GLASS STRUCTURE (TC03)

List of members

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MAIN GOALS OF THE TC

The activity of the TC03 committee is focused on the discussion of the basics aspects of glass structure as well as on the experimental collaboration throughout Round Robin tests of model glasses, for which atomistic simulation and thermodynamic modelling techniques are also used.

PLANS FOR 2012

Round-robin test

Structural characterisation of the four sodium borosilicate glasses will be completed not only through more advanced NMR methodologies but also with complementary techniques such as FTIR, Raman or XAFS spectroscopy. It has been thought that Round Robin tests will be extended in a near future to other glass systems of common interest for the members of the committee. Samples of the Na_2O-B_2O_3-SiO_2 Round Robin glasses have already been distributed to other laboratories to follow their characterisation. In order to complete the qualitative information about the B-Si connectivity scheme deduced from the $^{11}B\{^{29}Si\}$ D-HMQC experiments already performed, the following NMR techniques could be applied:

(i) ^{11}B MQ-MAS: this technique allows reaching the high resolution for the quadrupolar ^{11}B nucleus and could be used to unambiguously determined the number of tri- and tetra-coordinated boron sites. It is worthy to note that these experiments could be performed on the very high static field spectrometer (21.1 T) of the University of Lille 1.

(ii) $^{11}B\{^{29}Si\}$ HMQC-ST: at the light of the previous results, a re-investigation of the B-Si correlation could be performed with a correlation techniques providing high resolution for ^{11}B, such as the $^{11}B\{^{29}Si\}$ HMQC-ST sequence.
(iii) $^{11}B\{^{29}Si\}$ REDOR: a more quantitative investigation will be necessary in order to determine the number of silica connected to each boron species ($B(OSi)_n$). This information could be retrieved from $^{11}B\{^{29}Si\}$ REDOR experiments but will require the preparation of ^{29}Si-enriched NBS samples. This possibility would also be investigated. It is worth noting that the preparation of the ^{29}Si-enriched samples will also allow investigating the chemical environment of the different silicate species present in the glass structure. The $^{29}Si\{^{11}B\}$ REAPDOR or RESPDOR techniques could be used to characterise the silica network with the $Si(OB^{IV})_{4-n}(OB^{III})_n$ notation, giving thus access to the medium rage order structure of the glasses. This information could be then used to correlate the structure to the macroscopic properties and to the phase separation process.
Therefore, it has been proposed to continue the investigation of the glass microstructure due to its important influence into the structural speciation. High Resolution TEM characterisation coupled with microanalysis of properly prepared samples will also be scheduled.

Computer modelling of glass structure
Atomistic simulation will be performed to obtain new structural information complementary to the round robin tests and the thermodynamic calculation.

Meeting and symposium
At least one business meeting will be organised during 2012 where most of the members are able to join. In principle, this meeting will be held at the 11th European Society of Glass conference from 3 to 6 june 2012 in Maastricht (NL), where the ICG will also celebrate its annual meeting.

Education
Preparation for a course on glass structure to be held during the next ICG Conference in 2013.

ACTIVITIES in 2012

Round-robin test
During the present year, some more data have been obtained on the structural characterization of the four sodium borosilicate glasses. In particular, the group of Prof. Hiromichi Takebe at the University of Ehime (Japan) carried out FTIR spectroscopy and Prof. Giuseppe Dalba, from University of Trento (Italy) performed XANES measurements in collaboration with Dr. Toshihiro Okajima, of Kyushu Synchrotron Light Research Center (Japan) and Dr. Pierre Lagarde, from Soleil facility, in Paris (France). The results are currently under discussion and the relationships between these new data and those obtained by Nuclear Magnetic Resonance experiments will be soon established. Figure 1 of Annex 2 shows the FTIR spectra of the four NBS glasses under study, whose compositions are reported in Table 1 of annex 2. Table 2 of the Annex 2 gathers the IR band assignments of NBS glasses.

Computer modelling of glass structure

The glasses have also been investigated through molecular dynamics simulation. The ratio of N4 groups (BO4) was calculated for the four round-robin compositions. The calculated values could reproduced well those estimated from the NMR measurements and from the thermodynamic calculations. In order to investigate the structure change in the wider composition range, the N4 and Si-O-B were calculated for additional four compositions. The standard MD simulation provided the glass structure close to the ideal mixing of SiO4 and BOn (n=3 or 4) units, probably due to the extremely fast quenching rate. Figure 1 of Annex 3 presents the equilibrium phase diagram with the compositions of the NBS glasses studied by MD simulation as well as the % of boron in BO4 groups with respect to the total of boron atoms.

Meeting and symposium
A meeting was held at the 11th ESG conference on June 3, in Maastricht, the Netherlands. Seven members of the committee were present and three new colleagues joined the meeting, coming from Slovakia, Japan and Germany. The discussion was focused on the last results of the Round Robin tests performed by some of the members. In particular, new data were presented on the FTIR characterization of the sodium borosilicate glasses as well as the calculations carried out by means of thermodynamic and molecular dynamics modelling. The minutes of this meeting are annexed at the end of the document.

PLANS FOR 2013

Round-robin test
A technical report with a compilation of all measurements performed so far on the four sodium borosilicate glasses is intended to be prepared during the next year.

Once the round robin experiments on the Na2O-B2O3-SiO2 glasses are accomplished, new action lines should be envisaged on this point. For instance, a set of *glass structure problems* will be defined where all members can work by groups of interest. Therefore, all people should be working actively in any of the groups depending on their own research experience and capabilities.

Computer modelling of glass structure
A more detailed structural analysis of the sodium borosilicate glasses of the Round Robin test will be performed by means of molecular dynamics simulations in terms of clustering tendency of SiO4 and BOn (n=3 or 4) units.

Meeting and symposium
A business meeting will be organised during the next 23rd International Congress on Glass to be held in Prague, 1-5 July 2013. It is expected that most, if not all, members of TC03 committee will be joining the meeting. One of the main objectives of the committee is to attract new members and interested people in the activities of the group. While the core of activities remains a fundamental topic in Glass Science and Technology, a key issue will be recruiting more people

from Industry, in order to establish stronger links between academia and glass producers.

A session on Glass Structure will be co-organized by the TC03 committee at the 23rd International Congress on Glass, to be held in Prague during July 2013.

Education
A course on Glass Structure is not going to be finally held during the ICG congress in Prague, as it was previewed last year. However, an alternative is being studied for the coming years.

Website
It is the purpose of the members of TC03 to do their best in improving the access of everyone to the activities of the committee. Works are underway to use the facilities of the main ICG website for the publication of TC03 results as well as other additional means that can help.

Annex 1

Minutes of the TC03 meeting held in Maastricht (NL), on June 3rd 2012, with the occasion of the 11th European Glass Society Conference.

Members present: Akira Takada, Adrian Wright, Natalia Vedishcheva, Hiromichi Takebe, Gregory Tricot, Marek Liska and Francisco Muñoz. Three new persons joined the meeting: Doris Möncke (University of Erlangen, Germany), Maria Chromcikova (Institute of Inorganic Chemistry, Slovak Republic) and Akira Saitoh (Ehime University, Japan).

Apologies for absence were received from Laurence Galoisy, Natalia Karpukhina, Giuseppe Dalba, Alex Hannon, Ondrej Gedeon, Efstratios Kamitsos, Liu Qiming, Lionel Montagne and Steve Feller.

1. TC activities in 2011.
A review of the work performed and meetings held during the year 2011 was presented and, in particular, all results of the Round Robin experiments achieved on the NBS model glasses were described. It was pointed out that the choice of sodium borosilicates where phase separation occurred made the work too complicated and that further Round Robin studies should be conducted on homogeneous glasses when possible. A. Wright suggested that any type of industrially employed glass would be a more interesting choice in view of potential collaboration with other technical committees. The aim of performing Round Robin experiments by means of NMR in different laboratories was initially planned only for inter-calibration purposes; however, there has been a big step forward on the characterization of the NBS model glasses through the use of two-dimensional NMR techniques that allowed the determination of the boron and silicon structural sites. G. Tricot D-HMQC NMR experiments could be carried out for analysis of the phase separation in the glasses but only from a qualitative point of view. As reported in previous reports the glasses have been analyzed by four different laboratories, with demonstrated good correlation. In any case, high field ^{11}B NMR allows for more accurate determination of the N_4 borate groups. Concerning the N_4 determination, N. Vedishcheva recalled on the goodness of the N_4 values. Following the discussion on the N_4 determination and its correlation with the thermodynamic calculations that N. Vedishcheva co-workers have performed during the last years, she pointed out to the necessity of having a complete set of reliable thermodynamic data for other glass-forming systems if, in addition to experimental methods, the relevant glasses are to be studied by thermodynamic modelling.
The committee was also informed on the ICG website and TC's pages, where documents can be uploaded and the activities of the TC can be updated at any time.

2. Presentation of new results on the NBS Round Robin study in 2012.
Short talks were given to report on the new results or potential contributions that could be made to the Round Robin study by of TC03. These were as follows:
1. M. Liska: Glass structure and thermodynamic modelling applied to glasses. A SWOT (Strengths-Weaknesses-Opportunities-Threats) analysis was presented and CaO-P_2O_5 glasses results were presented as an example.
2. N. Vedishcheva: Thermodynamic modelling of B and C NBS Round Robin glasses. The thermodynamic usefulness of the modelling has been assessed throughout the short- and intermediate range order structure in glasses B and C. It is possible to calculate the equilibrium concentration of all components; however, even though the total number of structural units is known, no information on phase separation can be extracted from the results.

3. H. Takebe: FTIR characterization of NBS glasses. The results showed lower values of N_4 groups with respect to those determined by NMR and glasses B and C presented SiO_2 and Na_2O-SiO_2 enriched regions, respectively.
4. A. Takada: Molecular dynamics technique applied to NBS glasses. The MD technique, though it uses very fast quenching rates, it has provided quite good results. However, the tendency to phase separation can not be studied yet but it is planned as a next target as well as the morphology. The results on determination of the N_4 groups are quite similar to those determined through NMR, and it has been observed that SiO_4 units favour BO_4 groups more than BO_3 ones in NBS glasses.

3. Organization of the course on Glass Structure at the next ICG conference (Prague, 1-5 July 2013).
A draft of the course that is planned to be given during the 2013 ICG conference in Prague has been developed. It should be a one day course with 5 or 6 lectures, 50 min each. The talks would be focused on experimental techniques for the study of the structure of glass, e.g. NMR, optical spectroscopies, diffraction techniques, electron microscopy and modelling. The organizing committee of the ICG 2013 congress, as well as the TC23 committee on Education of the ICG, has been conveniently informed and they both showed their approval and support for the organization of the course.

4. Meetings.
It was proposed that the next annual meeting of the TC03 committee is to be held during the next ICG conference, Prague (SK), in 2013.

Madrid, July 27th 2012

Francisco Muñoz
TC03 – Glass Structure

Annex 2

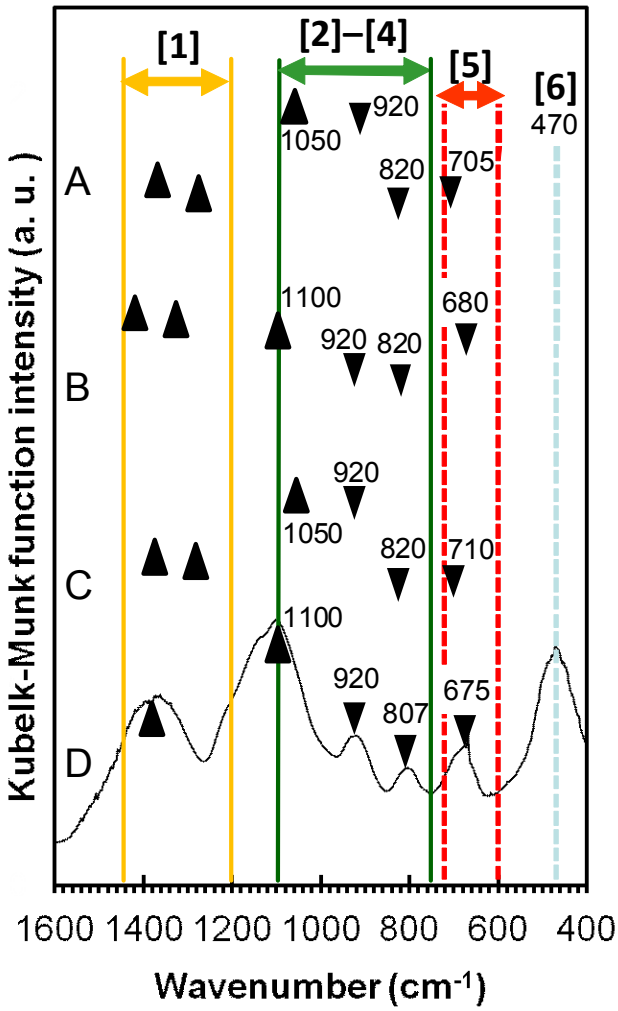


Figure 1. FTIR spectra of sodium borosilicate glasses NBS-A,B,C,D.

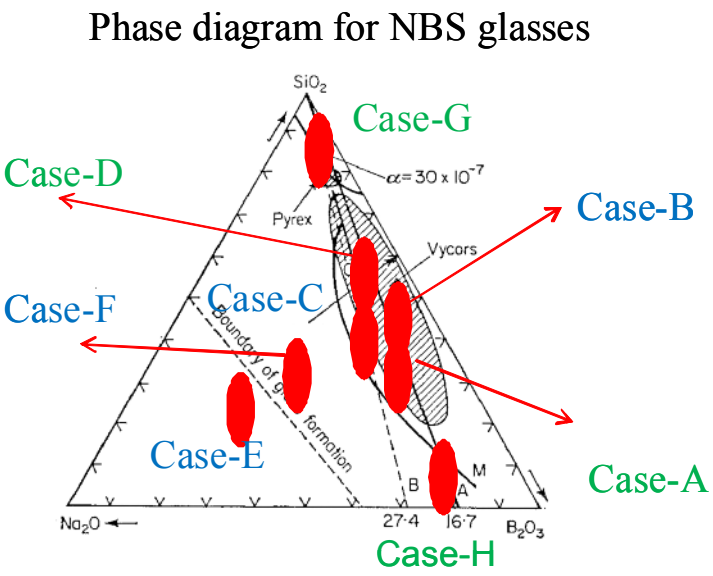
Table 1. Composition of sodium borosilicate glasses.

		Composition (mol%)			
Sample	Appearance	Na_2O	B_2O_3	SiO_2	N_4 *1
NBS-A	Transparent	12.5	62.5	25.0	0.20~0.25
NBS-B	Opaque	3.0	48.5	48.5	0.08~0.10
NBS-C	Transparent	15.0	42.5	42.5	0.30~0.40
NBS-D	Opaque	6.5	33.5	60.0	0.17~0.21

Table 2. IR band assignments.

No.	Peak position, cm^{-1}	Assignments
[1]	1450–1200	B-O stretching of trigonal BO_3 units[2]
[2]	1100–930	Si-O ν_3 vibrations[3]
[3]	1100–850	B-O stretching of tetrahedral BO_4 units[2]
[4]	800–740	Si-O ν_1 vibrations[3]
[5]	ca. 710	B–O–B bending[2]
[6]	470	Si–O–Si bending[3]

Annex 3



4-fold B atoms/ Total B atoms (%)

K=1	CaseB	Case-C	Case-F	Case-E
	12	36	67	81
R=0.2	Case-G	Case-D	Case-A	Case-H
	6	19	27	27

Figure 1. Equilibrium phase diagram with NBS glasses and % factions of BO4 groups.