_{14}^- \tag{10}$$

for good (dense) glass formers and

$$T_{ch} \ll T_{14}^- \tag{11}$$

for reluctant glass formers.

Consequently, eqs. (8)–(11) can substitute Mackenzie's empirical eqs. (5) and (6).

3. Conclusions

The fact that the same eqs. (8)–(11) indicate which materials are good or reluctant glass formers, for melt-derived as well as for gel-derived materials, indicates that similar results (in this sense) are expected for both processes, at least for stoichiometric and homogeneous materials. Obviously the presence of heterogeneous nucleation centers (impurities) may stimulate crystallization at rather low temperatures, including the gel state. Overall, the present paper demonstrates that the gel route cannot lead to dense glasses of unusual, reluctant glass forming compositions.

References

[1] E. Meyer, J. Cryst. Growth 74 (1986) 425; 76 (1986) 525.
[2] E.D. Zanotto, J. Non-Cryst. Solids 89 (1987) 361.
[3] E. Meyer, in: Instabilities and Nonequilibrium Structures, eds. E. Tirapegui and D. Villarroel (Reidel, Dordrecht, 1987) p. 311.
[4] E. Meyer, J. Cryst. Growth 84 (1987) 533.
[5] E. Meyer, J. Non-Cryst. Solids 102 (1988) 148.
[6] E. Meyer, J. Non-Cryst. Solids 107 (1989) 163.
[7] J.D. Mackenzie, J. Non-Cryst. Solids 100 (1988) 162.
[8] M. Decottignies, J. Phalippou and J. Zarzycki, J. Mater. Sci. 13 (1978) 2605.
[9] B.J.J. Zelinski, B.D. Fabes and D.R. Uhlmann, J. Non-Cryst. Solids 82 (1986) 307.
[10] O. Yamaguchi and K. Shimizu, Adv. Ceram. (Am. Ceramic Soc.) 21 (1987) 163.
[11] F. Branda, A. Aronne, A. Marotta and A. Buri, J. Mater. Sci. Lett. 6 (1987) 203.
[12] Thermodynamic Data Bank, Finnish Society of Metallurgy.
[13] D.E. Clark and J.J. Lanutti, in: Ultrastructure Processing of Ceramics, Glasses and Composites, eds. L.L. Hench and D.R. Ulrich (Wiley, New York, 1984) ch. 10.
[14] R. Roy et al., in: Science of Ceramic Chemical Processing, eds. L.L. Hench and D.R. Ulrich (Wiley, New York, 1986) ch. 27.
[15] D. Kundu and D. Ganguli, J. Mater. Sci. Lett. 5 (1986) 293.
[16] H.C. Ling et al., in: Science of Ceramic Chemical Processing, eds. L.L. Hench and D.R. Ulrich (Wiley, New York, 1986) ch. 31.
[17] F. Ribot, C. Sanchez and J. Livage, Mater. Res. Soc. Symp. Proc. 121 (1988) 139.
[18] C. Sanchez, M. Nabavi and F. Taulelle, Mater. Res. Soc. Symp. Proc. 121 (1988) 93.
[19] A. Shaikh, and G. Vest, J. Am. Ceram. Soc. 69 (1986) 682.
[20] R.W. Schwartz and D. Payne, Mater. Res. Soc. Symp. Proc. 121 (1988) 199.
[21] S. Hirano and K. Kato, J. Non-Cryst. Solids 100 (1988) 538.