Non-equilibrium materials from high temperature liquids

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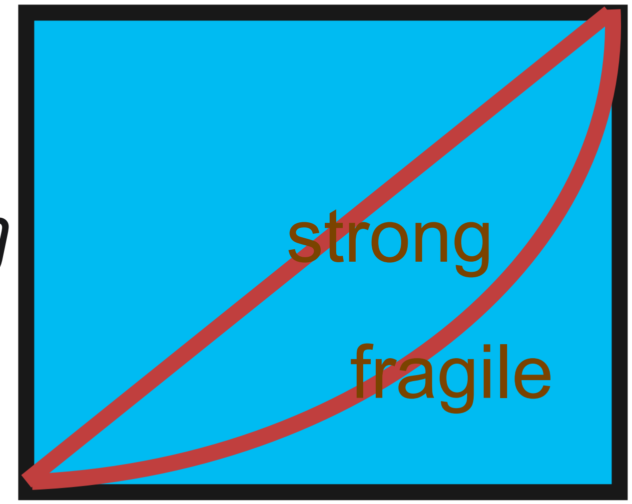
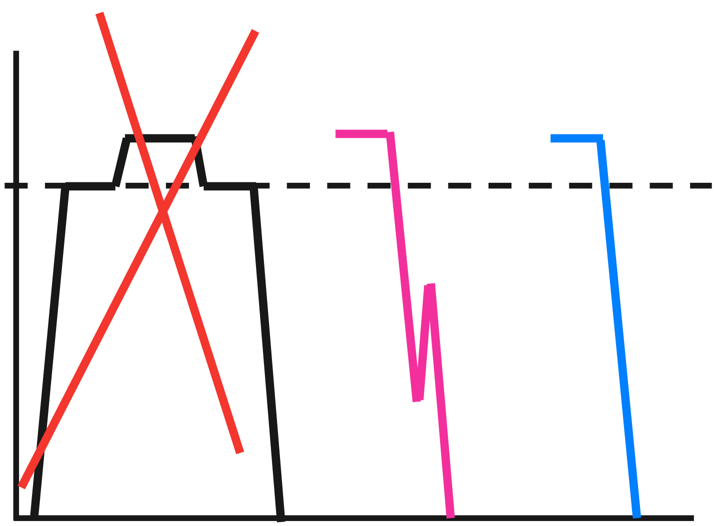
Background/motivation

- To investigate structural evolution in high temperature liquids and nucleation in glasses/liquids, including photonic and geological materials

- To improve materials processing – quality, performance, energy and raw materials use





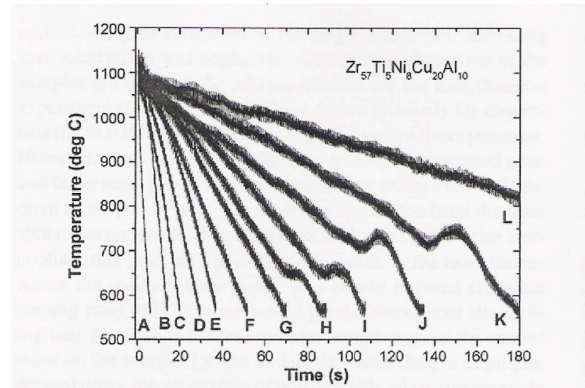
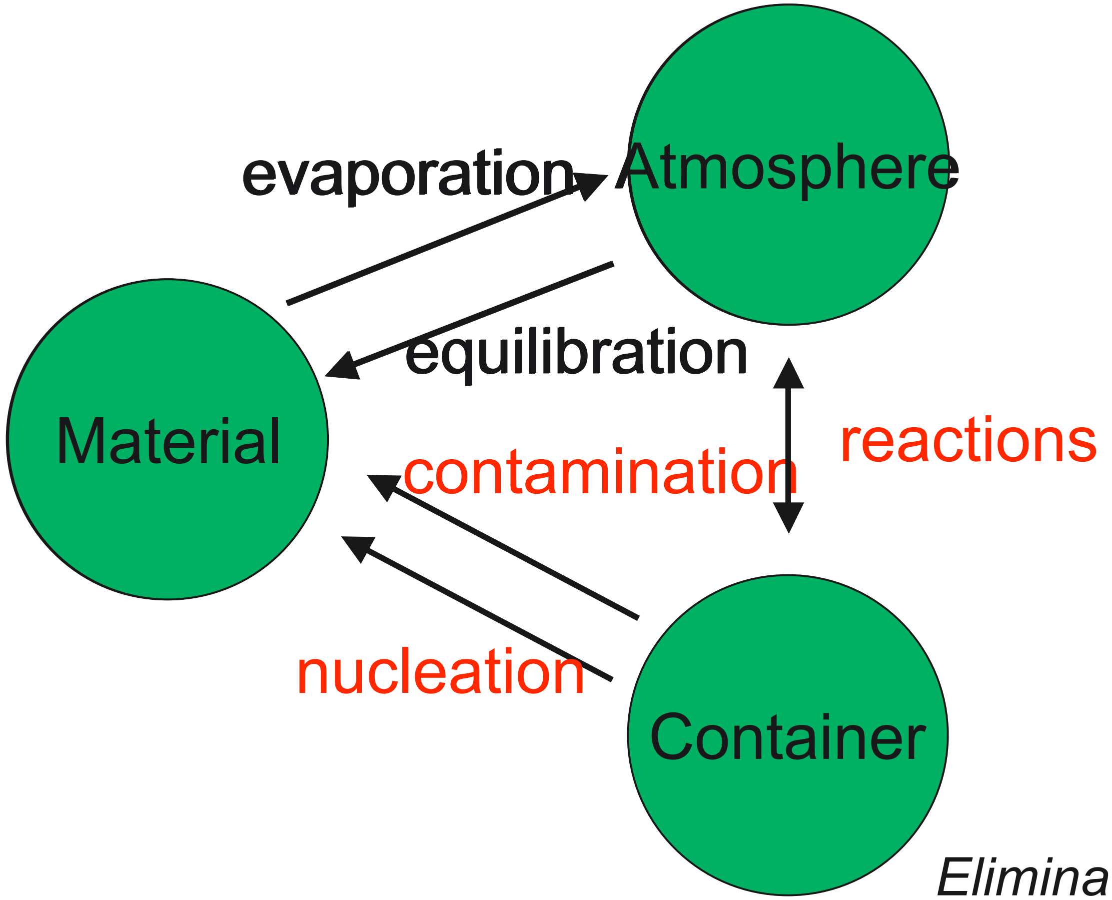


Fig. 2. Time–temperature curves of $Zr_{57}Ti_5Ni_8Cu_{20}Al_{10}$ spheres processed with 69–1.2 K/s cooling rates. The process cooling rates (slopes of the respective curves) are: A, 69 K/s; B, 38 K/s; C, 23 K/s; D, 16 K/s; E, 13 K/s; F, 11 K/s; G, 8 K/s; H, 6 K/s; I, 4.5 K/s; J, 3.5 K/s; K, 2.7 K/s; L, 1.2 K/s (recalesced at $t = 220$ s, $T = 730$ °C). Note that curve "G" exhibits a slight exotherm at ~625 °C, which is not clearly visible in the scale used here.

Wall, *et al*, Mater. Sci. Eng. A, **445-446**, 219-222 (2007).

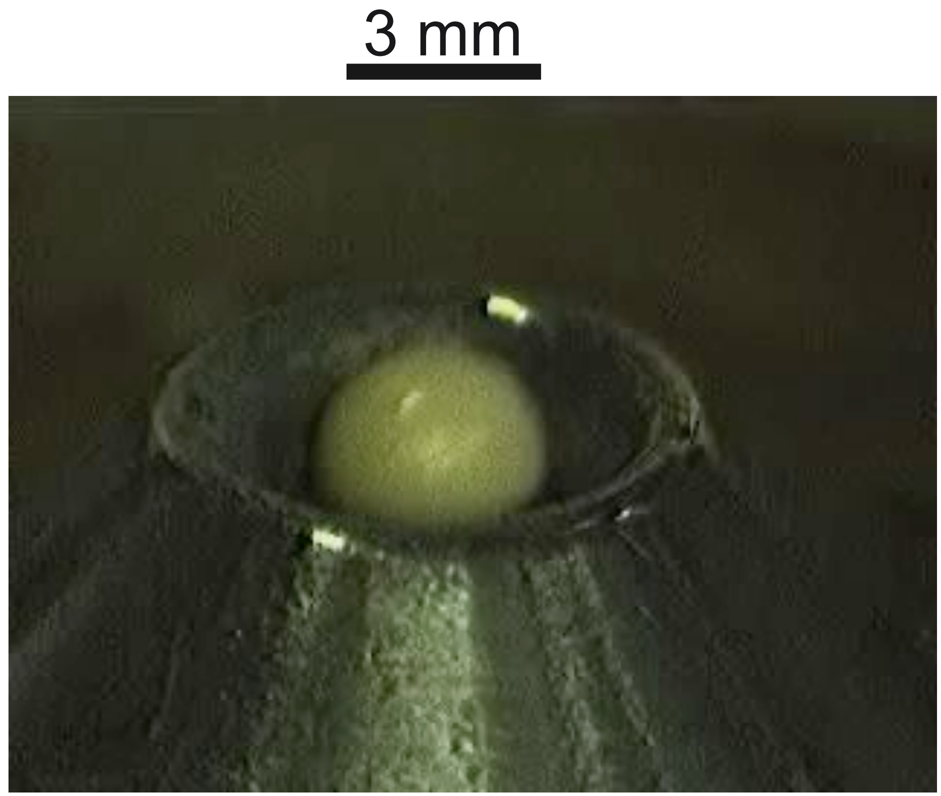
Containerless processing/levitation



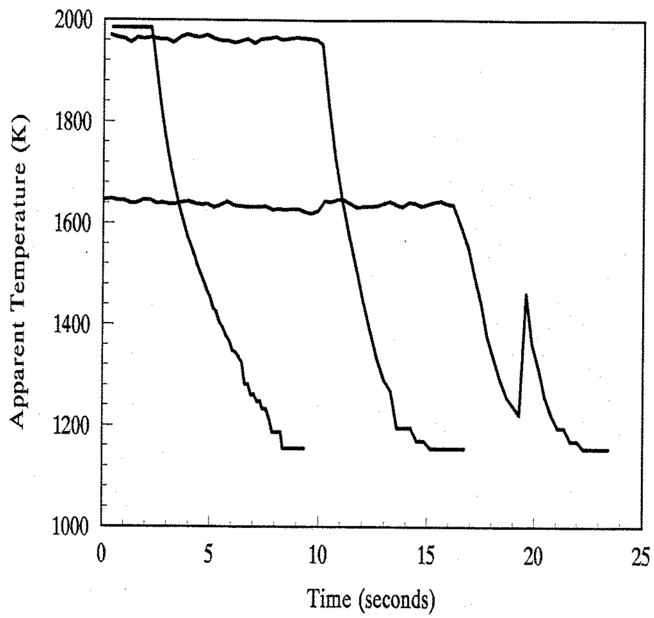
$$F = -mg$$

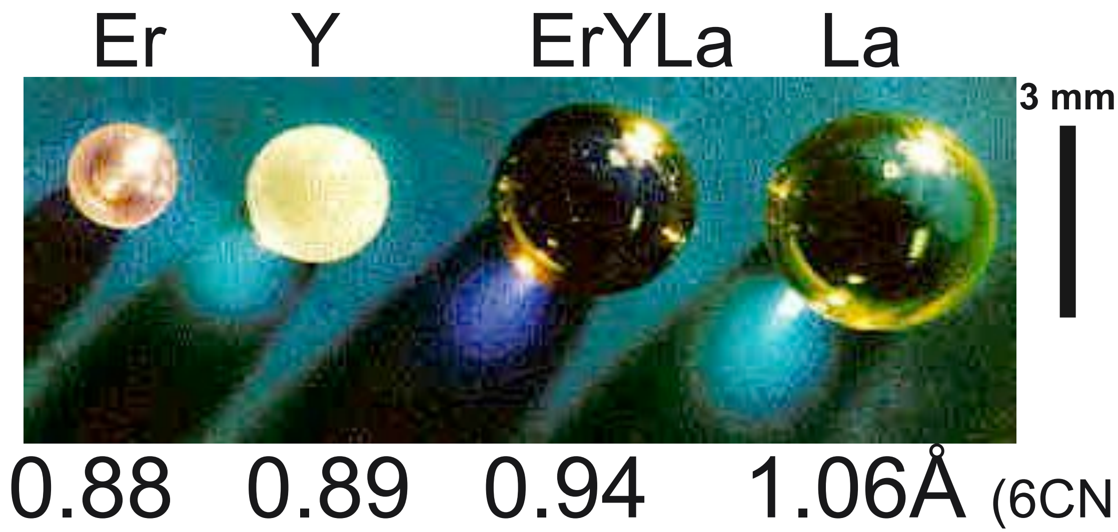
Elimination of the container provides access to high purity, non-equilibrium liquids and pristine liquid surfaces and maintains chemical purity.

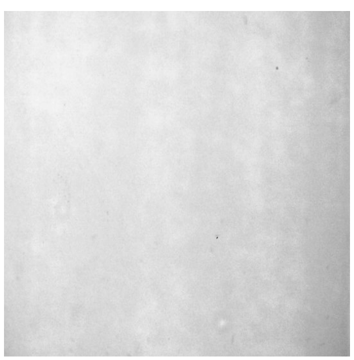
Methods for containerless processing/levitation



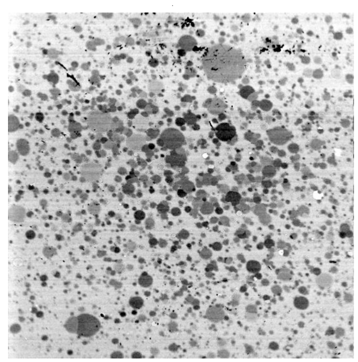
“Garnet glasses” : 3:5 R_2O_3-Al_2O_3



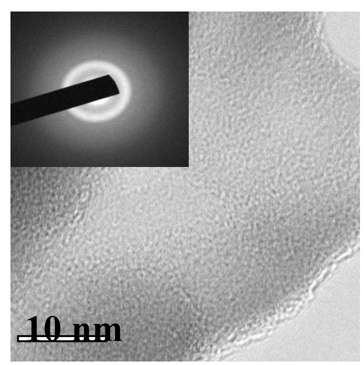




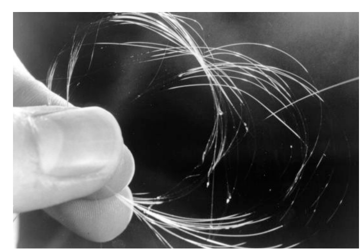
1-phase glass



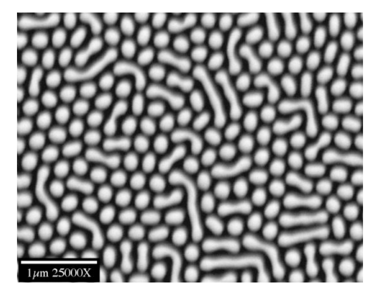
2-phase glass



TEM ht. treated gl.



Fibers from u/c liq.



SEM fast sol. liquid

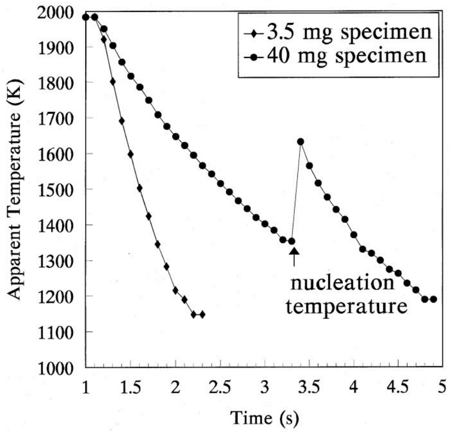
Weber, *et al.* J. Am. Ceram. Soc., **83**, 1868 (2000), Weber, *et al* Nature, 393, 769 (1998).

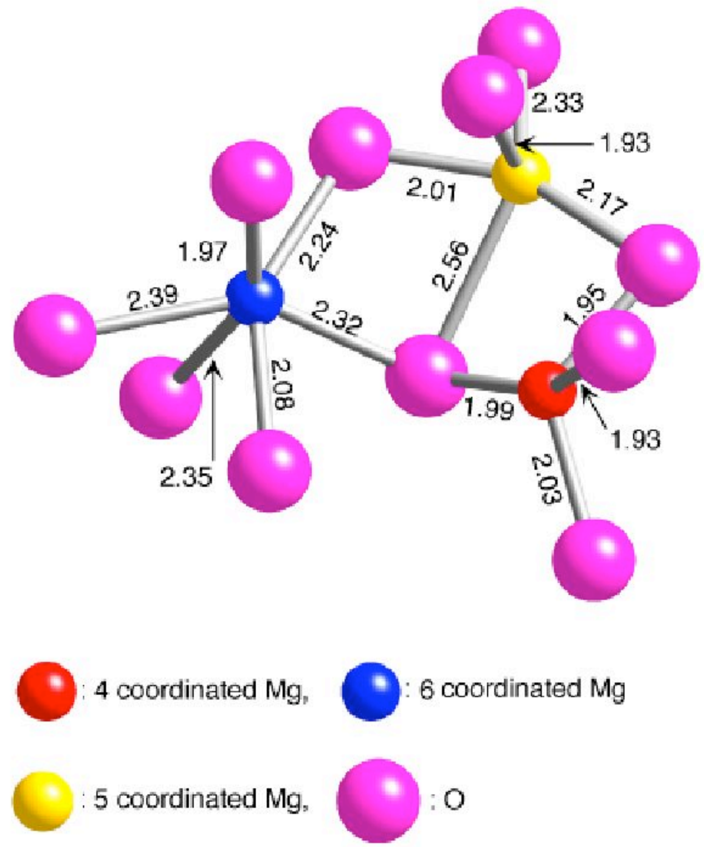
Process parameters for several glass compositions

Composition	***Approx. R_C (K/s)***	***Approx. SCL (K)***
Alum. Orthosil. 67 A 33 S	1000	10
Forsterite 67 M 33 S	700	10
Mullite 60 A 40 S	500	10
YAG 62.5 A 37.5 Y	100	10
LAG 62.5 A 37.5 L	50	80
55 A 35 Y 10 S	25	150
50 A 20 L 10 Y 20 S	10	150
55 A 30 RE 20 S	5-10	200

ΔC_P at T_g from ~80 to 20 J/M_2O_3 going down series

“Orthosilicate glass”: Mg_2SiO_4





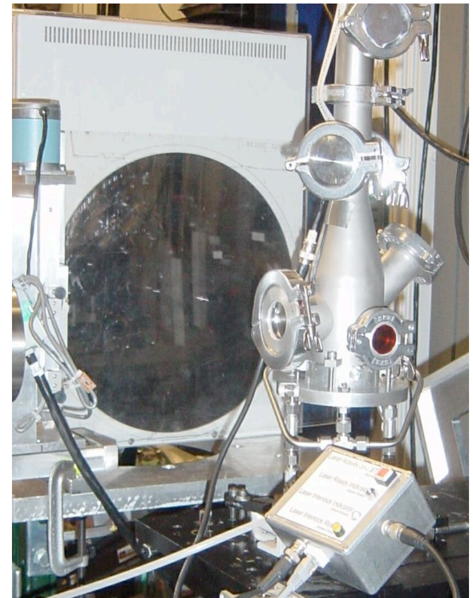
$2\ SiO_4^{4-} \rightarrow Si_2O_7^{6-}$ [corner] + O^{2-}
$Mg_2O_9^{14-}$ [edge] + $O^{2-} \rightarrow Mg_2O_{10}^{16-}$ [corner]

Forming Si-O-Si bridges frees oxygen that can increase Mg-O CN or “open up” Mg-O-Mg bonds

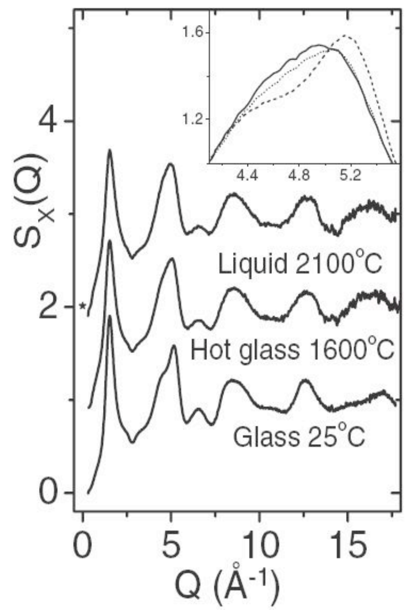
Tangeman, *et al*. GRL, **28**, 2517 (2001), Kohara, *et al*, Science, **303**, 1649 (2004).

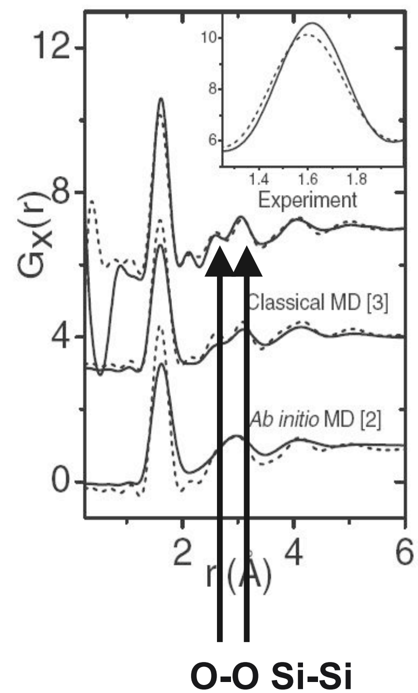
High energy X-ray measurements on liquids at APS

- Collaboration with Chris Benmore, Qiang Mei and Martin Wilding + outside users.
- 4 campaigns so far, 5 collaborating groups
- Investigated: SiO_2, CaO-Al_2O_3, MgO-SiO_2, Al_2O_3-SiO_2, RE_2O_3-Al_2O_3 and metallic alloys
- Using ~115 keV X-rays and Mar345 image plate at 11 ID-C
- Provides bulk probe, X-rays penetrate the sample, fast measurements (minutes), high Q-range



Structure of liquid SiO_2

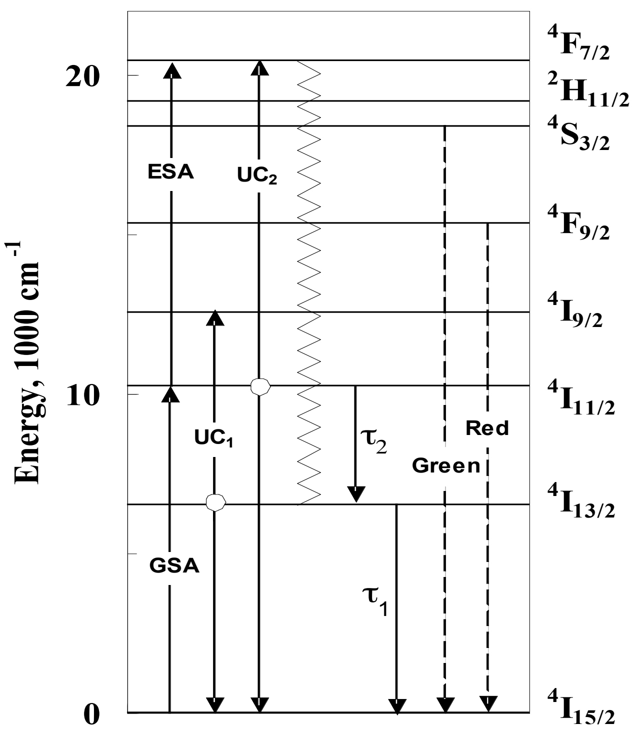


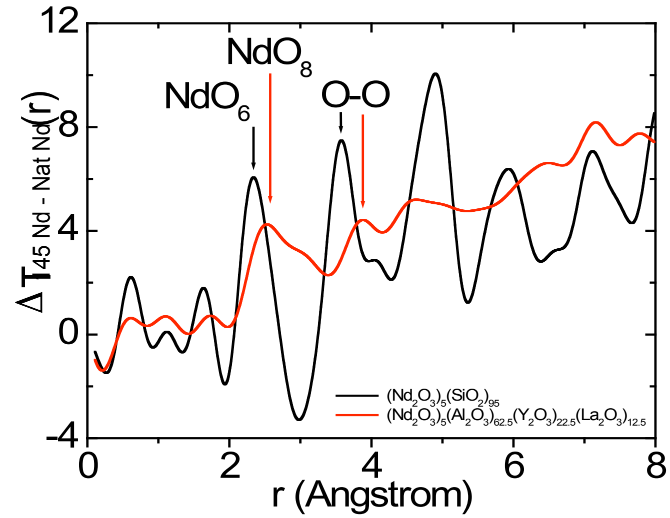


Mei, *et al*, PRL, 98, 057802 (2007).

- Main change is in shape of 2^{nd} peak in S(Q)
- Strong FSDP suggests robust network at high T
- Differences 1600-2100°C small 25-1600°C
- 2% increase in Si-O bond length from 25 to 1600°C
- Ave. bond angle decreases ~9° with T – small changes in polymer ring size

Dopant ions in glasses





- Studies using natural and ^{145}Nd enriched
- Predominantly NdO_8 in RE-Al and NdO_6 in SiO_2 host
- Increased intermediate range order in SiO_2 host consistent with Nd-O-Nd bonding (clustering)

Benmore, *et al*, Appl. Phys. Lett. **24**, 4954-56 (2003)

Summary and outlook

- Extreme sample environment can access deeply undercooled liquids, allow controlled nucleation of crystallites, and synthesize novel glassy and NE materials

- High energy, high flux X-rays can probe structures *in-situ* but not yet in real time – *more flux and faster detection are desirable*

- Plans to set up lab-based levitator at APS for glass synthesis and processing and to upgrade SE control, heating and measurement

- Area of interest: Nano-nucleation/crystallization of “extreme” glasses, dopant ion environment in glasses, “ambiguous” polyamorphic/ glacial/quasi-crystal states formed from non-equilibrium liquids

Thanks!

- Funding: Department of Energy, NSF, NASA

- Collaborators: Beamline experiments: Chris Benmore, Qiang Mei, Argonne, Martin Wilding U. Wales, Jim Rix MDI. Glass synthesis: Kirsten Hiera, April Hixson, Tom Key, Jean Tangeman.