Microgravity Studies of Liquid-Liquid Phase Transitions in Undercooled Alumina-Yttria Melts

NASA Contract number NAS8-98092
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Containerless Research, Inc.

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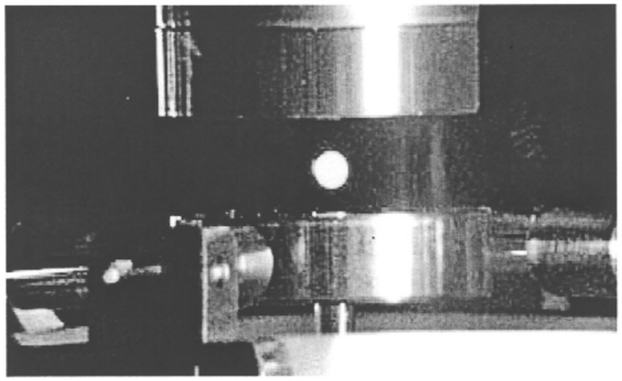
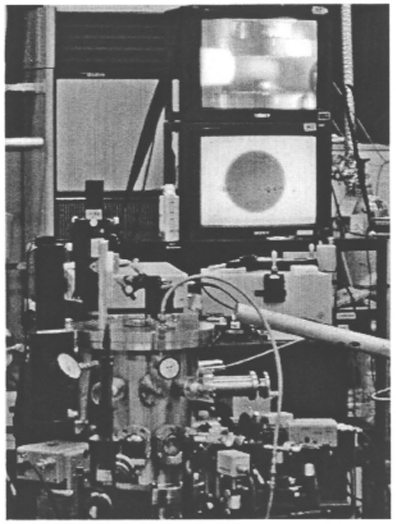
Outline

- Background
  - techniques
  - undercooling, glass formation, applications
  - role of low gravity experiments
- Current activities
  - melt structure
  - glass structure
  - melt properties
- Future/ongoing activities
  - kinetics of L-L transition
  - measurements of liquid properties
  - detailed structure model

Containerless techniques used to avoid contamination of corrosive melts, control melt chemistry, and access highly non-equilibrium oxide liquids

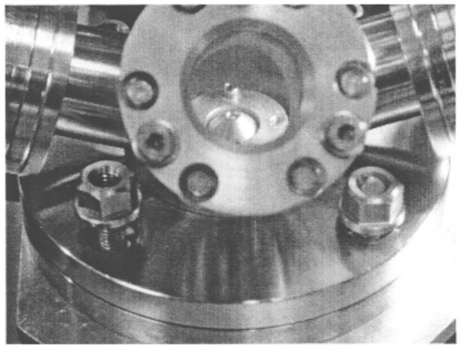


Electrostatic Levitation (ESL) at NASA Marshall Space Flight Center [RSI, **64**, 2961 (1993)]



Pressurized ESL at NASDA Tsukuba Space Center [RSI, **72**, 2811 (2001)]

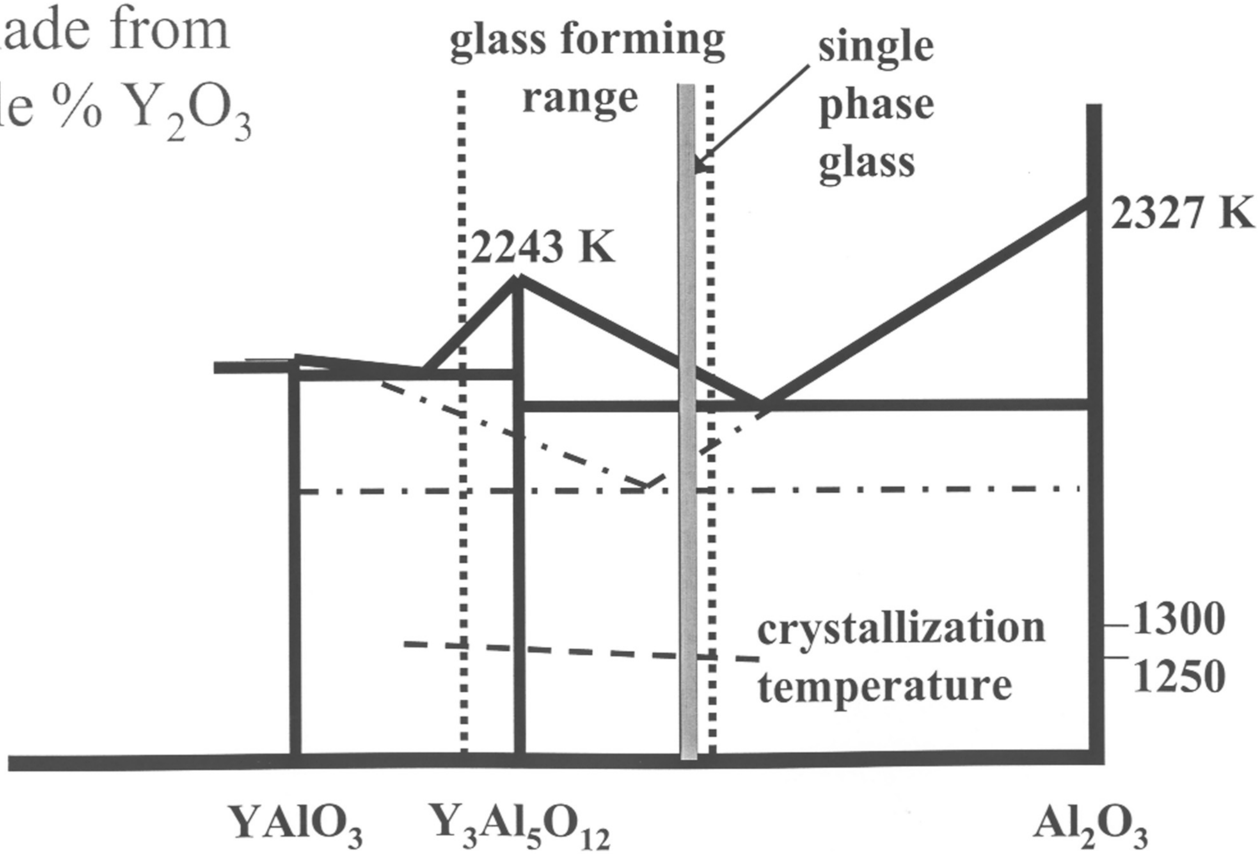
Aero-acoustic Levitation [Science, **287** (2000), RSI, **65**, 456 (1994)]



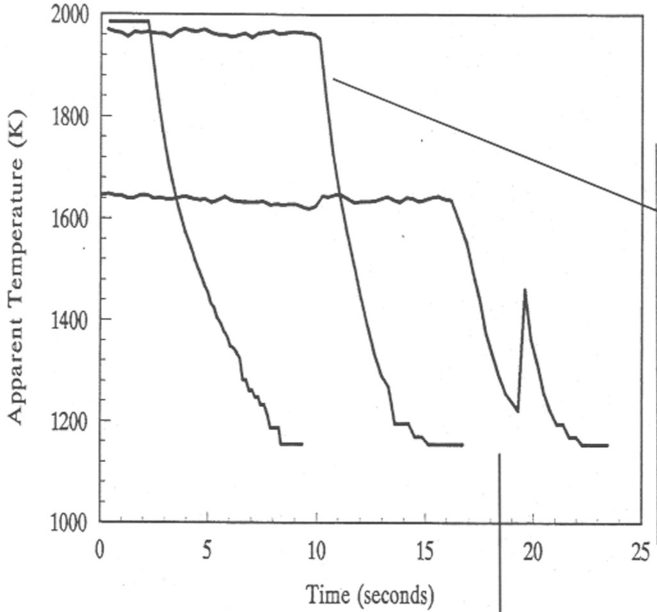
Aerodynamic Levitation [Microg. Sci. Tech., **7**, 279 (1995)]

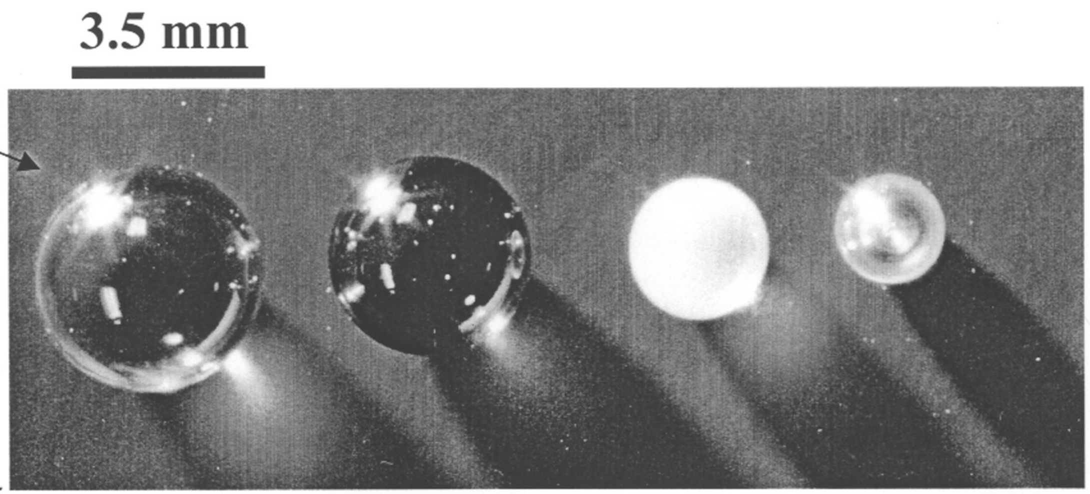
Compositions under investigation

Glasses made from 23-42 mole % Y_2O_3

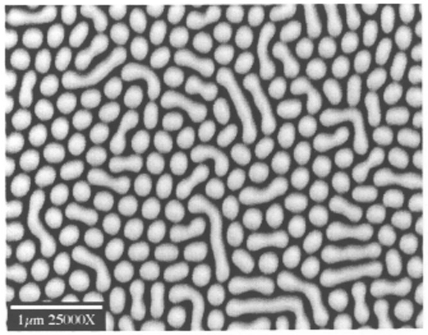


Glasses made from RE-Al oxide materials



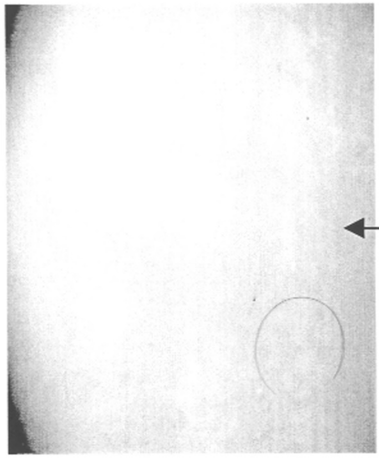


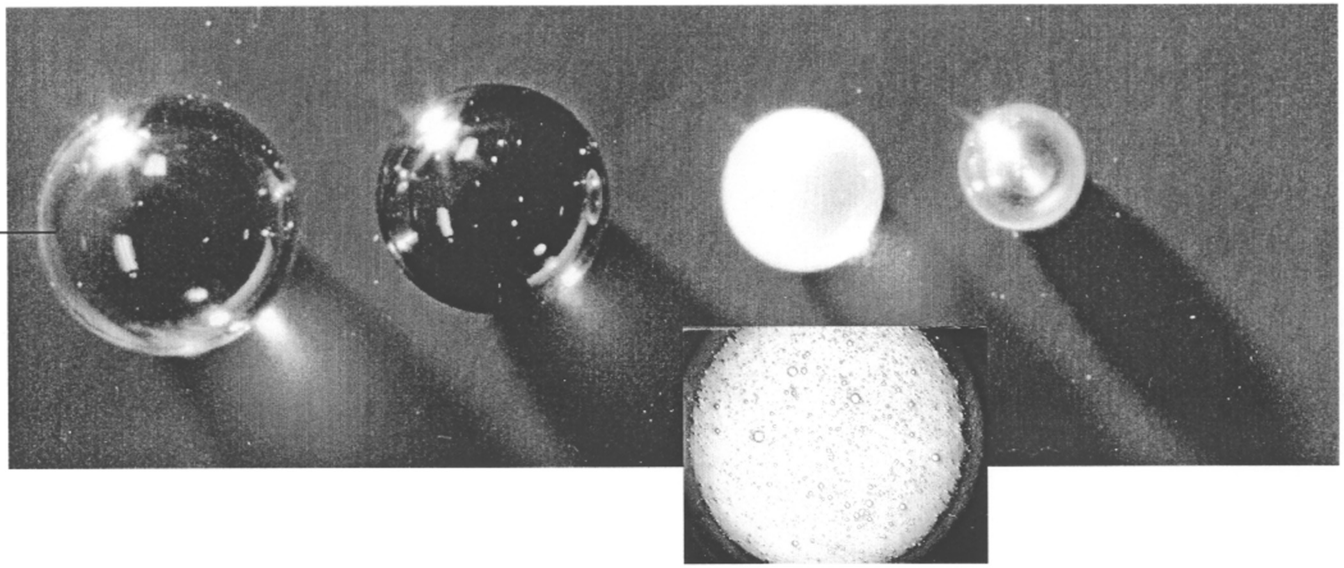
$La_3Al_5O_{12}$ $LaErYAl_5O_{12}$ $Y_3Al_5O_{12}$ $Er_3Al_5O_{12}$



BSE YAG-alumina eutectic
by Greg Jerman, NASA MSFC

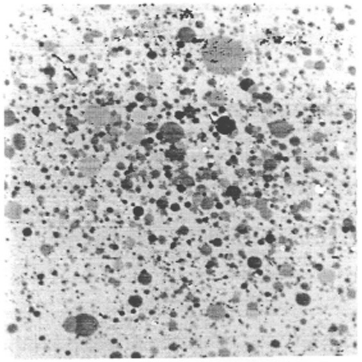
Glasses made from RE-Al oxide materials

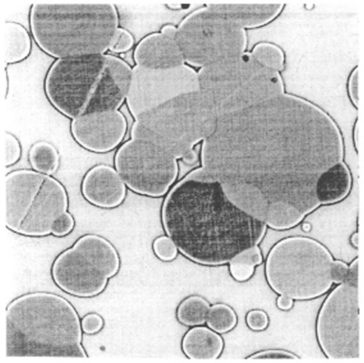




WDS analysis results, average of 10 points

Area of sample	O (At%)	SD	Al (At%)	SD	Y (At%)	SD
Matrix	58.91	0.12	26.34	0.08	14.75	0.09
Light spheroids	58.70	0.10	26.45	0.06	14.86	0.05
Dark spheroids	58.61	0.09	26.55	0.06	14.84	0.09

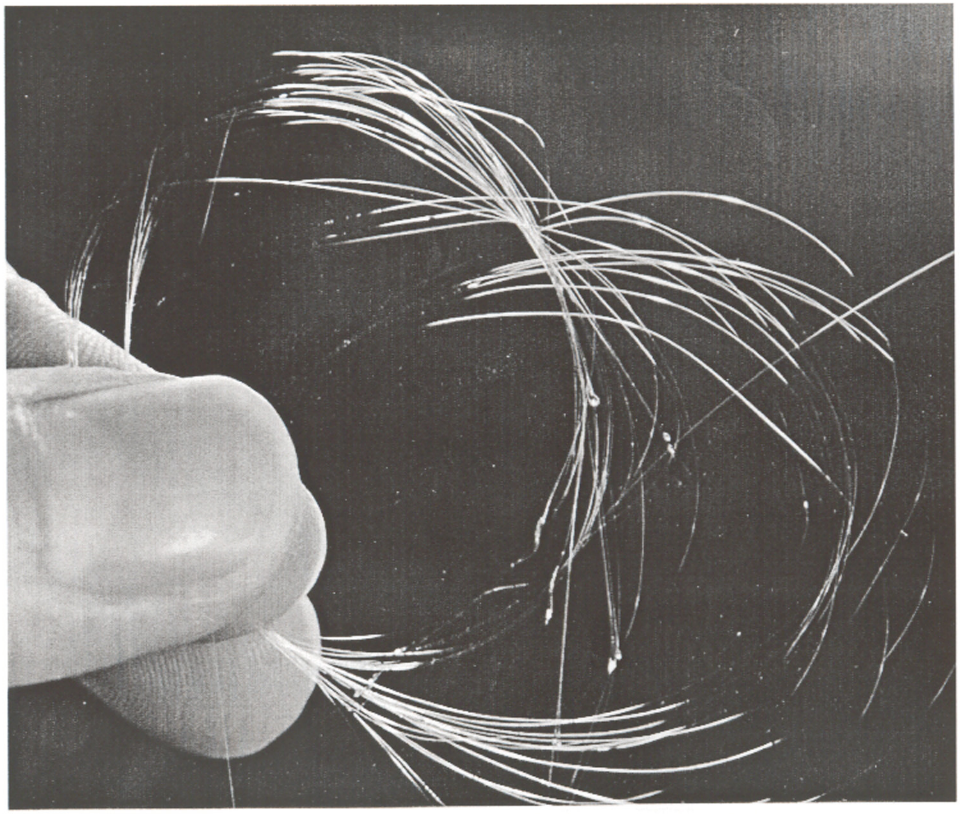




BSE

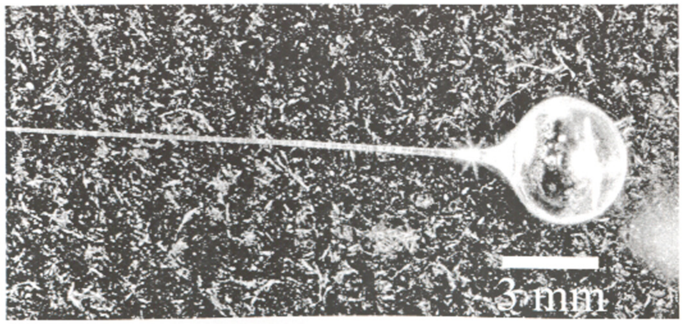
[J. Am. Ceram. Soc., **83**, 1868 (2000)]

$Y_3Al_5O_{12}$-composition Glass Fibers

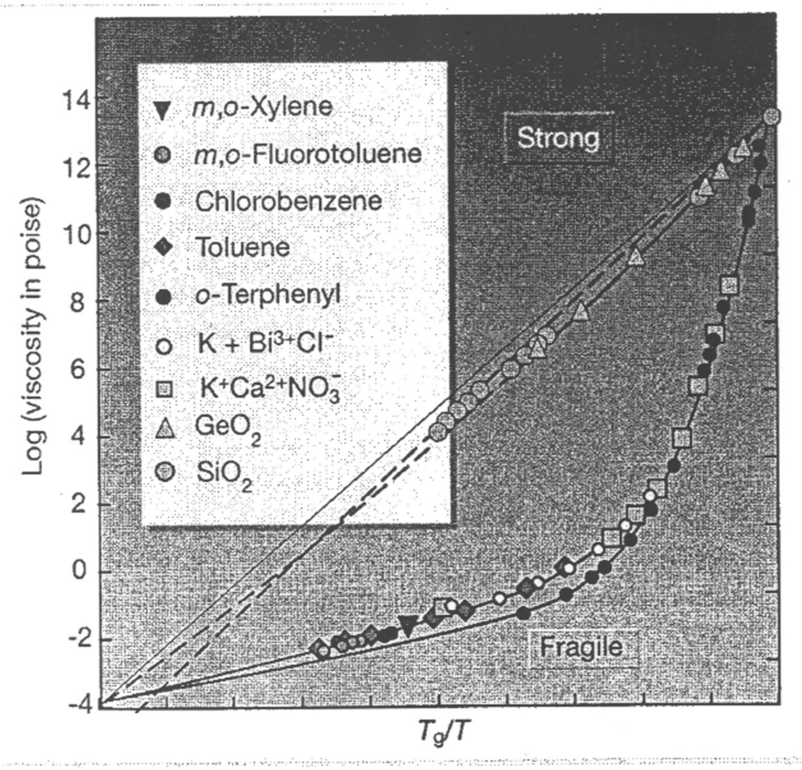


[Nature, **393**, 769 (1998)]

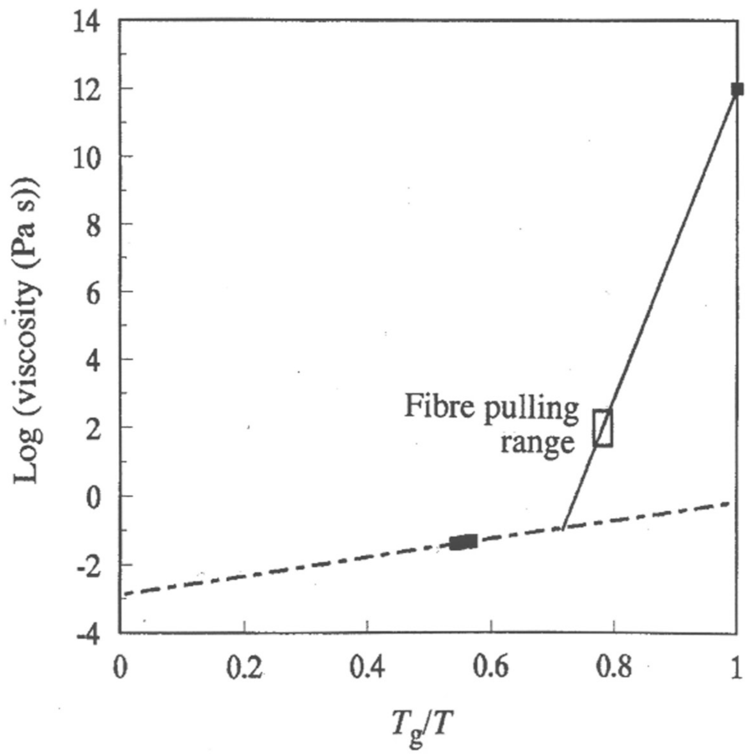
- Glass fibers pulled from liquid at 1600-1650 K (600 below Tm)
- Er-doped glass spheroid showing attenuation of a fiber.



Strong and Fragile Liquids



[Adapted from Angell, Science, **267**, 1924 (1995)]



[Nature, **393**, 769 (1998)]

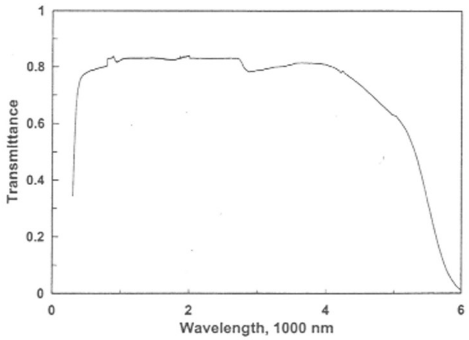
Fragility index, $2(Tg/T_{1/2}) - 1$, of YAG is about 0.65

Some properties of REAl^{TM} glass materials

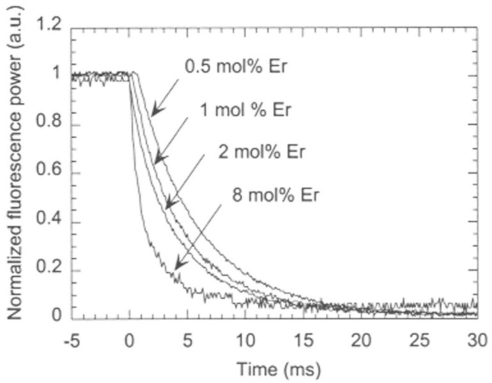
* REAl glasses are: hard (900 Hv), strong, high refractive index (1.7), thermally (Tg >1100 K),chemically and mechanically stable, good solvents for RE ions, homogeneous dopant distribution

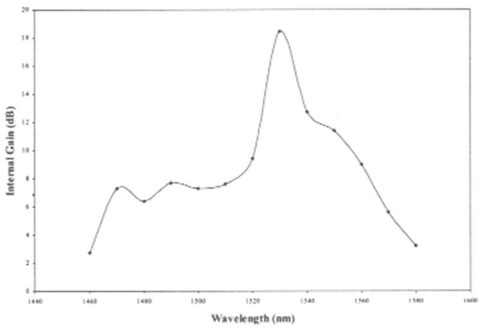
* One of the first "new" oxide glasses in about 30 years -- patents pending

* Applications include high power density lasers for *communications, surgery and rangefinding/detection*



[J. Am. Ceram. Soc., **85**, 1309 (2002)]



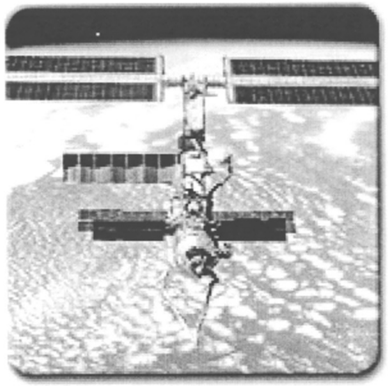


$^4I_{13/2} > {}^4I_{15/2}$ transition in Er^{3+} ions

Experimental Hypotheses

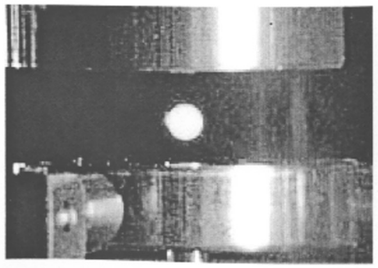
- A liquid-liquid phase transition can occur in undercooled A-Y melts by a diffusionless process

- Onset of the liquid-liquid phase transition is accompanied by a large change in the temperature dependence of viscosity

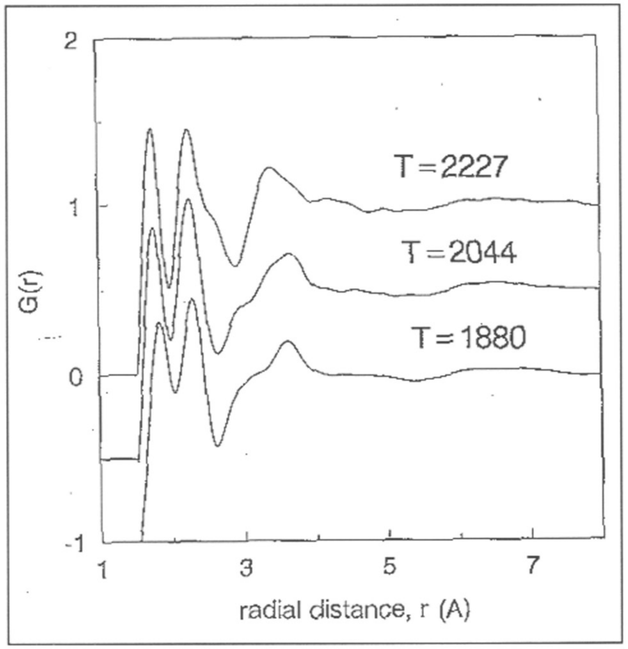


Role of low gravity experiments

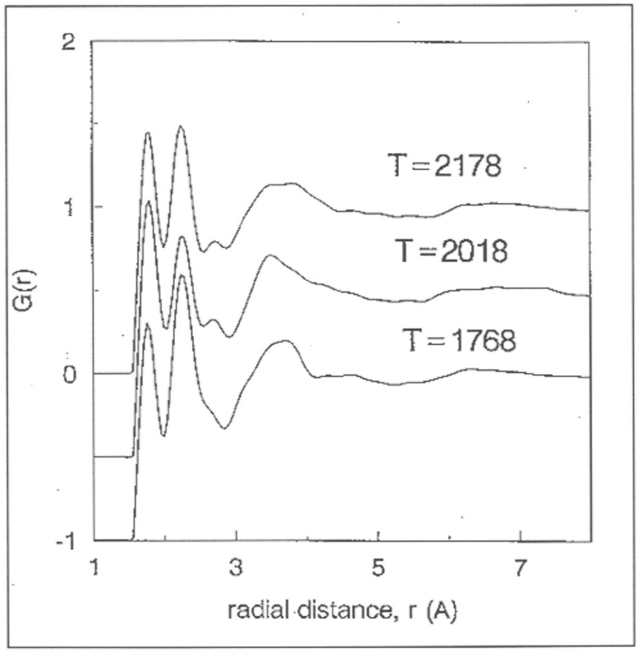
- We are studying kinetics in a liquid-liquid system: *it is essential to decouple diffusion and convection transport*
- The two phases have different densities: *sedimentation occurs on earth unless the melt is well stirred*
- Accurate measurement of melt viscosity requires a large and "quiescent" sample: *positioning forces can be minimized in low gravity allowing large samples to be used*



Structure of molten $Y_3Al_5O_{12}$



Argon



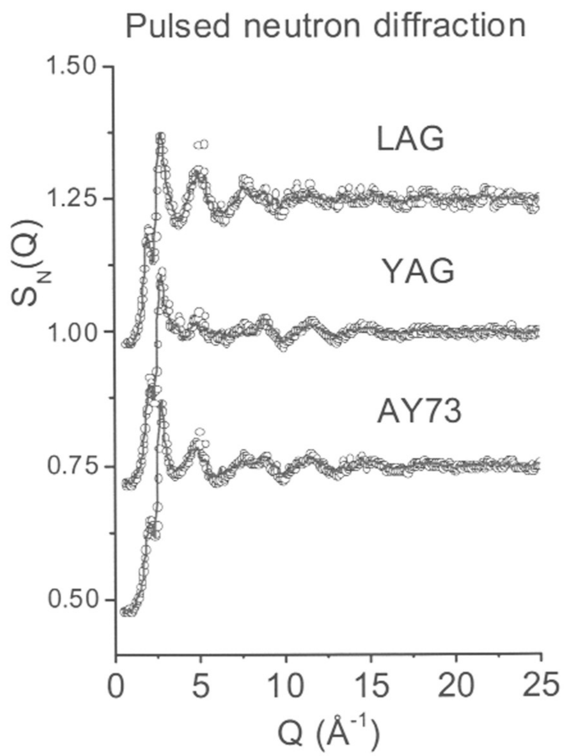
Oxygen

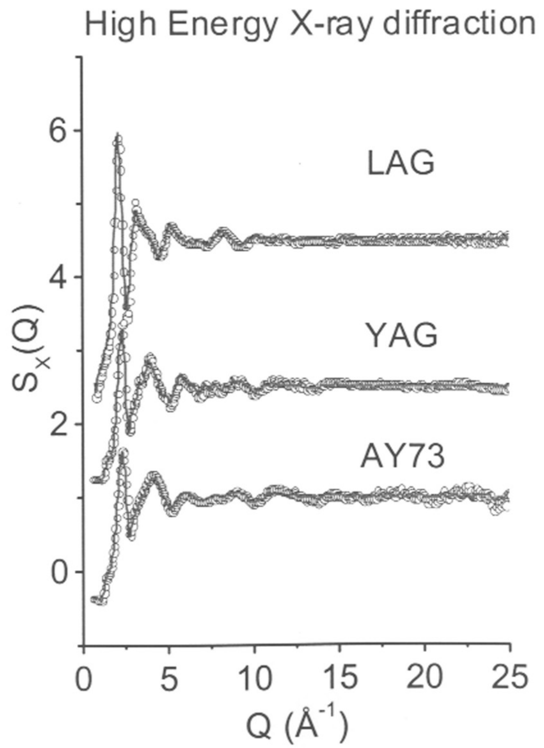
[Phys. Rev. Lett., **84**, 3622 (2000)]

Mainly 4CN Al-O and 6CN Y-O, changes with undercooling. In argon, which favors the L-L also increases population of 6 CN Al.

Is AlO_4>AlO_6 important in the L-L transition?

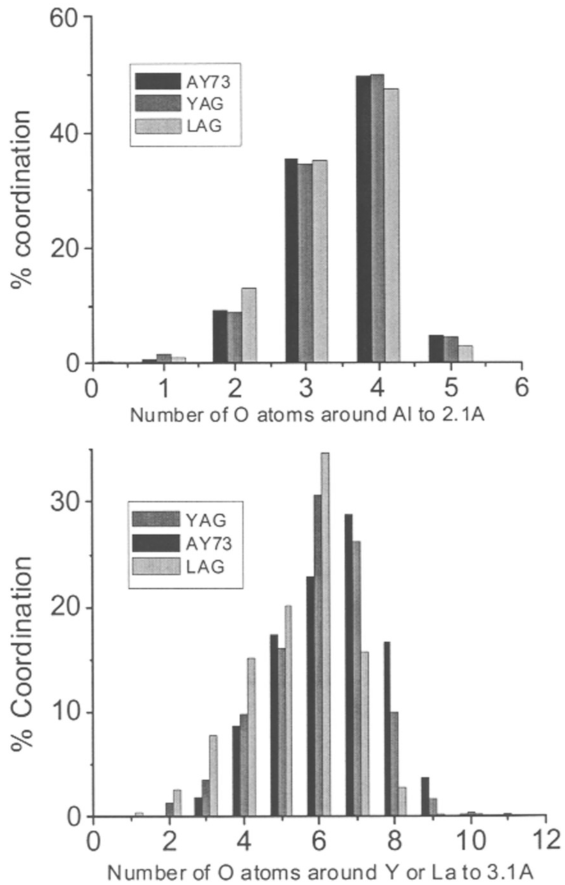
Pulsed Neutron and H-E X-ray Structure Factors and RMC Simulation

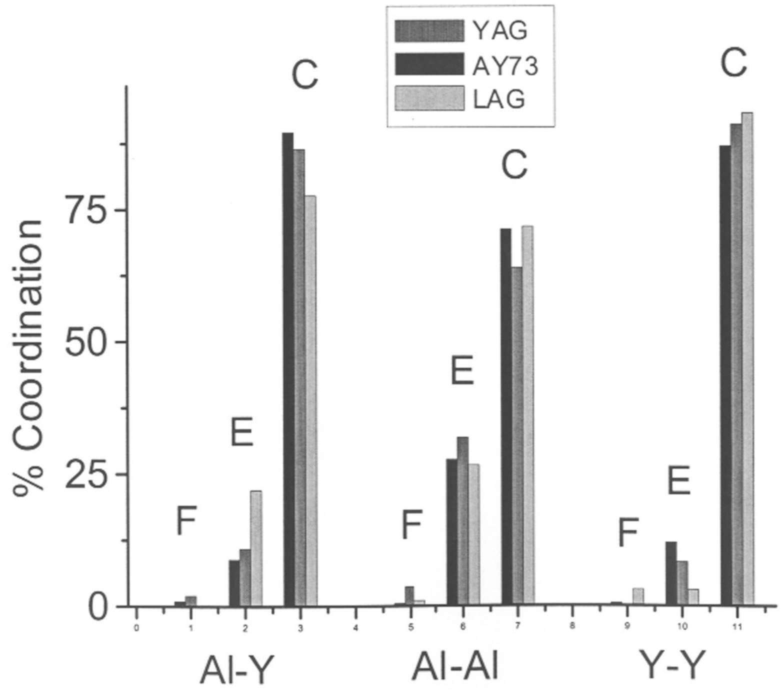




[Phys. Rev. Lett., submitted]

Connectivity of M-O species and maintenance of M-O stoichiometry





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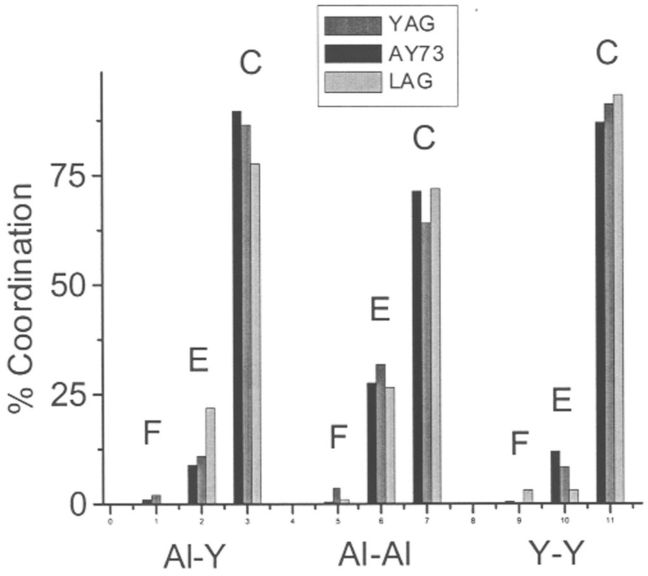


O^{2-}-generating reactions:

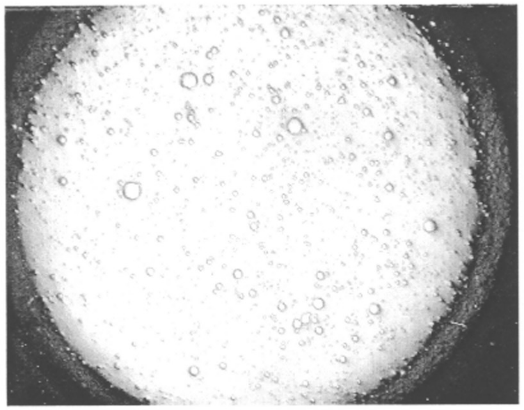
$YO_7^{11-} = YO_6^{9-} + O^{2-}$
$AlYO_9^{12-}$ [corner] = $AlYO_8^{10-}$ [edge] + O^{2-}

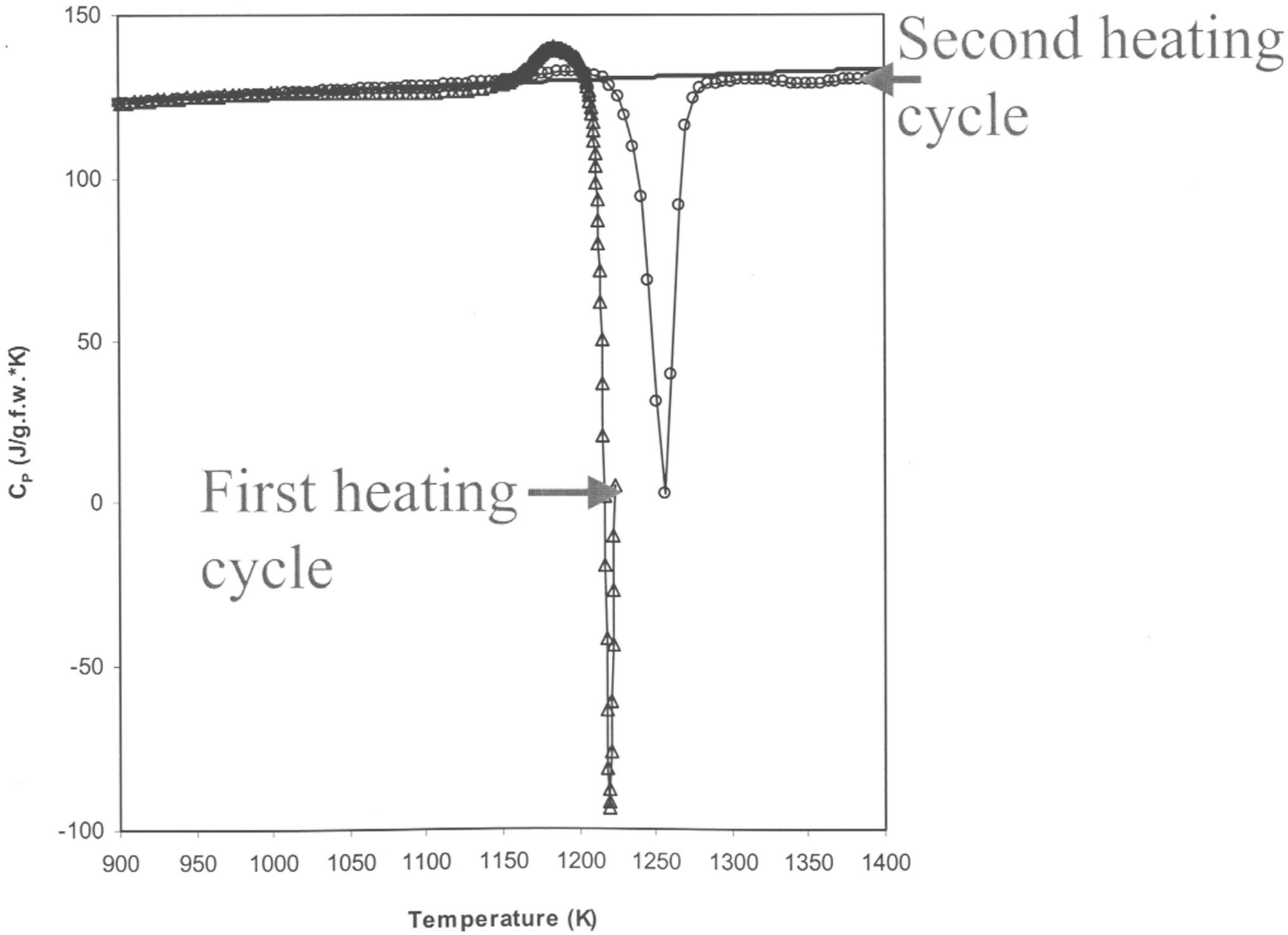
O^{2-}-consuming reaction:

$Y_2O_{10}^{14-}$ [edge] + O^{2-} = $Y_2O_{11}^{16-}$ [corner]

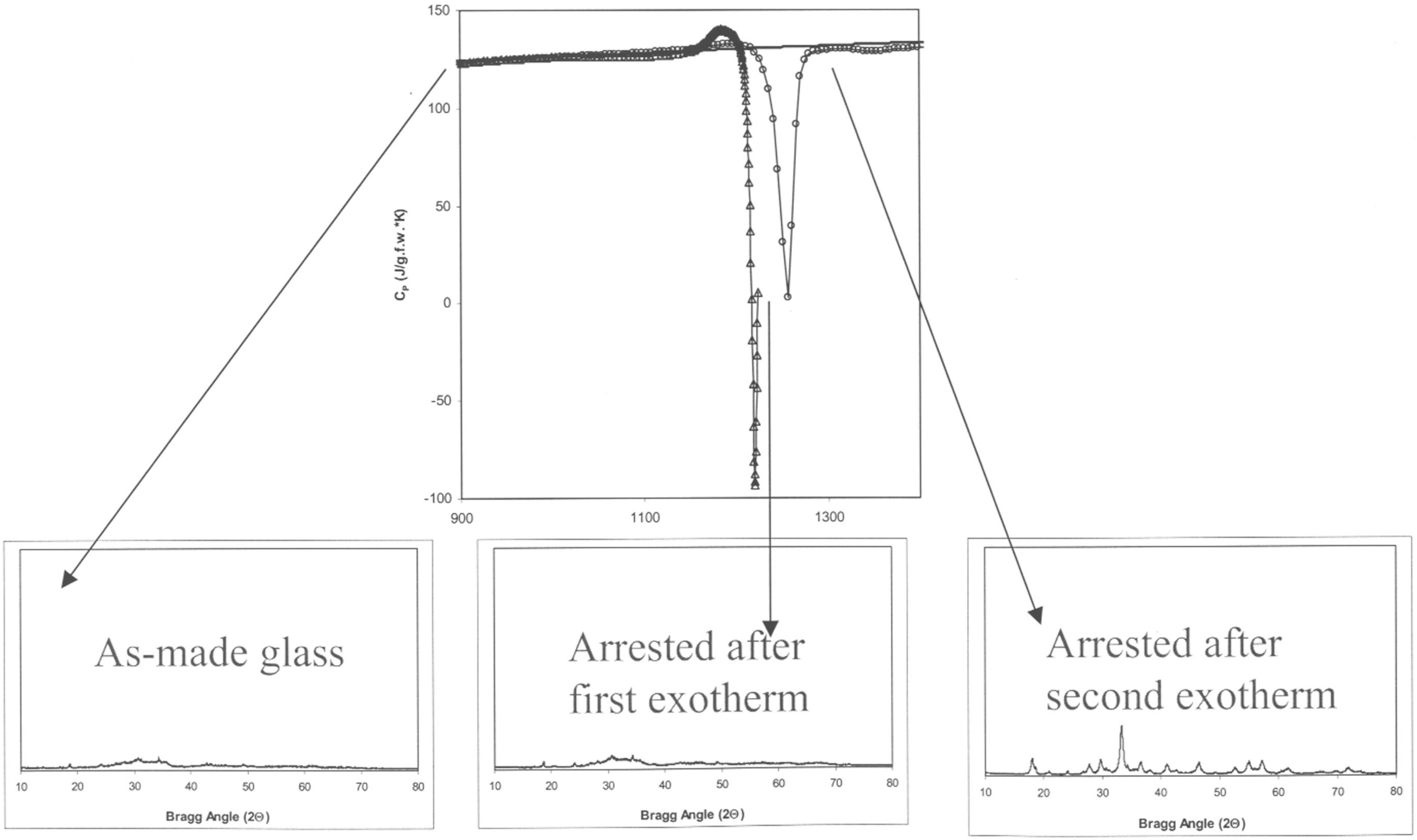
There is about 15% edge-shared YO species, after these are consumed, oxygen must be rejected if the $YO_7 > YO_6$ reaction proceeds
- *how does this affect the phase transformation kinetics*?

DSC on two-phase Y + 76 A-composition glass

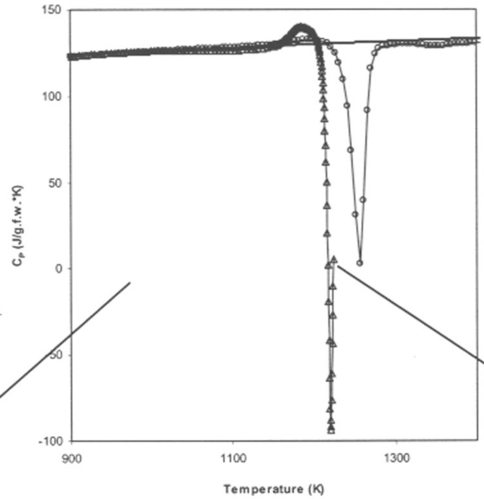




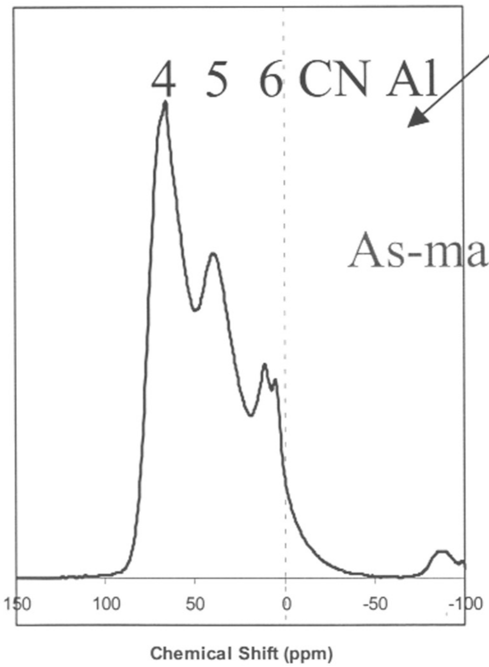
XRD on as-made and heat treated Y + 76 A-composition glasses



High-Field ^{27}Al NMR on as-made and heat treated Y + 76 A-composition glasses

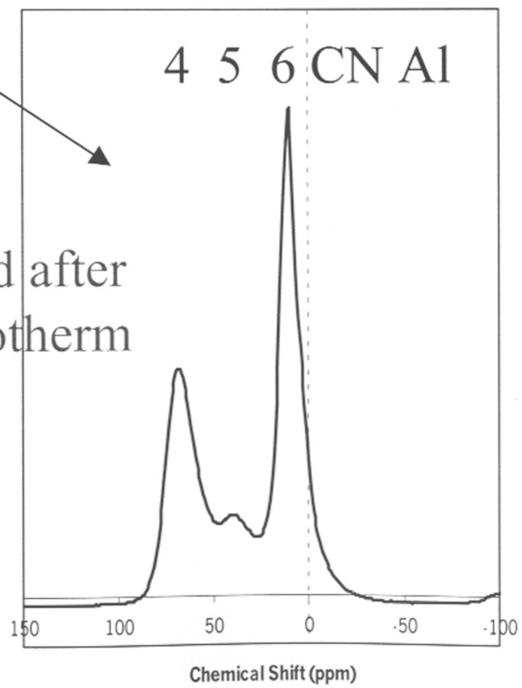


Analysis shows about 75/20/5% 4-,5- and 6-CN Al



As-made glass

Analysis, microstructure, X-ray and neutron studies in progress….



Arrested after first exotherm

Summary of structure results

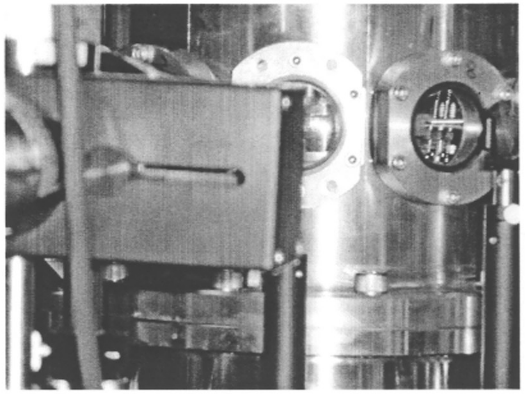
* Transition involves both changes in CN and connectivity of polyhedra

* Stoichiometry can be preserved by edge- to corner-shared transformation/s to consume O^{2-}

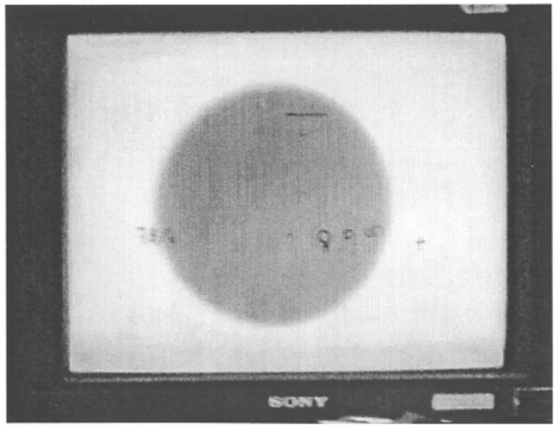
* Changes in Al CN are seen in NMR results

* Structure models are being optimized

Measurements of melt properties



[RSI, **72**, 2811 (2001), Jap. J. Appl. Phys.,**41,** 3030 (2002)]

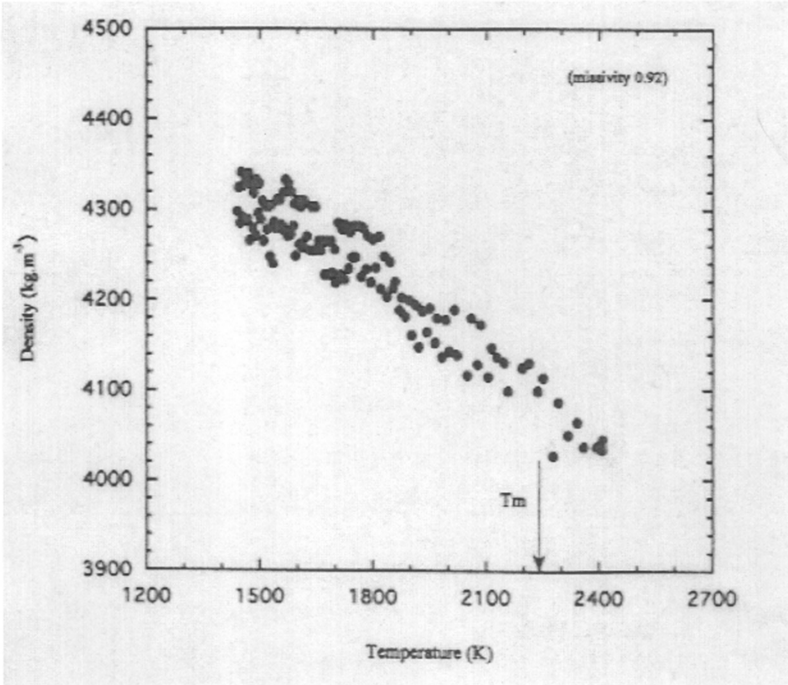


UV-backlit molten YAG sample

Density

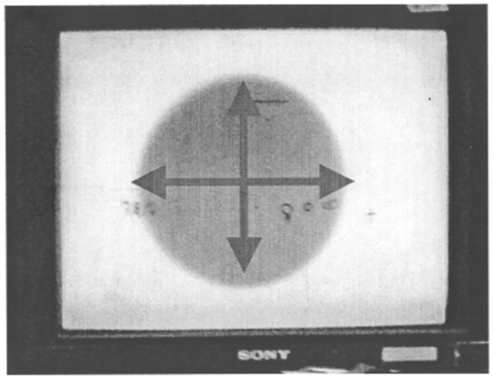
$$\rho = \frac{m}{4/3\pi r^3}$$

Preliminary measurements of the density of YAG(l) in pressurized ESL



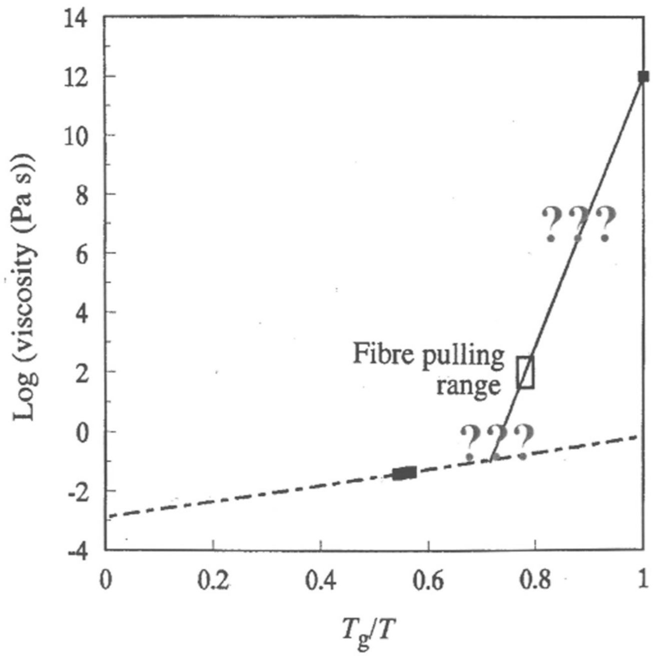
[P-F. Paradis, *et al*, in prep.]

Measurements of melt properties



Surface tension $\omega_l^2 = \dfrac{l(l-1)(l+2)\gamma}{\rho R_o^3}$

Viscosity $\tau_l = \dfrac{\rho R_o^2}{(l-1)(2l+1)\mu}$



$$\alpha^2 = \frac{\omega_R \rho R_o^2}{\mu} = \frac{\sqrt{l(l-1)(l+2)\gamma\rho R_o}}{\mu}$$

For $\alpha^2 > 3.69$ undamped

For damped ($\alpha^2 < 3.69$) oscillations, measurements of shape relaxation *via* "polar altitude" can be used to determine viscosity. Very high viscosity region from creep if xtals do not form.

Future/ongoing activities

* Investigation of transition kinetics by thermal processing of liquids and glasses

* Studies of liquid properties - *viscosity is a high priority* to establish correlation with str.

* Enhancement of structure models to enable a fuller understanding of CN and connectivity

* Establish detailed protocols/requirements for low gravity experiments