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MDSC and DSC studies on sol–gel lithium triborate glass and glass-ceramics: a comparison

Corrado Tomasi[a,*], Piercarlo Mustarelli[a], Eliana Quartarone[a], Renzo Pepi[b]

[a] *C.S.T.E.-C.N.R. and Dipartimento di Chimica Fisica, Università di Pavia, Viale Taramelli 16, 27100 Pavia, Italy*
[b] *R Scientifica s.a.s., Via E. Curiel 12, 53034 Colle di Val d'Elsa (SI), Italy*

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Abstract

Glasses prepared following a sol–gel route must be thermally treated to evacuate solvent and organic radicals. They often undergo phase transitions in the same temperature range where the weight losses occur. When applied to these systems, conventional differential scanning calorimetry (DSC) may lead to deceiving interpretations. In this paper the transformations of a sol–gel lithium triborate glass, annealed up to 500°C, have been investigated by Modulated DSC (MDSC). We show how the reversing heat flow signal obtained by temperature modulation may give valuable information. Upon annealing, the system undergoes phase separation and partial devitrification to give crystalline lithium diborate. A careful comparison with the misleading conclusions offered by conventional DSC is performed. © 1997 Elsevier Science B.V.

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1. Introduction

Several inorganic and organic systems exhibit phase transitions or transformations whose thermal effects can easily be detected and separated by differential scanning calorimetry. However, some other complex systems undergo more than one reversible and/or irreversible transformation in the same temperature range. Among irreversible processes, moreover, one can distinguish thermal events with mass conservation, such as cold crystallisation of polymers and glasses, and others accompanied by a partial mass loss, for instance release of solvent or gas evolutions.

It should be pointed out, in addition, that DSC behaves like a destructive technique when the sample undergoes permanent modifications during the heating run. For metastable and unstable materials, the sample deterioration entails that only single DSC runs on fresh specimens may supply significative data. Further, great care must be devoted to evaluate the influence of kinetic parameters (mostly the heating rate) on the attainable experimental resolution. Modulated DSC (MDSC) [1] is well suited to investigate systems in which reversible and irreversible phase transformations occur, whereas conventional DSC can hardly provide useful information.

Inorganic (or organic–inorganic) materials prepared by sol–gel synthesis from organic precursors are typical systems in which weight losses and structural rearrangements may easily take place over the same temperature range [2]. Alkali borate glasses, in particular, are of interest for applications in electrochemi-

*Corresponding author. Tel: +382-507 214

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cal devices and as coatings in electronic industry. When prepared by sol–gel, they show physico–chemical properties which usually differ from those of the same glasses obtained by quenching a melt [3].

Generally speaking, sol–gel synthesis presents a number of advantages: it allows to prepare glasses as a fine powder with high degree of purity, homogeneity, and solubility in organic solvents. Nevertheless, the organic residues due to the precursors employed in the preparation are often difficult to remove, and require complex thermal treatments. The release of volatile compounds may also be accompanied by a partial structural reordering. The related thermal effects broadcast over a wide range of temperature and, sometimes, can mask the glass transition.

In this paper we investigate the thermal properties of lithium triborate glass prepared via sol–gel, both by conventional and modulated DSC. Our first aim is to address the potential of MDSC in studying sol–gel prepared glasses. In particular, attention is focused on some misleading results arising from a conventional DSC analysis and on the related benefits which are provided by MDSC. Different mathematical approaches have been recently proposed in order to interpret the MDSC experimental data [4,5]; in the present work we will follow the notation introduced by Reading [6], which is employed in the analysis package offered by TA Instruments.

2. Experimental

2.1. Sample Preparation

Lithium triborate was prepared via sol–gel by a two step procedure [7]. The first step consisted in adding 0.090 moles of trimethoxyboroxine to a solution of 0.085 moles of lithium methoxide in 32 ml of absolute methanol (<5 ppm H_2O, Aldrich, 99%), and stirring the sol for 1 h under dry atmosphere (≈38 ppm V. of H_2O). The second step concerned the sol hydrolysis at room temperature and in ambient atmosphere (70% relative humidity) for 48 h. In order to remove the residual solvent, the obtained gel was first dried at rt in air and then kept at 90°C for 24 h under vacuum. The product, in form of glassy powder, is nominally composed by six-membered B–O rings (boroxols), each retaining 2 methoxy groups which can be removed by thermal treatment. Finally, different aliquots of glass were annealed at 100°C, 200°C, 300°C, 400°C, and 500°C for 6 h. For the sake of simplicity the samples will be called G-100,..., G-500 depending on the annealing temperature.

2.2. Apparatus

A DSC 910 and a MDSC 2910, equipped with a 2000 Thermal Analyst (TA Instruments, USA), were used for all sample measurements. MDSC was fitted out with an auto-fill liquid nitrogen cooling accessory (LNCA). A nitrogen gas flow of 30 ml min^{-1} was used as a purge gas. DSC measurements were run at 5°C min^{-1}. The MDSC ones were also performed at a heating rate of 5°C min^{-1} by imposing a temperature modulation with a period of 40 s and an amplitude of ±0.5°C. The relatively high heating rate has been chosen to match the operating conditions of our DSC. On the other hand, our MDSC preliminary results on melt-quenched borate glasses showed no remarkable differences in the T_g region between runs at 2°C min^{-1} and 5°C min^{-1} (work in preparation). All samples were kept in desiccator and crimped in standard aluminium pans just before measurements.

3. Results and Discussion

Fig. 1 shows several conventional DSC runs performed on the samples G-100 (a), G-200 (b), G-300 (c), G-400 (d), and G-500 (e). Curve (a) presents a single broad endothermic peak, which is probably due to water and methanol release [8], followed by some thermal effects above 450°C. A similar behaviour is given by the sample treated at 200°C (curve (b)), whose thermogram displays a double peak profile in the range 100°C –300°C. In both cases the thermal events take place at a temperature lower than the annealing one: in particular, curve (b) shows its first endotherm well below 150°C.

Since the samples were carefully held in a desiccator after the end of the annealing, this result calls for a high rate of moisture absorption. In order to check this assumption, the annealing procedure were simulated in the DSC cell, under N_2 atmosphere. An aliquot of the glass as prepared was kept at 200°C for 30 min,

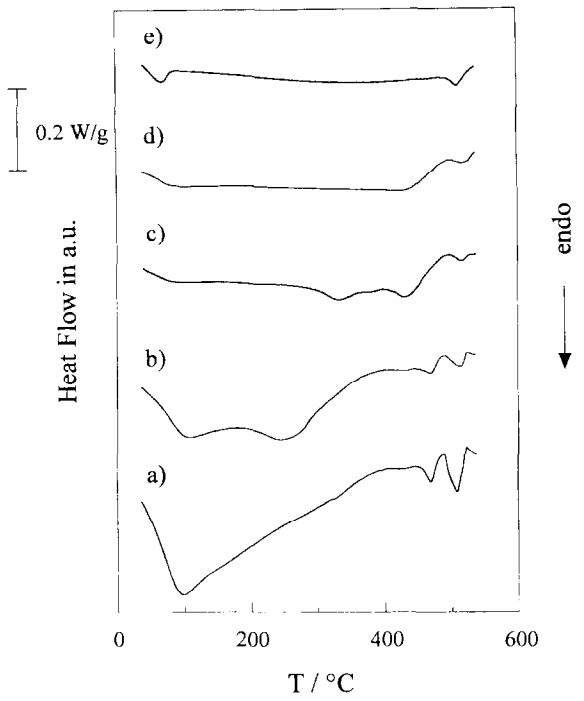

Fig. 1. DSC scans of the sol–gel glass annealed at different temperatures for 6 h: SG-100 (a), G-200 (b), G-300 (c), G-400 (d), and G-500 (e).

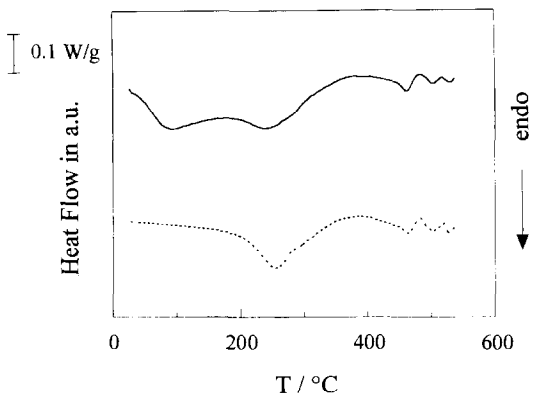

Fig. 2. Comparison between the DSC curve of sample G-200 (solid line), and of a fresh sample kept in the DSC cell for 30 min at 200°C under N_2 atmosphere (dashed line).

then the DSC was allowed to thermalise and the measuring run was started. Fig. 2 shows the comparison between the measurements performed on sample G-200 (curve a), and on the sample treated in DSC (curve b). The lack of the first peak in curve (b) confirms the presence of moisture in the sample G-200.

Fig. 1c displays no endotherms for $T<250$°C, whereas two abrupt changes of the baseline slope and an exothermic complex profile (possibly two peaks) appear at higher temperatures. This may suggest that a phase separation occurred during the annealing at 300°C. A possibility is to relate the first slope change to the glass transition, T_g, of vitreous B_2O_3, which is given in literature [9], near ~270°C, and the second slope change to the transition of a remaining glass phase of unknown composition. We recall that lithium borate glasses with an alkali oxide fraction, x, ranging from 0.2 to 0.33 display the glass transition in the interval 400–500°C [10]. The exothermic peaks could be assigned to the crystallisation of the two glassy phases. Incidentally, we note that phase separation seems to make the glass more resistant against moisture absorption (see Fig. 2).

The analysis of curve (d) puts into evidence that no changes in baseline slope are present, but for an exothermic profile in the range between 450°C and 550°C. A first puzzling question arises about the absence of glass transitions corresponding to the presumed crystallisation peaks which are still observable.

Finally, curve (e) is nearly flat up to ~500°C, where an endothermic baseline change is followed by an incipient exothermic phenomenon. It is possible to suppose that the annealing performed at this temperature gives origin to a single glassy phase that crystallises just above its T_g.

Our X-ray diffraction data clearly showed the progressive growth of a crystalline phase (lithium diborate, $Li_2B_4O_7$) in the samples G-300, G-400 and G-500 (see Fig. 3). On the contrary, no peaks were observed in samples G-100 and G-200. It is of evidence that neither the DSC curves by themselves offer clear trends, nor a simple comparison with X-ray diffraction patterns allows to understand the complex transformations of the sol–gel glass when subjected to different thermal treatments. A significative help in understanding the relationships among structural rearrangements, phase crystallisations and weight losses may come from Modulated DSC.

Compared to conventional DSC, MDSC produces two additional signals, reversing and non-reversing heat flows, which let to separate thermodynamically reversible and irreversible transformations, at least in

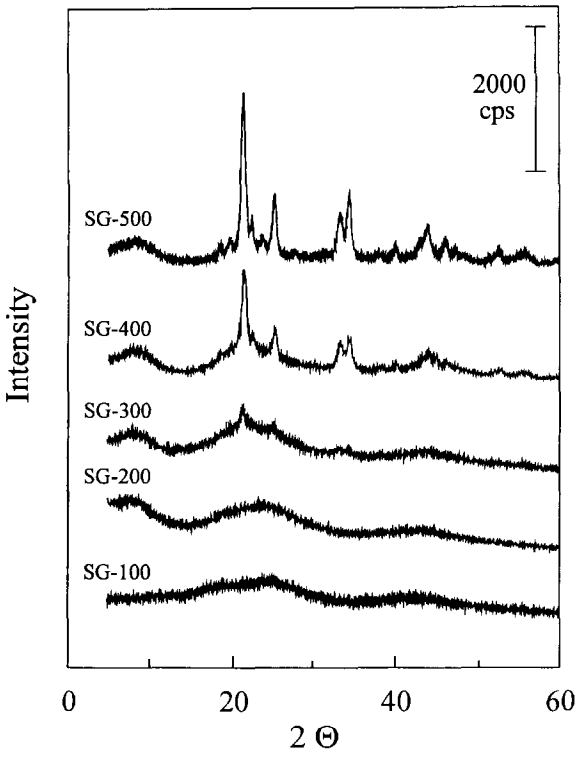

Fig. 3. X-ray diffractograms of the samples after annealing at different temperatures.

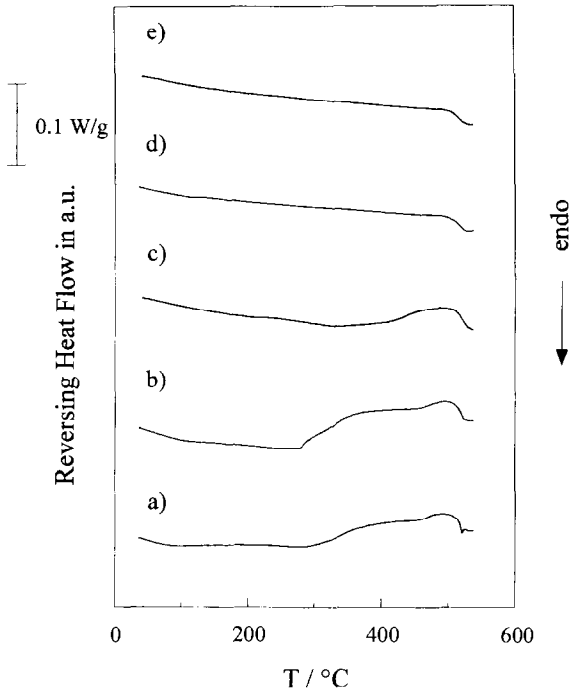

Fig. 4. MDSC reversing signal of the sol–gel glass annealed at different temperatures for 6 h : SG-100 (a), G-200 (b), G-300 (c), G-400 (d), and G-500 (e).

the "time scale" of the experimental parameters [11]. Reversing signal is related to the sample heat capacity and, hence, does not only provide information about reversible phenomena, but also allows to detect irreversible events leading to heat capacity changes. For instance, when a weight loss occurs, the amount of heat required to increase the sample temperature of 1°C decreases and a smaller signal is recorded, even if the true C_p is constant. Further, when amorphous samples undergo cold crystallisation, the specific heat capacity decreases because of the reduced configurational entropy of the crystalline state with respect to the vitreous one.

Fig. 4 shows the reversing component of the heat flow for samples G-100 (a), G-200 (b), G-300 (c), G-400 (d), and G-500 (e). The reversing heat flow of G-100 is almost flat in the region below 300°C. Since our thermogravimetric measurements show that sample undergoes a relevant weight loss due to moisture and methanol release [8], we can state that the constant virtual C_p is the result of two contrasting effects: sample mass reduction and actual C_p augmentation. Similar considerations hold for sample G-200. Both (a) and (b) curves present a slope change at 300°C, corresponding to a decrease of the sample heat capacity. This can be explained by considering the partial crystallisation of the specimen, that takes place near 300°C, as evidenced by XRD.

A careful analysis of curve (c) above 300°C reveals a gradual reduction of C_p that can be related both to the residual crystallisation and to the loss of methoxy groups still bonded to the boroxol rings. In contrast with conventional DSC results, MDSC reversing signal does not show endothermic baseline changes in the range between 250°C and 450°C. This confirms that the DSC data may be strongly misleading, in the sense that the observed baseline steps are evidently due to an overlap of the irreversible processes above described.

Both (d) and (e) curves exhibit no remarkable baseline changes up to 450°C, as expected for samples annealed at 400°C and 500°C. The well-evident tran-

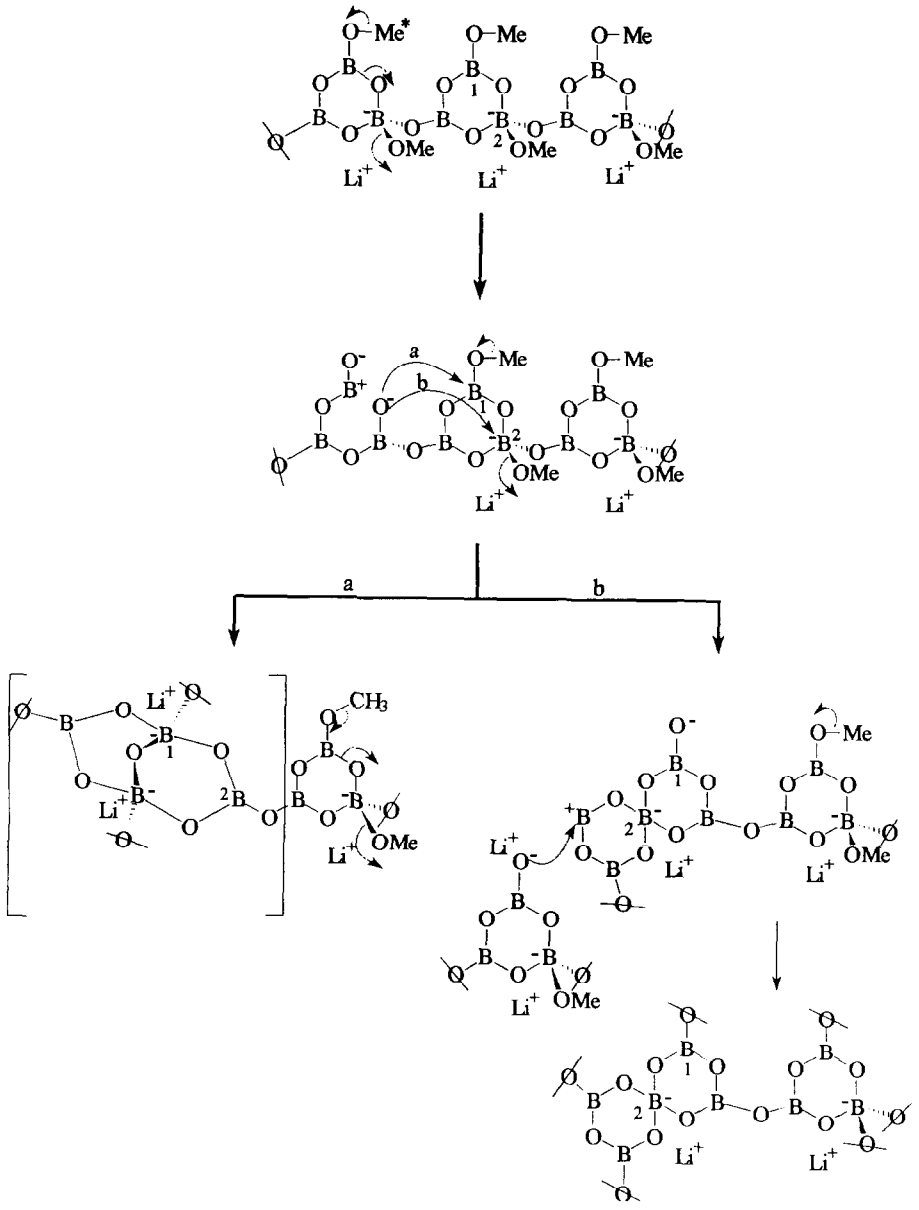

Fig. 5. Pictorial representation of thermally-induced phase separation with formation of crystalline lithium diborate (a), and glassy lithium tetraborate (b).

sition steps appearing in both the curves at 500°C represent the glass transition of a single amorphous phase, whose nature cannot be simply investigated by thermal analysis. In fact, XRD patterns clearly show the growth of crystalline $Li_2B_4O_7$, i.e. of a phase whose composition differs from the starting one. On this basis only, and in absence of reliable quantitative data on the crystallised fraction, we are not able to state what is the stoichiometry of the remaining glassy phase. A decisive help may come from spectroscopic techniques such as NMR and IR: in a previous work we have demonstrated that our data are in agreement

with the model depicted in Fig. 5 [2], which shows how the bulk may reorganise itself to give a glass harder (= more connected) than the starting one.

We stress that the pictorial representation of Fig. 5 is only one of the possibilities fitting our overall findings, although the T_g behaviour well supports the formation of a glassy phase with x≅ 0.2 (lithium tetraborate). The advantages offered by MDSC, however, are well evident: in this case, the reversing signal "removes" the residual crystallisation and allows to highlight the glass transition, whereas the complexity of the DSC curves may lead to deceiving interpretations.

4. Conclusions

The utility of MDSC in studying samples that undergo weight losses and both reversible and irreversible structural rearrangements, in the same temperature range, has been demonstrated. The task to separate reversible (in the experimental timescale) phenomena from the irreversible ones may give a substantial help in understanding temperature-driven transformations in complex systems such as supramolecular structures, clathrates and sol–gels. An educated choice of complementary spectroscopic and diffractometric techniques is however needed.

In this case, conventional DSC analysis depicted the formation of one or more glassy phases depending on the annealing temperature. The MDSC reversing signal suggests the more reliable idea of a single phase separation taking place slightly above 250°C, that leads to the formation of a crystal and a residual glassy phase, whose composition does not ever abruptly change with the annealing.

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