Phase II SBIR Final Technical Report

Manipulation of Samples at Extreme Temperatures for Fast *in-situ* Synchrotron Measurements

Grant Number: DE-SC0007564

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Period of performance: 4/23/2013 - 4/22/2016

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April 22, 2016

Distribution: Unlimited

Preface

This SBIR project was performed by Materials Development, Inc. over the period from 4/23/2013 - 4/22/2016. This period included a one year non funded extension to allow completion of beamline experiments. Work was performed mainly at MDI's facilities in Evanston, Illinois and the Advanced Photon Source (APS) at Argonne National Laboratory in Illinois. The following MDI staff worked on the project: Dr. Oliver Alderman, Ms. Danni Jin, Mr. Alex Lin, Mr. Samuel Sendelbach, Mr. Amit Tailor, Mr. Anthony Tamalonis, Ms. Sonia Tumber, Dr. Richard Weber, and Ms. Alison Whale. Ms. Jin and Mr. Lin were employed full time at MDI through the Northwestern University Walter P. Murphy Cooperative Science and Engineering program. Ms. Whale worked full time for a summer during her undergraduate degree in Physics at Coe College in Cedar Rapids, IA. Dr. Lawrie Skinner worked on the project under a subcontract to Stony Brook University. Some work on beamline integration was subcontracted to Argonne National Laboratory. The project employed two consultants who assisted with analysis of data and by providing advice on instrument function and design.

Executive Summary

An aerodynamic sample levitation system with laser beam heating was integrated with the APS beamlines 6 ID-D, 11 ID-C and 20 BM-B. The new capability enables *in-situ* measurements of structure and XANES at extreme temperatures (300-3500 °C) and in conditions that completely avoid contact with container surfaces. In addition to maintaining a high degree of sample purity, the use of aerodynamic levitation enables deep supercooling and greatly enhanced glass formation from a wide variety of melts and liquids.

Development and integration of controlled extreme sample environments and new measurement techniques is an important aspect of beamline operations and user support. Processing and solidifying liquids is a critical value-adding step in manufacturing semiconductors, optical materials, metals and in the operation of many energy conversion devices. Understanding structural evolution is of fundamental importance in condensed materials, geology, and biology. The new capability provides unique possibilities for materials research and helps to develop and maintain a competitive materials manufacturing and energy utilization industry.

Test samples were used to demonstrate key features of the capability including experiments on hot crystalline materials, liquids at temperatures from about 500 to 3500 °C. The use of controlled atmospheres using redox gas mixtures enabled *in-situ* changes in the oxidation states of cations in melts. Significant innovations in this work were:

(i) Use of redox gas mixtures to adjust the oxidation state of cations *in-situ*
(ii) Operation with a fully enclosed system suitable for work with nuclear fuel materials
(iii) Making high quality high energy *in-situ* x-ray diffraction measurements
(iv) Making high quality *in-situ* XANES measurements
(v) Publishing high impact results
(vi) Developing independent funding for the research on nuclear materials

This SBIR project work led to a commercial instrument product for the niche market of processing and studying materials in extreme conditions. MDI registered the trademark “Instruments for Innovation®” and sells products under this trademark. SBIR is the ideal vehicle for funding developments such as this since the total market size is relatively small meaning that venture investments to develop products cannot typically be obtained. The sale of niche market instruments for work in extreme conditions has been several million dollars over the last decade. The work to develop and build and sell this instrument has created stable high paying jobs in the technology manufacturing sector.

Outreach enabled by this research helped with PhD thesis research, supported three undergraduate interns and one local high school student. In addition several scientific articles were published, papers were presented at international conferences and a workshop was held.

Introduction: This project addressed the need to access and control samples at extreme temperatures that are important in many research applications at x-ray beamline facilities. Development and integration of well controlled extreme sample environments and new measurement techniques is an important aspect of beamline operations and user support. The goal of this project is to enable the investigation of the structure of materials when they respond to their sample environment, in particular the local order structure and structural evolution in liquids, metastable materials, glasses and nano-crystalline materials. Processing and solidifying liquids is a critical value-adding step in manufacturing semiconductors, optical materials, metals and in the operation of many energy conversion devices. Understanding structural evolution is of fundamental importance in condensed materials, geology, and biology. Despite these strong drivers, studies of the structural evolution in metastable liquids, which are a key to understanding nucleation, crystallization, clustering, nano-crystallization, and vitrification behavior, are limited by the lack of experimental techniques.

The technology employed MDI's proprietary aerodynamic levitation technology that was integrated with a high flux neutron instrument to achieve unprecedented performance. The project was performed over the period 8/15/2011 - 2/15/2015 that included a 12 month non-funded extension to allow completion of beamline testing at the APS, analysis of data, and preparation of several publications. Work was performed mainly at MDI's facilities in Evanston, Illinois and the APS at Argonne National Laboratory in Illinois. The project employed two consultants and subcontracted help from an expert on x-ray scattering from Stony Brook University.

MDI delivered a test instrument to APS. Title to the instrument is being transferred to APS during the close out of this project. The instrument is being placed in the user program as a specialized sample environment. Plans are being made for MDI to contract to provide service and support when the instrument transfer is completed.

Proposed Research: The research as proposed was performed and completed on budget. The following four research tasks were performed:

Task 1 – Complete design analysis and perform Critical Design Review (CDR) at APS.

Task 2 - Construct Phase II test instrument.

Task 3 – Characterize instrument and perform test experiments at MDI.

Task 4 - Install test instrument at APS and perform experiments to validate instrument concept.

Task 5 - Analyze data and publish/present results.

The work performed is described in more detail in the following section.

Activities Performed and Results: This section provides a brief summary of the project research activities and results. Several significant scientific results have already been published in high profile peer reviewed journals. Additional publications are in preparation of review. As we stated in the Phase II proposal, peer reviewed publications are one of the most effective ways to generate interest in the novel research technology. Publication is a central component of the commercialization of the technology.

Task I – A detailed Critical Design Review (CDR) was held at APS on July 1, 2013. The review was illustrated with detailed 3D CAD images of the proposed instrument design and integration. Topics covered included: overall instrument layout, integration with the beamlines, utility requirements, storage of the instrument, laser, materials and x-ray safety, shipping and delivery, schedule, and candidate sample materials for testing during the beamline experiments. Following successful completion of the CDR, design work for the test levitator was completed.

Task 2 – Based on the requirements identified during the design phase, final parts were specified and ordered. Instrument assembly and testing were started as parts were delivered from vendors and machine shops. Photographs of the instrument and the computer control program user interface are presented in Figs.1 and 2.

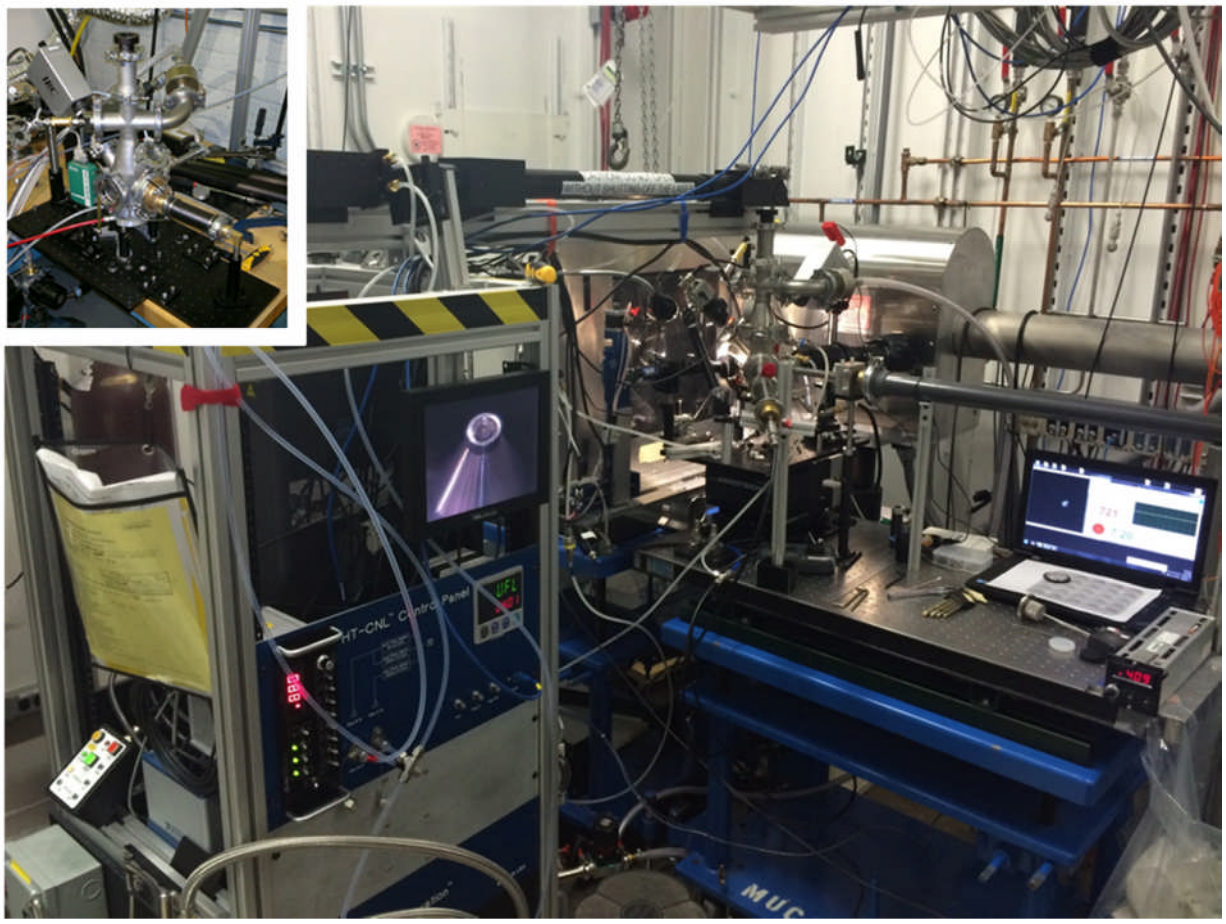

Fig. 1. Photograph of the levitator system installed at beamline 6 ID-D of the Advanced Photon Source. The laser system is mounted on a movable frame and directed onto the sample using mirrors. The sample is housed in a hermetically sealed chamber that is located on a table in the beamline hutch. The chamber is sealed onto a plenum base that houses the levitation nozzle. The frame houses a small monitor, gas flow controls and other ancillary components and power supplies. The inset shows a chamber set up for testing in MDI laboratories. The instrument is described in detail in our paper recently submitted to the Review of Scientific Instruments.

Fig. 2. Screen shot of the LabVIEW control panel screen. The program enables control and monitoring of the instrument functions and acquisition of the temperature data.

The instrument construction included development of new levitation nozzle designs, development, testing and integration of control software used to operate the instrument systems and acquire temperature data, and testing of all subsystems. The instrument integration was "mocked up" in MDI's facility and tested under a variety of operating conditions.

Task 3 – The test instrument was delivered to APS in late 2013. A total of 12 experimental campaigns were performed at APS. Most of these involved high energy diffraction at beamline 6 ID-D. Two campaigns were performed at beamline 20 BM-B to makes XANES measurements and on campaign at beamline 11 ID-C. 5 campaigns supported outside users from Aberystwyth University, Stony Brook University, University of California-Davis and University of Illinois Urbana-Champaign. Experiments were performed in support of work by Dr. Anna Prnova who from Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia who worked at APS on a Fulbright scholarship from October 2015-March 2016.

Samples were prepared from high purity metal oxide powders that were blended, fused on a laser hearth and formed into spheroidal samples approximately 3 mm in diameter. Samples were loaded into the levitation nozzle using an extended vacuum chuck. Some examples of sample materials investigated at the beamline are listed in Table I.

Table I. Composition of samples investigated at NOMAD using the aerodynamic levitation melting instrument.

Composition	Result

$CaSiO_3$	Published
Y_2O_3	Published
ZrO_2	Measurements on liquid and hot solid
UO_2	Published
FeO-SiO_2 binaries	XRD and XANES submitted and in preparation papers.
MgO-SiO_2 binaries	Measurements on normal and supercooled liquid
TiO_2	Published
Yttrium iron garnet	Measurements on liquid
Ca and Na borates	Published
Na_2CO_3	Published
Titanate liquids	XANES

The experiments at APS provided performance data and enabled detailed improvements in the precise design, operation and data analysis needed to exploit the sample environment. These aspects and the iteration of the designs are presented under Task 4.

Task 4 - Analyze experimental results and refine approach.

The research at APS resulted in significant improvements in the implementation of the aerodynamic levitation experiments. The principal advances were in the following areas:

1. Improving ease of installation of the levitator.
2. Improving stability and range of conditions that could be accessed.
3. Improving sample temperature control.
4. Providing precise control of gas chemistry.

The laser beam delivery system was redesigned using a two element lens system with an aperture. The new arrangement enabled precise delivery of the laser beam heating power to the sample with minimal heating of the levitation nozzle. By using the Stefan-Boltzmann relationship, the calculated radiative heat flux from a 3 mm diameter sample at 3500 ºC would be 324 W for a blackbody. In addition, some convective heat losses would occur due to the flowing levitation gas. In order to attain a sample temperature of 3500 ºC, the laser was operated at about 80% of full power – approximately 400 Watts. This result indicates that the laser beam power delivery is efficient with most of the laser power reaching and being absorbed by the sample. An increase in laser power beyond about 80 % power setting did not increase the sample temperature. We attribute this result to the beam diameter increasing at the maximum laser power setting such that the delivery optics do not transmit more power to the sample.

Commercial Development: MDI participated in the DOE Commercial Assistance Program (CAP) and worked with Dawnbreaker to implement a commercialization strategy. A central component of this strategy was the publication of scientific data in peer reviewed papers. This has been found to be an effective way to reach the target market and develop the product pedigree. As part of the CAP work, MDI's website, www.matsdev.com, was extensively updated to reflect the commercial availability of the new instrument.

MDI offers the extreme environment processing instrument under the trademark "Instruments for Innovation®" that was registered with the US Patent and Trademark Office on 11/19/2013.

MDI is currently building an instrument for customer in the US. We expect to close a sale to a customer in India in the near future. We have bids out for two additional instrument one in the US and one in Sweden. The use of the instrument has leveraged new R&D business, MDI is developing a capability for handling nuclear fuel materials in work funded by Argonne National Laboratory.

Outreach: MDI is actively engaged in a variety of outreach activities. MDI staff are members of professional societies and they regularly present results at scientific meetings and publish peer reviewed articles. This project supported work by Ms. Danni Jin and Mr. Alex Lin both of whom were Northwestern University Co-op undergraduate interns. They helped with sample preparation, instrument testing at MDI and experiments at the SNS. Ms. Alison Whale, an undergraduate at Coe College in Cedar Rapids, IA worked at MDI for a summer and assisted with sample preparation and offline characterization. Mr. Sam Sendelbach is a local high school student who assists MDI part time with lab duties.

List of publications that resulted from this work:

1. L.B. Skinner, A.C. Barnes, P.S. Salmon, L. Hennet, H.E. Fischer, C.J. Benmore, S. Kohara, J.K.R. Weber, A. Bytchkov, M.C. Wilding, J.B. Parise, T.O. Farmer, I. Pozdnyakova, S.K. Tumber, and K. Ohara, "The structure of liquid alumina: A joint diffraction and modeling approach," Phys. Rev. B. **87**, 024201(2013).

2. L.B. Skinner, C.J. Benmore, J.K.R. Weber, M.C. Wilding, S.K. Tumber and J.B. Parise, "A time resolved high energy X-ray diffraction study of cooling liquid SiO_2," Phys. Chem. Chem. Phys., **15**, 8566-72 (2013).

3. M.C. Wilding, M. Wilson, C.J. Benmore, J.K.R. Weber and P.F. McMillan, "Structural Changes in Supercooled Al_2O_3–Y_2O_3 Liquids," Phys. Chem, Chem. Phys., **15**, 8589 - 8605 (2013).

4. J.K.R. Weber, C.J. Benmore, L.B. Skinner, J. Neuefeind, S.K. Tumber, G. Jennings, L.J. Santodonato, D. Jin, J. Du and J.B. Parise, "Measurements of liquid and glass structures using *in-situ* high energy x-ray and neutron scattering," J. Non-cryst. Solids, **383**, 49-51 (2014).

5. J. Akola, S. Kohara, K. Ohara, A. Fujiwara, Y. Watanabe, A. Masuno, T. Usuki, T. Kubo, A. Nakahira, K. Nitta, T. Uruga, J.K.R.Weber and C.J. Benmore, "Network topology for

the formation of solvated electrons in binary $CaO–Al_2O_3$ composition glasses," Proc. Nat. Acad. Sci., **110**, 10129-10134 (2013).

6. L.B. Skinner, C. J. Benmore, J.K.R. Weber, J. Du, J. Neuefeind, S.K. Tumber, and J.B. Parise, "Low Cation Coordination in Oxide Melts," Phys. Rev. Lett., **112**, 157801 (2014).

7. O.L.G. Alderman, L.B. Skinner, C.J. Benmore, A. Tamalonis and J.K.R. Weber, "Structure of Molten Titanium Dioxide," Phys. Rev. B, **90**, 094204 (2014).

8. L.B. Skinner, C.J. Benmore, J. K.R. Weber, M.A. Williamson, A. Tamalonis, A. Hebden, T. Wiencek, O.L.G. Alderman, M. Guthrie, L. Leibowitz and J.B. Parise, "Molten Uranium Dioxide Structure and Dynamics," Science, 346, 984-87 (2014).

9. P.S. Maram, S.V. Ushakov, J.K.R. Weber, C.J. Benmore and A. Navrotsky, "*In Situ* Diffraction from Levitated Solids under Extreme Conditions - Structure and Thermal Expansion in the $Eu_2O_3–ZrO_2$ System," J. Am. Ceram. Soc., **98**, 1292-99 (2015).

10. M.C.Wilding, M. Wilson, P. F. McMillan, C. J. Benmore , J.K.R.Weber, T. Deschamps, and B. Champagnon, "Structural properties of $Y_2O_3–Al_2O_3$ liquids and glasses: An overview," J. Non-cryst. Solids, **407**, 228-34 (2015).

11. O.L.G. Alderman, G. Ferlat, A Baroni, M. Salanne, M. Micoulaut, C.J. Benmore, A. Lin, A. Tamalonis and J.K.R. Weber, "Liquid B_2O_3 up to 1700 K: x-ray diffraction and boroxol ring dissolution," J. Phys. Cond. Matt., 27, 455104 (2015).

12. M.C. Wilding, C.J. Benmore, J.K.R. Weber, J.B. Parise, L. Lazareva, L.B. Skinner, O.L.G. Alderman and A.J. Tamalonis, "Exploring the structure of high temperature, iron-bearing liquids," Mats. Today: Proceedings, 2S, 358 - 363 (2015).

13. O.L.G. Alderman, Oliver; M. Liška, J. Machacek, C.J. Benmore, A. Lin, A. Tamalonis and J.K.R. Weber, "Temperature-Driven Structural Transitions in Molten Sodium Borates Na_2O-B_2O_3: X-Ray Diffraction, Thermodynamic Modelling and Implications for Topological Constraint Theory," J. Phys. Chem. C, **120**, 553-560 (2016).

14. M.C. Wilding, M. Wilson, O.L.G. Alderman, C. Benmore, J.KR. Weber, J.B. Parise, A. Tamalonis and L.B. Skinner, "Low-Dimensional Network Formation in Molten Sodium Carbonate," Sci. Rep., **6**, 24415; doi: 10.1038/srep24415 (2016).

Appendix I

Headers and abstracts from selected publications.

PRL **112,** 157801 (2014) PHYSICAL REVIEW LETTERS week ending 18 APRIL 2014

Low Cation Coordination in Oxide Melts

L. B. Skinner,[1,2,3,*] C. J. Benmore,[2] J. K. R. Weber,[2,3] J. Du,[4] J. Neuefeind,[5] S. K. Tumber,[3] and J. B. Parise[1]
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(Received 12 September 2013; published 17 April 2014)

The complete set of partial pair distribution functions for a rare earth oxide liquid are measured by combining aerodynamic levitation, neutron and x-ray diffraction on Y_2O_3, and Ho_2O_3 melts at 2870 K. The average Y-O (or Ho-O) coordination of these isomorphic melts is measured to be 5.5(2), which is significantly less than the octahedral coordination of crystalline Y_2O_3 (or Ho_2O_3). Investigation of La_2O_3, ZrO_2, and Al_2O_3 melts by x-ray diffraction and molecular dynamics simulations also show lower-than-crystal cation-oxygen coordination. These measurements suggest a general trend towards lower coordination compared to their crystalline counterparts. It is found that the coordination drop is larger for lower field strength, larger radius cations and is negligible for high field strength (network forming) cations, such as SiO_2. These findings have broad implications for predicting the local structure and related physical properties of metal-oxide melts and oxide glasses.

DOI: 10.1103/PhysRevLett.112.157801 PACS numbers: 61.20.-p, 61.25.-f, 64.70.dj

Science AAAS

Molten uranium dioxide structure and dynamics

L. B. Skinner *et al.*
Science **346**, 984 (2014);
DOI: 10.1126/science.1259709

L. B. Skinner,[1,2,3]* C. J. Benmore,[1] J. K. R. Weber,[1,3] M. A. Williamson,[4] A. Tamalonis,[1] A. Hebden,[4] T. Wiencek,[5] O. L. G. Alderman,[1,3] M. Guthrie,[6] L. Leibowitz,[4] J. B. Parise[2,7]

Uranium dioxide (UO_2) is the major nuclear fuel component of fission power reactors. A key concern during severe accidents is the melting and leakage of radioactive UO_2 as it corrodes through its zirconium cladding and steel containment. Yet, the very high temperatures (>3140 kelvin) and chemical reactivity of molten UO_2 have prevented structural studies. In this work, we combine laser heating, sample levitation, and synchrotron x-rays to obtain pair distribution function measurements of hot solid and molten UO_2. The hot solid shows a substantial increase in oxygen disorder around the lambda transition (2670 K) but negligible U-O coordination change. On melting, the average U-O coordination drops from 8 to 6.7 ± 0.5. Molecular dynamics models refined to this structure predict higher U-U mobility than 8-coordinated melts.

Structure of molten titanium dioxide

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(Received 29 July 2014; revised manuscript received 27 August 2014; published 18 September 2014)

The x-ray structure factor of molten TiO_2 has been measured, enabled by the use of aerodynamic levitation and laser beam heating, to a temperature of $T = 2250(30)$ K. The Ti-O coordination number in the melt is close to $n_{TiO} = 5.0(2)$, with modal Ti-O bond length $r_{TiO} = 1.881(5)$ Å, both values being significantly smaller than for the high temperature stable rutile crystal structure ($n_{TiO} = 6.0$, $r_{TiO} = 1.959$ Å). The structural differences between melt and crystal are qualitatively similar to those for alumina, which is rationalized in terms of the similar field strengths of Ti^{4+} and Al^{3+}. The diffraction data are used to generate physically and chemically reasonable structural models, which are then compared to the predictions based on various classical molecular dynamics (MD) potentials. Interatomic potentials, suitable for modeling molten TiO_2, are introduced, given the inability of existing MD models to reproduce the diffraction data. These potentials have the additional advantage of being able to predict the density and thermal expansion of the melt, as well as solid amorphous TiO_2, in agreement with published results. This is of critical importance given the strong correlation between density and structural parameters such as n_{TiO}. The large thermal expansion of the melt is associated with weakly temperature dependent structural changes, whereby simulations show that $n_{TiO} = 5.85(2) - [3.0(1) \times 10^{-4}]T$(K, 2.75 Å cutoff). The TiO_2 liquid is structurally analogous to the geophysically relevant high pressure liquid silica system at around 27 GPa. We argue that the predominance of fivefold polyhedra in the melt implies the existence of as-yet-undiscovered TiO_2 polymorphs, based on lower-than-octahedral coordination numbers, which are likely to be metastable under ambient conditions. Given the industrial importance of titanium oxides, experimental and computational searches for such polymorphs are well warranted.

DOI: 10.1103/PhysRevB.90.094204 PACS number(s): 61.43.−j, 61.05.cp, 61.20.Ja

IOP Publishing

Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **27** (2015) 455104 (15pp)

doi:10.1088/0953-8984/27/45/455104

Liquid B_2O_3 up to 1700 K: x-ray diffraction and boroxol ring dissolution

O L G Alderman[1,2], G Ferlat[3], A Baroni[3,4,5], M Salanne[4], M Micoulaut[5], C J Benmore[2], A Lin[1,6], A Tamalonis[1] and J K R Weber[1,2]

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Received 26 August 2015
Accepted for publication 30 September 2015
Published 29 October 2015

Abstract

Using high energy x-ray diffraction, the structure factors of glassy and molten B_2O_3 were measured with high signal-to-noise, up to a temperature of $T = 1710(20)$ K. The observed systematic changes with T are shown to be consistent with the dissolution of hexagonal $[B_3O_6]$ boroxol rings, which are abundant in the glass, whilst the high-T ($\gtrsim$1500 K) liquid can be more closely described as a random network structure based on $[BO_3]$ triangular building blocks. We therefore argue that diffraction data *are* in fact qualitatively sensitive to the presence of small rings, and support the existence of a continuous structural transition in molten B_2O_3, for which the temperature evolution of the 808 cm^{-1} Raman scattering band (boroxol breathing mode) has long stood as the most emphatic evidence. Our conclusions are supported by both first-principles and polarizable ion model molecular dynamics simulations which are capable of giving good account of the experimental data, so long as steps are taken to ensure a ring fraction similar to that expected from Raman spectroscopy. The mean thermal expansion of the B-O bond has been measured directly to be $\alpha_{BO} = 3.7(2) \times 10^{-6}\ K^{-1}$, which accounts for a few percent of the bulk expansion just above the glass transition temperature, but accounts for greater than one third of the bulk expansion at temperatures in excess of 1673 K.

Keywords: liquid structure, boron oxide, borate, aerodynamic levitation, laser heating, glass structure, molecular dynamics

The Journal of Physical Chemistry C 2016 *120* (1), 553-560

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Temperature-Driven Structural Transitions in Molten Sodium Borates $Na_2O-B_2O_3$: X-ray Diffraction, Thermodynamic Modeling, and Implications for Topological Constraint Theory

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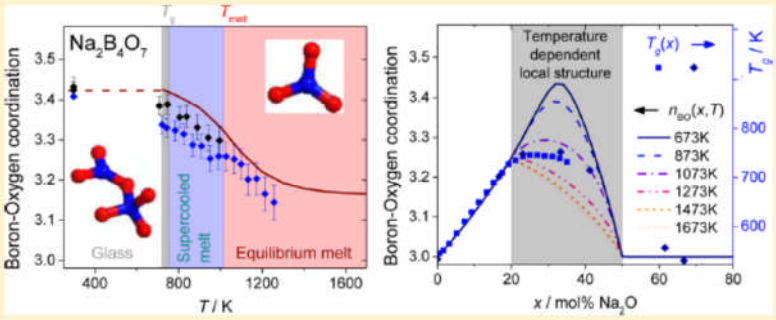

ABSTRACT: Temperature-dependent measurements of the X-ray structure factor of molten $Na_2B_4O_7$ reveal a continuous structural transition. We demonstrate that the thermodynamic model of ideal associated solutions is capable of predicting this evolution of melt structure, between a low density, depolymerized melt at $\gtrsim$300 K above the liquidus, toward a dense, polymerized melt close to the glass transition. This temperature-dependent nature of melt structure is predicted to be strongly composition-dependent, with the B−O coordination number depending on temperature only in the range 20−50 mol % Na_2O, which appears to be manifest in the broad maximum observed in the glass-transition temperatures. We discuss the ramifications of these findings for the application of topological constraint theory, with relevance to industrial glass design and manufacture, crystal growth from melts of nonlinear optical materials, geochemistry, and the understanding of melt fragility and the glass transition.

Sci. Rep., 6, 24415; doi: 10.1038/srep24415 (2016).

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SCIENTIFIC REPORTS

OPEN

Low-Dimensional Network Formation in Molten Sodium Carbonate

Received: 06 December 2015
Accepted: 17 March 2016
Published: 15 April 2016

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Molten carbonates are highly inviscid liquids characterized by low melting points and high solubility of rare earth elements and volatile molecules. An understanding of the structure and related properties of these intriguing liquids has been limited to date. We report the results of a study of molten sodium carbonate (Na_2CO_3) which combines high energy X-ray diffraction, containerless techniques and computer simulation to provide insight into the liquid structure. Total structure factors ($F^x(Q)$) are collected on the laser-heated carbonate spheres suspended in flowing gases of varying composition in an aerodynamic levitation furnace. The respective partial structure factor contributions to $F^x(Q)$ are obtained by performing molecular dynamics simulations treating the carbonate anions as flexible entities. The carbonate liquid structure is found to be heavily temperature-dependent. At low temperatures a low-dimensional carbonate chain network forms, at $T = 1100$ K for example ~55% of the C atoms form part of a chain. The mean chain lengths decrease as temperature is increased and as the chains become shorter the rotation of the carbonate anions becomes more rapid enhancing the diffusion of Na^+ ions.