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CONTAINERLESS SYNTHESIS

OF

INTERESTING GLASSES

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CONTAINERLESS GLASS PROCESSING AND STUDIES

Motivations:

*Novel glasses and enhanced glassforming ability

Ultrapure glasses

Gas bubbles and microballoons

Phase separation

Foams

Composite materials (suspensions)

Surface tension

Surface (free) crystallization

High temperature thermophysical properties

OUTLINE

I.   Standard Arguments for Containerless Processing (C.P.) of Glasses

II. Flight Results

III. Re-examination of Motivations for C.P.

IV. Two Interesting Candidate Systems

I. <u>Why do containerless processing of glasses?</u>

    A. Standard argument

        1. Kinetic viewpoint - glass-forming ability, competition of cooling rate

            vs. crystallization rate

        2. Thus, to form new glasses one wishes to suppress crystallization

        3. First step in crystallization is nucleation; i.e. preventing nucleation could stop devitrification

        4. Nucleation can be greatly aided by liquid being in contact with solid (foreign) surfaces (so called heterogeneous nucleation)

        5. The container and impurities from container can be effective heterogeneous nucleation sites

Thus,   6. Containerless processing could prevent crystal nucleation and lead to new family of glasses

B. Required Cooling Rate

1. Define: x = volume fraction of crystals formed

   I = crystal nucleation rate

   g = crystal growth rate

   t = time; T = temperature

   R = dT/dT = cooling rate

2. Say for non-isothermal transformation desire $X \leq X_c$ (where $X_c \ll 1$)

$$X = \frac{4\pi}{3} \int_{t_i}^{t_f} dt \; I(t) \left[\int_{t}^{t_f} g(t')\,dt' \right]^3$$

$$= \frac{4\pi}{3} \int_{T_i}^{T_f} R^{-1}(T)\,I(t)\,dT \left[\int_{T}^{T_f} g(T')\,R^{-1}(T')\,dT' \right]^3$$

3. For $X = X_c$, defines integral equation for $R(T)$

4. If functional form of $R(T)$ given, then parameters in $R(T)$ can be found

5. For $R = $ constant

$$R_c^4 = \frac{4\pi}{3X_c} A$$

$$A = \frac{4\pi}{3} \int_{T_i}^{T_f} dT \, I(T) \left[\int_T^{T_f} g(T') \, dT \right]^3$$

6. (Aside: cooling rate in microgravity situation not constant and fixed unless special cooling apparatus.)

7. From above we note that as $I(T)$ diminishes, required R_c is reduced

C. Nucleation

1. Steady State Homogeneous

$$I^o_{Hom} = Z \cdot D^* \cdot N^*_e$$

$Z \equiv$ Zeldovich factor

$D^* \equiv$ interfacial transport and attempt term and most important term (for present discussion)

$$N^*_e = N^o exp^{(-W^*/kT)}$$

where $W^* =$ thermodynamic barrier to form critical radius

$N^o \equiv$ number of sites/volume (available for nucleation)

2. Steady State Heterogeneous

$$I^o_{Het} = Z' \cdot D^* * N'_e$$

$$N'_e = n_s \exp(-W^* f(\theta)/kT)$$

n_s = number of sites available for heterogeneous nucleation/volume

$0 \le f(\theta) \le 1$, where $f(\theta) = (2 - \cos\theta + \cos^3\theta)/4$

θ = contact angle

Thus, the effective lowering of barrier due to $f(\theta)$ makes heterogeneous nucleation the commonly observed crystal nucleation mehanism.

D. Comments:

1. Removal of heterogeneous sites can be very effective in reducing x since I,g overlap important.

2. Above particularly true for marginal glass formers where g expected to be large.

3. Homogeneous nucleation could prevent glass formation, but many compositions "immune" due to meager I,g overlap.

4. Containerless processing may not guarantee homogeneous nucleating conditions.

II. Flight Experiments

A. Delbert Day, P.I.

Mission: D-1 SLM on MEA/A-2

Experiment: 81F01

Sample Characteristics

#	Composition (mol. %)	Diameter (nm)	Rc (earth)
2	$39.3Ga_2O_3$ - $35.7CaO$ - $25SiO_2$ (hot pressed)	6	11 ± 2 °C/sec.
6	$56Ga_2O_3$ - $44CaO$ (devitrified melt)	6	550 ± 50 °C/sec.
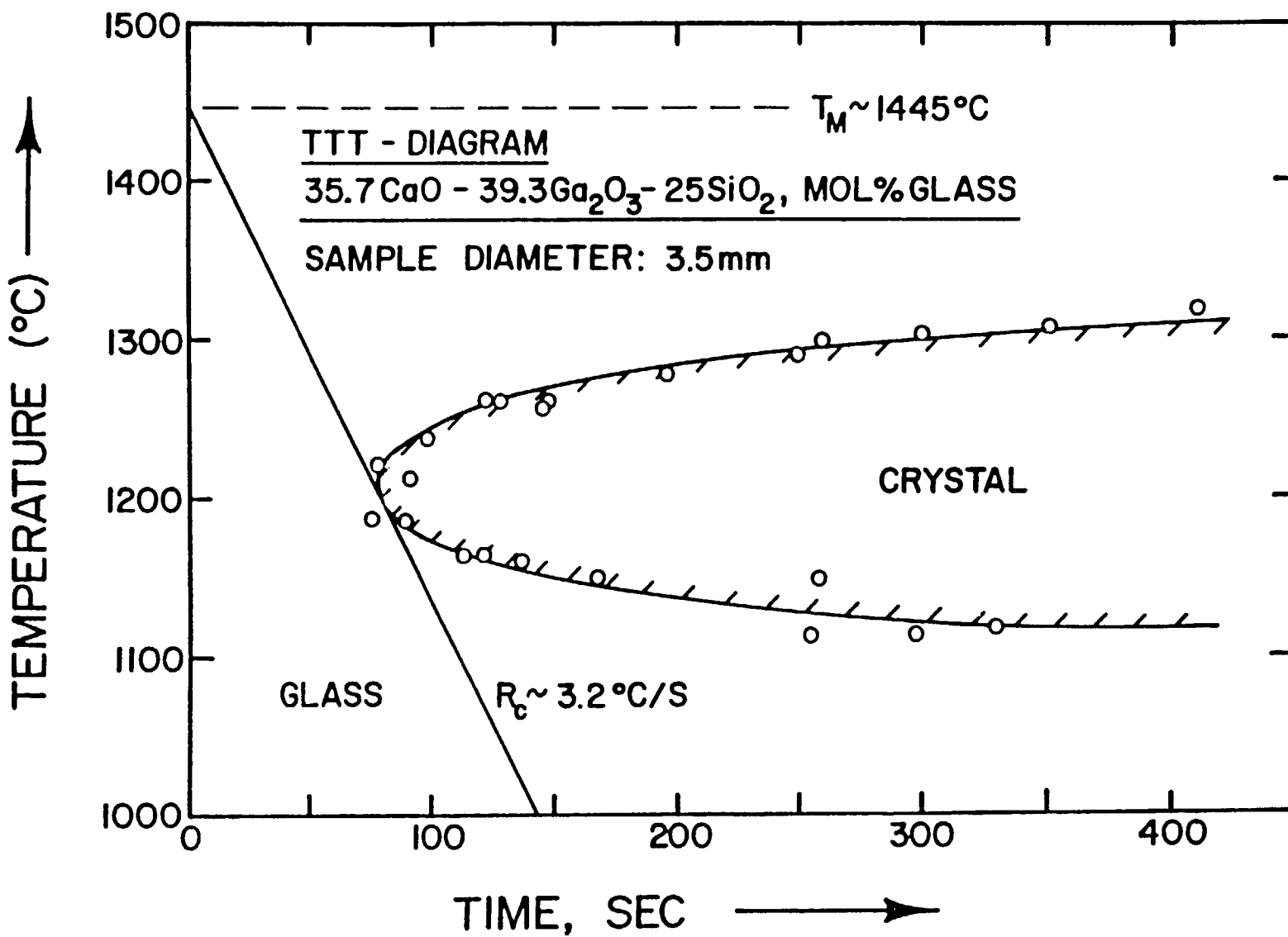
Figure 6. TTT diagram for the 35.7 CaO-39.3 Ga_2O_3-25 SiO_2, mol%, composition for sample diameter $\sim$3.5 mm.
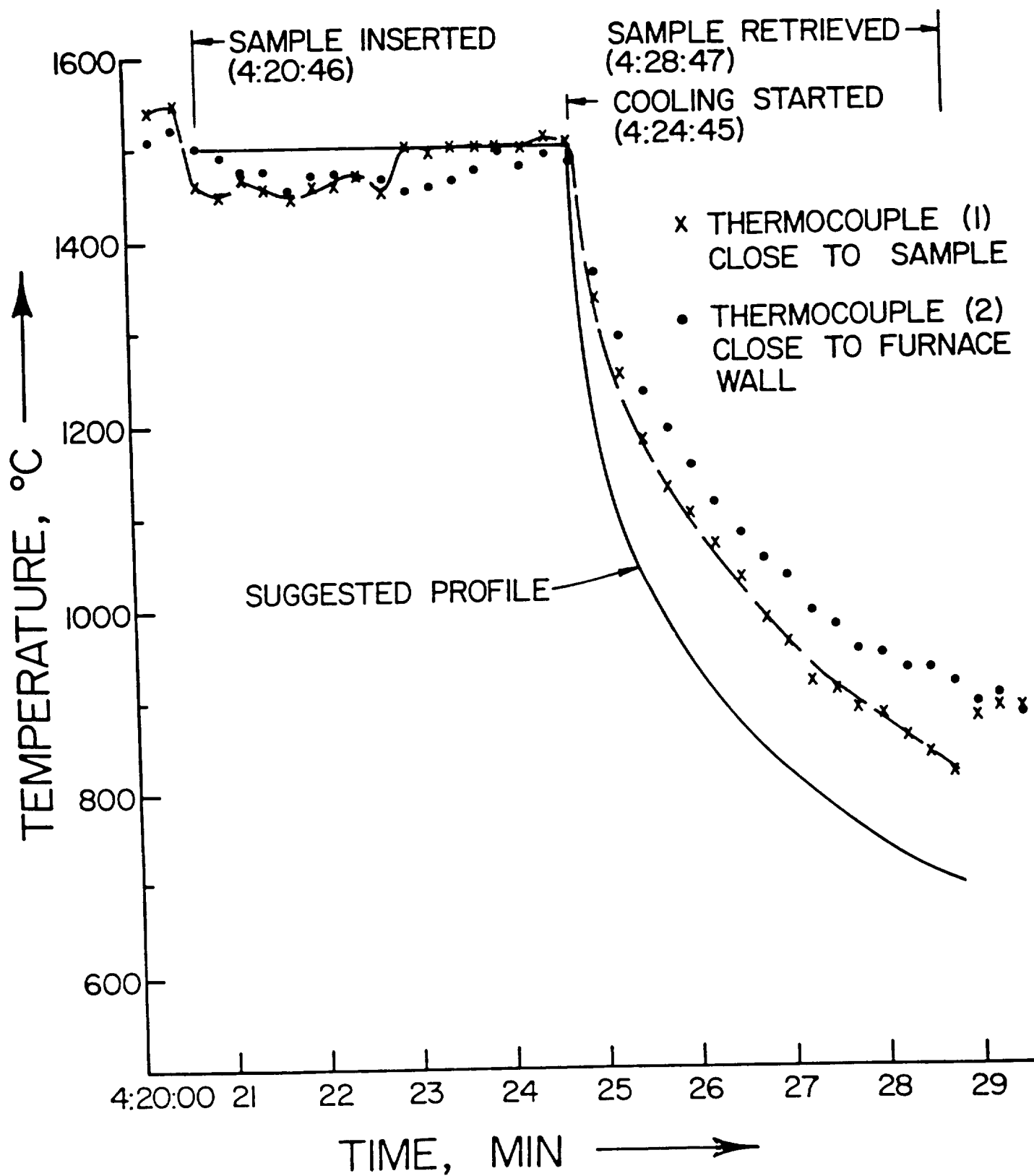
Figure 13. The planned and observed time-temperature profile for 35.7 CaO-39.3 Ga$_2$O$_3$-25 SiO$_2$, mol%, hot pressed sample (#2) when processed in the single axis acoustic levitator, MEA/A-2.
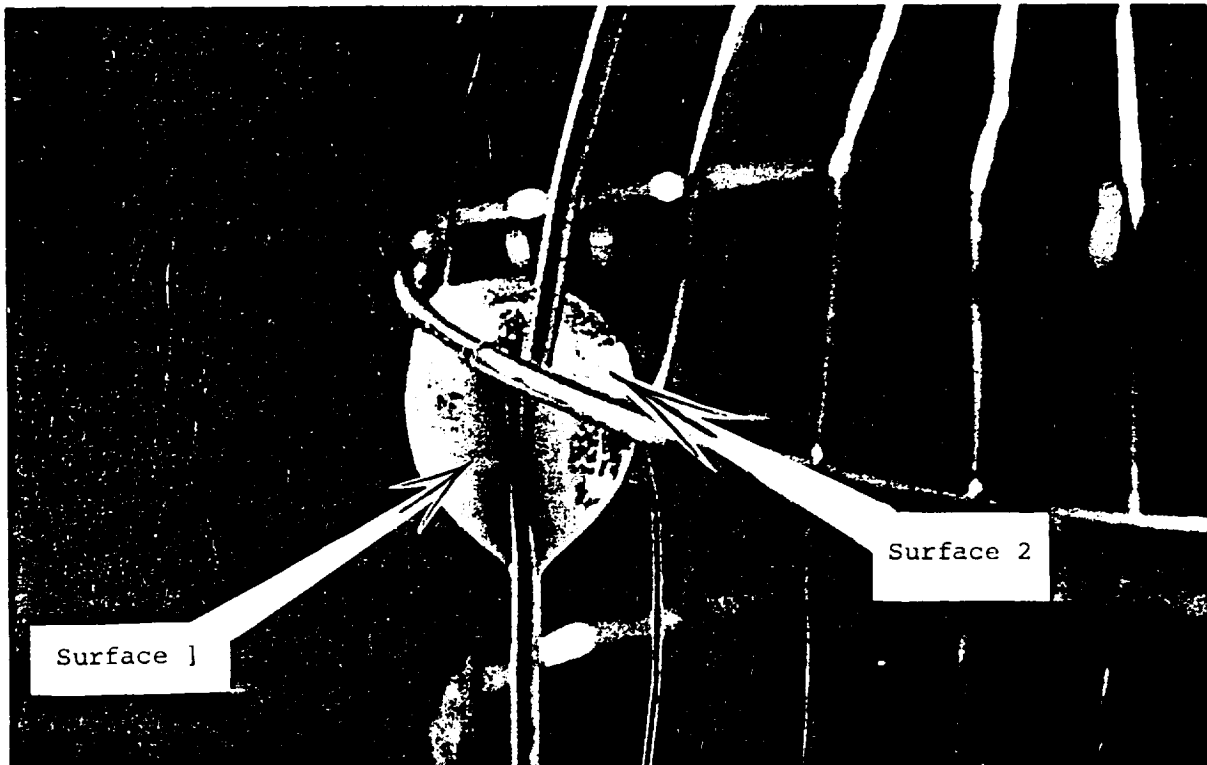
Surface 1

Surface 2

Figure 11. Flight sample 2 (35.7 CaO-39.3 Ga_2O_3-25 SiO_2, mol%, hot pressed) stuck to platinum wire cage while levitated and melted in space (MEA/A-2). The sample crystallized where it contacted the cage wires.
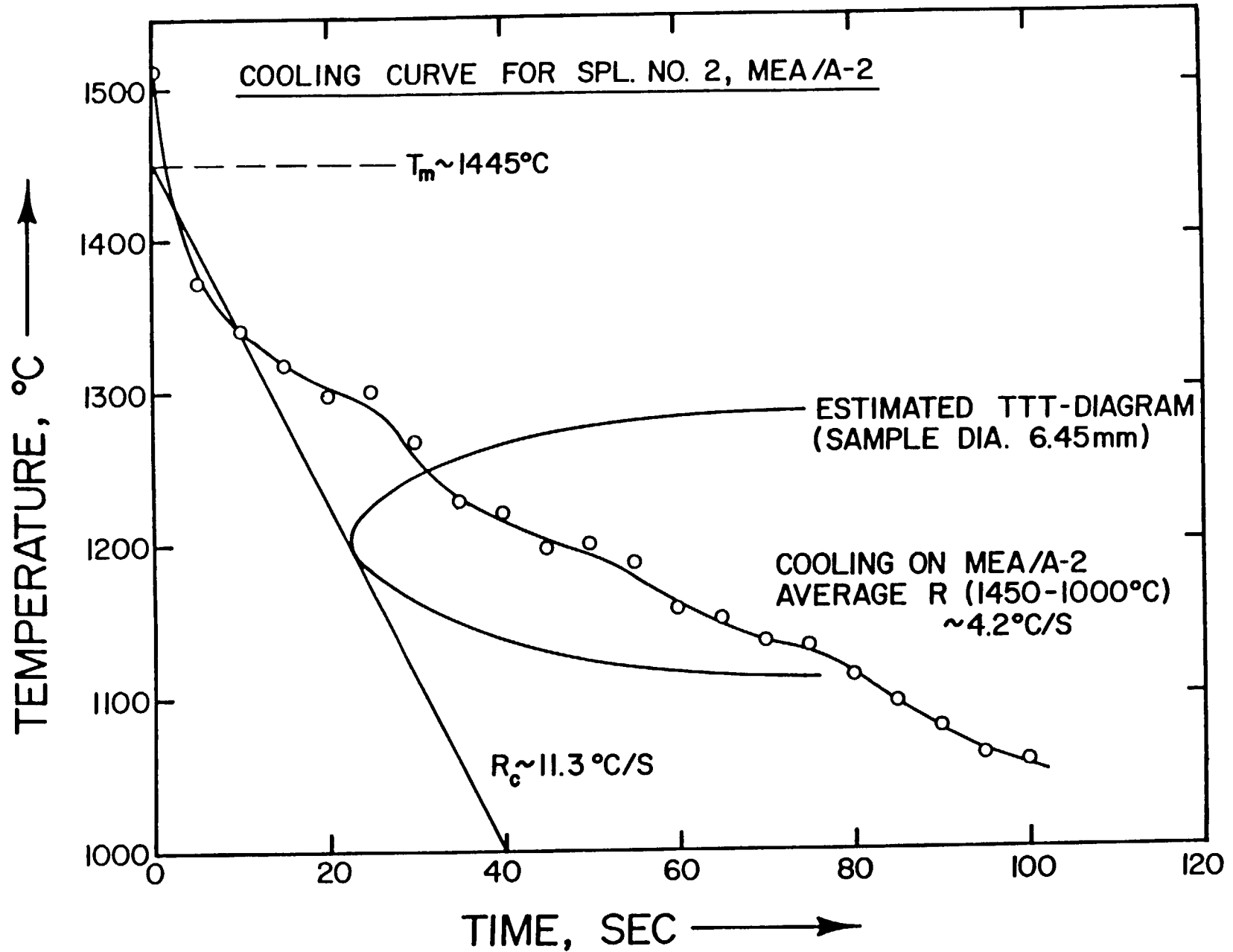
Figure 25. The estimated TTT diagram for the 35.7 CaO-39.3 Ga_2O_3-
25 SiO_2, mol%, composition for sample diameter $\sim$6.5 mm
and the cooling rate measured for sample 2 in MEA/A-2.

TABLE XII. Results for the hot pressed calcia-gallia-silica sample (#2)

processed on MEA/A-2 experiment.

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1. The sample escaped the acoustic energy well and stuck to the cage wires while

   levitated in the SAAL in space. Escape was clearly associated with the opening of

   the SAAL cooling shroud gate.

2. 70 to 80% of the sample was glassy. Partial crystallization ($\approx$20%) was observed

   where the melt touched the platinum wires of the cage. Examination by SEM and

   EDAX showed that the crystalline phases were Ga_2O_3 and $Ca_2Ga_2SiO_7$.

3. Comparison of the critical cooling rate for glass formation of this glass on earth

   with the cooling rate used in the flight experiment, showed a 2 to 3 times

   enhancement of glass formation for this composition melted in space.

III. The Other Side of The Coin

A. Since glass-forming is a contest between cooling and crystallization, why not rapid cooling (on earth)?

B. It has been employed:

Technique	Typical Compositions
Liquid Quenching	$TiO_2 + RO$, $Al_2O_3 + Gd_2O_3$
Splat Cooling	Metal Alloy Glasses; L_2O_3-Al_2O_3
	$L = La, Nd, Gd, Er, \ldots$
Cold Rollers	R_2O-TaO_3; R_2O-NbO_3
	$R = Li, Na, K$
Spinning Wheel	Metal Alloy Glasses
Laser Film Melting	Ge, Si, Mixed Chalcogenides

C. Other Novel-"Non-Melting" Techniques

1. Sol-gel

2. Gas Phase Deposition Methods

    (a) Evaporation

    (b) Sputtering

    (c) Reactive Sputtering

    (d) CVD

          etc.

3. Solid State Methods

    (a) High Pressure

    (b) Shock Tube

    (c) Solid State RXS

Ask again: Why do containerless processing of glasses?

Let us primarily focus on rapid cooling techniques--

A. Limited to ribbon, fragments, etc. - no bulk material

B. No contact could be of greater importance than splat cooling

   e.g. Li_2O-B_2O_3 glass

C. Glass properties can depend on sensitively upon history; i.e. rapidly cooled glass

   will behave differently from ordinary glass. Also, more generally properties can

   depend on how glass is made.

   e.g. Weeks et. al. - electrical conductivity of GeO_2 can depend upon

      melting T

      Galeener et. al. - Raman scattering function of Fictive Temperature

      Hench et. al. - Sol-gel SiO_2; different ρ, uv-cutoff

D. Difference in Properties Imply Structural Differences

   i.e. One is preparing different materials

IV. Two Examples of Interesting Glass Systems

A. CaO-Al$_2$O$_3$ System

1. Why interesting?

    Technological: (a) very good IR transmission for oxide glass

          cutoff ~ 6 μ

          (b) High Young's Modulus - use for reinforcement in

          structural composites

    Scientific: (a) Unusual glass-forming system

          (b) Questions regarding structure

2. Glass-Forming Ability

    (a) By normal coating: Narrow region around 65 mole % CaO

    (b) By melt quenching: CaO (59-70%)

    (c) By Splat Cooling (Slivers): CaO (19-81%) (super-quench)

3. Structure/Properties

(a) Structural studies mainly by Raman

(b) Thermal expansion and index measurements of "stable" glasses

(c) Studies have been performed on ternaries (SiO_2 or CaF_2 additions)

4. Future Work

Ground based: (a) Alternate preparation methods

(b) Study of crystallization behavior

(c) More detailed structural studies (NMR)

Flight opportunities: (a) Glass-forming ability

(b) Bulk samples for structural studies and

mechanical property measurements

(c) Optical performance

B. Li$_2$O-B$_2$O$_3$ System

1. Why interesting?

   (a) Base composition for wide variety of FIC glasses
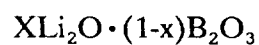
   (b) Borate structures more varied and complex than silicates due to 3 or

   4 fold coordination of B

   (c) LB$_2$ first simple borate which seems to exhibit homogeneous crystal

   nucleation

2. Glass-forming Ability

   $$XLi_2O \cdot (1-x)B_2O_3$$

   (a) Bulk samples ($0 \leq x \leq .42$) (but special care for larger x)

   (b) Splat cooling (virtually no advantage)

   (c) Quench crucible + dry N$_2$ ($0 \leq x \leq .6$)

   (d) Roller method ($0 \leq x \leq .7$)

3. Structure/Properties

   (a) Activation energies for DC conductivity appear to decrease

   monotonically with increasing Li_2O content

   (b) High Li_2O content glasses appear to devitrify via surface mechanism -

   avoidance of contact with substrate important

   (c) Detailed IR, Raman and NMR studies have been performed as function

   of composition

4. Future Work

   Ground based: (a) Crystallization studies as a function of

   composition

   (b) Effects of quench rate on structure and

   properties (electrical)

   (c) Effect of nucleation upon conductivity

   Flight opportunities: (a) Glass-forming ability

   (b) Crystallization behavior

   (c) Structure/properties of slowly cooled glasses

V. Summary

1. We have focused on <u>one aspect</u> of containerless glass experimentation: glass-forming ability

2. We have argued that although containerless processing will abet glass formation, other ground-based methods can do the "job" better

3. However, these methods have limitations re: sample dimensions and concomitant ability to make property measurements (e.g. fracture)

4. Most significantly, perhaps, is the observation that glass properties are a function of preparation procedure

5. Thus, in conclusion, it seems as though there still is an argument for use of containerless processing for glass-forming

ACKNOWLEDGEMENTS