Influence of Radiation and Multivalent Cation Additions on Phase Separation and Crystallization of Glass

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Research Objectives

The major objectives of this proposed investigation are as follows:

- To investigate the influence of multivalent cations on the thermodynamics and kinetics of phase separation and crystallization in simple model glasses.
- To study the influence of α and β particles, heavy ion bombardment and γ irradiation on phase separation and crystallization in simple model glasses.

Research Objectives (cont.)

- To examine the structural changes produced by radiation just prior to the onset of phase separation and/or crystallization.
- To develop models to explain the observed effects of multivalent cations and radiation on phase separation and crystallization.
- To utilize the results of these experimental and modeling studies to provide guidelines for the allowed range of composition choices and processing conditions in order to avoid the formation of unwanted phases in nuclear waste disposal glasses.

Glass Systems Selected:

A. Influence of Radiation on Phase Transformation Behavior:

- Composition families - Na_2O-SiO_2, Li_2O-SiO_2, and K_2O-SiO_2(called NS, LS, and KS); Na_2O-P_2O_5(NP) and K_2O-P_2O_5(KP); and Na_2O-B_2O_3(NB).

Composition	Rationale
LS_2	metastable phases
NS_2, .43N-.57S, .41N-.59S	nucleation mechanism
.185N-.815S	phase separation
NP, KP	crystallization behavior
.09K-.91S, .1N-.9B, .2N-.8S	incipient phase separation

Glass Systems Selected: (cont.)

B. Effect of Valence State of Multivalent Ion Upon Crystallization Kinetics and Mechanisms and Phase Separation Behavior:

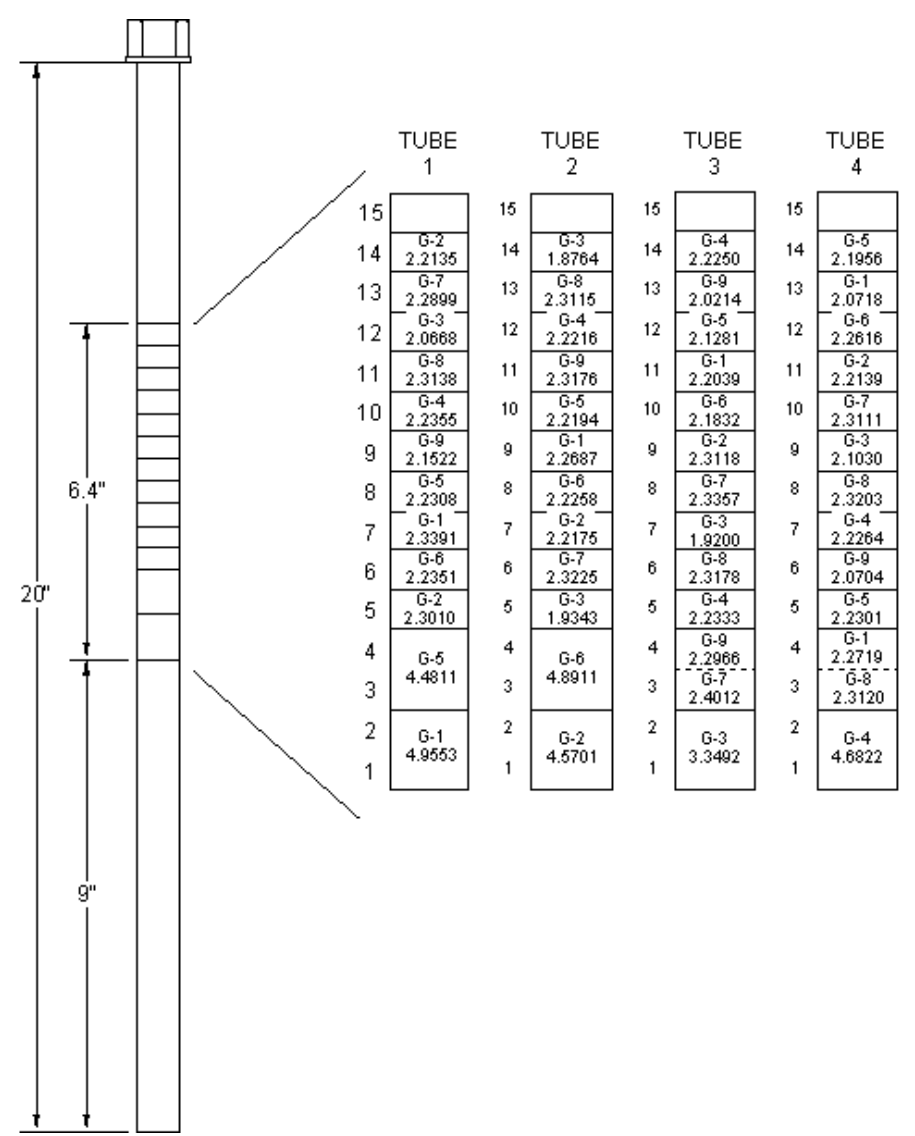
- Composition families - Na_2O-SiO_2, Li_2O-SiO_2, and K_2O-SiO_2(called NS, LS, and KS); Na_2O-P_2O_5(NP) and K_2O-P_2O_5(KP); and Na_2O-B_2O_3(NB).

Composition	Rationale
.2N-.8S	phase separation behavior
(+ 1, 2, and 4 mol % Fe_2O_3)	
$5Na_2O$-Fe_2O_3-$8SiO_2$	nucleation mechanism

Influence of γ Irradiation: Phase Separation & Crystallization

- Irradiation - On June 26, 1998 fifty glass samples were inserted into the gamma irradiation facility at PNNL. The samples were placed in four aluminum tubes (the next page illustrates the sample configuration and gives the weights and compositions of the samples). The Al tubes and samples holders were cleaned with acetone before loading. The tubes were back flushed with high purity, dry nitrogen before sealing. Thermocouples were placed near the top and bottom samples, as shown in the schematic drawing. The samples span a height of approximately six inches.

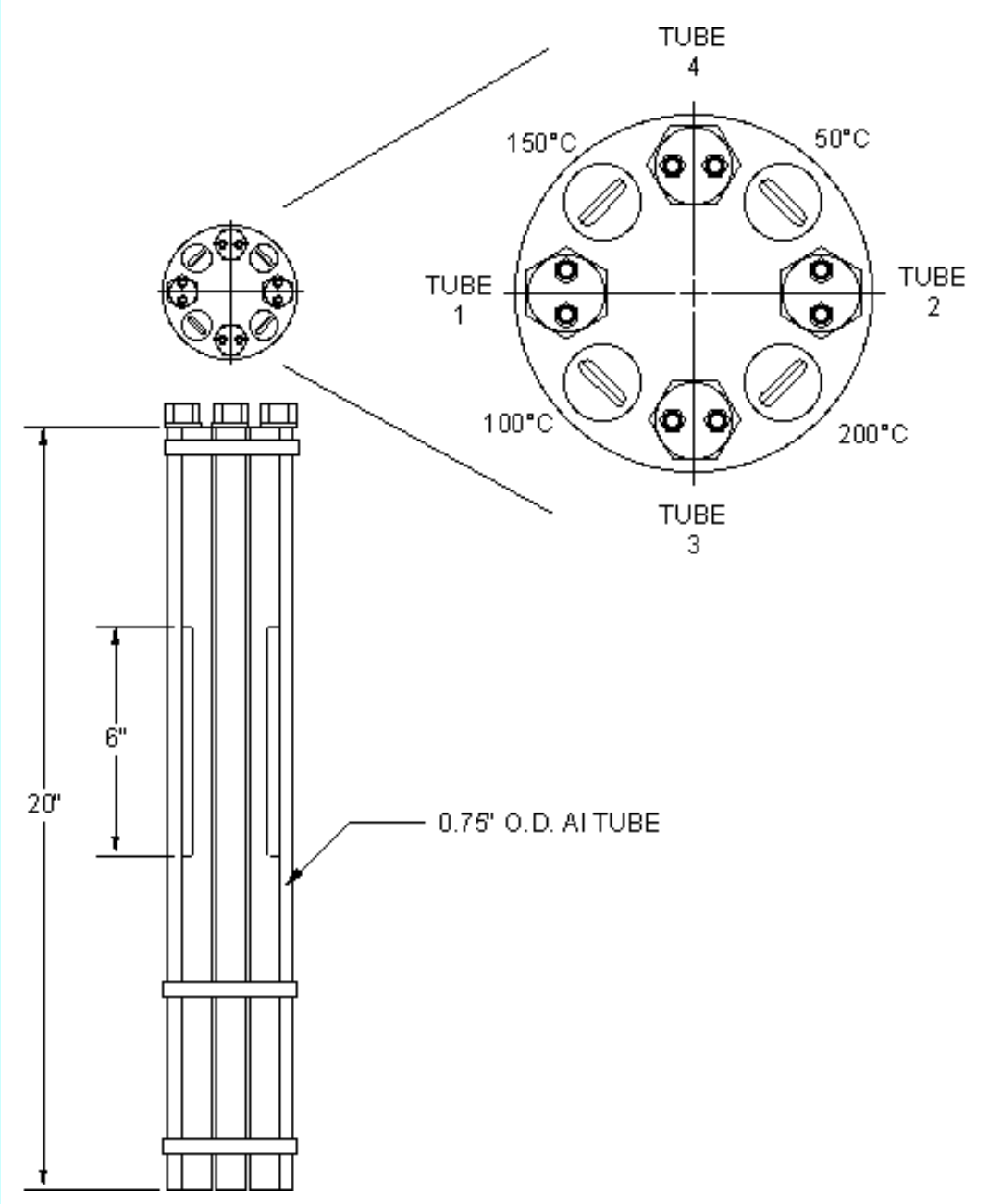
Gamma Irradiation Sample Tubes



Glass ID	Glass Composition
G-1	$Li_2O{\bullet}2SiO_2$ (LS_2)
G-2	$.09K_2O{\bullet}.91SiO_2$ (.09K-.91S)
G-3	$.1Na_2O{\bullet}.9B_2O_3$ (.1N-.9B)
G-4	$.2Na_2O{\bullet}.8SiO_2$ (.2N-.8S)
G-5	$.185Na_2O{\bullet}.815SiO_2$ (.185N-.815S)
G-6	$Na_2O{\bullet}.8SiO_2$ (NS_2)
G-7	$.43Na_2O{\bullet}.57SiO_2$ (.43N-.57S)
G-8	$.41Na_2O{\bullet}.55SiO_2$ (.41N-.59S)
G-9	$Na_2O{\bullet}P_2O_5$ (NP)

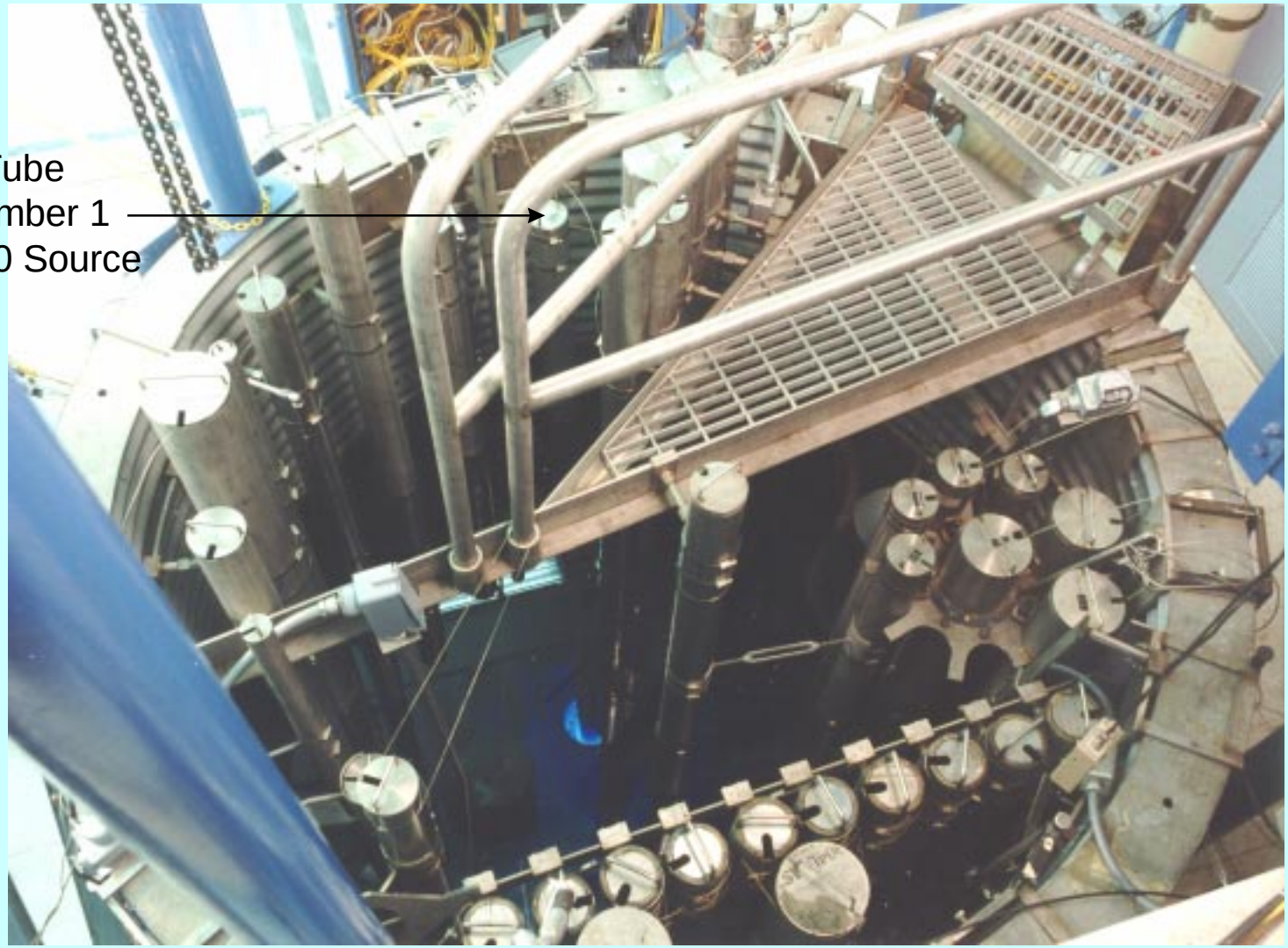
Note: Values under each Glass ID No. are the weight of the glass cube; approximately 2 grams for a 1 cm cube and 4.5 grams for a 1 cm $\times$ 1 cm $\times$ 2 cm sample for SAXS.

Gamma Irradiation Sample Package



PNNL Gamma Irradiation Facility

PNNL Gamma Irradiation Facility



Influence of γ Irradiation: (cont.)
Phase Separation & Crystallization

Benchmark Samples - Half of the glass prepared was used for irradiation with the other half saved for characterization purposes. Glasses will be analyzed by the following techniques with the indicated motives:

IR spectroscopy - Water content, structure

- Raman spectroscopy - structure
- Optical microscopy - devitrification
- DTA/DSC - crystallization, glass transition temperature
- SAXS - Phase separation
- Chemical analysis - heavy metal impurities
- SEM - crystallites, inclusions, etc.
-

$5Na_2O$-Fe_2O_3-$8SiO_2$: Glass Crystallization

a. Under conditions where the iron is predominantly in the Fe^{3+} oxidation state:

<u>Experimental</u> - glass preparation

Raw materials: Fe_2O_3, SiO_2, and Na_2CO_3

Crucible type: quartz

Melting: 1200°C for 1.5 hours

<u>Heat Treatments</u>

Nucleation: 500°C (6, 21, and 66.5 hours)

Growth: 685°C (1 hour)

Phase Diagrams: Na_2O-Fe_2O_3-SiO_2 System

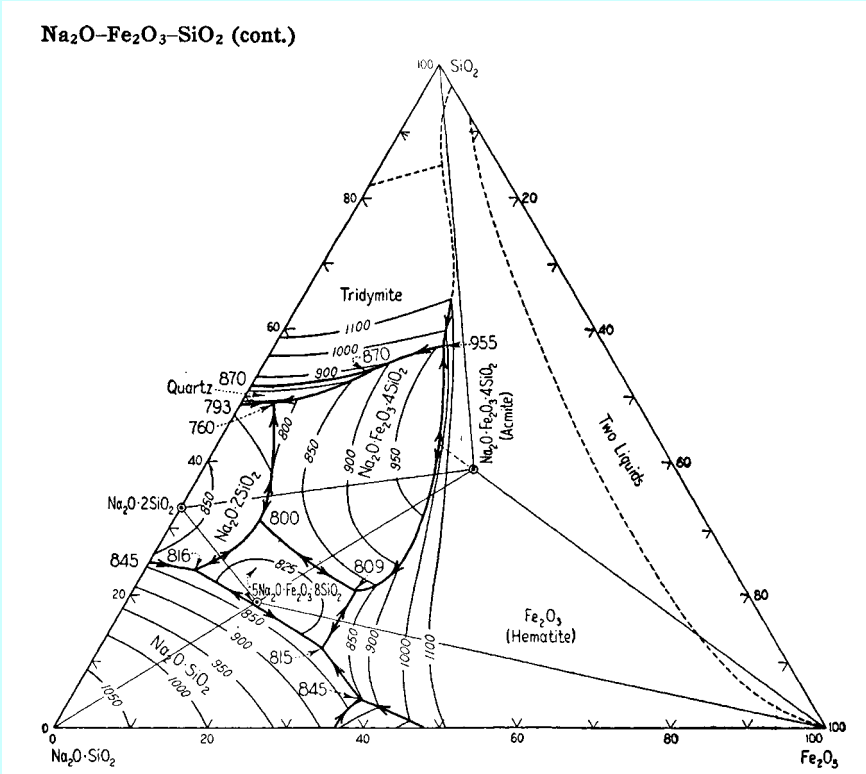


FIG. 520.—System Fe_2O_3–SiO_2–$Na_2O \cdot SiO_2$.

N. L. Bowen, J. F. Schairer and H. W. v. Willems *Am. J. Sci.*, 5th Ser., **20**, 419 (1930); two-liquids lines from *ibid.*, p. 425.

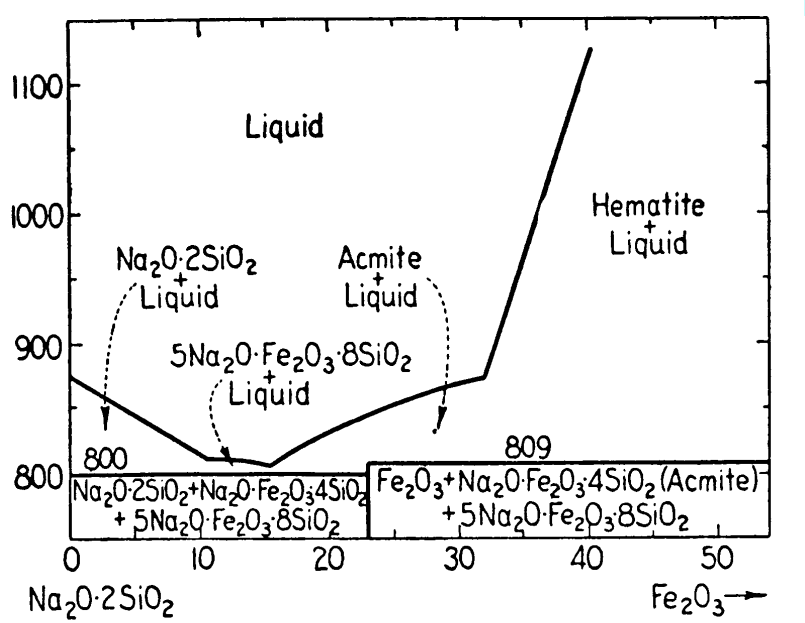


FIG. **524.**—Join Fe_2O_3–$Na_2O \cdot 2SiO_2$, Fig. 519

Drawn from data of Bowen, *et al.*, *ibid.* p. 435.

$5Na_2O$-Fe_2O_3-$8SiO_2$: Crystallization Results

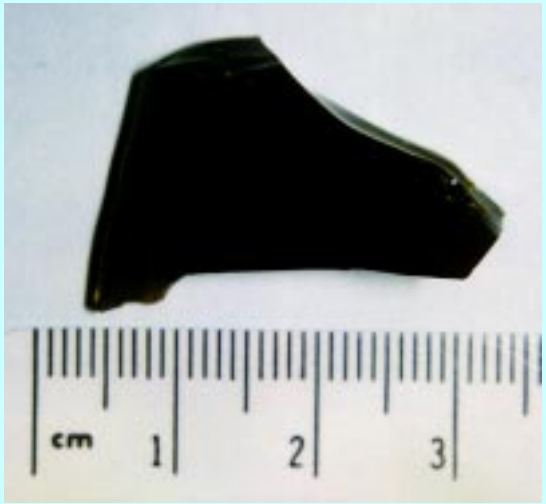
Oxidized Glass:

- No internal nucleation
- Needle-like surface crystals observed
- Crystals grew from the surface with a growth rate of approximately 50µm/s.
-

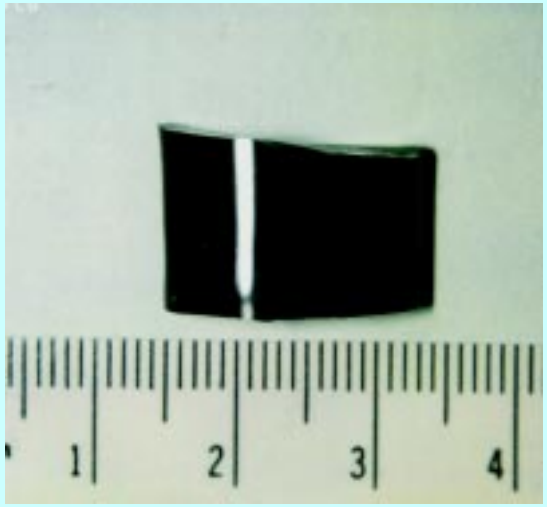
A second glass batch of 5-1-8 composition was melted using iron oxalate as a source with a mixture of H_2/N_2 gas flowing through the furnace in order to produce a glass containing predominantly Fe^{2+}.

- Liquidus measurements of the two glasses indicated that very little of the reduced species was produced.
- As expected, the second glass did not exhibit internal nucleation either.

$5Na_2O$-Fe_2O_3-$8SiO_2$: Oxidized & Reduced Glass



Oxidized Glass



Reduced Glass

Melt History

<u>500 g Batch</u>
SiO_2 : 252.88 g
Na_2CO_3 : 278.78 g
Fe_2O_3 : 84.10 g

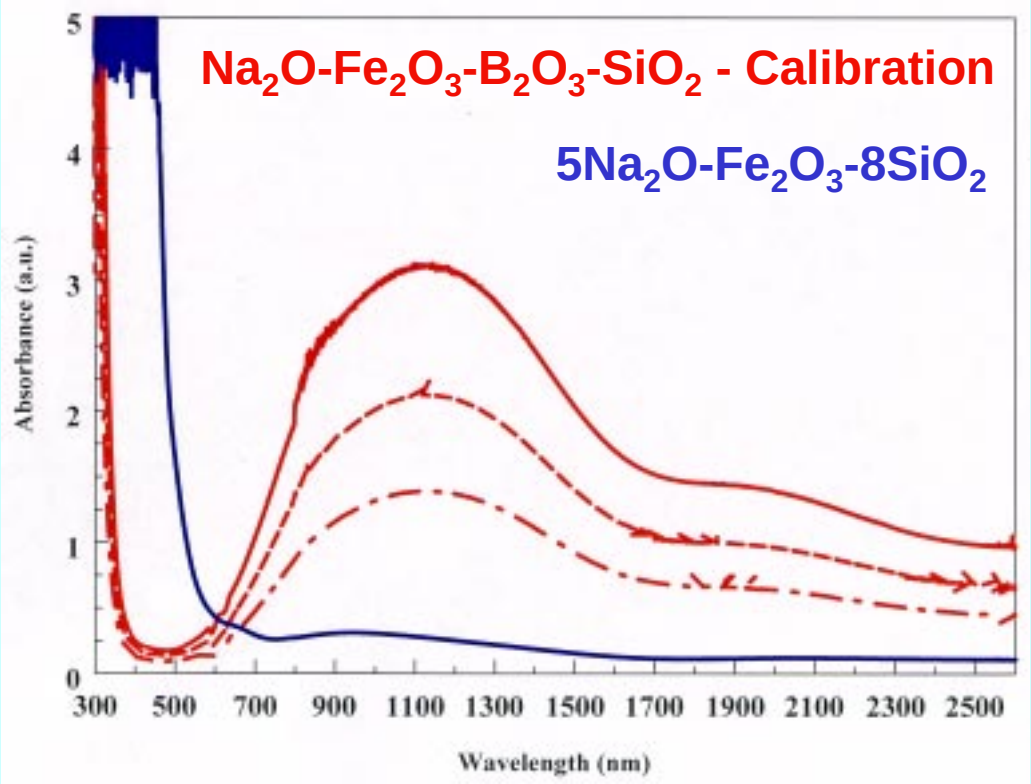
→

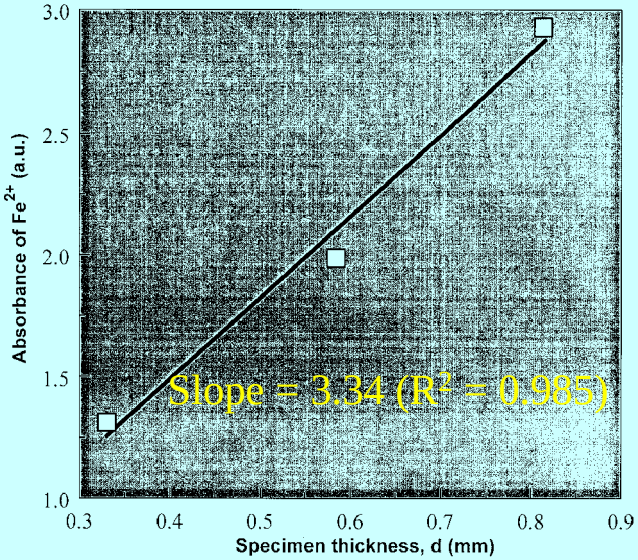
<u>Oxidized Melt (500 g)</u>
1130 C - 1 h (bubbles)
1200 C - 1 h (fined)
Quenched
Dark Brown in Color

→

<u>Reduced Melt (200 g)</u>
1200 C - 2 h
Bubbled with 4% H_2 & 96 % Ar
Quenched
Dark Green in Color

Redox Measurement: Oxidized & Reduced





Beer's law:

$$[Abs]_{Fe^{2+}} = \varepsilon \cdot C_{Fe^{2+}} \cdot d$$

ε : extinction coeffcient, 1.031 (abs/mm–wt%)

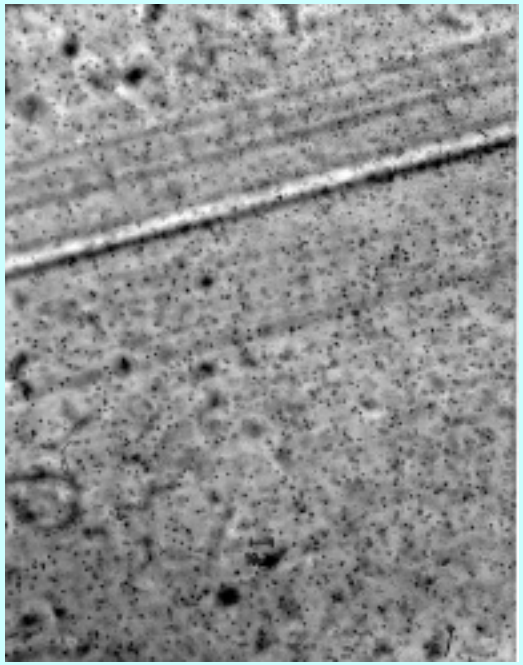
$C_{Fe^{2+}}$: concentration of Fe^{2+} in glass (wt%)

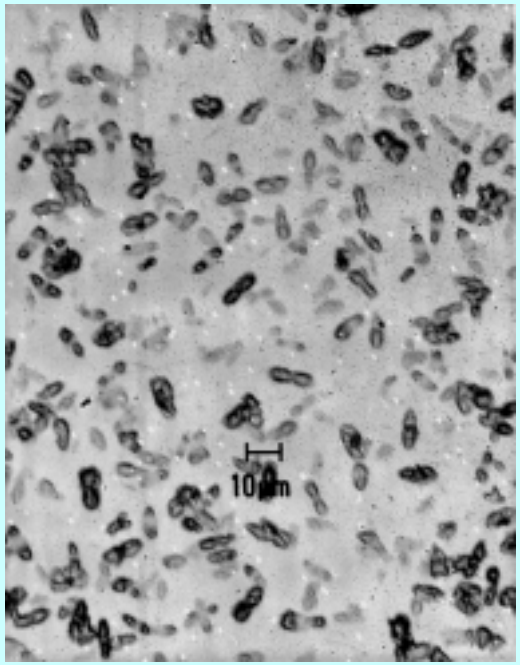
d : specimen thickness (mm)

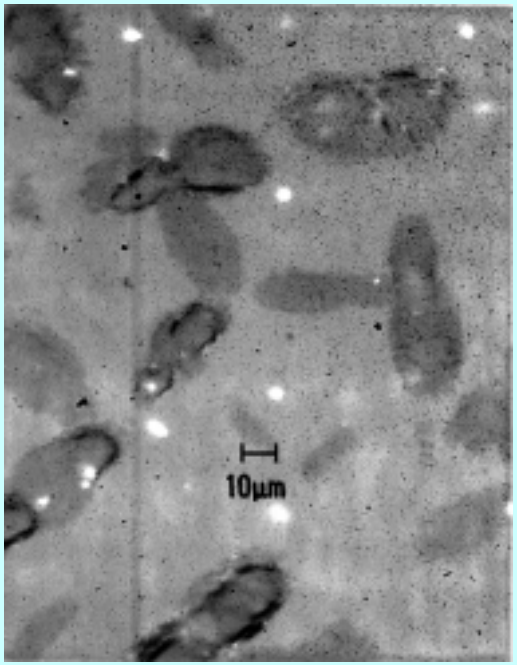
$5Na_2O$-Fe_2O_3-$8SiO_2$

Oxidized Glass	Reduced Glass
Transparent:	Opaque:
UV/VIS - Beer's law	UV/VIS - Colorimetric
Fe^{2+}/Fe_{total} = 0.025	Fe^{2+}/Fe_{total} = 1.00

$5Na_2O$-Fe_2O_3-$8SiO_2$: Reduced Glass







Quenched

Annealed (500°C-2 h, cooled in oven over-night)

Na_2O-SiO_2 Glasses + Fe_2O_3 : Immiscibility

<u>Objectives</u> - To study the influence of Fe oxidation state on the thermodynamics and kinetics of phase separation.

- Glasses - $.2Na_2O$- $.8SiO_2$ + 1, 2, and 4 mole% Iron Oxide

<u>Oxidation State</u> - modification via thermal history, choice of raw materials, and gas atmosphere.

Heat treatments have been initiated to investigate the movement of the binodal boundary as a function of iron oxide concentration and Fe^{2+}/Fe^{3+}.