Stability of High-Level Nuclear Waste Glass

Theodore M. Besmann and Nagraj Kulkarni
Metals and Ceramics Division, Oak Ridge National Laboratory
Karl E. Spear
Pennsylvania State University
John D. Vienna and Pavel R. Hrma
Glass Development Laboratory, Pacific Northwest National Laboratory

PENNSTATE

1855

ornl

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

EMSP
Environmental Management Science Program

Objective of EMSP Research Project

Develop practical models for calculating thermodynamic stabilities of components in complex waste glasses.

- Work with large number of components
- Easy to understand and use
- Reliable
- Extrapolatable and interpolatable (T, x_i)

Relevance

- Work will provide a thermochemical model for waste glass/melts
- Model allows prediction of liquidus temperatures (T_L) and formation of undesirable phases
- Model can be used to evaluate the driving force for glass corrosion in repository environments
- Can supply understanding necessary for waste form development with strong technical basis
- Will point the way toward studies of component association in melt which may significantly improve the understanding of waste glass melt chemistry

Associate Species Approach Originally Applied by Hastie and Bonnell Simplifies Modeling

- The liquid/melt phase thermochemistry is modeled as an ideal solution of associate species
  - e.g., Soda-alumina glass modeled as ideal solution of
    $Na_2O + AlNaO_2 + Na_{2/3}Al_{4/3}O_{7/3} + Al_2O_3$ :: each with 2 non-oxygen atoms
- Accurately represents behavior of chemically complex systems
- Accurately predicts activity in glass phases (not stable phase)
- Logically allows estimation of thermodynamic values with an accuracy greater than that required for predicting useful engineering limits on activities in solutions
- Relatively easy for non-specialists in thermochemistry to understand and use

Associate Species Approach For Modeling the Na_2O-Al_2O_3 System

- Liquid associate species with well-known thermodynamic properties are derived by "melting" crystalline phases

$$AlNaO_{2(s)} = AlNaO_{2(l)}$$

$$\Delta G^\circ_{fusion} = 0 \text{ at } T_{fusion}$$

$$\Delta H^\circ_{fusion} = T_{fusion} \times \Delta S^\circ_{fusion}$$

$$\Delta H^\circ_{f(l)} = \Delta H^\circ_{f(s)} + \Delta H^\circ_{fusion}$$

$$\Delta S^\circ_{f(l)} = \Delta S^\circ_{f(s)} + \Delta S^\circ_{fusion}$$

Binary Solutions Ideal Mixing

- Ideal solutions ($\Delta H_{mix} = 0$)

$$\Delta H_{mix} = 0$$

$$\Delta G_{mix} = - T\Delta S_{mix}$$

$$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

$$G = G_{soln} = G_{pure} + \Delta G_{mix}$$

$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$G = (1-X_B)G_A + X_B G_B + RT((1-X_B)\ln(1-X_B) + X_B \ln X_B)$$

A Modified Associate Species Approach is Necessary To Accommodate Immiscible Liquids

- The presence of two immiscible liquids makes impossible the use of the pure ideal solution
- Positive interaction parameters are therefore used to model a two liquid phase system with identical constituents
- Free energy minimization routines determine the composition and quantity of each liquid
- Simple manual fitting to the phase diagram yields excellent results

To Model A Complex System The First Step Is to Build Up the Model From Constituent Species

- Models for subsystems must be generated
- The models must be checked against established phase equilibria
- For glass, this means using the "solution" model for the liquid phase in calculations and determining if the liquidus (melting points) in the system reflect reality
- The ChemSage software allows us to quickly assess the phase equilibria and determine the "goodness" of the fit

Current Database For Na_2O-Al_2O_3-Cr_2O_3-MnO-NiO-B_2O_3-SiO_2

Glass/Liquid

Si_2O_4
Al_2O_3
B_2O_3
Cr_2O_3
Ni_2O_2
Mn_2O_2
$Al_6Si_2O_{13}$:/4
$Na_4B_2O_5$:/3
$NaBO_2$
$Na_2B_4O_7$:/3
$Na_2B_8O_{13}$:/5
Na_2O
$NaAlO_2$
$Na_2Al_4O_7$:/3
Na_4SiO_4 :2/5
Na_2SiO_3 :2/3
$Na_2Si_2O_5$:/2
$NaAlSiO_4$:2/3
$NaAlSi_2O_6$:/2
Al_2NiO_4:2/3
Al_2MnO_4:2/3
Mn_2SiO_4:2/3
$MnNiO_2$

Solution Phases

Mullite:
$Al_6B_{1.33}O_{11}$
$Al_6Si_2O_{13}$

Nepheline:
$NaAlSiO_2$
$NaAlSi_2O_6$
$NaAlO_2$

Corrundum:
Al_2O_3
Cr_2O_3

Crystalline Phases

Al_2O_3
B_2O_3
SiO_2 (cris)
SiO_2 (trid)
SiO_2 (quar)
Na_2O
NiO
Cr_2O_3
MnO
Na_3BO_3
$Na_4B_2O_5$
$NaBO_2$
$Na_2B_4O_7$
NaB_3O_5
$Na_2B_8O_{13}$
NaB_5O_8
NaB_9O_{14}
Na_4SiO_4
Na_2SiO_3
$Na_2Si_2O_5$
$NaAlO_2$
$Na_2Al_{12}O_{19}$
$Na_2Al_{22}O_{34}$
$NaAlSiO_4$
$NaAlSi_2O$
$NaAlSi_3O_8$
Al_2NiO_4
Cr_2NiO_4
Ni_2SiO_4
Al_2MnO_4
$MnSiO_3$
Mn_2SiO_4
$Al_4Mn_2Si_5O_{18}$
$Al_4Mn_3Si_3O_{12}$

Examples of Associate Species

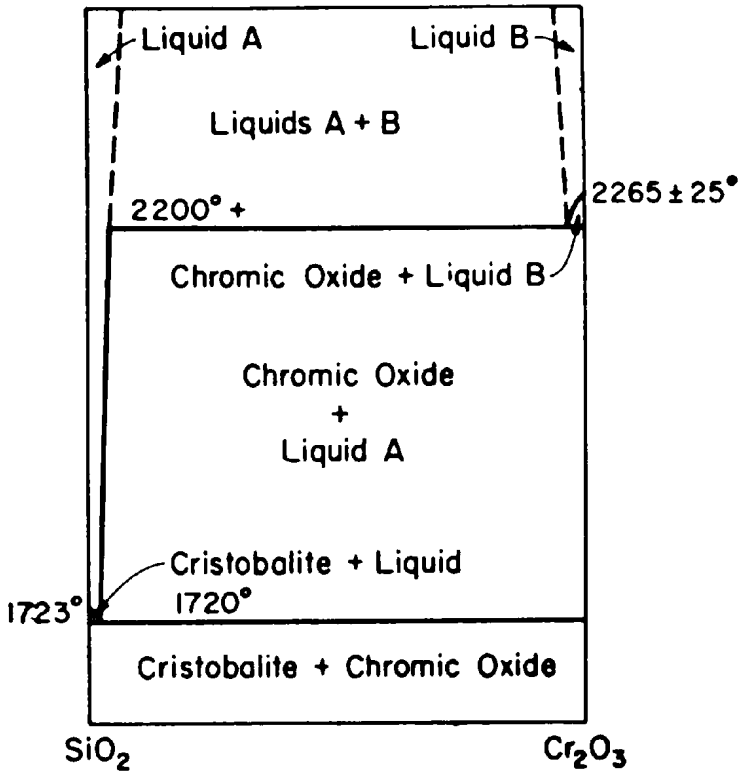
- Liquids
  - $NaAlSiO_4$:2/3
  - $NaAlSi_2O_6$:/2
- Crystalline Phases
  - $NaAlSiO_4$
- Solid Solutions
  - $Al_2O_3 \cdot Cr_2O_3$, corrundum

Recent Accomplishments

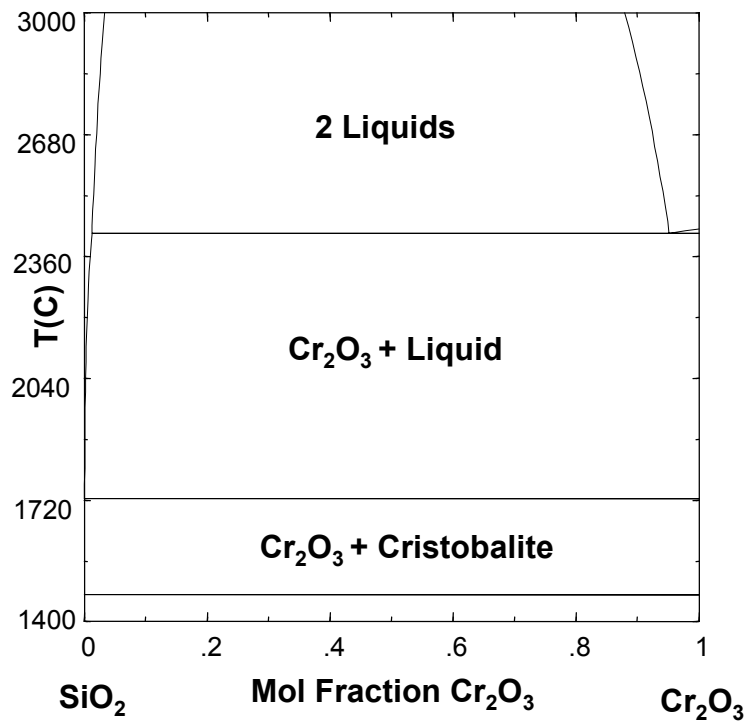
- Model Expansion
  - Inclusion of CaO-containing systems
  - Inclusion of spinel formers (Cr_2O_3, MnO, NiO)
  - Development of ZrO_2-containing systems
- Experimental
  - Completion of liquidus measurements for a Na_2O-Al_2O_3-CaO-B_2O_3-SiO_2 base system
  - Measurement of Cr_2O_3 solubilities
  - Expansion of database in spinel and zircon primary phase fields
- Initial Comparisons of Model and Experiment

The Cr_2O_3-SiO_2 Is An Example of a System Modeled With Positive Interaction Parameters to Reproduce the 2 Liquid Region

Published (No. 332)



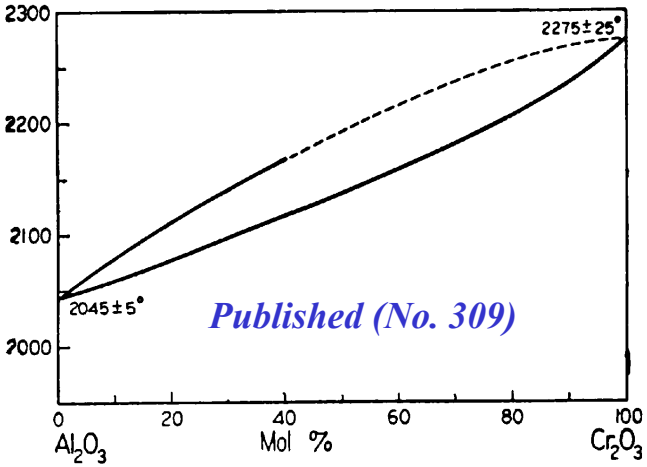
Computed Phase Diagram

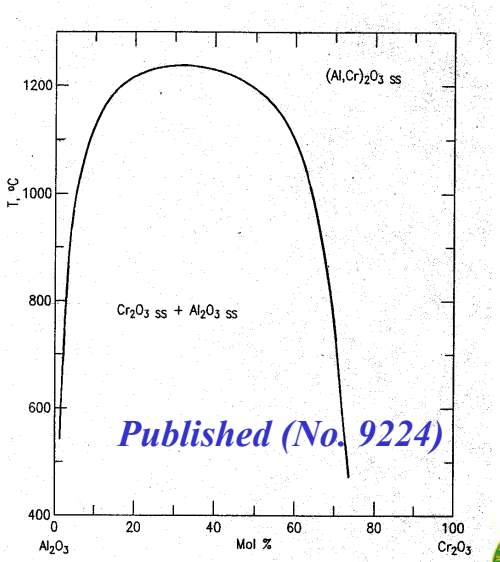


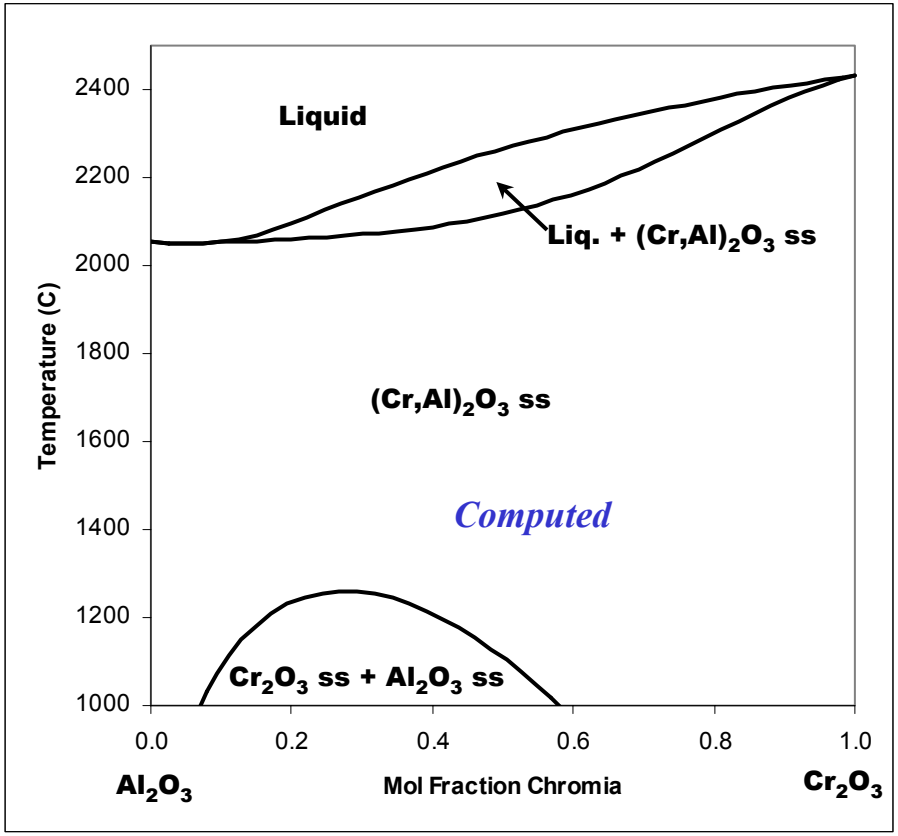
For the liquid $G_{ex} = X(1-X)[100{,}000-5T)$, where X is the mol fraction of SiO_2

The computed diagram reflects the newer melting point of Cr_2O_3 of 2432°C

Modeling the Cr_2O_3-Al_2O_3 System Was Challenging Due to the Solid Solutions and 2-Solution Phase Regions

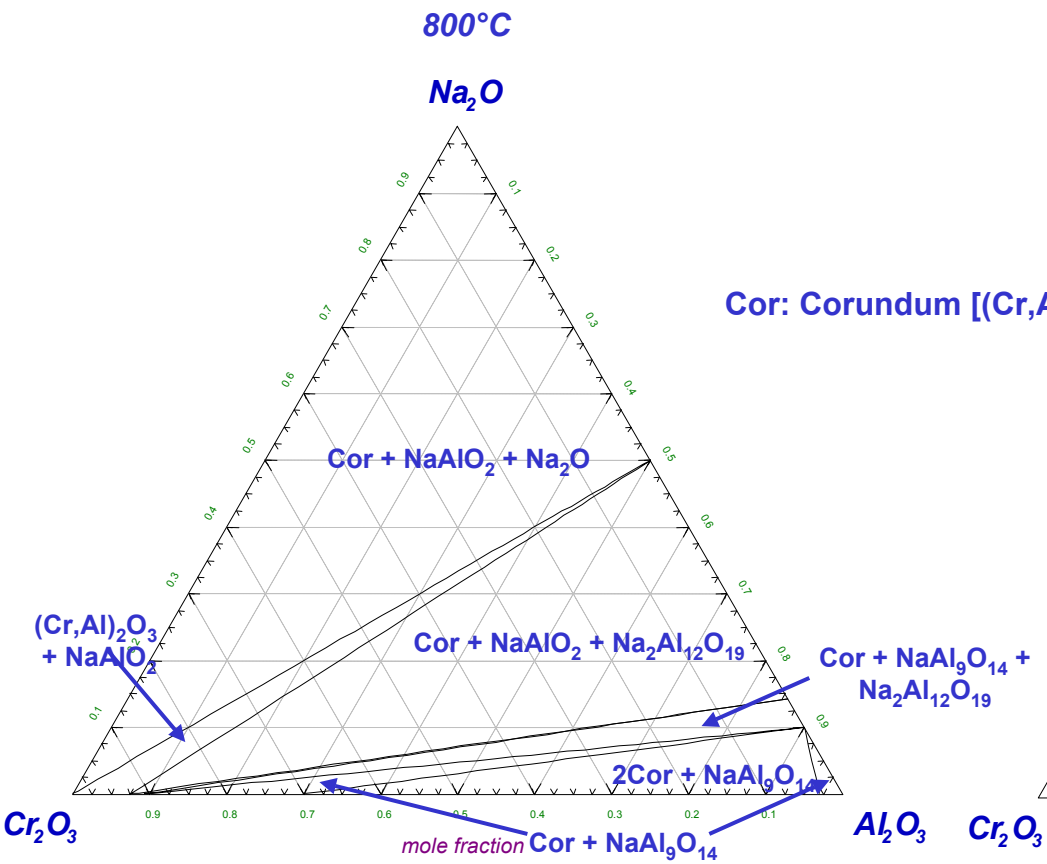




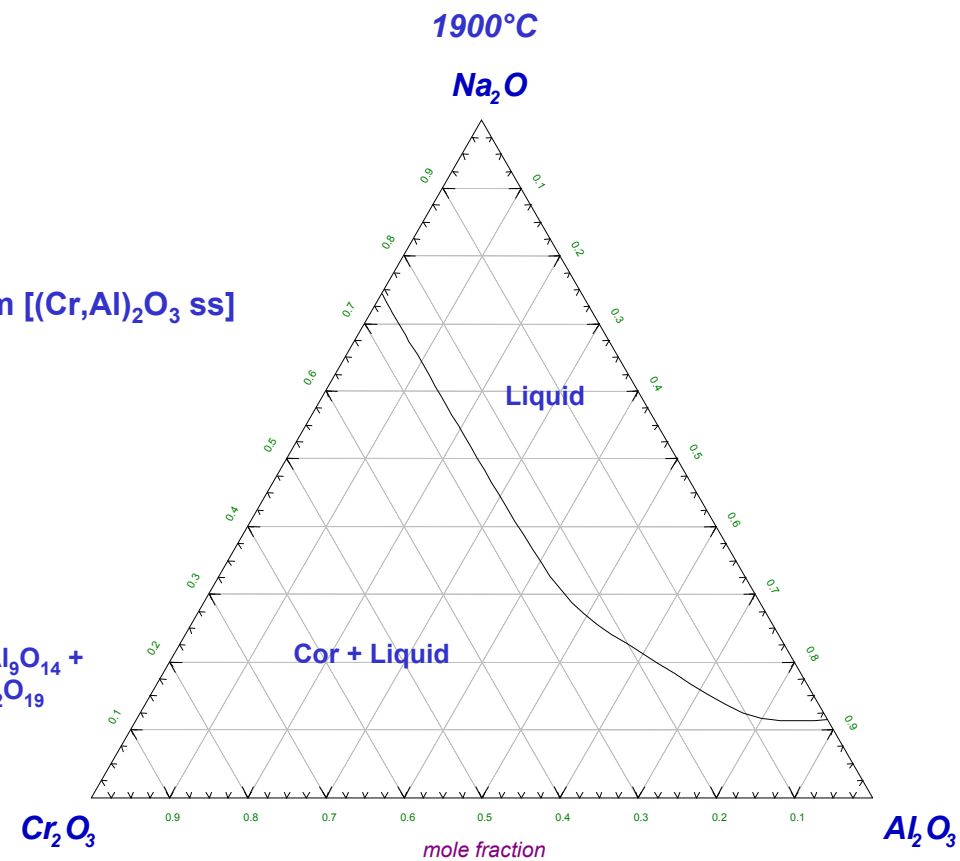


EMSP
Environmental Management Science Program

Examples: Computed Ternary Phase Diagrams for the Na_2O-Cr_2O_3-Al_2O_3 System

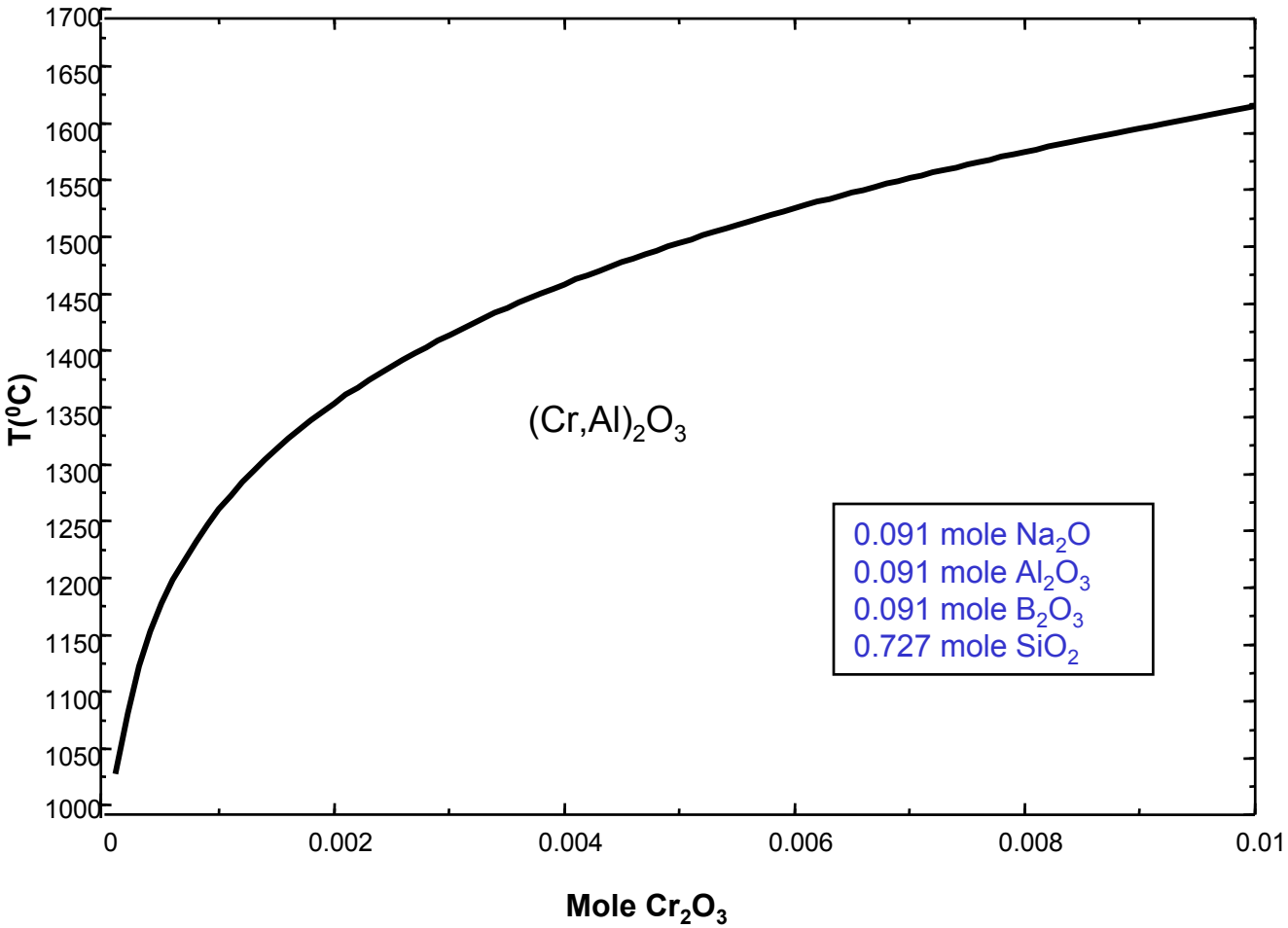


Cor: Corundum [$(Cr,Al)_2O_3$ ss]



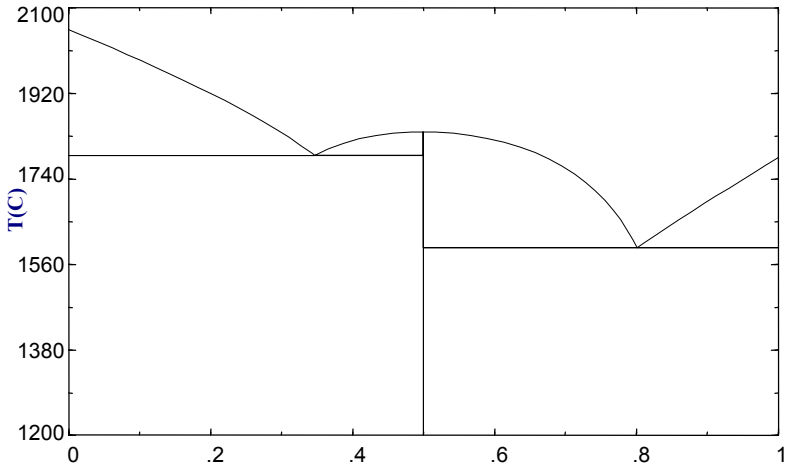
There are no published diagrams for this system

Liquidus Curve for the Na_2O-Cr_2O_3-Al_2O_3-B_2O_3-SiO_2 System as a Function of Cr_2O_3 Content

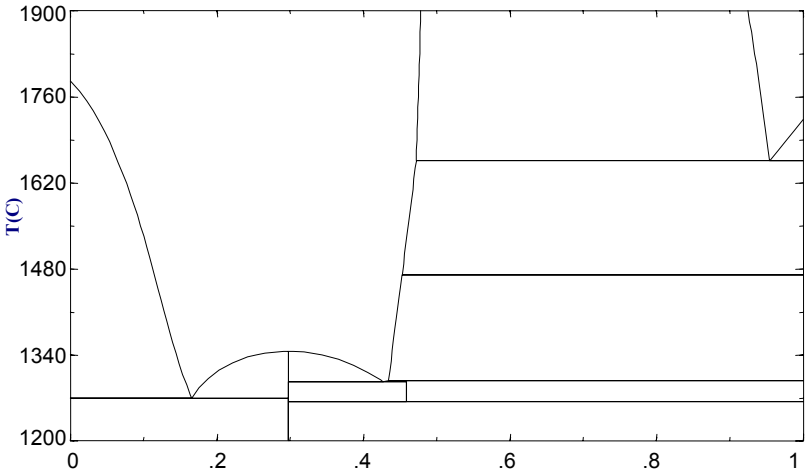


Published and Computed Phase Diagrams for Al_2O_3-MnO and -SiO_2 Are Comparable

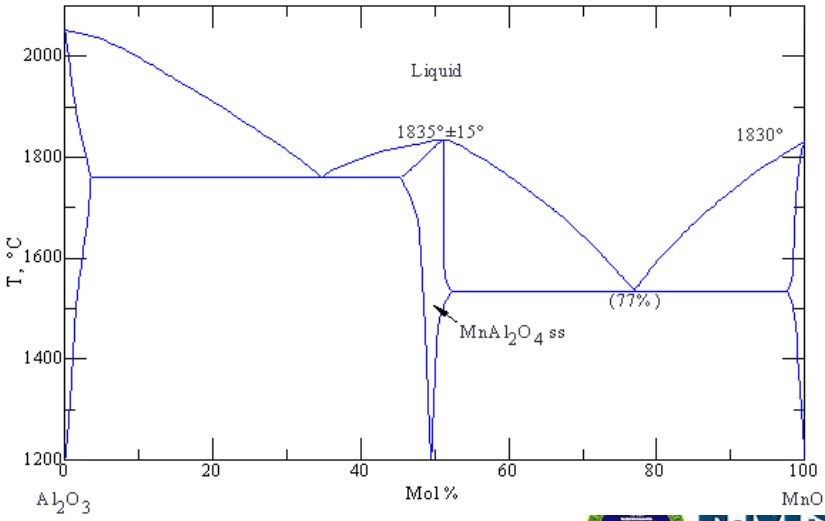
Computed



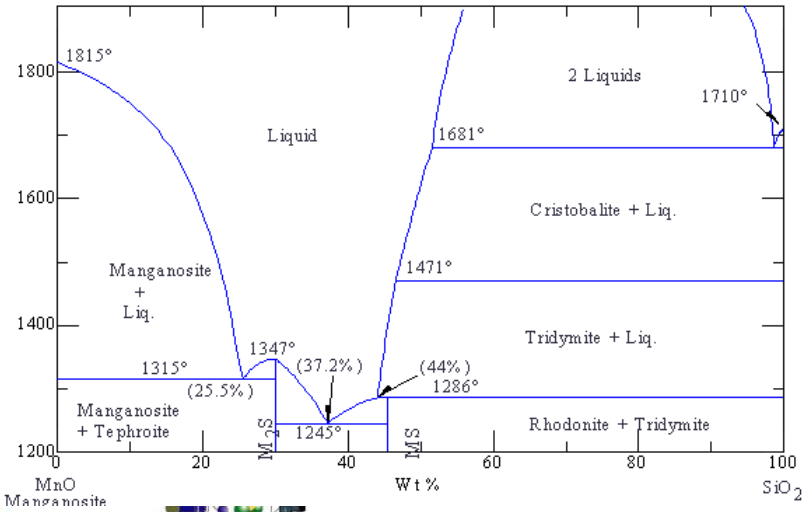
Computed



Published No. 92-004



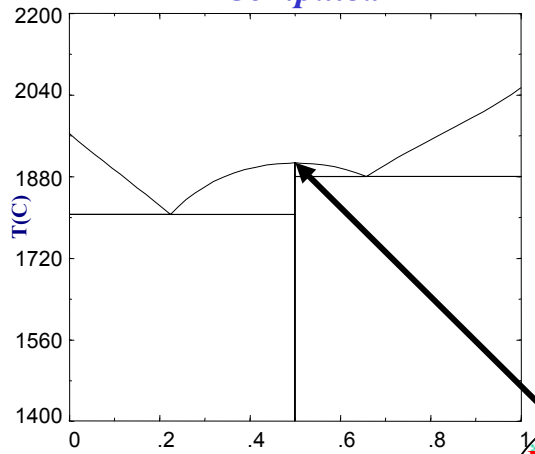
Published No. 6411



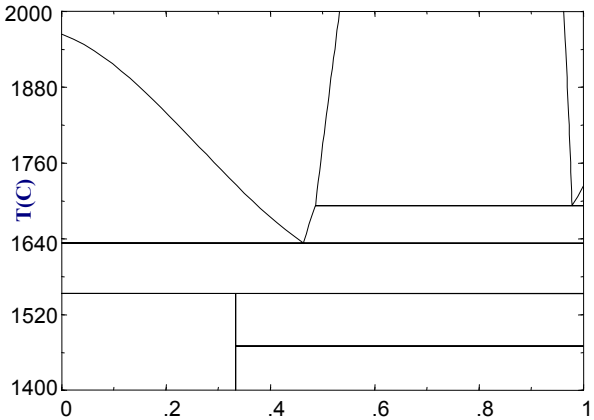
EMSP
Environmental Management Science Program

Published and Computed Phase Diagrams for Al_2O_3-NiO and NiO-SiO_2 Show Good Agreement

Computed

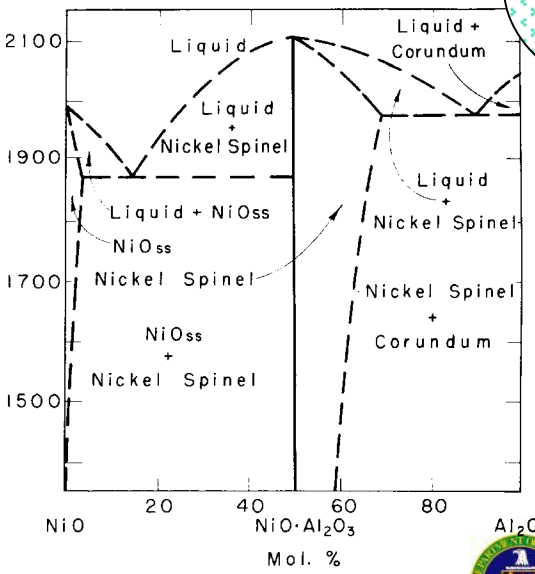


Computed

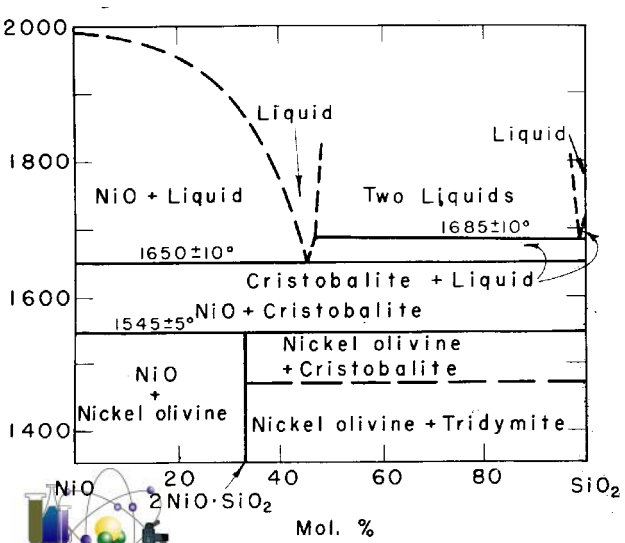


Lower melting point of $NiO \cdot Al_2O_3$ based on more recent data

Published No. 2323

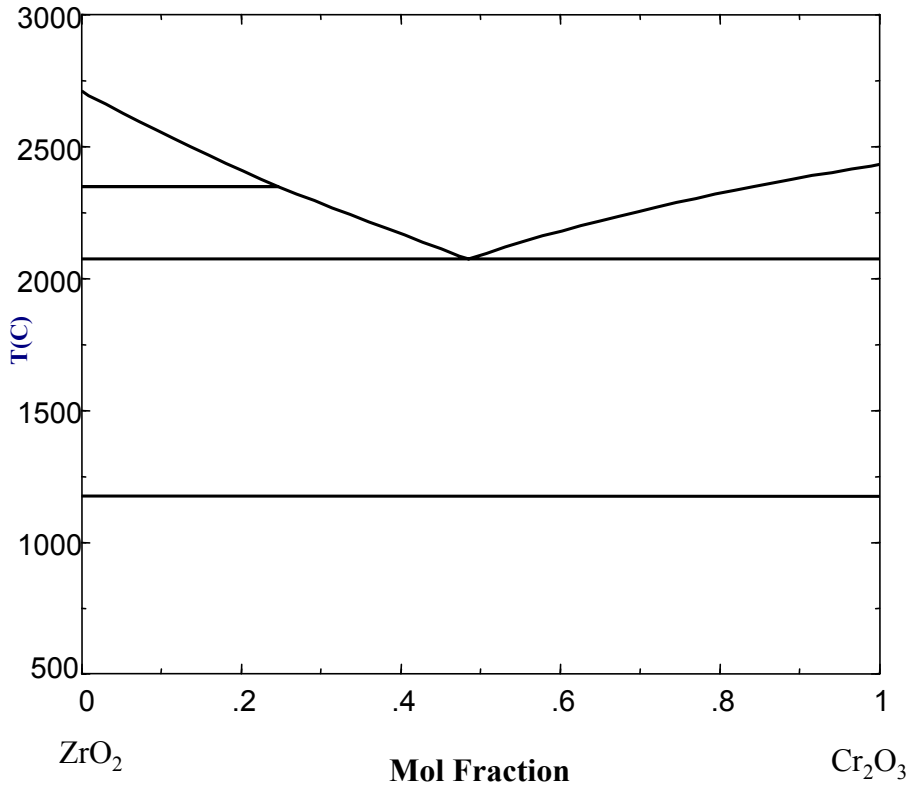


Published No. 2324



EMSP
Environmental Management Science Program

Computed Phase Diagram for the ZrO_2-Cr_2O_3 System Agrees With Existing Data

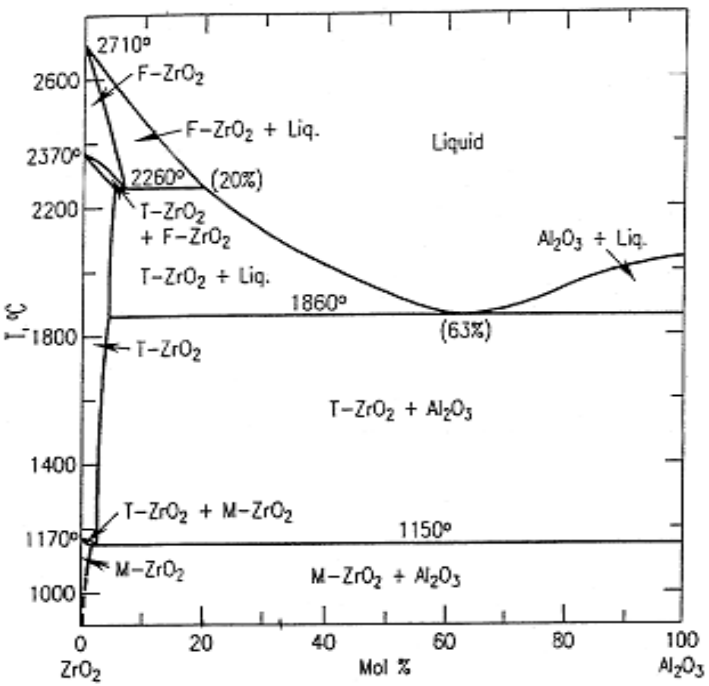


- No published phase diagram
- DTA analysis indicates eutectic at 1950°C and 0.5 mol fraction
- Liquid treated as ideal solution of end member liquids (ZrO_2, $CrO_{1.5}$)
- Cr_2O_3 melting point of 2432°C from SGTE compared to 2330°C from JANAF

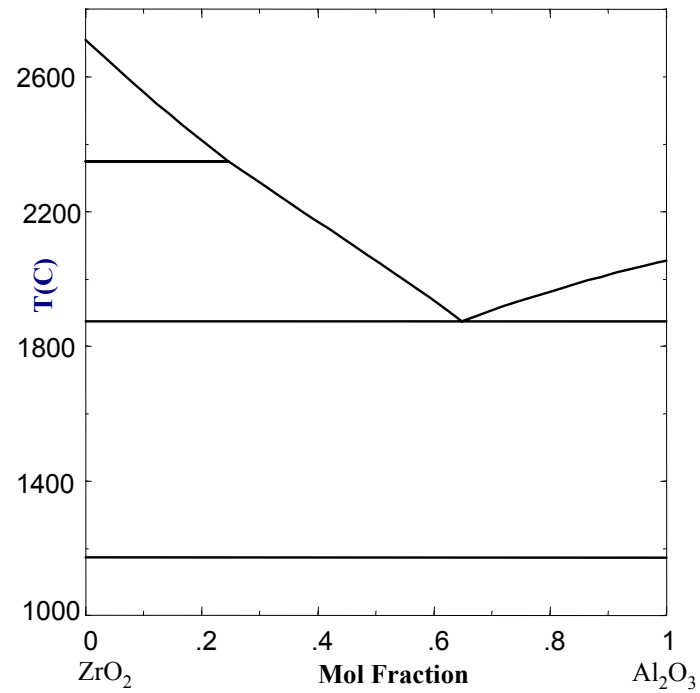
ZrO_2-Al_2O_3 System With No Solid Solution Matches Published Diagram

Published

Lakiza & Lopato, J. *Am. Ceram. Soc.*, 80 [4] 893 (1997)



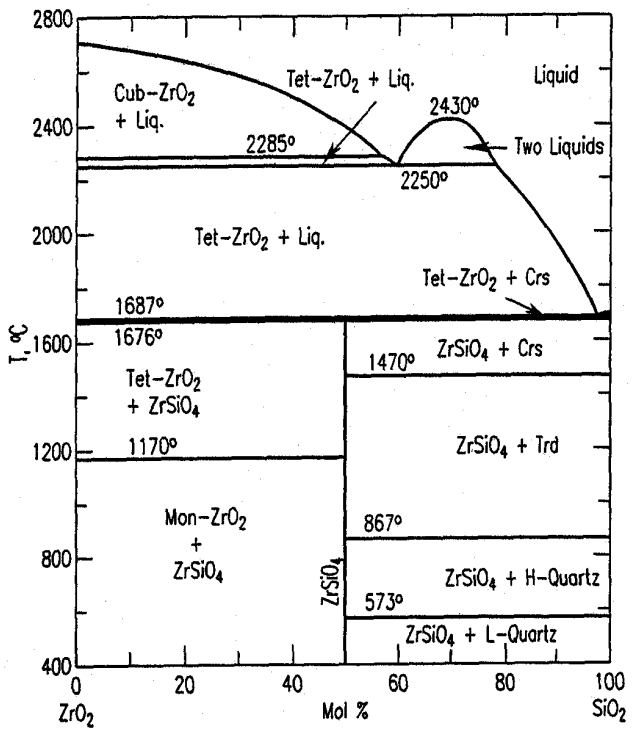
Computed



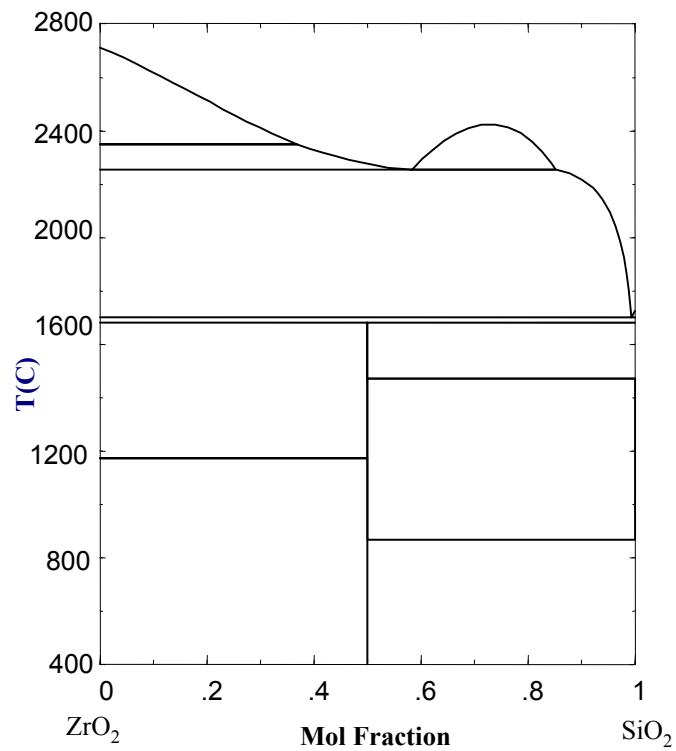
- Solid solubility of Al_2O_3 in ZrO_2 ignored
- Ideal mixing of liquid ZrO_2 and $AlO_{1.5}$

ZrO_2-SiO_2 System Well-Fits Published Diagram, With Corrected Transformation Temperature

Published (No. 2400)



Computed

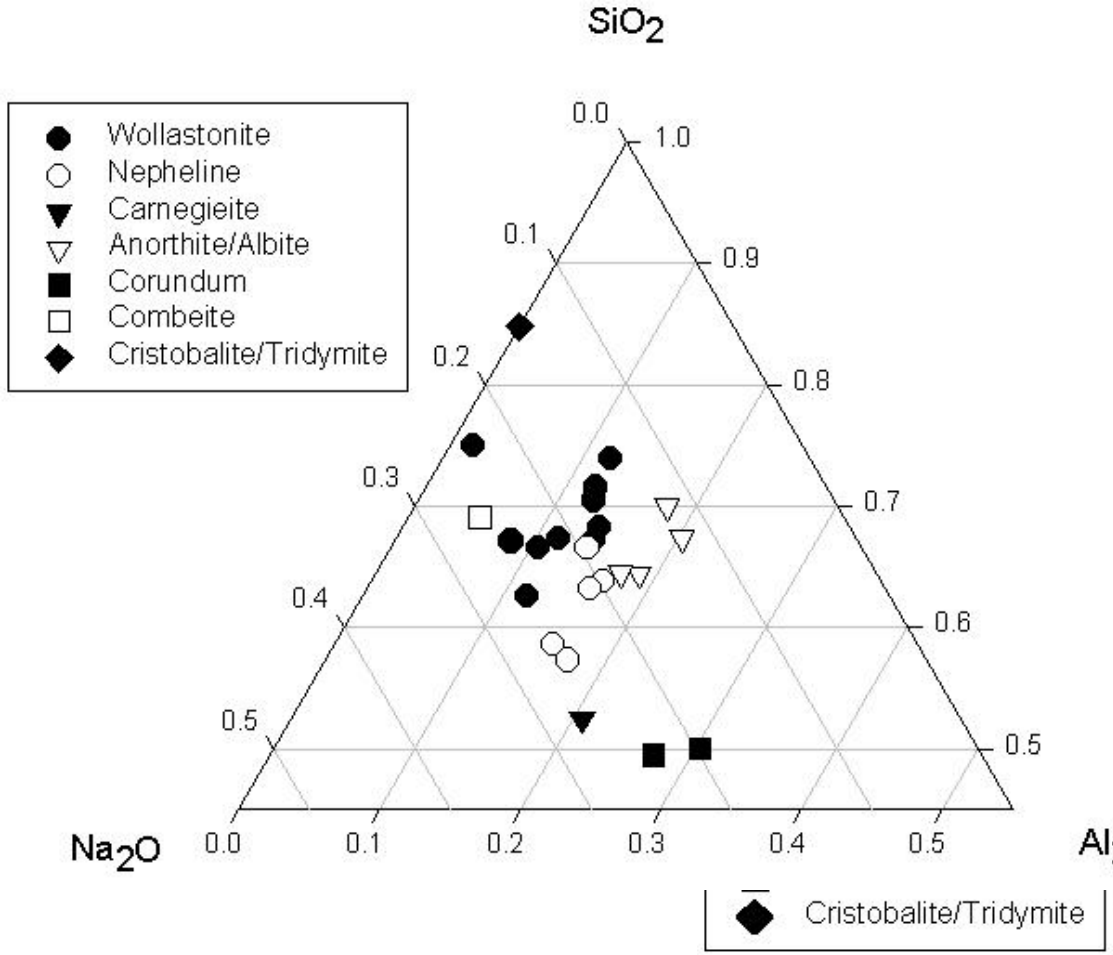


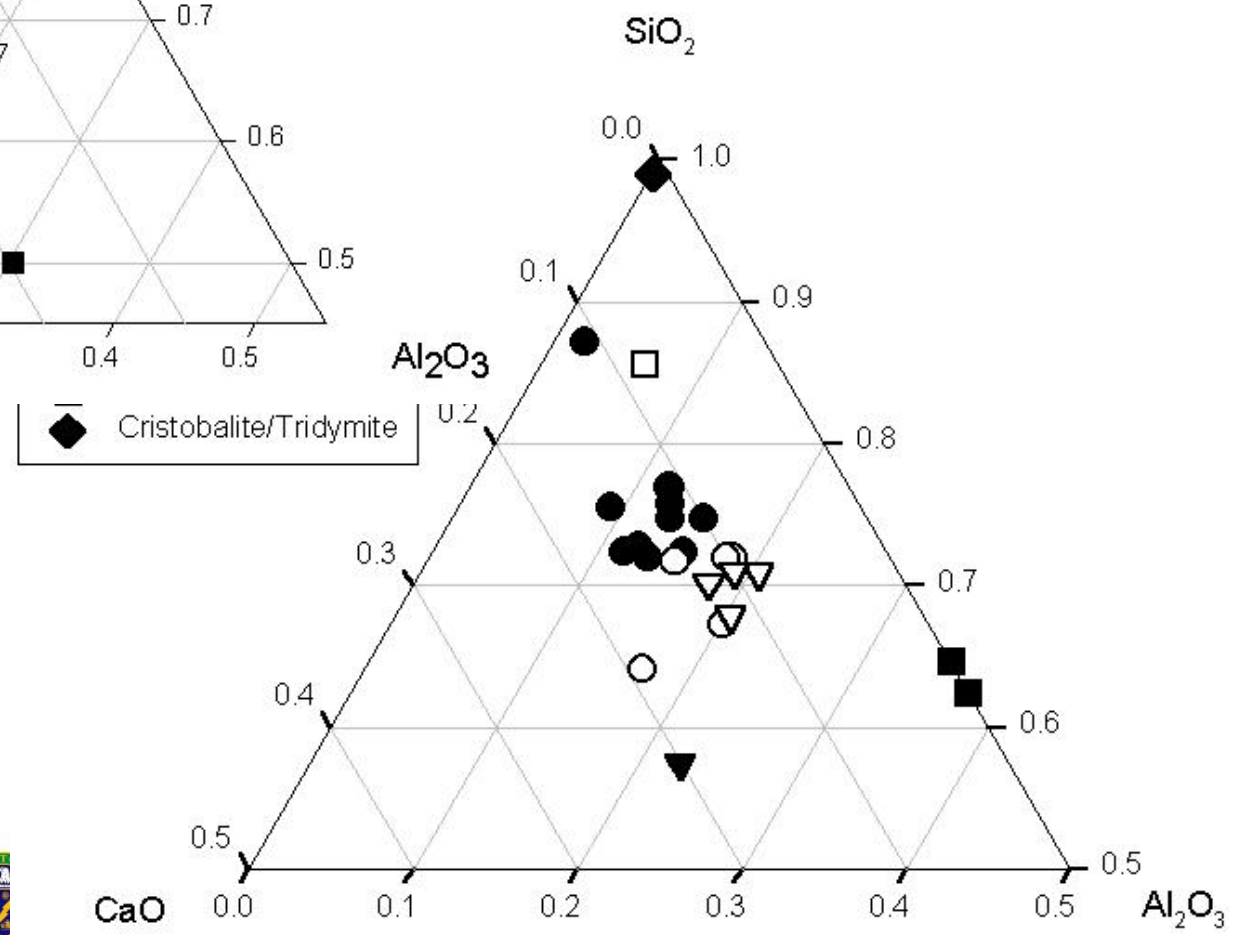
- Liquid solution model has positive excess terms
- ZrO_2 (t) to (c) transformation temperature (2347°C) from SGTE

Experimental Data

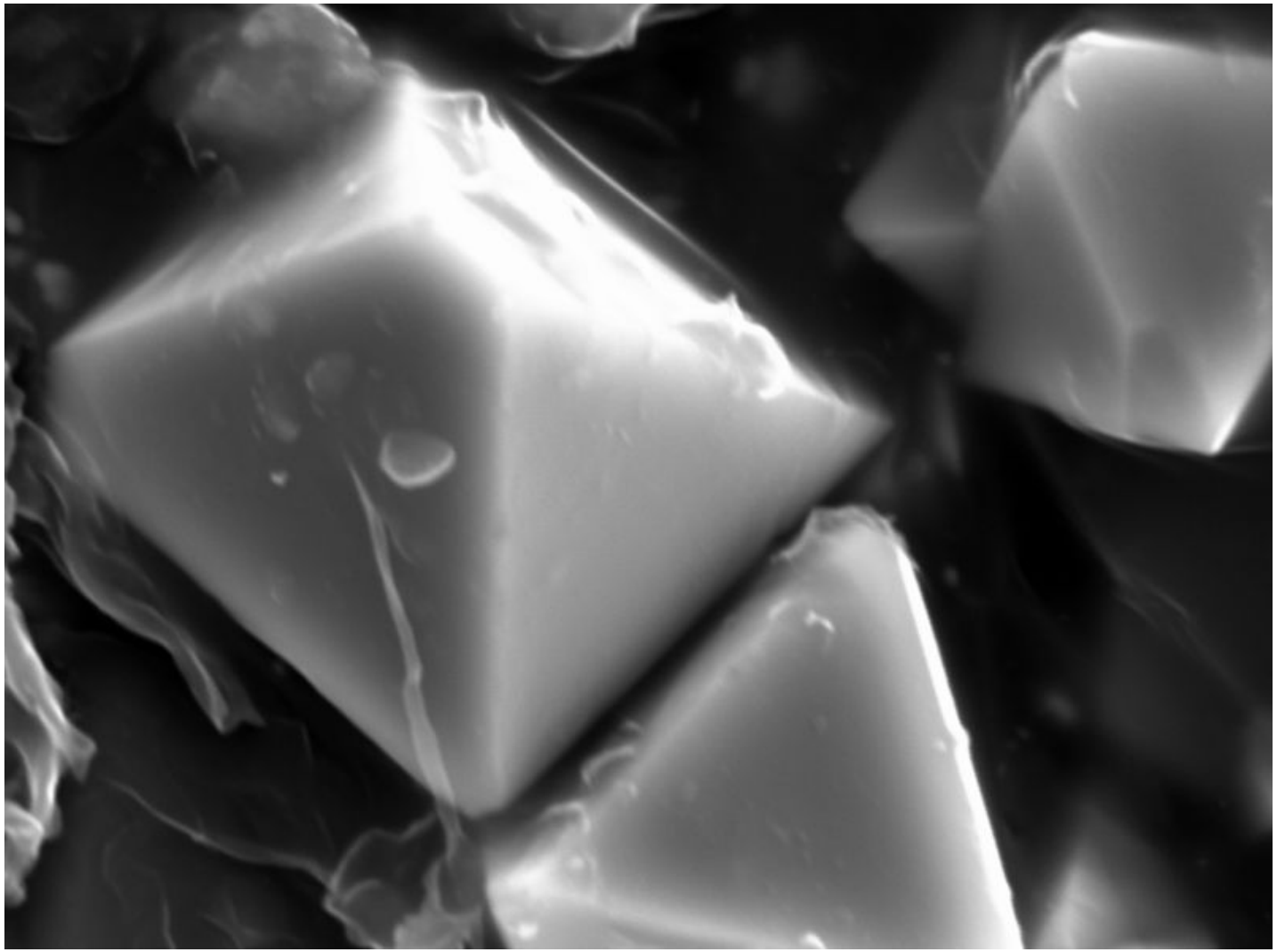
- Initial focus on Al_2O_3-B_2O_3-CaO-Na_2O-SiO_2 system
  - system forms the foundation of waste glass melts
  - fabricated and tested roughly 50 glass compositions
  - measured T_L, C_P, and primary phases
- Expanded to include multi-component melts in spinel and eskolaite primary phase fields

Ternary Projections

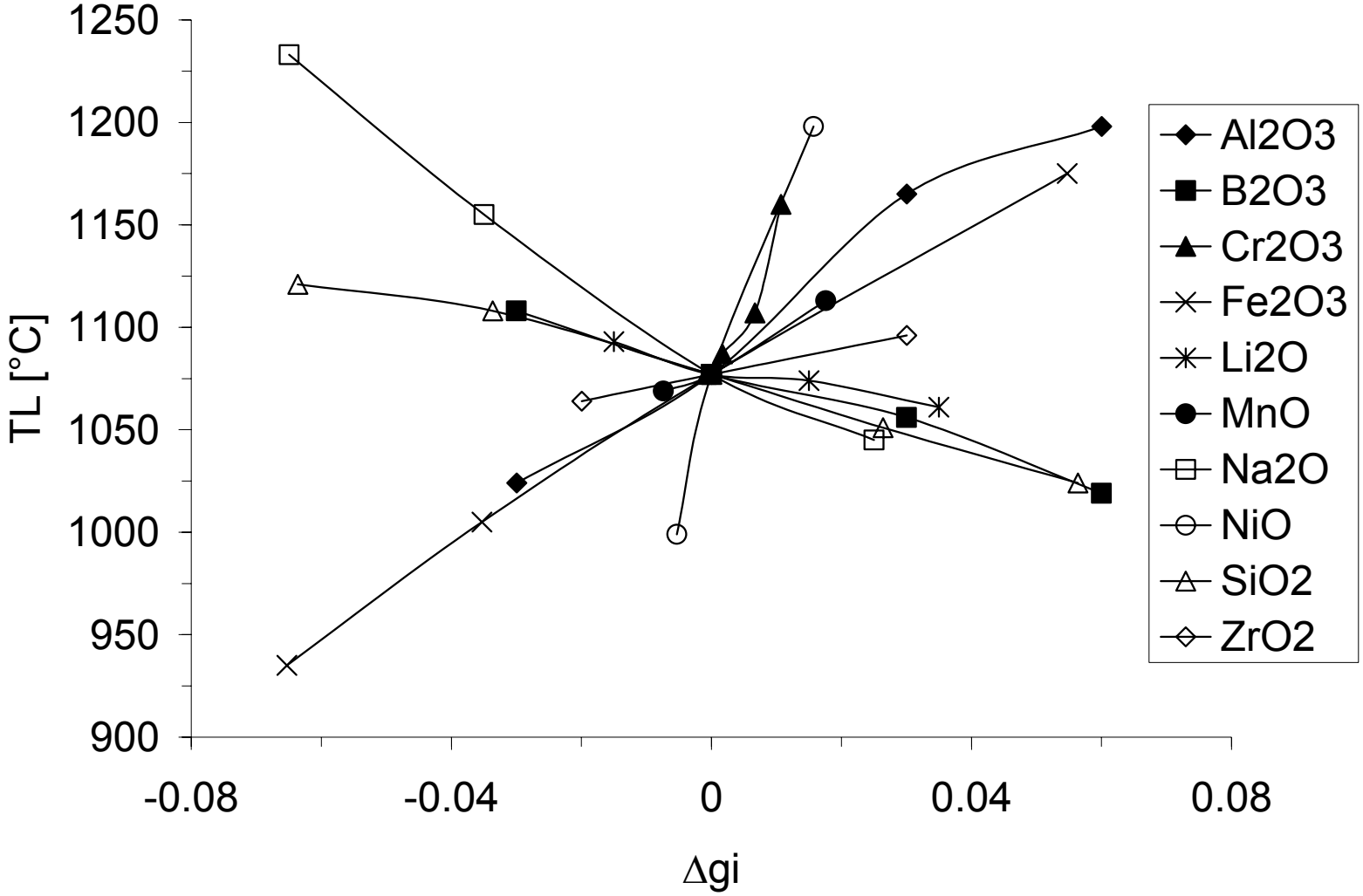




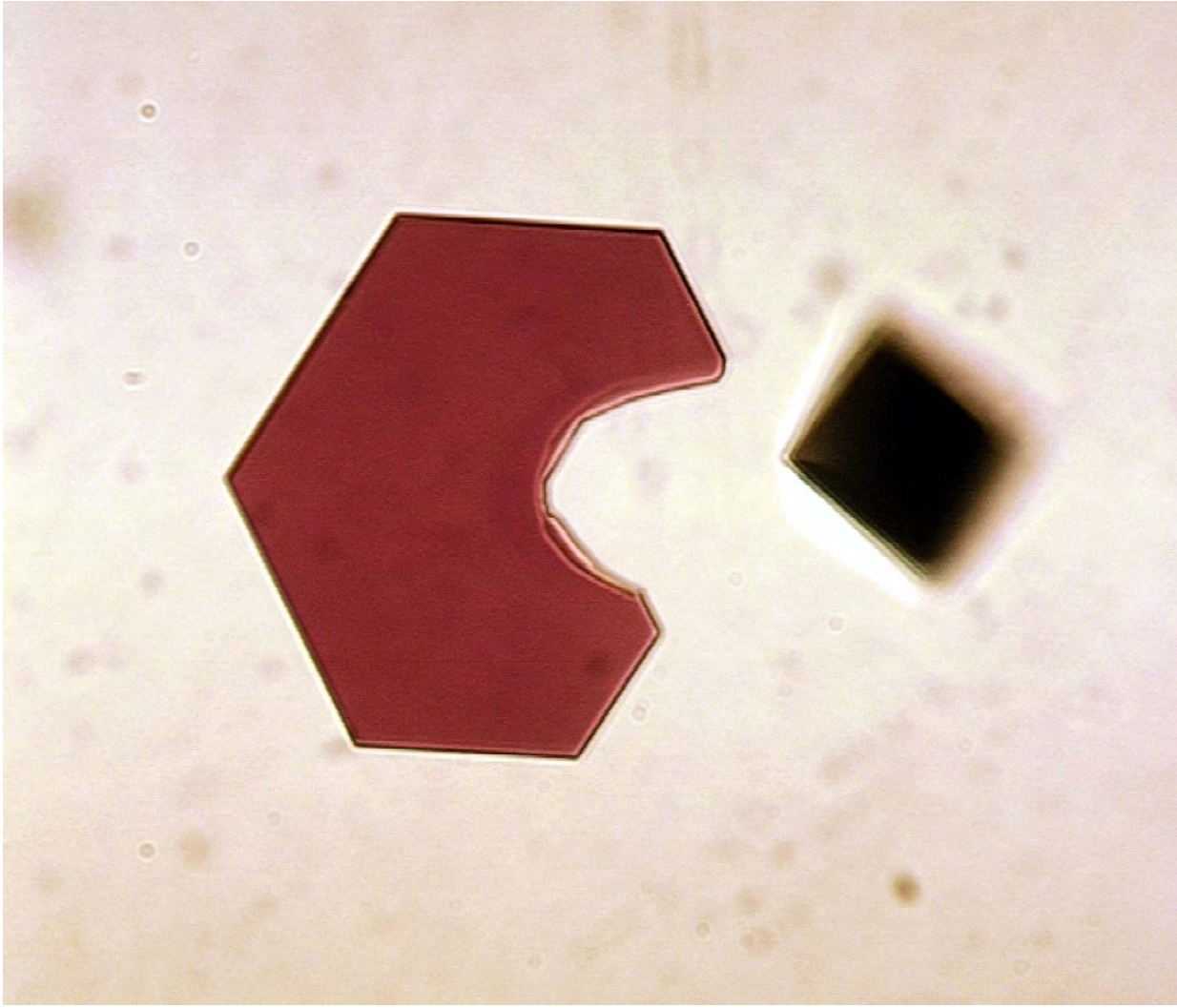
Spinel is One of the Phases Added



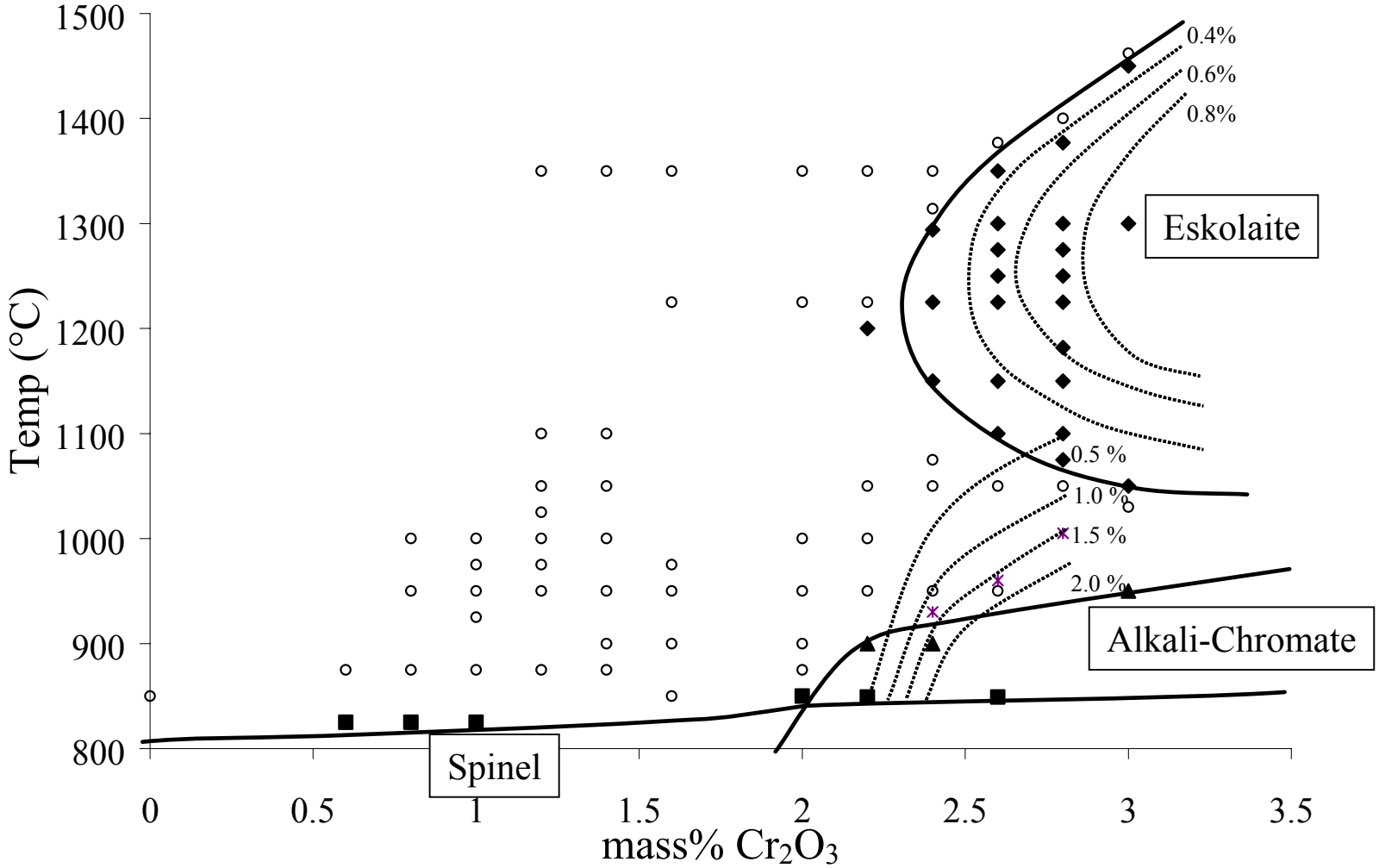
It Can Pose a Problem


1250
1200
1150
1100
1050
1000
950
900
TL [°C]
-0.08
-0.04
0
0.04
0.08
Δgi
Al2O3
B2O3
Cr2O3
Fe2O3
Li2O
MnO
Na2O
NiO
SiO2
ZrO2

Eskolaite vs. Spinel



Cr_2O_3 Solubility



Comparison of Experimental and Computed Liquidus Temperatures and Primary Phase Formation

Al_2O_3	Na_2O	SiO_2	B_2O_3	M-T_L,°C	C-T_L, °C	Phase
25.0	25.0	50.0	0.0	1510	1528	Carnegiete
16.7	16.7	66.7	0.0	1124	1096	Nepheline
12.5	12.5	75.0	0.0	1085	1118	??
20.0	20.0	40.0	20.0	875	1329	Nepheline

Issues that need resolution include the strong effect of boria on depressing the liquidus temperature and some discrepancy in primary phase formation

Summary of Status

- The associate species approach for complex systems is simple, relatively accurate, and highly usable for describing
  - Liquidus surfaces
  - Conditions for crystalline phase formation
  - Chemical activities of glass constituents
- We have developed a base model for waste glass systems that agrees reasonably with published phase diagrams
- The model has been extended in to include Cr_2O_3, MnO, and NiO
- The example of the effect of Cr_2O_3 content on T_L demonstrates the strong effect of this constituent, and illustrates the difficulty experienced with Cr_2O_3 content in waste glass fabrication.
- It is expected that use of the model can aid in finding compositional-temperature regimes that will avoid problematic Cr-containing phase precipitation.
- ZrO_2 has been modeled with Cr_2O_3, SiO_2, and Al_2O_3 by using single metal atom end members
- When the spinel-forming systems are completed they will also support efforts to avoid spinel formation in melters, which can be problematic.

Current Efforts

- Data collection
  - Add additional major components to glass basic system (Fe, Zr, Li, etc.)
  - Study solubility of minor components (additional work on Cr and begin S, Ni, Mn)
- Model development
  - Attempt single metal oxide method for boron species
  - Complete spinel/corrundum forming system ss and melt components model
  - Add Zr containing phases
  - Sulfur solubility
- Model validation and enhancement

Recent Publications Data Development

Hrma, P., P. Izak, J. D. Vienna, G. M. Irwin, and M. L. Thomas. 2002. "Partial Molar Liquidus Temperatures of Multivalent Elements in Multicomponent Borosilicate Glass," *Phys. Chem. Glasses* **43** [2] 128-136.

Jiricka, M. P. Hrma, and J. D. Vienna. 2003. "The effect of composition on spinel crystals equilibrium in low-silica high-level waste glasses," in *J. Non-cryst. Sol.*, **319** [3], 280-288.

Izak, P., P. Hrma, B. K. Wilson, and J. D. Vienna. 2001. "The Effect of Oxygen Partial Pressure on Liquidus Temperature of a High-Level Waste Glass with Spinel as the Primary Phase," in *Ceramic Transactions* **119**, pp. 309-316, American Ceramic Society, Westerville, OH.

Li, H., P. Hrma, and J. D. Vienna. 2001. "Sulfate Retention and Segregation in Simulated Radioactive Waste Borosilicate Glass," in *Ceramic Transactions* **119**, pp. 237-246, American Ceramic Society, Westerville, Ohio.

Vienna, J. D. 2002. *The Effects of Temperature and Composition on the Solubility of Chromium in Multi-component Alkali-borosilicate Glass Melts*, Ph.D. Dissertation, Washington State University, Pullman, WA.

Vienna, J. D., P. Hrma, J. V. Crum, and M. Mika. 2001. "Liquidus Temperature-composition Model for Multi-component Glasses in the Fe, Cr, Ni, and Mn Spinel Primary Phase Field ," *J. Non-cryst. Sol.*, **292** [1-3], p 1-24.

Wilson, B. K., P. Hrma, J. Alton, T. J. Plaisted, and J. D. Vienna. 2002. "The Effect of Composition on Spinel Equilibrium and Crystal Size in High-Level Waste Glass," in *J. Matl. Sci.*, **37** [24], pp 5327-5331. T. M. Besmann and K. E. Spear, "Thermochemical Modeling of Oxide Glasses," J. Am. Ceram. Soc., 85 [12] 2887-94 (2002)

Recent Publications, Model Development

K. E. Spear and M. D. Allendorf, "Thermodynamic Analysis of Alumina Refractory Corrosion by Sodium or Potassium Hydroxide in Glass-Melting Furnaces," *J. Electrochem. Soc.*, **149** (12) B551-B559 (2002).

M. D. Allendorf and K. E. Spear, "Thermodynamic Analysis of Silica Refractory Corrosion in Glass-Melting Furnaces," *J. Electrochem. Soc.*, **148** (2) B59-B67 (2001).

T. M. Besmann, K. E. Spear, and E. C. Beahm, "Assessment of Nepheline Precipitation in Nuclear Waste Glass via Thermochemical Modeling," *Mat. Res. Soc. Symp. Proc.* **608** (2000).

T. M. Besmann, K. E. Spear and E. C. Beahm, "Thermochemical Models for Nuclear Waste Glass Subsystems - MgO-CaO and MgO-Al2O3," *Mat. Res. Soc. Symp. Proc.* **556** (1999).

K. E. Spear, T. M. Besmann, and E. C. Beahm, "Thermochemical Modeling of Glass: Application to High-Level Nuclear Waste Glass," *MRS Bulletin*, **24**(4) 37-44 (1999).

K. E. Spear, T. M. Besmann, and E. C. Beahm, "Thermochemical Modeling of Nuclear Waste Glass," *Proc. Symp. High Temperature Corrosion and Materials Chemistry*, The Electrochemical Society, Pennington, NJ (Fall 1998).