JOURNAL OF MATERIALS SCIENCE 29 (1994) 1330–1335

X-ray structural investigation on sodium borate samples prepared by the sol–gel method

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Amorphous samples of sodium and lithium di- and triborate were prepared by the sol–gel method. The structural characterization of sodium borate glasses was carried out by X-ray diffraction and the radial curves obtained were compared with those determined for glasses of equal composition prepared by melt quenching. The small differences observed do not reveal any systematicity; evaluation of the errors involved suggests that they are within the limits of the experimental uncertainty.

1. Introduction

Borate glasses containing alkaline or silver oxides have been investigated over the past decades [1–5] on account of their ionic conductivity and their potential use in the field of solid-state batteries. In these cases, boron oxide was often mixed to other network formers, mostly SiO_2, in order to obtain materials with low melting temperatures and good chemical durability. Apart from technological aspects, the ease of preparation of borate vitreous samples in a wide range of compositions has suggested the use of borate glass as model system for investigations on basic aspects of the vitreous state [6]. Some workers have exploited this possibility with the purpose of verifying whether glasses of equal compositions but quenched at different rates would show different structural characteristics to X-ray diffraction determinations [7]. The answer to this question is important with regard to model interpretation of amorphous structures. If the short- and medium-range order appear to be unaffected by the thermal history, and only to depend on composition, then one structural model would be able to describe the amorphous system, however obtained. If not, the modellistic approach to the amorphous structure has a very limited validity. In the case mentioned above, we investigated the structure of several alkaline borate glasses prepared by quenching the melts with rates about three orders of magnitude apart. It was found that the short- and medium-range structures were not affected by the different thermal treatments. Continuing along the same lines, we now want to compare the structure of glasses of equal composition prepared by totally different routes. As known, vitreous materials can now be obtained following several procedures. We chose the sol–gel method which has proved to be quite versatile as regards both systems and compositions [8]. In its more common form, it is based on hydrolysis and condensation reactions between metalorganic precursors in organic solution, which in the end give rise to amorphous networks. Removal of solvent and of organic residuals generally requires mild thermal treatments, while further thermal processing is often necessary to obtain the final product [9].

In this paper we present an X-ray diffraction investigation on sodium borate glasses prepared by the sol–gel method. For calculation requirements, borate samples of lithium were also prepared by the same route. The sample nominal composition was Me_2O–nB_2O_3. where Me is the alkaline metal (sodium or lithium) and $n = 2$ or 3. With reference to the composition, the samples are named BONA2, BONA3, BOLI2 and BOLI3, followed by the suffix SG for sol–gel. To our knowledge, only one paper describing the preparation via the sol–gel route of sodium borate glasses of composition Na_2O–$4B_2O_3$ has been published so far [10], while several cases of lithium borate preparations have been reported in the literature [11–15].

Step by step, the structural analysis of these samples is compared with the results, reported in detail elsewhere [7], obtained for melted glasses of the same nominal composition; in this paper, these are labelled with the same acronyms already mentioned for sol–gel materials, followed by suffixes FQ for fast-quenched and SQ for slow-quenched glasses.

2. Experimental procedure

Tri-*n*-butyl borate, $B(OBu)_3$, and sodium and lithium methoxides, $NaOCH_3$ and $LiOCH_3$, were used as starting materials, with anhydrous methanol as solvent. Methanol solutions of the alkaline methoxides of $1.11\ mol\,l^{-1}$ concentration were prepared in a dry nitrogen atmosphere. These solutions were then mixed with butyl borate in teflon beakers under stirring, in such amounts as to give about the same quantity of each final product. The beakers were then covered with filter paper and left in an ambient atmosphere for hydrolysis. The gels were formed in about 2 days at room temperature. The drying step also took place under the same conditions. When the weight of the dried gels was reduced to about three times that of the expected final products, the samples were subjected to heat treatment in a dry oxygen flow to eliminate as much as possible of the organic residuals. The step sequence was the following: 24 h at 40, 60, 80, 100, 200, 300 °C and 400 °C, 3 days at 450 °C and finally 24 h at 500 °C. The heat treatment of the samples with lithium was stopped at 400 °C because of their tendency to crystallize at higher temperature [11]. At this point, all the samples, which were in the form of small irregular pieces light grey (sodium borate) or light brown (lithium borate) in colour because of the organic residuals, were put in a desiccator to avoid attack from atmospheric moisture.

The above sequence follows closely the experimental procedure used by Tohge and Mackenzie [10]. However, not all the preparations proceeded without problems. The gel formation appeared to be the most delicate step for obtaining amorphous materials. The necessary presence of humidity in the atmosphere caused the formation of non-negligible quantities of small crystals with needle shape, which grew preferentially on the filter paper used as a cover. These crystals, easily recognized as boric acid, did not influence the gel below; rather, their formation reduced in the solution the concentration of boron available for the vitreous network, thus giving rise in the end to samples of composition different from that expected. The presence of other unknown crystalline forms on the surface of the gels was also detected in some cases, but the small humps they caused in the X-ray spectra tended to disappear with thermal treatments. Sharp crystalline peaks were instead obtained in the spectra of sodium borate gels when a few drops of HNO_3 or of water were added to the starting solution, so that these materials were not processed further. The hydration conditions also proved to be very important in the preparation of lithium borate samples: here, amorphous materials were readily obtained with an atmospheric humidity of about 30%, while a saturated atmosphere produced good examples of syneresis [9, 16], but the gels, after mild thermal treatment, were shown to have crystallized completely.

The composition of the amorphous samples was carefully determined. The content of the alkaline oxide was obtained by acid–base titration. The amount of boron was determined by hydrolysing the borate to H_3BO_3. As the boric acid is too weak for direct titration, the solution was then treated with mannitol to form a mannito–boric complex ($pk_A \approx 4$), which in turn was titrated by potentiometry. The small amount of carbon present in every sample was calculated by the difference. As expected, in all cases the analytical results showed loss of boron. In Table I batch and actual compositions are given, together with the apparent densities (solid and closed pores) of the samples, as determined using a helium stereopicnometer. These values are different from those obtained for the corresponding melt-formed samples (about 2.34 $\mathrm{g\,cm^{-3}}$ was, in fact, obtained for BONA2 and about 2.24 $\mathrm{g\,cm^{-3}}$ for BONA3 [7]), probably indicating that the porosity of sol–gel samples is strongly affected by preparation details [9].

The structure of the glasses was investigated by X-ray diffraction (XRD), which is particularly suitable for studying the short-range order [2, 17] and also permits a general view of medium-range interactions.

The diffraction experiments were performed in a nitrogen flow and at room temperature. Diffraction data were collected by a θ–2θ diffractometer Siemens D500 equipped with a graphite monochromator on the diffracted beam; using $\mathrm{Mo}K_\alpha$ radiation and a step-scan mode, a number of counts ranging from 80 000–200 000 were collected at each pre-set point in the angular range $\theta = 2°$–$70°$, corresponding to the s range $s_{\min} = 6$–$165\ \mathrm{nm^{-1}}$ ($s = 4\pi\sin\theta/\lambda$, where θ is half the scattering angle and λ is the wavelength).

The observed intensities were corrected for background, absorption and polarization [18]. As a large portion of incoherent radiation was still present in the diffracted intensities, and considering that real peaks at low r were expected in the radial curves due to the shortest B–O distances, the method proposed by Habenschuss and Spedding [19, 20] was used for normalization, because it takes the incoherent contribution into account and also minimizes spurious ripples in the low r region.

From the normalized intensities, I_{eu}, the structure functions were obtained according to

$$i(s) = I_{\mathrm{eu}} - \sum_{i=1}^{m} n_i f_i^2(s) \qquad (1)$$

and the radial distribution functions, $D(r)$, were then evaluated by a Fourier transformation

$$D(r) = 4\pi r^2 \rho_0 + 2r/\pi \int_{s_{\min}}^{s_{\max}} s i(s) M(s) \sin(sr)\,\mathrm{d}s \qquad (2)$$

where n_i are the stoichiometric coefficients of the assumed unit containing m kinds of atoms; f_i is the scattering factor, ρ_0 is the average electronic number density, $M(s)$ is a modification function of the form $\{[\sum n_i f_i(0)]^2/[\sum n_i f_i(s)]^2\}\exp(-ks^2)$, ($k = 5\times10^{-5}$ $\mathrm{nm^2}$).

TABLE I Density (g/cm³), batch and actual compositions (mol %) of the glasses investigated; n indicates the actual ratio B_2O_3/Me_2O

Sample	Density ($\mathrm{g\,cm^{-3}}$)	B_2O_3		Na_2O		Li_2O		C		
		Batch	Actual	Batch	Actual	Batch	Actual	Batch	Actual	n
BONA2SG	1.79(1)	75	61(3)	25	25(1)	–	–	–	13(4)	2.4
BONA3SG	2.08(1)	80	71(3)	20	22(1)	–	–	–	7(4)	3.2
BOLI2SG	2.05(1)	75	55(2)	–	–	25	23(1)	–	21(3)	2.4
BOLI3SG	2.10(1)	80	66(3)	–	–	20	22(1)	–	12(4)	3.0

3. Results

Figs 1 and 2 show the structure functions, $si(s)$, and the radial functions, $D(r)$, of BONA samples obtained by the sol–gel method. These curves indicate that the samples are amorphous.

In the same figures, functions obtained for melt-quenched samples of similar composition and prepared using two different quenching rates are also reported [7]. The figures show clearly the close similarity of the structures of sodium borate glasses obtained by such different routes. All the peaks describing the borate vitreous network and the alkaline ion interactions are present in the radial functions; the small discrepancies exhibited do not seem to follow any pattern hinting at a physical meaning. For example, among the structure functions of Fig. 1, the SG curve is almost indistinguishable from the SQ function in the BONA3 case; however, in BONA2 case it is the FQ curve which follows more closely the function from the sol–gel glass. Nor is any systematic behaviour detectable at varying s, because the apparent small differences appear randomly distributed over the functions.

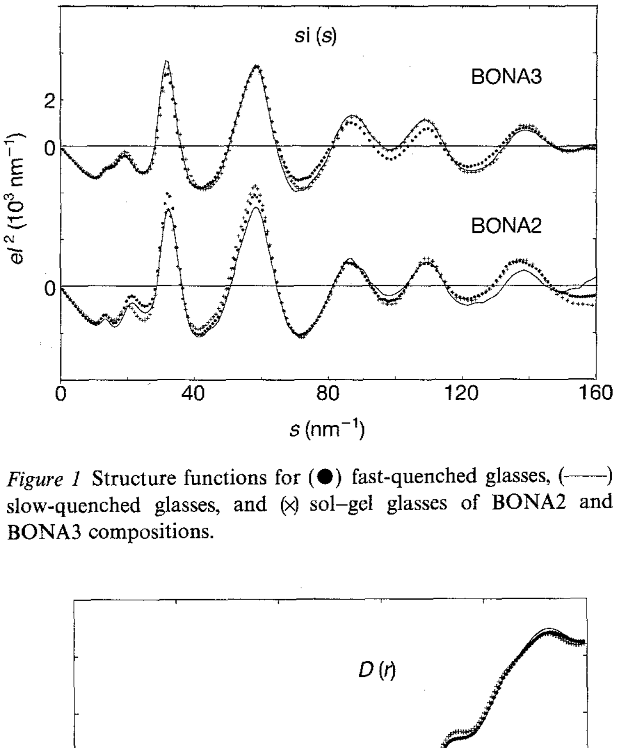

Figure 1 Structure functions for (●) fast-quenched glasses, (——) slow-quenched glasses, and (x) sol–gel glasses of BONA2 and BONA3 compositions.

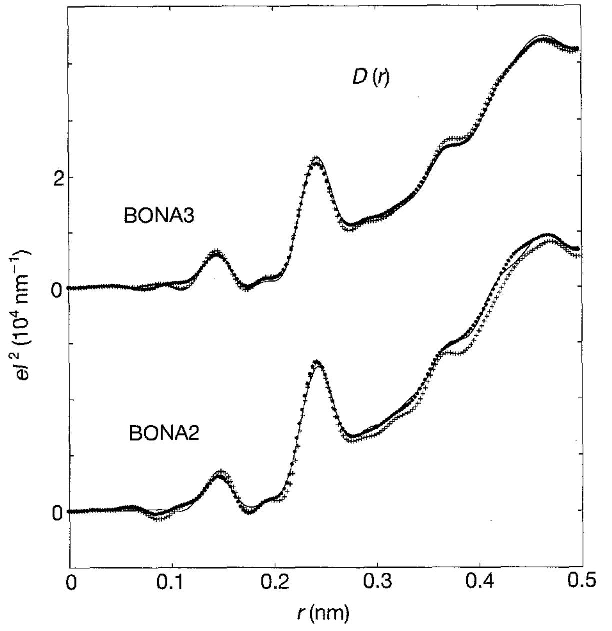

Figure 2 Radial distribution functions for (●) fast-quenched glasses, (——) slow-quenched glasses, and (x) sol–gel glasses of BONA2 and BONA3 compositions.

At this point we could already infer that the structure of sodium borate glasses as determined by X-ray diffraction, that is, at atomic level organization, is essentially independent of the preparation method. However, we chose to carry out an accurate quantitative analysis on sol–gel functions following the lines of the investigative work already performed on the melt-quenched samples, with the aim to visualize numerically through comparison of physical parameters, the extent of the structural similarity qualitatively observed.

To this purpose, the Debye scattering equation modified by a Gaussian distribution of interatomic distances was used for the simulation of the main interactions [2, 18]

$$i(s) = \sum_{i=1}^{m}\sum_{j=1}^{N_j} n_i f_i f_j \exp[(-\tfrac{1}{2})\sigma_{ij}^2 s^2][\sin(sr_{ij})/(sr_{ij})] \quad (3)$$

where N_j is the number of atoms with discrete structure "seen" by an origin atom of the i type, r_{ij} is the mean distance of the jth atom from an origin atom of the i type, and σ_{ij} is the mean square deviation of r_{ij}.

The first quantitative check on the borate network was performed on the peak at 0.140 nm in the radial functions (Fig. 2), interpreted, as usual, as due to B–O interactions. This was backtransformed into s-space to produce a "filtered" structure function $si(s)_F$; this was then used as the experimental reference for the simulation of the interaction, carried out using the Debye scattering Equation 3 and least-square fitting procedures. The final values of the three independent parameters used, that is, the distance r_{B-O}, its mean square deviation σ_{B-O}, and the frequency factor N_{B-O}, are reported in Table II, together with those obtained previously for the melt-quenched [7] samples. The errors given in parentheses were determined by comparing parameter values obtained in several calculations carried out using different ranges of experimental data. In the same table, the agreement factors, R, defined as

$$R^2 = \sum[si(s)_{sim} - si(s)_{exp}]^2 / \sum[si(s)_{exp}]^2 \quad (4)$$

are also reported for all cases. An example of reference and simulated curves is given in Fig. 3.

To evaluate the nearest environment of the sodium ions, a difference method was used [2]. It is, in fact,

TABLE II Final values of mean distances, r, frequency factors, N, and mean square deviations, σ, describing the shortest B–O interaction in sol–gel and melt-quenched [7] glasses. Limit errors are given in parentheses; agreement factors R (see text) are also reported

Sample	r (nm)	N	σ (nm)	$R(\times 100)$
BONA2FQ	0.1452(4)	3.0(2)	0.008(1)	7.8
BONA2SQ	0.1438(3)	3.1(2)	0.008(1)	8.1
BONA2SG	0.1461(3)	3.2(2)	0.008(1)	8.3
BONA3FQ	0.1428(3)	2.9(2)	0.010(1)	4.9
BONA3SQ	0.1425(3)	3.0(2)	0.009(1)	5.7
BONA3SG	0.1424(3)	3.0(2)	0.009(1)	4.8

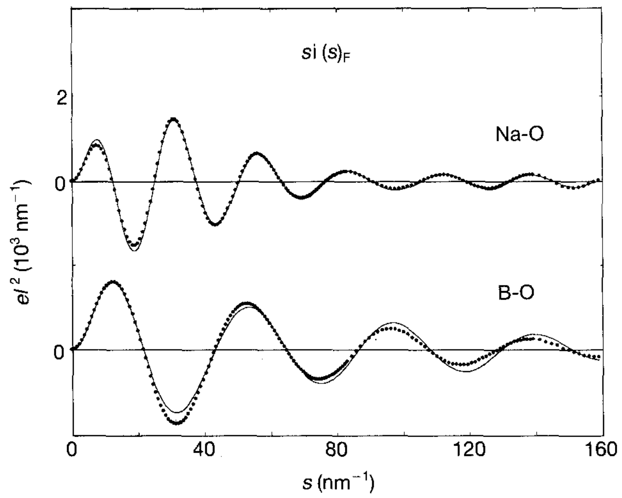

Figure 3 Comparison of (●) the backtransforms of the Na–O and B–O peaks with the simulated functions for BONA2 sol–gel glass.

necessary to single out the contribution deriving from the interactions of the sodium ions from all the others falling in the same distance range (0.2–0.3 nm). If the structure of the vitreous matrix B_2O_3 were preserved in BONA glasses, simple subtraction of a B_2O_3 function from that of a BONA sample would give the interactions of sodium ions only, at least in the r range where the nearest-neighbour distances fall [2]. This condition is not fulfilled in the case of borate glasses, because the addition of Me_2O to B_2O_3 causes structural variations which are significant, even at the level of the boron first coordination distance. However, the required result can be achieved by subtracting BOLI (lithium borate) from BONA functions, because it is known from nuclear magnetic resonance (NMR) and infrared (IR) studies that glasses with the same Me_2O/B_2O_3 ratio have practically identical boron coordination [21–24]. This procedure was carried out on BONA–BOLI radial functions; as expected, the resulting $\Delta D(r)$ curves display features originated by the sodium interactions and, as negative values, features produced by the lithium ions, while the interactions due to the borate network have disappeared.

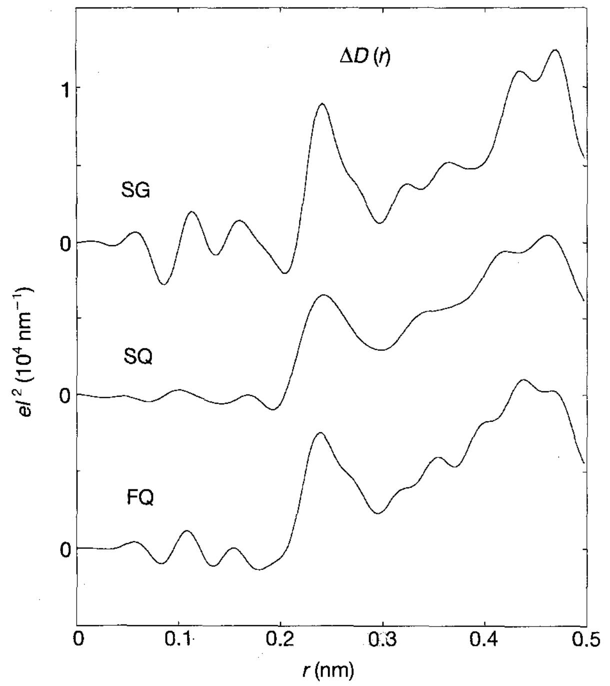

Figure 4 Difference radial curves $\Delta D(r) = D(r)_{\mathrm{BONA2}} - D(r)_{\mathrm{BOLI2}}$ for fast-quenched, slow-quenched, sol–gel glasses.

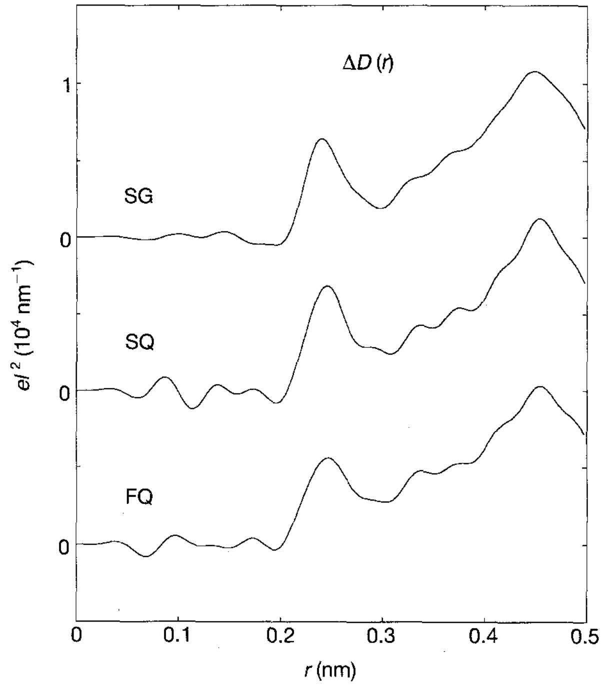

Figure 5 Difference radial curves $\Delta D(r) = D(r)_{\mathrm{BONA3}} - D(r)_{\mathrm{BOLI3}}$ for fast-quenched, slow-quenched, sol–gel glasses.

The difference radial curves $\Delta D(r)$ are reported in Figs 4 and 5 for the compositions BONA2 and BONA3, respectively: besides the functions obtained from sol–gel samples (SG), those calculated for the FQ and SQ samples are also shown. In all cases the small negative peak due to Li–O interactions is evident at about 0.190 nm, bordering, at low r, residual spurious details. The well-resolved peak produced by Na–O interactions follows, centred around 0.240 nm; it is asymmetric, similar to that found in many oxide crystal structures and in other borate glasses as well [2, 25–27]. Again, the Na–O peak in the SG curves does not show any distinctive feature with respect to the other samples. The peak was backtransformed and used as experimental reference in the least-square fitting procedure applied to the simulation of the interaction. Two terms, with different distances, root mean square deviations and frequency factors, were best fitted to the "filtered' structure function $si(s)_F$. As an example, the final result of this procedure is given in Fig. 3 for one case, while the best-fit parameters are reported in Table III.

4. Discussion

As shown qualitatively in Figs 1 and 2, the glasses with the same compositions but prepared by different methods have very similar functions. Minor differences are observable by superposing these functions, but no trend is evident. We cannot say whether these differences are meaningful, as they look comparable to the uncertainty shown by different data sets obtained

TABLE III Best-fit mean distances, r, root mean square deviations, σ, and frequency factors, N, for the Na–O interactions. Limit errors are given in parentheses; total coordination numbers and agreement factors R (see text) are also listed

Sample	r_1 (nm)	σ_1 (nm)	N_1	r_2 (nm)	σ_2 (nm)	N_2	N_{tot}	$R(\times 100)$
BONA2FQ	0.2372(5)	0.009(1)	2.6(2)	0.272(1)	0.009(1)	1.4(1)	4.0	2.8
BONA2SQ	0.2368(5)	0.012(1)	2.4(3)	0.273(1)	0.014(1)	1.6(1)	4.0	3.1
BONA2SG	0.2400(5)	0.007(1)	2.7(3)	0.271(1)	0.011(1)	1.6(1)	4.3	4.4
BONA3FQ	0.2421(5)	0.014(1)	3.6(2)	0.284(1)	0.011(1)	1.6(1)	5.2	3.3
BONA3SQ	0.2426(5)	0.011(1)	3.8(3)	0.285(1)	0.014(1)	1.7(1)	5.5	3.5
BONA3SG	0.2388(5)	0.014(1)	3.1(3)	0.274(1)	0.007(1)	1.6(1)	4.7	4.2

on the same sample by different diffractometers [28]; in addition, the composition values of sol–gel samples and melt quenched ones are not coincident.

Therefore, let us take a closer look at the quantitative determinations listed in Tables II and III. The parameters describing the boron coordination (Table II) are quite convincing. Distance values are very similar for samples of the same composition, independent of their preparation, and increase with the amount of alkaline oxide. This effect is expected, as the modifier oxide gives rise to the formation of BO_4 units; crystallographic investigations of alkaline borates show, in fact, that the B–O distance in BO_4 units is about 0.010–0.015 nm longer than in BO_3 units [29]. Frequency factors, N, are also very similar but systematically lower (about 10%–15%) than expected. This is not surprising though. It is known that the evaluation of coordination numbers involves, in general, errors greater than those connected to distance determinations. Furthermore, in this case they are also affected by another factor, that is, by the use of the boron scattering factors reported in the International Tables [30] which have been calculated for spherical free atoms; here they should represent atoms bonded covalently [6] to a highly electronegative element such as oxygen, with consequent heavy distortion of the electron cloud . Looking at Equation 3, it is easy to understand that if the weight of B–O contribution to the diffraction, given by the product $f_B f_O$ for neutral atoms, is overestimated, the frequency factor, N, comes out smaller than it should.

Even as far as the Na–O interaction is concerned, the parameters reported in Table III appear to describe one physical situation occurring in all the samples. At closer observation, the two sol–gel samples of different composition seem to be more similar to each other than they are to the melt-quenched ones of equal composition. This is the case with r_1 distances, with values of about 0.239–0.240 nm (SG samples) compared with the distinct 0.237 nm (BONA2) and 0.242–0.243 nm (BONA3) for melt-quenched samples; the same occurs with r_2 distances: 0.271 and 0.274 nm for SG samples, while for melt-quenched ones the values group around 0.272 and 0.284 nm, respectively; the same trend again occurs with coordination numbers, but no trend at all is seen with standard deviations. However, these numerical coincidences do not seem to provide enough grounds for any particular physical interpretations. In fact, because of the difficulties met during the preparations, the actual compositions of SG samples show small deviations with respect to the nominal ones (see last column of Table I), which, instead, correspond perfectly to the values determined in the melt-quenched glasses. These compositional differences are also present within the pairs BONA–BOLI used in the difference method, thus preventing the complete cancellation of the common structural terms in the calculation of the $\Delta D(r)$ functions, and somehow affecting the results for sodium coordination.

Finally, a comment must be made about the error values associated with the parameters describing the sodium interactions, which are listed in parentheses in Table III. As mentioned above, these figures come from different best-fitting calculations carried out on several data ranges in the reciprocal space and different strategies. But they are not comprehensive of other error sources, such as the mentioned compositional differences. A further contribution to the total error might also come from neglecting the term representing the interactions of lithium ions which, in negative form, are present in the $\Delta D(r)$, in the r range just neighbouring that corresponding to Na–O interactions. To verify the influence of such a term, a new set of calculations was carried out, in which both lithium- and sodium-nearest neighbour contributions were best-fitted by the usual least-square procedures to the backtransforms of proper ranges of $\Delta D(r)$. As expected, the parameterized description of lithium interactions were shown to be quite unreliable; its small contribution centred at about 0.20 nm is, in fact, influenced by the spurious oscillations at lower r and by the presence of the much bigger peak at higher r. But, more important, the coordination of the sodium ions was modified in this procedure, particularly in the values of first distance (about 0.003 nm shorter) and first coordination number (about 0.5 units greater). While these calculations certainly suggest that the errors given in parentheses in Table III are underestimated, on the other hand they do not change the conclusion given above. On the contrary, as sodium coordination parameters in all cases have displayed the same behaviour, these calculations further support the idea that the same amorphous structure is set up both in samples prepared by the sol–gel method and in samples of equal composition prepared by traditional melt-quenching techniques.

Probably some difference exists, but in a distance range longer than that examined here. Although we do not have experimental data to prove it, with the exception of the few density values which may support such an hypothesis, strong indications in this direction come from investigations of the sol gel method itself, though carried out essentially on systems based on SiO_2. The relevant literature, extensively discussed by Brinker and Scherer [9], warns about the extreme sensitivity of this preparation procedure to the experimental conditions (pH, humidity, temperature, nature and concentration of reactants, type of solvent, etc.). Proper combinations of these actually give rise to final products which differ from each other in terms of type and length of polymers formed, porosity and pore distribution, "texture" of the samples, etc, which in the end favour the formation of fibres, or thin films or bulk gels.

Even more so, in comparing glasses prepared from melts with glasses obtained from solutions, we may think that they must differ in some way, perhaps in a distance range of a few units or of some tens of nanometres, but other types of investigations are needed to provide evidence of this aspect.

5. Conclusion

Two amorphous samples of sodium di- and triborate were prepared by the sol-gel method. Their X-ray diffraction spectra were shown to be quite similar to those obtained from glasses of the same composition prepared by classical melt-quenching procedures. With the purpose of verifying numerically the similarities observed, a quantitative analysis was carried out on the first distance interactions appearing in sol–gel radial functions. Using the Debye scattering equation, the peaks due to B–O and Na–O interactions were simulated and compared with their respective experimental references. In the case of the Na–O peak, a difference procedure involving radial functions from sodium and lithium borate samples was used to eliminate other interactions falling in the same r region. Taking into account the incidence of several error sources, it is concluded that the vitreous network in borate glasses is the same at the level of first distances whatever preparation method is used. Further investigations using other techniques are, however, needed to evince possible structural differences which might set up in a longer distance range.

Acknowledgement

This work was carried out within the project "Materiali Speciali per Technologie Avanzate" of the Italian Consiglio Nazionale delle Ricerche.

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Received 15 February
and accepted 26 August 1993