GLASS STRUCTURE (TC03)

List of members

Francisco Muñoz* (CSIC, Spain), Chair
Akira Takada* (Asahi Glass, Japan), Vicechair
Adrian C. Wright* (Reading University, UK)
Natalia Vedishcheva* (Institute Silicate Chemistry, Russia)
Ondrej Gedeon* (Institute of Chemical Technol., Czech Republic)
Gregory Tricot* (Lille University, France)
Hiromichi Takebe* (Ehime University, Japan)
Giuseppe Dalba* (University of Trento, Italy)
Marek Liska (Inst. Inorg. Chem., Slovak Republic)
Alex Hannon, (Rutherford Appleton Laboratory, UK)
Laurence Galoisy (IMPMC CNRS 7590, France)
Natalia Karpukhina (Queen Mary University of London, UK)
Joe Zwanziger (Dalhousie University, Canada)
Liu Qiming (Wuhan University of Technology, China)
Efstratios Kamitsos (Nat. Hellenic Research Foundation, Greece)
Steve Feller (Coe College, USA)
Lionel Montagne (Lille University, France)
* Core group members

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 2011

The main objectives to be carried out during 2011 were the following:

Round-robin test

Round Robin Test on the four samples of Na_2O-B_2O_3-SiO_2 glasses should see further progress throughout NMR characterisation.

Computer modelling of glass structure

This objective was adapted to establish a correlation between the results on NMR characterisation and those obtained through modelling techniques that could be successfully applied. At the same time, the results of atomistic modelling would be compared with those of the chemical structure thermodynamic modelling.

Glass microstructure

It was proposed that the subject under study of TC03 could be extended to Glass Microstructure and the relationship between atomic structure and phase separation behaviour.

Education

The intention is that a series of workshops/seminars could be planned with the topic “Glass Structure”.

Meeting and symposium
A meeting was planned for 2011 in Oxford (UK) within the framework of the **International Conference on the Chemistry of Glasses and Glass forming Melts**, together with a session on the **Chemical Aspects of Glass Structure**.

ACTIVITIES in 2011

New results on the Round-robin test
1. Data of the N_4 (BO_4) groups in the Na_2O-B_2O_3-SiO_2 glasses under study have been complied from four different laboratories.

2. In order to investigate the mixing between the silicate and the borate species, the through space correlation technique D-HMQC was applied by the group of Lionel Montagne and Gregory Tricot at the University of Lille (France). This 2D NMR pulse sequence creates correlation signals only in case of very close nuclei. The very short B-Si distances highlighted by the experiments can then be interpreted as chemical connectivity. The 2D D-HMQC spectrum obtained on the NBS-A glass shows significant interactions between the silicate species and BO_4 and a complex correlation scheme between the silicate species and BO_3. More precisely, it appears that a silicate moieties (-110 ppm) is connected to a first trigonal borate group whereas another silicate group (-100 ppm) is connected to another borate group. The correlation scheme seems to be simpler for the NBS-B sample. Indeed, the 2D D-HMQC spectrum only shows a correlation signal involving silicate and trigonal boron. The lack of signal between silicate and BO_4 group suggests that the two networks are completely dissociated and could be related in some extent to phase separation.

Computer modelling of glass structure

Results on the thermodynamic calculations by using the model by N. Vedishcheva and coworkers [N.M. Vedishcheva *et al.*, J. Non-Cryst. Solids 345&346 (2004) 39-44] have been obtained for the four Na_2O-B_2O_3-SiO_2 glasses. The results agree quite well with the experimental data obtained by NMR characterisation.

Meeting and symposium

A meeting was held at the International Conference on the Chemistry of Glasses and Glass forming Melts, in Oxford (UK) on September 4th, where 12 members from TC03 were present. A set of short presentations were given by nine of the members of TC03 with the aim of letting know on the particular research interests of each member in view of promoting potential future collaborations. The most important aspects of the Round Robin tests and modelling of the sodium borosilicate glasses were reviewed. Professor Adrian Wright and the members of the TC03 committee contributed to the organisation of two sessions at the Lomonosov Conference on Glass Chemistry focused on the Chemical aspects of glass structure and computer modelling of glasses and glass-forming melts.

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.

Annex 1: Minutes of the TC03 business meeting, held at Oxford (UK), on September 4th with the occasion of the international conference on glass and glass-forming melts.

Members present: Akira Takada, Adrian Wright, Natalia Vedishcheva, Ondrej Gedeon, Hiromichi Takebe, Alex Hannon, Giuseppe Dalba, Gregory Tricot, Natalia Karpukhina, Laurence Galoisy, Marek Liska and Francisco Muñoz.

Apologies for absence were received from Efstratios Kamitsos and Liu Qiming.

New members have joined TC03 from beginning 2011: Alex Hannon, Gregory Tricot and Natalia Karpukhina, who have also actively participated of the TC03 meeting at the Lomonosov conference.

The composition of the TC03 committee up to date is as follows:

Francisco Muñoz (CSIC, Spain), Chair
Akira Takada (Asahi Glass, Japan), Vice-chair
Joe Zwanziger (Dalhousie University, Canada)
Adrian C. Wright (Reading University, UK)
Natalia Vedishcheva (Institute Silicate Chemistry, Russia)
Ondrej Gedeon (Ins. of Chem. Technol., Czech Republic)
Doris Ehrt (Otto-Schott Institute, Germany)
Liu Qiming (Wuhan University of Technology, China)
Hiromichi Takebe (Ehime University, Japan)
Efstratios Kamitsos (Nat. Hellenic Research Foundation, Greece)
Laurence Galoisy (IMPMC CNRS 7590, France)
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TC22 meeting during the conference was not possible to be held due to organisation issues during the Lomonosov conference, so it was agreed with the members of TC22 technical committee to celebrate a joint TC03-TC22 meeting. Members from TC22 committee were: Georges Calas, Maire-Helene Chopinet, Bruce Aitken and Neville Greaves.

Update of TC03 status after 2011

Due to the fact that no meetings of TC03 were organised in 2010, and also that very few members were attending the meeting held at the 8th PACRIM conference of Vancouver in 2009, it was appropriate to inform all former and new members of TC03 committee the changes at the technical committee's structure of the ICG. The reasons for a change of committee's name and newly defined objectives were explained. After reviewing the composition of the committee, it was exposed that most of the members were European, and that the committee should continuously attract new members.
The report of the Coordinating technical committee meeting, held on 31st march 2011, in Shenzhen (P.R. China) was reviewed with respect to the situation and progress of the TC3.

Presentations by TC03 members

Short presentations were given by some of the members of the TC03 on their main research topics in relationship with the objectives of the committee. These were:

1. Francisco Muñoz, (CSIC, Spain)

2. Akira Takada, (Asahi Glass, Japan)
3. Ondrej Gedeon (Inst. Chem. Technol. Prague, Czech Republic)
4. Giuseppe Dalba (University of Trento, Italy)
5. Alex Hannon (Rutherford Appelton Laboratory, UK)
6. Hiromichi Takebe (Ehime University, Japan)
7. Gregory Tricot (Lille University France)
8. Natalia Karpukhina (Queen Mary University of London, UK)
9. Natalia Vedishcheva (Institute Silicate Chemistry, Russia)

Round Robin of NBS glasses

Active discussions were maintained on the status of the NMR round robin experiments that were being carried out in several laboratories, as presented in the last reports. The glass composition of the four borosilicate glasses is given in Table I.

Table I. Composition of NBS round robin glasses.

	Composition (mol %)		
Samples	**Na_2O**	**B_2O_3**	**SiO_2**
NBS-A	12.5	62.5	25
NBS-B	3	48.5	48.5
NBS-C	15	42.5	42.5
NBS-D	6.5	33.5	60

New data on the N_4 speciation were provided from experiments performed at the University of Lille 1 (France), by Gregory Tricot, and CSIC (Spain), by Francisco Muñoz. These new data on N_4 groups are presented in Figure 1. However, no new data were reported from the laboratories chosen at the beginning of the NMR round robin, appart from the first reported last year and performed by the laboratories of Joe Zwanziger and Scott Kroeker.

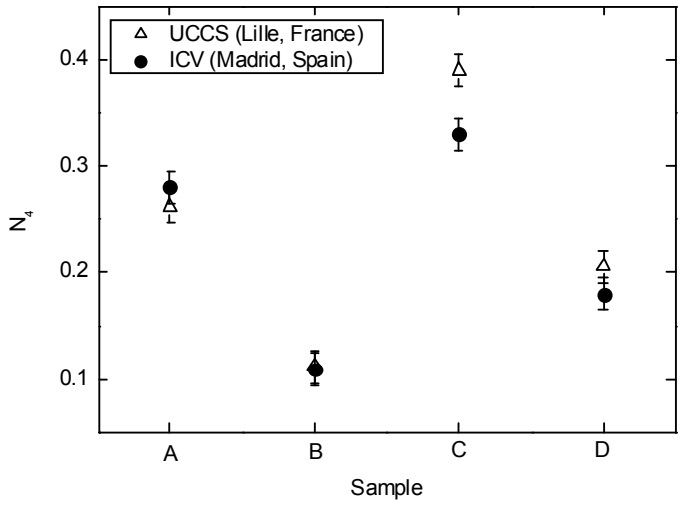

Figure 1. Fraction of N_4 groups in NBS-1,2,3,4 glasses as determined from experiments in the Universities of Lille 1 (France) and CSIC (Spain).

In particular, Gregory Tricot, presented new and very valuable results for the advance on the NMR round robin of the NBS glasses, from which some comments are presented below.

In order to investigate the mixing between the silicate and the borate species giving rise to the mixed boro-silicate network, the through space correlation technique D-HMQC was applied to the samples. This 2D NMR pulse sequence creates correlation signals only in case of very close nuclei. The very short B-Si distances highlighted by the experiments can then be interpreted as chemical connectivity. The 2D D-HMQC spectrum obtained on the NBS-A sample (Fig. 2a) shows significant interactions between the silicate species and BO_4 and a complex correlation scheme between the silicate species and BO_3. More precisely, it appears that a silicate moiety (-110 ppm) is connected to a first trigonal borate group whereas another silicate group (-100 ppm) is connected to another borate group. The correlation scheme seems to be simpler for the NBS-B sample. Indeed, the 2D D-HMQC spectrum (Fig. 2b) only shows a correlation signal involving silicate and trigonal boron. The lack of signal between silicate and BO_4 group suggests that the two networks are completely dissociated and could be related in some extent to phase separation process.

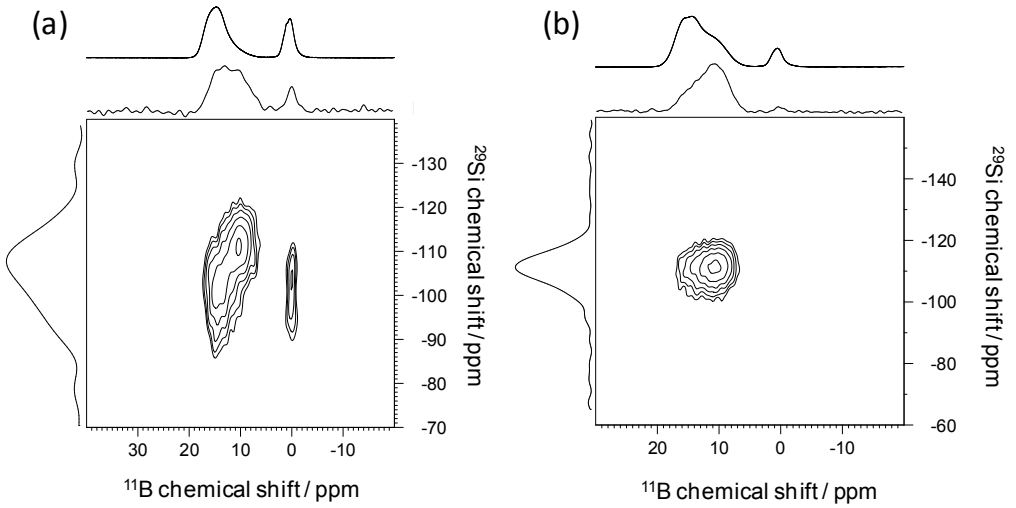

Figure 2: $^{11}B\{^{29}Si\}$ *D*-HMQC spectra recorded on the NBS-A (a) and NBS-B (b) samples. In the direct dimension (^{11}B) are reported the 2D spectrum projection (lower part) and the ^{11}B 1D MAS-NMR acquisition (upper part). In the indirect dimension (^{29}Si) is reported the 2D spectrum projection. The 2D spectra have been recorded after 30 and 10 hours of acquisition, respectively, by using the pulse sequence described in references[1, 2].

Computer modeling and thermodynamic calculations

During the last years, the connection between experimental data on structure of glasses and the atomistic calculations, as well as thermodynamic modelling, has been explored by the members of the TC03 committee. During the meeting, all possible relationships between the NMR data of the Round Robin on sodium borosilicate glasses and modelling were evaluated. From the theoretical point of view, there may be two main approaches, clasical and ab-initio. Classical molecular dynamics calculations can give information on the distribution of Q^n species reasonably for borate systems. As the next step some calculations on borosilicate system are ongoing. From the point of view of the ab-initio approach, the main conclusion is that new people experienced with such a methodology should be involved in TC03 in order to investigate the local structure more precisely and NMR spectra in the chosen system.

On the other hand, the thermodynamic model established and presented by Natasha Vedishcheva at the meeting can also provide such information from a different point of view. Then, it is now the task of the members to establish proper correlations between the NMR data and molecular and thermodynamic modelling calculations.

The last point on this topic, is the fact that all the supported glasses present phase separation. It has been suggested that it would be more appropriate first to simulate the particular phases that present typical morphology. The experts on this particular topic think

[1] Trebosc et al., J. Magn. Reson. 186, 2007, 220.

[2] Tricot et al., Phys. Chem. Chem. Phys 13 (37), 2011, 16786.

that it is a great challenge for atomistic simulation to realistically describe phase separated glasses due to the restriction of simulated time span and simulation box size. Alternative challenge is to develop a mesoscopic methodology for estimate morphology of separated glass.

As an example of the combination between NMR experiments and thermodynamic calculations performed by N. Vedishcheva on the Round Robin glasses, Table II gathers the N_4 fractions in NBS glasses A to D, which compositions are given in Table I. The thermodynamic calculations can reproduce N_4 fractions reasonably.

Table II. N_4 fractions by thermodynamic calculations following model by N. Vedishcheva *et al.*[3]

Glass	NBS-A	NBS-B	NBS-C	NBS-D
N_4 ($\pm$ 0.05)	0.20	0.06	0.35	0.19

Discussions on the next important points

A review on the up-to-date NMR round robin experiments should be soon produced in conjuction with chemical analysis and characterisation of phase separation of the NBS glasses.

Samples of NBS glasses will be distributed to other laboratories among the TC03 members. FTIR, Raman as well as EXAFS experiments will be of valuable interests in order to be able to characterise the Na_2O-B_2O_3-SiO_2 system of glasses in complementary ways.

Madrid, October 17th 2011

Francisco Muñoz
TC03 – Glass Structure

[3] N.M. Vedishcheva *et al.*, J. Non-Cryst. Solids 345&346 (2004) 39-44.