Thermal characterization of glasses and polymers by temperature modulated differential scanning calorimetry: glass transition temperature

D. Tonchev & S. O. Kasap
Department of Electrical Engineering, University of Saskatchewan, Saskatoon, Canada

Abstract

Temperature Modulated Differential Scanning Calorimetry (TMDSC) is a relatively new thermal analysis technique that incorporates not only the ability of conventional DSC, but also provides significant and distinct advantages over traditional DSC. We first review the principles of TMDSC and then provide a number of characterization-type applications to glasses and polymers. The glass transition temperature T_g measurements by conventional DSC usually involve heating scans and, consequently, the measured T_g depends sensitively on the thermal history and aging. We demonstrate that, in contrast to DSC, TMDSC measurements can conveniently provide a more meaningful and reproducible characterization of the glass transition properties of glasses and amorphous polymers, without the complications arising from thermal history and aging.

1 Introduction

Differential scanning calorimetry (DSC) is a well established thermal characterization technique that has been extensively used to measure heats and temperatures of various transitions; it has been recognized as a very useful tool for the interpretation of thermal events as discussed by a number of authors (see for example [1]). In the last ten years, a greatly enhanced version of the DSC method called the *Temperature Modulated Differential Scanning Calorimetry* (TMDSC) has been introduced through the pioneering works of Reading and coworkers [2-7]. The MDSC method incorporates not only the ability of

High Performance Structures and Materials II, C.A. Brebbia & W.P. De Wilde (Editors)
ISBN 1-85312-717-5

conventional DSC but it also provides significant and distinct advantages over traditional DSC. The benefits of MDSC technique have been discussed in several recent papers (*e.g.* [3-11]). One of the most important benefits is the separation of complex transitions such as the glass transition into more easily interpreted components [7,8,12]. Recent applications of MDSC to glasses has shown that it can be very useful for the interpretation of thermal properties, such as the heat capacity, in relation to the structure as, for example, in the case of chalcogenide glasses As-Se [13] Se-Te [14], Ge-Se [15-17], Ge-S [16,17] and Ge-As-S [18]

Glass transition phenomenon is a characteristic property of all glasses and amorphous polymers, and is of considerable interest in materials engineering, especially for applications at elevated temperatures, near the glass transition temperature T_g. Conventional DSC has been widely used to measure the glass transition temperature T_g of glasses as a function of thermal history, aging, composition, and heating and cooling rates. While DSC T_g measurements during heating depend on thermal history and aging, T_g measurements from cooling scans are generally independent of thermal history and aging provided that the cooling scan starts from a liquid-like equilibrium state above the glass transformation region but below the crystallization temperature. The problem with cooling scans is that the experiments are difficult to perform, and sometimes the sample crystallizes while being equilibrated at a temperature above T_g. The effect of thermal history and aging on DSC T_g measurements makes it difficult to compare small changes in T_g due to small compositional changes only.

The purpose of this paper is two fold: first it provides an overview of the principles of the TMDSC technique, and the interpretation of the measured TMDSC quantities (such as the reversing heat capacity) and, secondly, typical applications of the TMDSC to glasses and polymers in terms of the measurement and characterization of the glass transition temperature. We present typical results obtained not only in our own laboratories to highlight the usefulness of the TMDSC in materials characterization. We show results that while T_g as measured by conventional DSC depends on aging and thermal history, T_g as measured on TMDSC is relatively insensitive to aging and thermal history.

2 TMDSC

In TMDSC measurements, the sample temperature is modulated sinusoidally about a constant ramp so that the temperature T at time t is

$$T = T_o + rt + A\sin(\omega t) \qquad (1)$$

where T_o is the initial (or starting) temperature, r is the heating rate (which may also be a cooling ramp, q), A is the amplitude of the temperature modulation, $\omega = 2\pi/P$ is the angular frequency of modulation and P is the modulation period. It should be emphasized that Eq. (1) is a simplified statement of the fact that the cell has reached a steady state operation and that the initial temperature transients have died out. The resulting instantaneous heating rate dT/dt therefore varies sinusoidally about the average heating rate r and is given by

$$dT/dt = r + A\omega\sin(\omega t) \qquad (2)$$

At any time, the apparatus measures the sample temperature and the amplitude of the instantaneous heat flow and then by carrying out a suitable Fourier deconvolution of the measured quantities it determines two quantities (which have been termed by *TA Instruments*):

Reversing heat flow (RHF)
Nonreversing heat flow (NHF)

Fourier transforms are made on one full cycle of temperature variation which means that the average quantities refer to moving averages. The average heat flow which corresponds to the average heating rate (r) is called the *total heat flow* (HF). Total heat flow is the only quantity that is available and hence it is the only quantity that is always measured in conventional DSC experiments. TMDSC determines the heat capacity using the magnitudes of heat flow and heating rate obtained by averaging over one full temperature cycle. Suppose that Q' is the rate of heat flow. If triangular brackets are used for averages over one period P, then $\langle Q' \rangle$ is the average heat flow per temperature cycle. The heat capacity per cycle is then calculated from

$$m_s C_P = \langle \text{Heat flow} \rangle \,/\, \langle \text{Heating rate} \rangle \tag{3}$$

where m_s is the mass of the sample. This C_P has been called the *reversing heat capacity*, though Schawe has defined as the *complex heat capacity* [19]. The reversing in this context refers to a heat flow that is reversing over the time scale of the modulation period. Furthermore, it is assumed that C_P is constant, that is, it does not change with time or temperature over the modulation period. The *reversing heat flow* is then obtained by

$$\text{RHF} = C_P \langle dT/dt \rangle \tag{4}$$

The nonreversing heat flow (NHF) is the difference between the total heat flow and the reversing heat flow and represents heat flow due to a kinetically hindered process such as crystallization. There are a few subtle issues in the above condensed discussion. First is that the method requires several temperature cycles during a phase transition to obtain RHF and NHF components which sets certain requirements on r, A and ω. The second is that the phase difference between the heat flow and the heating rate oscillations is assumed to be small as it would be the case through a glass transition region or crystallization; but not through a melting process. (A semiquantitative description and discussion of TMDSC have been given in reference [20].)

At present there is considerable scientific interest in applying TMDSC measurements to the study of glass transformation kinetics in glasses and polymers. The interpretation of TMDSC measurements in the glass transition regions has been recently discussed and reviewed by Hutchinson and Montserrat [21-23]. In Section 4 we present results where TMDSC technique has been applied to a number of glasses and polymers to show the usefulness of TMDSC in T_g measurements.

3 Experimental procedure

Thermal analysis experiments were performed on a temperature-modulated DSC apparatus (TA Instruments Inc. DSC 2910 system) using a liquid nitrogen cooling accessory. With this system both heating and cooling scans in the modulated (TMDSC) and in non-modulated (conventional DSC) regime were made. The instrument was calibrated by multiple-point calibration. We used two standards - elemental gallium and indium (Ga and In). Calibration standards were chosen with melting points close to the glass transitions observed for the glasses and polymers reported in this paper. The instrument was also calibrated for specific heat capacity measurements (C_p) using a standard sample of sapphire.

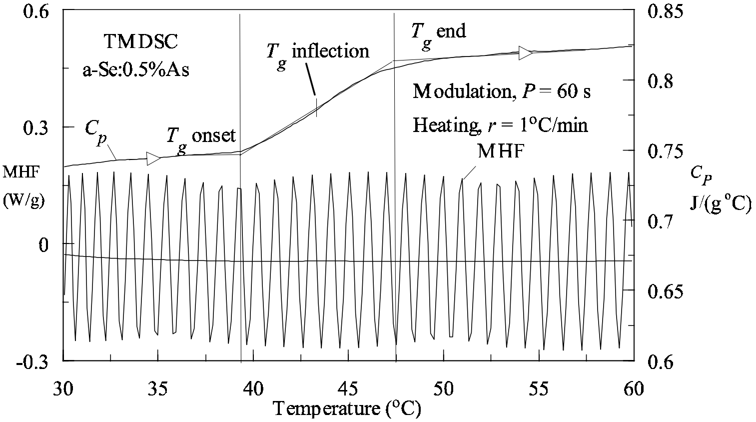

Figure 1: A typical TMDSC scan.

It is important to emphasize that ideally the underlying heating rate in TMDSC experiments should be as small as possible. In this way we can separate the conventional DSC experiment, which also takes place during TMDSC measurements, from the dynamic, frequency controlled TMDSC experiment. The oscillation amplitude A in the TMDSC was typically ±1.0 °C for all modulation modes, unless otherwise stated. We observed that TMDSC measurements did not depend on the modulation amplitude for $A = \pm 0.2$ °C to $A = \pm 5$ °C as reported previously [10]. The oscillation period P was chosen to ensure that there were at least four full modulations within the halfwidth of the temperature transition, that is, a minimum of 8 oscillations over the T_g range as it can be seen in one of the worst case examples as shown in Figures 1 for a-Se:0.5%As which has a particularly narrow glass transition range, and required a $P = 60$ s. Figure 1 shows the modulated heat flow (MHF) signal and C_P versus temperature results for $A = \pm 1$ °C. The reversing heat flow, RHF, and the nonreversing heat flow, NHF, were deconvoluted from the modulated heat flow, MHF, in both the heating and cooling scans along with the underlying or total TMDSC heat flow, THF, and the heat flow, HF, from conventional DSC. The specific complex heat capacity (mass normalized heat capacity), C_p, was obtained from the RHF. The difference between the average specific capacity, as determined from the DSC HF, and the complex heat capacity, as determined from TMDSC RHF, in the T_g region is substantial as shown by Hutchinson [23].

4 Results and applications

4.1 Glasses: chalcogenides

4.1.1 Stabilized amorphous selenium: a-Se:0.5%As

Stabilized amorphous selenium (a-Se alloyed with 0.5%As) is a prototype inorganic polymer-type glass that exhibits glass aging that occurs over the time scale of hundreds of hours at room temperature, and thus allows the aging affects on the T_g measurements to be studied over a reasonable time scale. Figure 2 shows the dependence of T_g as measured by TMDSC and DSC on the aging period. TMDSC T_g was from the infection point, and the DSC T_g was from the usual endothermic T_g peak onset definition that is common in the literature. The sample was first heated at 20 °C/min to a temperature above T_g but below the crystallization temperature, *e.g.* 70 – 80 °C, equilibrated, and then cooled down to room temperature at 5 °C/min. It was then aged at room temperature for the aging times shown in Figure 2. The underlying heating scan was 1 °C/min in both techniques. It is clear that over an aging time of 100 hours. TMDSC-T_g changes by about 1 °C whereas DSC's T_g changes by about 5 °C. The endothermic relaxation that usually occurs during heating through the glass transition normally becomes larger as the glass is aged longer. This endothermic relaxation peak in the conventional DSC makes the T_g determination based on the onset definition highly sensitive on aging. Most significantly, though, there is a genuine relaxation effect on the T_g itself in DSC heating scans, because the T_g definition in the DSC case depends on the "starting structure", the initial enthalpy, $H(T_o,t)$, which changes with aging (time).

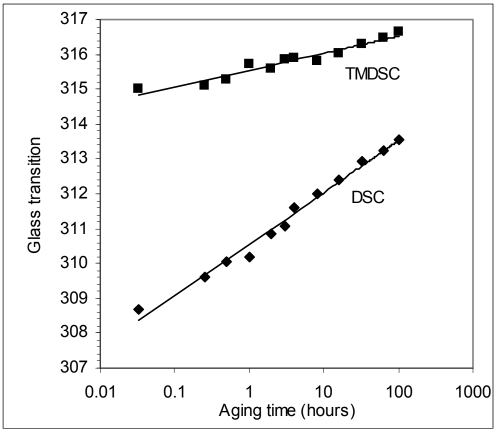

Figure 2: T_g dependence on aging for DSC and TMDSC.

4.1.2 Arsenic triselenide (As_2Se_3)

Glass transition temperature of As_2Se_3 glass as observed in DSC scans is well known to depend on thermal history; see, for example, [24]. The classical well known example is the fact that the T_g value determined by DSC under a heating scan at a given rate r is different than that determined under a cooling scan at a rate $q = r$. Further, T_g determined in a DSC heating scan also depends on aging. Figure 3 shows the clear difference between T_g values observed in heating and cooling scans in DSC experiments; T_g values from T_g-onset and T_g-inflection definitions are different in heating and cooling scans. In contrast, T_g values determined in TMDSC scans, whether by a heating or cooling scan, as shown in Figure 4, are the same for a given modulation period P, within experimental errors. T_g depends only on the modulation frequency ω (= $2\pi/P$) provided that the underlying heating or cooling scan is "slow"; usually less than 1 °C/min.

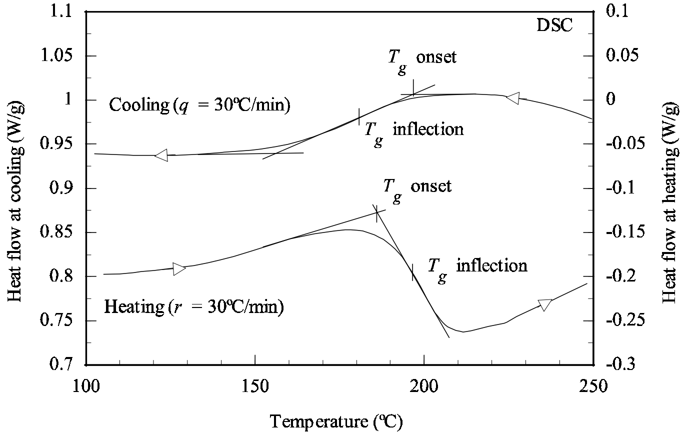

Figure 3: Typical DSC heating and cooling scans on As_2Se_3 glass.

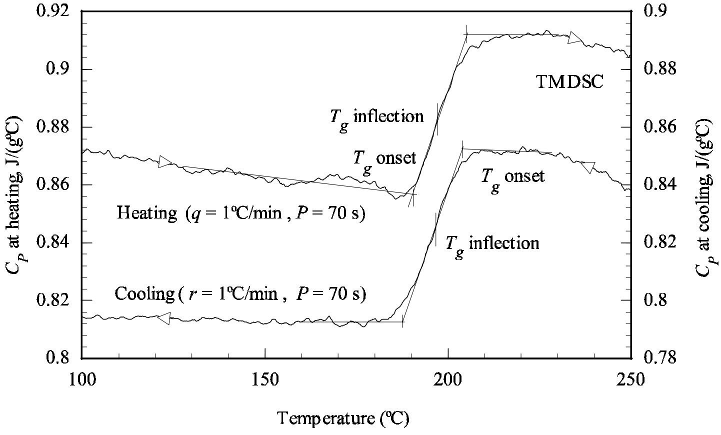

Figure 4: Typical TMDSC heating and cooling scans on As_2Se_3 glass.

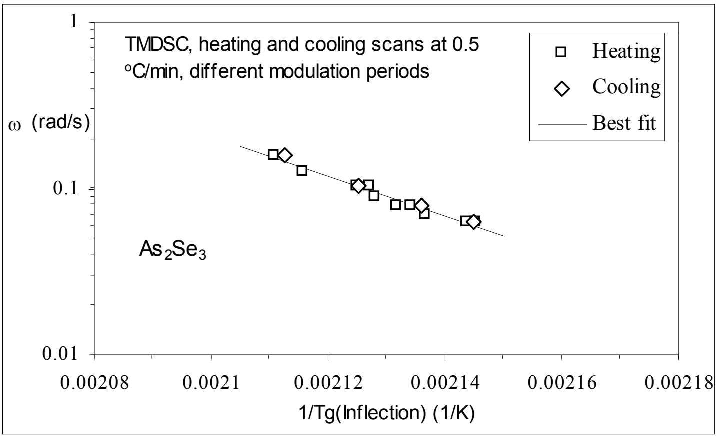

Figure 5: Semilogarithmic plot of the angular modulation frequency ω vs. reciprocal T_g (inflection point) for heating and cooling scans.

We have also examined the effect of A on the T_g measurements, and found that A values up to ±5 °C did not affect the T_g measurement. Thus, TMDSC experiments are in the linear region of the measurements and are not affected by nonlinearities as discussed by Schick et al. [25]. The T_g measurement in the TMDSC experiments represents the relaxation processes associated with the temperature modulation and not the underlying heating rate as in the conventional DSC. For example, T_g in TMDSC represents a temperature where the relaxation time τ is comparable with the modulation period P. Above T_g, $\tau << P$ and below T_g, $\tau >> P$, and in the T_g region $\tau \sim P$. As P (or ω) is varied, from experiment to experiment, different values of τ satisfy $\tau \sim P$ and hence T_g depends on ω as shown in Figure 5. It is possible to analyze the lnω vs. $1/T_g$ plots in Figure 5 in terms of a kinetic interpretation based on relaxation time τ that depends on the temperature and structure, usually expressed in a so-called Tool-Narayanaswamy-Moynihan relaxation time form (see [10] or As_2Se_3). τ for As_2Se_3 glass, as expected, is proportional to the viscosity of the glass [10].

4.2 Polymers

4.2.1 Polyethylene Terephthalate (PET)

PET samples for the TMDSC measurements were on samples taken from an amorphous sheet (2 mm in thickness) obtained from Goodfellow (England). The conventional DSC heating and cooling scans are sown in Figure 7 in which two heating schedules, labelled HA and HB, with different thermal histories are shown to highlight the dependence of T_g on the thermal history. In HA, the sample is equilibrated at 0 °C and then heated at 10 °C/min and in HB it is equilibrated at 50 °C, and then heated at 10 °C/min; the two T_gs from onset are different. HA exhibits an enthalpic relaxation. The TMDSC results are shown in

Figure 8 where it can be seen that C_P vs. temperature scans in TMDSC are the same whether the experiment is a heating or a cooling scan, and hence independent of the initial state.

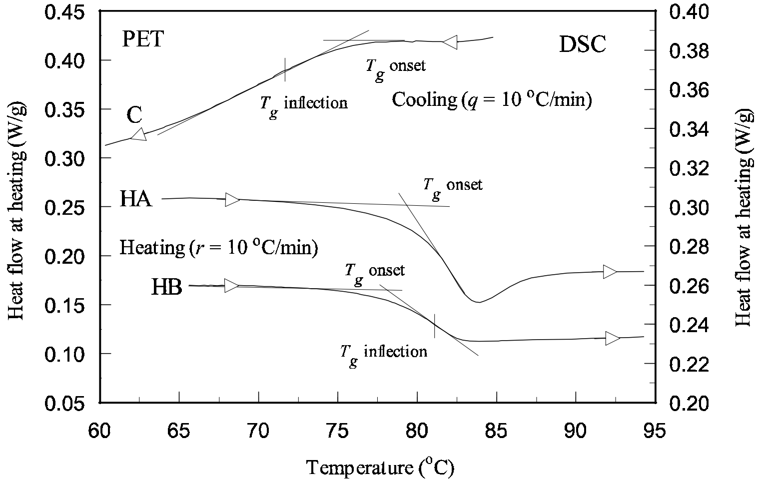

Figure 7: DSC T_g measurements on PET. (C: cooling; HA and HB: heating.)

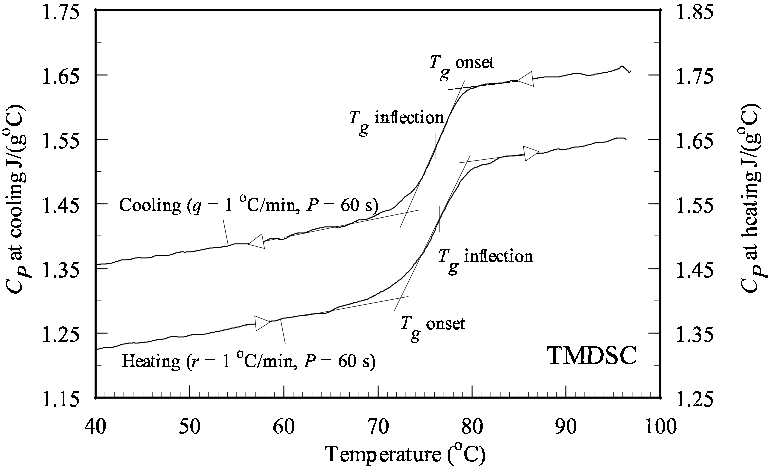

Figure 8: TMDSC T_g measurements on PET.

Table 1 provides a useful summary of the T_g measurements from thermal analysis (TA) using DSC and TMDSC experiments. T_g(I), corresponding to the inflection point has 10 °C difference between heating and cooling DSC scans with $r = q$, but the difference is less than 0.5 °C in the case of TMDSC heating and cooling scans. Clearly, the TMDSC provides a distinct advantage in providing T_g values that are independent of the underlying heating or cooling rate, and independent of the starting point of the scan, that is, thermal history.

Table 1: PET. Comparison of T_g measurements. T_g(I) = T_g at inflection point; T_g(O) = T_g at onset; r = heating and q = cooling, both in °C/min.

T_g	T_g(I)	T_g(I)	T_g(I)	T_g(I)	T_g(O) HB	T_g(O) HA	T_g(O)
TA	TMDSC $r = 1$	TMDSC $q = 1$	DSC $r = 10$	DSC $q = 10$	DSC $r = 10$	DSC $r = 10$	DSC $q = 10$
°C	76.16	76.05	81.41	71.51	77.80	80.73	75.29

4.2.2 Polycarbonate (PC)

Polycarbonate samples were taken from an amorphous sheet obtained from Goodfellow. Both the DSC and TMDSC experiments were similar to those on PET in terms of experimental conditions (r, q, P and A). Figure 9 shows the TMDSC results obtained with heating and cooling scans where it is apparent that the two C_P vs. T characteristics through glass transition are almost identical; the same T_g values as obtained from the inflection point, and independent of the starting state. Table 2 provides a useful summary of the T_g measurements from DSC and TMDSC experiments. T_g(I), corresponding to the inflection point, has 12 °C difference between heating and cooling DSC scans with $r = q$, but the difference is less than 0.25 °C in the case of TMDSC heating and cooling scans.

Table 2: PC. Comparison of T_g measurements. T_g(I) = T_g at inflection point; T_g(O) = T_g at onset; r = heating and q = cooling, both in °C/min

T_g	T_g(I)	T_g(I)	T_g(I)	T_g(I)	T_g(O)	T_g(O)
TA	TMDSC $r = 1$	TMDSC $q = 10$	DSC $r = 10$	DSC $q = 10$	DSC $r = 10$	DSC $q = 10$
°C	149.47	149.23	154.00	142.12	149.23	150.11

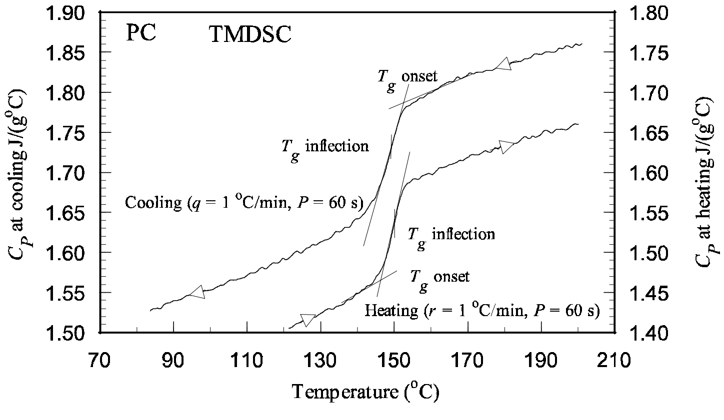

Figure 9: TMDSC T_g measurements on polycarbonate.

5 Summary and conclusions

Temperature modulated differential scanning calorimetry (TMDSC) experiments provide a more meaningful and reproducible characterization of the glass transition characteristics of glasses and polymers than the conventional DSC as demonstrated by its applications to chalcogenide glasses, PET and polycarbonate. T_g measurements by TMDSC show substantially reduced dependence on thermal history and aging. One of the fundamental reasons is that the experimental time scale in TMDSC experiments is well defined by the user set modulation period P, and the observed T_g corresponds to the temperature when the structural relaxation time $\tau \sim P$. In DSC experiments, on the other hand, the experimental time scale as determined by the underlying heating rate is ill-defined and leads to T_g observations that are particularly sensitive to thermal history and aging.

References

[1] Wunderlich, B., *Thermal Analysis*, Academic Press, Boston, MA, 1990.
[2] Reading, M., Elliott. D. and Hill, V.L., *J. Thermal Analysis,* **40,** 949, 1993.
[3] Reading, M., *Trends Poly. Sci* , **1**, 248, 1993.
[4] Reading, M., Luget, A., Wilson, R., *Thermochim. Acta*, **238,** 295, 1994.
[5] Sauerbrunn S., Thomas, L., *American Laboratory*, January 1995, p.19.
[6] Thomas, L., *NATAS Notes* (North American Thermal Analysis Society, Sacramento, CA,USA) **26,** 48, 1995.
[7] Jones, K.J., Kinshott, I. , Reading, M., Lacey, A.A., Nikopoulos, C., Pollosk, H.M., *Thermochim. Acta,* **304-305**, 187, 1997.
[8] Hassel B., *NATAS Notes* (North American Thermal Analysis Society, Sacramento, CA, USA) **26,** 54, 995.
[9] Wunderlich, B., Jin, Y., Boller, A., *Thermochim. Acta* **238,** 277, 1994.
[10] Kasap, S.O., Tonchev, D. *J. Mater. Res.* **16**, 2399, 2001.
[11] Tonchev, D., Kasap, S.O., *Mater. Sci. Eng.*, **A328**, 62, 2002
[12] Boller, A..,Schick, C., Wunderlich, B,, *Thermochim. Acta***,** **261**, 97, 1995.
[13] Wagner, T., Kasap, S.O., *Philos. Mag.* **B 74,** 667, 1996.
[14] Kasap, S.O., Wagner, T., Maeda, K., , *Jpn. J. Appl. Phys.* **35,** 1116, 1996.
[15] Wagner, T., Kasap, S.O., *J. Mater. Res.* **12,** 1892, 1997.
[16] Feng, X., Bresser, W.J., Boolchand P., *Phys. Rev. Lett.,* **78**, 4422, 1997.
[17] Boolchand, P., Feng, X. Bresser, W.J., Zhang, M., Goodman, B., *J. Non-Cryst. Solids* **222**, 137, 1997.
[18] Wagner, T., Kasap, S.O., Petkov, K., *J. Mater. Sci.,* **32,** 5889, 1997.
[19] Schawe, J.E.K., *Thermochim. Acta*, **260,** 1, 1996.
[20] Jian, Z., Inrie, C.T., Hutchinson J.M., *Thermochim. Acta*, **387**, 75, 2002.
[21] Hutchinson, J.M., Montserrat, S., *Thermochimica Acta,* **305**, 257, 1997.
[22] Hutchinson J.M., Montserrat, S. *J. Thermal Anal.,* **47**, 103, 1996.
[23] Hutchinson, J.M. *Thermochimica Acta,* **324**. 165, 1998.
[24] Kasap, S.O., Yannacopoulos, S., *Phys. Chem. Glasses*, **31**, 71, 1990.
[25] Schick, C., Merzlyakov, M., Hensel, A., *J. Chem Phys.* **111,** 2696, 1999.