Heat Capacities of Thermally Treated $Na_2O-3B_2O_3$ Glasses Above and Below T_g

Piercarlo Mustarelli[a], Corrado Tomasi[a], and Marco Villa[b]

[a] C.S.T.E.-C.N.R. and Dipartimento di Chimica Fisica dell'Università di Pavia
[b] Dipartimento di Fisica "A. Volta" dell'Università di Pavia

Z. Naturforsch. **51a,** 187–191 (1996); received January 11, 1996

Various contributions have been obtained from the heat capacities of "as quenched" and annealed $Na_2O-3B_2O_3$ glasses. It is shown that the enthalpic release gives a major contribution to the DSC curves obtained by reheating quenched glasses. Different relaxation processes are followed by comparing DSC scans of quenched and annealed samples in the vitreous state and around the glass transition temperature, T_g. As a function of the annealing time at $T = T_g - 30\,°C$, the specific heats at room temperature initially increase, due to the decrease of the exothermic contribution from quenched-in defects, which are absent in a fully annealed glass; over a month-long time scale these heat capacities drop, due to a partial ordering, which decreases the configurational contribution. Such a decrease is related with the "overshoot" which occurs above T_g and which attains a limiting value $\Delta H_g \cong 14\,J\,mol^{-1}$ in a matter of days. The heat capacities above T_g relax towards a value of C_p of $\cong 2.3\,J\,mol^{-1}\,K^{-1}$ after a few days of annealing, which is intermediate between the anomalously low C_p ($\sim 1.8\,J\,mol^{-1}\,K^{-1}$) of a fast quenched ($\sim 10^3\,K\,min^{-1}$) and that ($\sim 2.9\,J\,mol^{-1}\,K^{-1}$) of a sample annealed for one hour. These phenomena point to complex relationships among enthalpic relaxation, entropic relaxation and temperature in these glasses.

Key words: Glasses, borates, structural relaxation, annealing.

1. Introduction

The thermodynamic properties of glasses depend on the preparation method and thermal history [1]. Also the short range structure of $Na_2O-2B_2O_3$ is possibly influenced by the quenching rate. However, careful ^{11}B NMR MAS [2] and X-ray diffraction [3] experiments have shown that the distributions of the ^{11}B quadrupolar coupling parameters and the radial distribution functions are the same in "fast quenched" (FQ, average cooling rate $\sim 10^3$ K/min) and "slow quenched" (SQ, average cooling rate ~ 0.1 K/min) glasses. On the other hand, in that system we have shown that the excess entropy of a glass, relative to its crystalline counterpart, is fully used during a crystallization process occurring ~ 100 K above the glass transition temperature, T_g, no matter what the quenching rate was. Obviously, this finding simply means that above the crystallization temperature, T_c, a single, thermodynamically well defined crystalline state is attained. However, several details of our Differential Scanning Calorimetry (DSC) records could not be explained as superposition of the thermal response of a glass and its crystal; in particular, the shape of the thermograms both well below and around T_g is heavily influenced by the thermal treatment and reveals phenomena of relaxation and reordering which probably occur over a medium-range scale [4]. Many models have been developed to describe the non-exponential and often non-linear relaxation phenomena near and below the glass transition [5]. However, these models do not take into account what happens in the regions well below T_g.

In this paper the matter is further investigated by comparing the heat capacities, C_p, of a set of annealed sodium borates with composition $Na_2O-3B_2O_3$ which appear to be "stronger" glasses (in the sense of Angell's classification [6]) than those studied before. We recall that the strength of a glass reflects in some way the stability of its short- and medium-range order against temperature-induced degradation. In other words, a strong glass will retain a higher viscosity ($\sim 10^{13}$ Pa s) at the glass transition and undergo crystallization over a longer time scale than a "fragile" one.

Reprint requests to Dott. Piercarlo Mustarelli, CSTE-CNR – Via Taramelli 16, 27100 Pavia, Italy.

2. Experimental Procedures

Reagent grade $Na_2B_4O_7 \cdot 10H_2O$ and H_3BO_3 were used as starting materials in the glasses preparation. Weighted amounts of the proper mixtures were melted in a platinum crucible and kept for 60 min at 1000 °C. Fast quenched glass was poured on a stainless steel mould at room temperature; near T_g the cooling rate was estimated to be ~ 20 K s^{-1}. Slow quenched glass was obtained by leaving the melt inside the furnace with the power switched off; in this case, the cooling period down to 200 °C was about 4 hours, which corresponds to a cooling rate near the T_g of ~ 0.03 K s^{-1}. The samples were kept for 2 hours at 200 °C before X-ray analysis to determine the presence of crystallization. Annealing was performed on samples of glass (~ 50 mg in weight) kept in an oven at 430 °C (approximately 30 °C below T_g) for times ranging from 1 hour to 96 days.

Differential scanning analyses (DSC) were performed with a DSC 910 cell controlled by a TA 2000 system (TA Instruments, USA), under N_2 dry atmosphere. The FQ and SQ samples were kept for 36 hours at 150 °C to eliminate moisture, the they were analyzed at a heating rate of 10 °C/min. Annealed samples were ground immediately after the end of the annealing period and analyzed at the same heating rate. The DSC cell was calibrated before each run using Al_2O_3. To reduce the errors in determining the heat capacity, a procedure of baseline subtraction was used which required a DSC recording baseline made with two empty pans, one of which was later filled with the sample. These precautions reduce the C_p errors to below $\sim 2\%$. The heat capacities and other thermodynamic properties were calculated using a home-made program written in MS-Fortran and run on a 486 IBM-compatible personal computer. The program uses the C_p of sapphire as a reference.

3. Results

Figure 1 presents the DSC plots for FQ and 96 days annealed glasses. The differences among quenched and annealed glasses are summarized. The crystallization process (not fully seen in the figure) yields different peaks which suggest the existence of various crystalline phases, in agreement with the phase diagram [7]. The existence of a well defined glass transition even after ~ 100 days annealing suggests that this borate is an unusually strong glass.

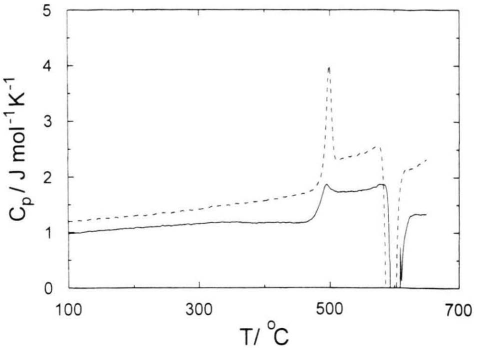

Fig. 1. DSC plots for fast quenched (FQ) (solid line) and 96 days annealed (dashed line) glasses.

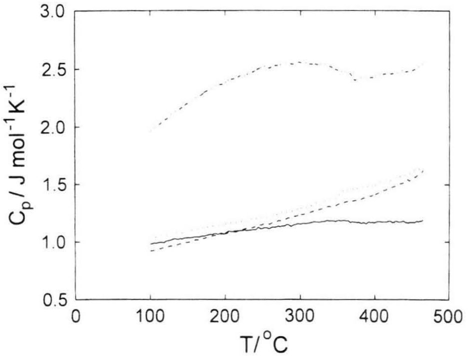

Fig. 2. Molar heat capacity below T_g for FQ (solid line), slow quenched (SQ) (dashed line), 1 hour (dashed-dotted line) and 21 days annealed (dots) samples.

Figure 2 shows the molar heat capacity below T_g for FQ, SQ, 1 hour and 21 days annealed samples. Plots for longer annealing times are essentially the same as that for 21 days. The FQ heat capacity displays an exothermic inflection at ~ 350 °C, which is generally observed in FQ glasses [8]. Avramov and Gutzow have recently described these features as the initial part of the transition region, where the investigated property deviates measurably from its glassy-state frozen value [9].

Figure 3 displays the enthalpic intake at T_g, which is currently named "overshoot", in FQ, SQ, 1 hour annealed and 96 days annealed samples. This sharp "melting" peak is very much reduced in the FQ sample, but about the same in all glasses annealed for 24 hours or more. Also the glass transition temperatures are essentially the same in all annealed glasses (see Table 1).

Table 1. Thermodynamic properties of as-quenched and annealed borate glasses.

Glasses	C_p (100 °C) ($J mol^{-1} K^{-1}$)	C_p (550 °C) ($J mol^{-1} K^{-1}$)	ΔC_p ($J mol^{-1} K^{-1}$)	ΔH_{ov} ($J mol^{-1}$)	T_g (°C)	T_f' (°C)	T_c (°C)
As-quenched							
FQ	0.98 ± 0.02	1.77 ± 0.03	0.56 ± 0.06	1.51 ± 0.08	474 ± 2	478 ± 3	592 ± 2
SQ	0.92 ± 0.02	2.53 ± 0.05	0.6 ± 0.06	4.66 ± 0.3	476 ± 2	469 ± 3	603 ± 2
Annealed							
1 hour	1.96 ± 0.04	2.88 ± 0.06	0.78 ± 0.08	6.24 ± 0.3	473 ± 2	454 ± 3	593 ± 2
24 hours	1.73 ± 0.03	2.58 ± 0.06	0.54 ± 0.05	12.53 ± 0.7	484 ± 2	454 ± 3	580 ± 2
3 days	1.54 ± 0.03	2.39 ± 0.05	0.40 ± 0.04	13.46 ± 0.7	484 ± 2	447 ± 3	570 ± 2
21 days	1.03 ± 0.02	2.37 ± 0.05	0.49 ± 0.05	14.86 ± 0.8	489 ± 2	457 ± 3	587 ± 2
47 days	1.19 ± 0.02	2.26 ± 0.05	0.54 ± 0.05	13.60 ± 0.7	486 ± 2	459 ± 3	581 ± 2
96 days	1.19 ± 0.02	2.45 ± 0.05	0.39 ± 0.04	15.95 ± 0.8	489 ± 2	443 ± 3	586 ± 2

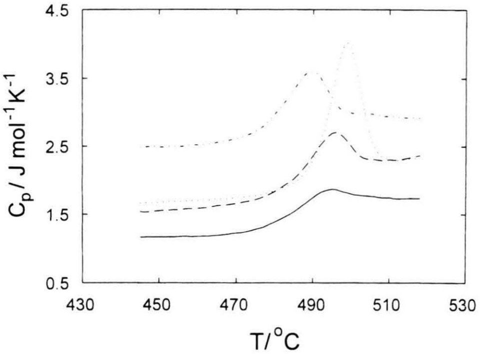

Fig. 3. Behaviour of the "overshoot" at T_g in FQ (solid line), SQ (dashed line), 1 hour annealed (dashed-dotted line) and 96 days annealed samples (dots).

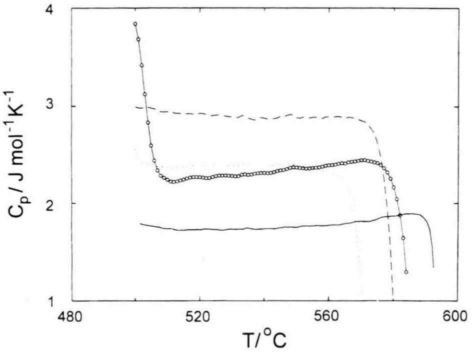

Fig. 4. Heat capacities behaviours above T_g in FQ glass (solid line), and in samples annealed 1 hour (dashed line), 4 days (dots) and 21 days (circles).

Figure 4 shows the heat capacity behaviour above T_g in FQ glass and in samples annealed for 1 hour, 4 days and 21 days. After a sudden increase (1 hour annealed glass), there is a reduction of C_p. For long annealing times, the C_p values in the metastable liquid state tend to that of SQ (not shown in the Figure for the sake of clarity).

Table 1 summarizes the data obtained from the DSC runs. Since after 1 hour of annealing FQ and SQ glasses yield the same results, within the experimental uncertainty, only annealed FQ glasses are listed. In the Table are reported: a) the heat capacities at 100 °C and at 550 °C, b) the T_g and the crystallization temperatures, T_c, c) the limiting fictive temperatures (see below), T_f', d) the "overshoot" areas, ΔH_{ov}, and e) the C_p difference between the glassy and the supercooled state, ΔC_p. T_g values have been determined with the onset method. The T_f' values have been determined using the algorithm proposed by Moynihan and coworkers [10].

4. Discussion

It is customary to describe the thermodynamic state of a glass with a single parameter, the limiting fictive temperature, T_f', the temperature at which an amorphous system with a given structure is at equilibrium [11]. However, as often reported [12, 13], in our case this parameter captures only a part of the complex thermal behaviour outlined above; the fictive temperature has "anomalous" values of ~478 °C and ~470 °C in the FQ and the SQ samples, respectively, and it remains nearly constant (~450 °C) for all annealed glasses. The fictive temperature depends upon both the "shape" of the glass transition and the heat capacities above and below T_g. Its apparent insensitivity to annealing points to the existence of some competing thermal effects, that will be qualitatively illustrated in the following with the aid of some simple pictorial views reported in Figure 5.

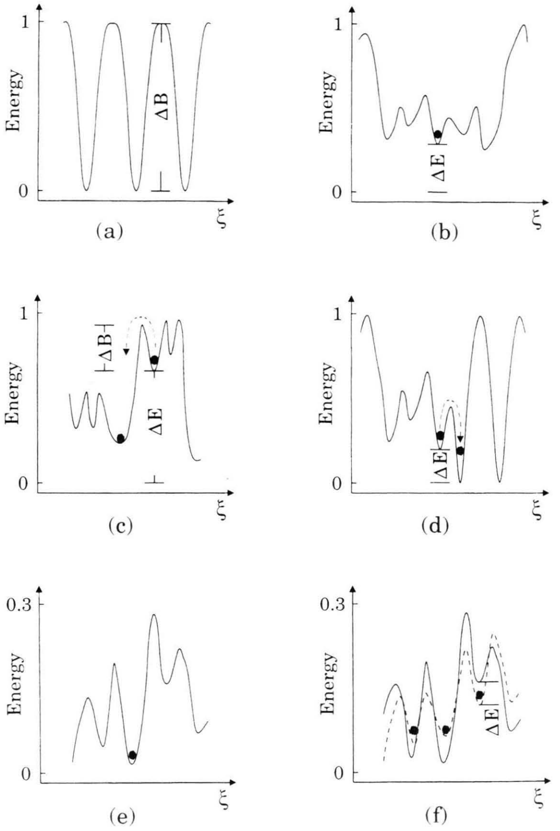

Fig. 5. Potential energy of a "particle" vs. a generalized coordinate, ξ, for different cases: a) ideal crystal, b) ideal metastable state, c) glass with many "freezed-in" defects, d) crystallization process, e) low-energy metastable configuration (rigid state, below T_g), f) entropic intake in the super cooled liquid state (above T_g).

In an ideal crystal (Fig. 5a), the "particles" are found at the bottom of regular energy wells, having a barrier height ΔB much higher than the thermal energy ($\sim kT$). In an ideal metastable glassy state, on the contrary, there are several shallow minima having a potential energy, ΔE, somehow above the ground state of the crystal which become progressively accessible as kT approaches the barrier height (Figure 5b). The heat capacity of this ideal metastable state is larger than that of the crystal for the following reasons:

a) there are many equivalent "positions" (configurations) that may be accessible to the "particle" (entropic contribution);
b) minima are shallower, i.e. there are degrees of freedom, already fully excited at relatively low temperature, with characteristic vibrational frequencies much smaller than those typical of a crystal;
c) there is a distribution of accessible states, lying above the ground state by ΔE, which adds an enthalpic term to the heat capacity.

We may expect that several high-energy defects, which have been frozen-in during a fast quenching, will eventually relax towards a more stable state (see Figure 5c). Following this model, the large differences in heat capacity below T_g between annealed and quenched glasses (see Fig. 2) are due to the absence in the annealed glasses of the exothermic contribution of the relaxing defects; since the annealing temperature is near T_g, all defects with ΔB comparable with kT_g relax in a very short time, which is below our minimum annealing time of 1 hour. If we suppose a defect energy $\Delta E \sim 1$ eV above the ground state, a simple estimate based on the C_p increase after 1 hour of annealing yields, for the FQ glass, a concentration of the "quenched-in" defects of $\sim 6 \times 10^{-3}$ mol^{-1}, which is too small to be detected by X-rays or NMR. By defining an "annealing rate", R_a, as

$$R_a \approx \nu_0 \exp\{-\Delta B/kT\}$$

for a defect with barrier height ΔB, we obtain a very reasonable average $\Delta B \sim 1.5$ eV for the FQ glass, when a vibrational attempt frequency $\nu_0 = 10^{-11}\ \mathrm{s}^{-1}$ is assumed. In this description, the exothermic inflection displayed by the C_p curve of 1 hour-annealed glass near 350 °C (see Fig. 2) is due to high-energy defects not yet removed by the annealing.

A competing, and different, process from defect annealing is that of relaxation of the ideal metastable state towards a crystal-like configuration (Figure 5d). This process, which involves a partial reordering of the energy wells, is expected to be very slow below T_c, and to give a negligible direct contribution to the DSC runs in terms of endo- or exothermic features. However, it reduces the configurational entropy of the ideal metastable state, causing a slow drop of C_p both below and above T_g. This effect is seen in the C_p(100 °C) and C_p(550 °C) behaviour of glasses annealed for more than one day. Furthermore, the crystal-like configurations produced by sub-T_g annealing (Fig. 5e) are partially incompatible with the situation we have above T_g (Figure 5f). The characteristic enthalpic "overshoot" at T_g is mostly due to the melting of these crystal-like configurations. It is not surprising, in this sense, that the area of the overshoot peak, ΔH_{ov}, increases as a function of the annealing time with roughly the same time constant of few days, with which the sub-T_g heat capacities drop to a stable value.

Figure 4 shows that the beginning of the crystallization process varies substantially in well-annealed glasses (from ~ 570 °C to ~ 590 °C) without following any defined trend. This random behaviour is probably due to some "accidents", such as roughness of the DSC pans, or irregular grinding of the samples. The influence of these factors in determining nucleation and crystals growth is well known [14]. If we disregard the quenched glasses, we may say that the C_p values above T_g generally have a tendency to decrease (up to ~ 20%) with the annealing time (see Table 1); however, the C_p apparently rebounds by ~ 10% in the sample annealed for three months.

5. Conclusions

We have studied the annealing behaviour of sodium triborate glasses and we have shown that a quenching rate of ~ 10^3 K min^{-1} "freezes-in" a small fraction (~ 0.6%) of defects, which are not detected by NMR or X-rays diffraction, but account for a substantial decrease of heat capacity below T_g. These defects are eliminated by a hour-long annealing at $T = T_g - 30$ °C, which produces an approximation of what we have called "the ideal metastable state". Further annealing at the same temperature below T_g creates "crystal-like" configurations, which again decrease, relative to the ideal metastable state, the C_p value and contribute to the endothermic overshoot at T_g. This last process is apparently completed in about a week, and is responsible for the drop of C_p's below T_g and for a three-fold increase of ΔH_{ov}.

After annealing, our samples are scanned from T_g to the crystallization temperature at a rate of 10 °C/min. Obviously, no equilibrium situation can be attained in the few minutes the system lives in the "under cooled" state. However, the complex thermal behaviour displayed by the DSC runs from T_g to T_c demonstrates that we begin with very different states, which produce systems having different crystallization behaviours and display C_p values which are non-linear functions of the annealing time. It may be argued that several metastable states may be produced below T_g, and that the range of possible structures is related to the unusually strong character of glassy Na_2O-$3B_2O_3$.

[1] A. K. Varshneya, Fundamentals of Inorganic Glasses, Acad. Press, San Diego 1994.
[2] P. Mustarelli, A. Magistris, and A. Musinu, Phys. Chem. Glasses **35,** 44 (1994).
[3] M. P. Medda, A. Musinu, G. Paschina, and G. Piccaluga, J. Non-Cryst. Solids **150,** 76 (1992).
[4] S. R. Elliott, Nature London **354,** 445 (1991).
[5] See, for example, 1) I. M. Hodge, J. Non-Cryst. Solids **131–133,** 435 (1991), and 2) Discussion Session, Phenomenology and models of the kinetics of volume and enthalpy in the glas transition range, ibid. p. 528.
[6] C. A. Angell, J. Non-Cryst. Solids **131–133,** 13 (1991).
[7] T. Milman and R. Bouaziz, Ann. Chim. **3,** 311 (1968).
[8] C. Tomasi, P. Mustarelli, and A. Magistris, Phys. Chem. Glasses **36,** 137 (1995).
[9] I. Avramov and I. Gutzow, J. Non-Cryst. Solids, **104,** 148 (1988).
[10] C. T. Moynihan, A. J. Easteal, J. Wilder, and J. Tucker, J. Chem. Phys. **82,** 2673 (1974).
[11] A. Tool and C. Eichlin, J. Amer. Ceram. Soc. **14,** 276 (1931).
[12] H. N. Ritland, J. Amer. Ceram. Soc. **39,** 403 (1956).
[13] O. S. Narayanaswamy, J. Amer. Ceram. Soc. **54,** 491 (1971).
[14] C. S. Ray, W. Huang, and D. E. Day, J. Amer. Ceram. Soc. **74,** 60 (1991).