Thermodynamic models for phase separation and crystallization in nuclear glasses

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[3] CEA, DES, ISEC,DPME, Univ. Montpellier, Marcoule, France

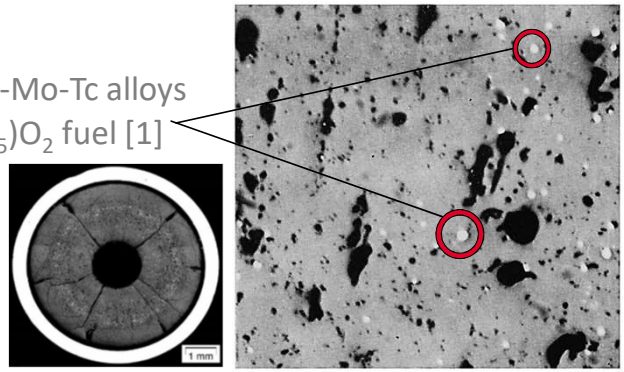
Context: The origin of some poorly soluble phases

Current nuclear French glass R7/T7 is homogeneous at its synthesis temperature…
But, in a view to increasing waste loading, typical insoluble precipitates can form such as:

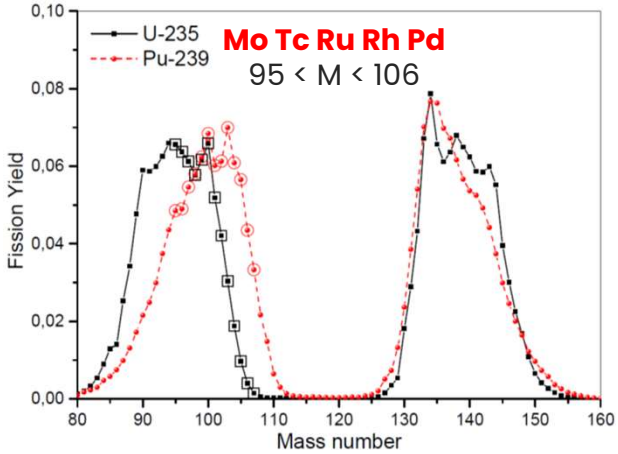
1. Platinum Group Metal (PGM),
2. Complex molybdates

These two types of phases come mainly from the “white phase” or “noble metal phase”
This alloy is made of Pd-Rh-Ru-Mo-Tc fission products

White phases: Pd-Rh-Ru-Mo-Tc alloys in irradiated $(U_{0,85}Pu_{0,15})O_2$ fuel [1]



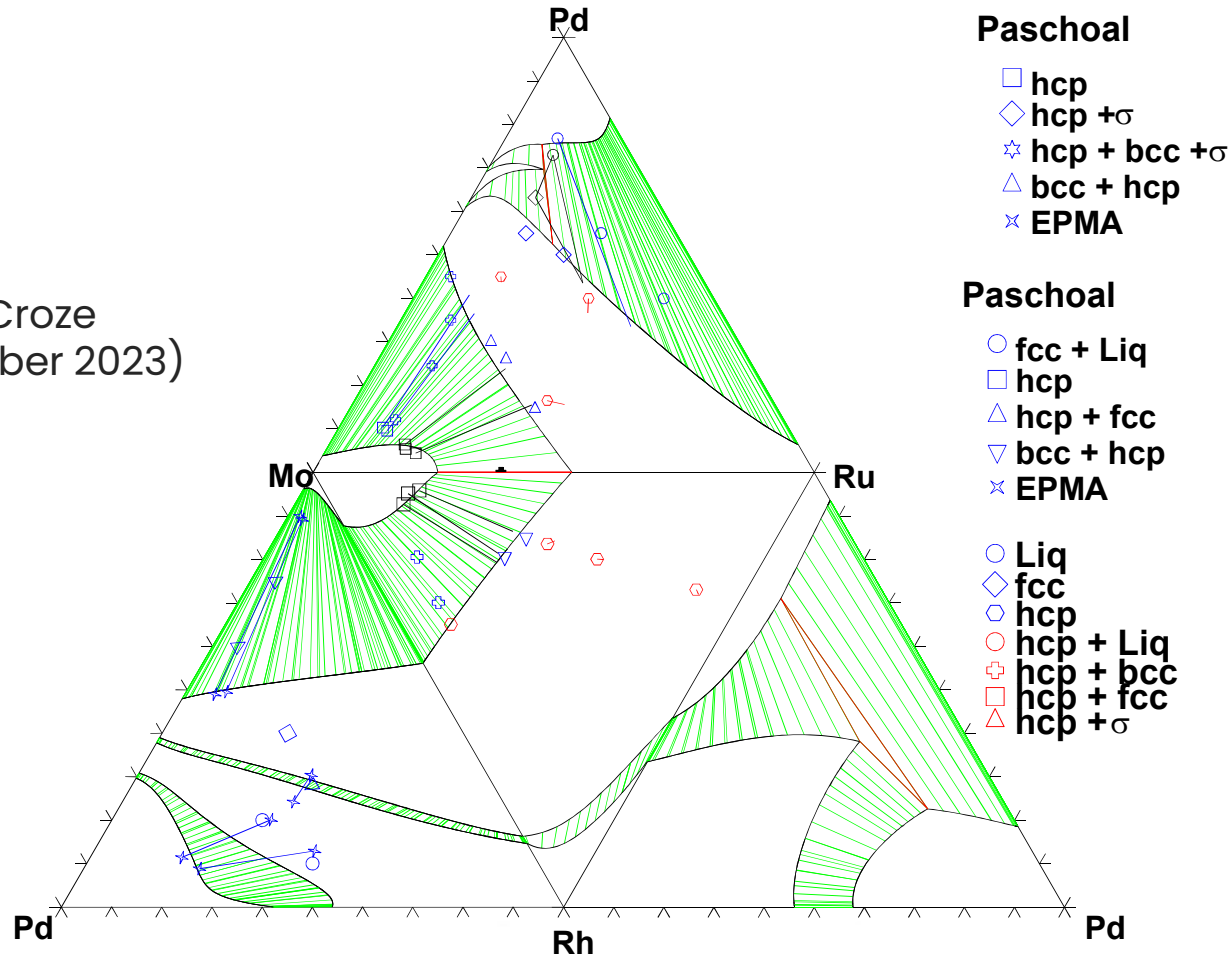
[1] Bramman & al. ; J. of Nuclear Materials (1968)



This study focuses on the fundamental research conducted to describe the thermodynamics of these complex phases formed from the noble metal phase: PGM alloys and molybdates

Context: Thermodynamics of “white phases”

Ph.D. work of Théo Croze
(Defense in December 2023)



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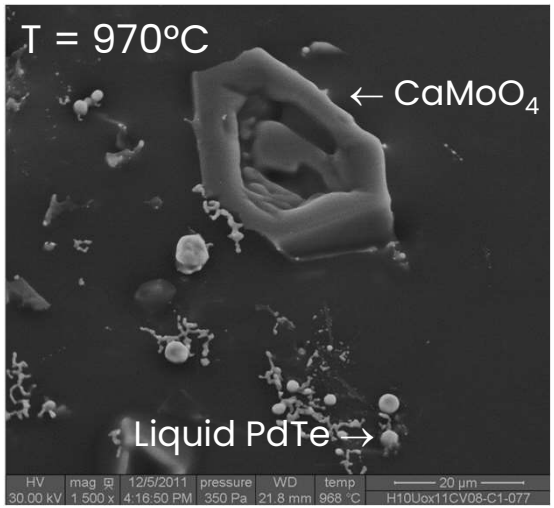
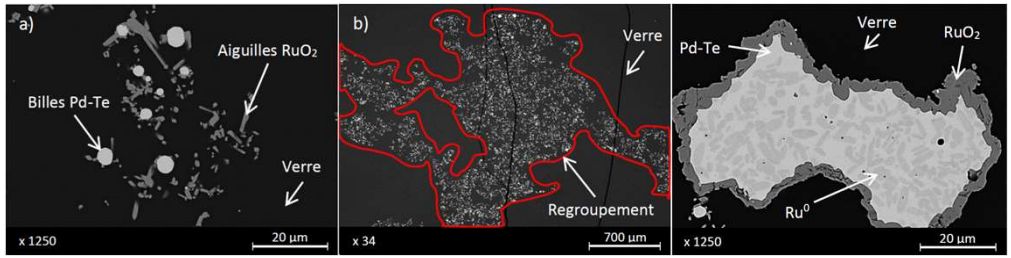
Objectives: acquisition and modelling of fundamental thermodynamic data

The objective of this work is to predict the formation and morphology of typical insoluble phases in prototypic nuclear glasses such as PGM precipitates and complex molybdates that can form beyond their solubility limits



$CaMoO_4$ observed by ESEM in situ in during UOX glass synthesis at 970°C

In the UOX glass without Rh, the metallic liquid containing mainly Pd-Te is liquid at 960 °C



Backscattered SEM images from C. Laurin PhD, 2019
a) typical shape of RuO_2 and Pd-Te particles,
b) a cluster of insoluble particles in an unstirred glass
c) Pd-Te-Ru cluster.

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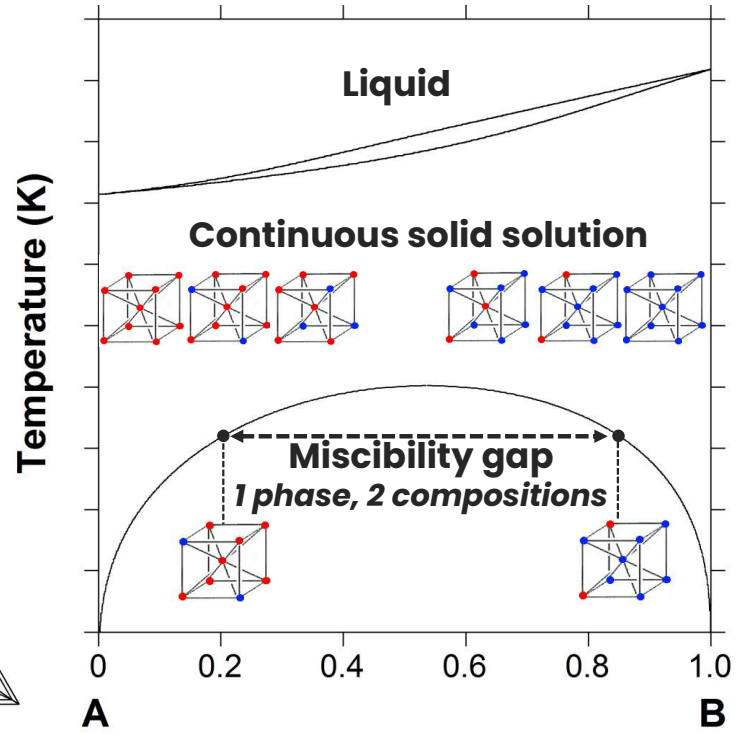
Figures: Courtesy o al. CEA ISEC/DPME

Thermodynamic origin of phase separation: Liquid miscibility gap

A single phase (liquid or solid) in which TWO distinct composition sets cannot mix:
ONE phase, **ONE** structure, **ONE** Gibbs energy function but **TWO** compositions

Liquid miscibility gap

Solid miscibility gap



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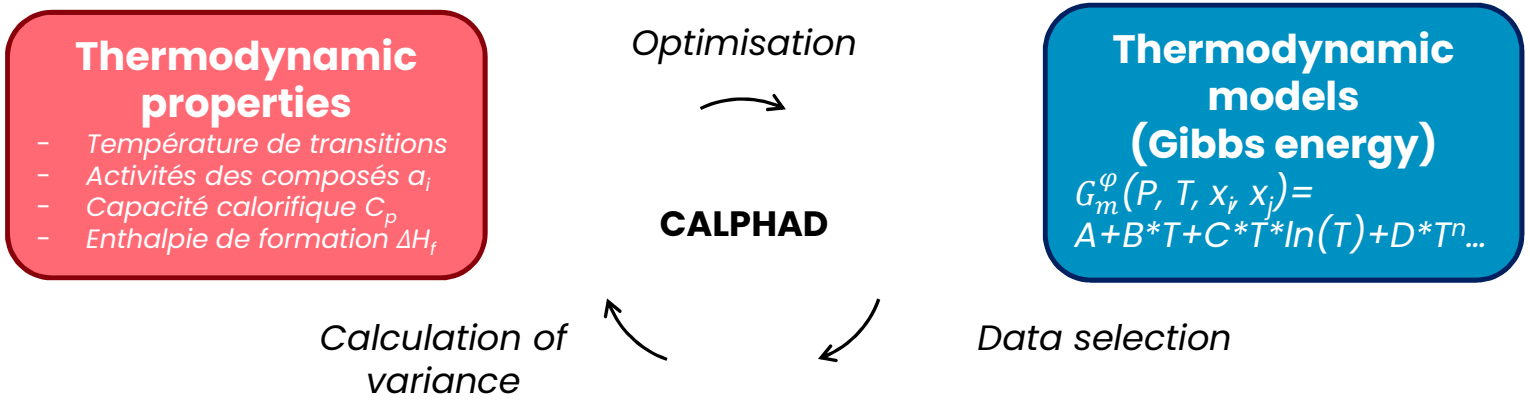
Approach: Thermodynamic modelling by the CalPhaD method (Calculation of Phase Diagram)



Available data
Experiments & Atomistic calculations

- *DTA*
- *DSC*
- *High temperature pyrometry*
- *XRD*
- *SEM-EDS*
- *ICP-MS*
- *DFT + MD*

Pd-Rh-Ru-Te:
- Heat treatments
- DTA

1. Critical analysis of literature data
2. If lack of data, new experiments are performed
3. Also atomistic – DFT - calculations

Calphad is the only predictive method for complex systems under all conditions: *P, T,* x_i
The developped database is used to perform application calculations: Phase diagram, thermodynamic properties

Some relevant data on PGM & chalcogen phases

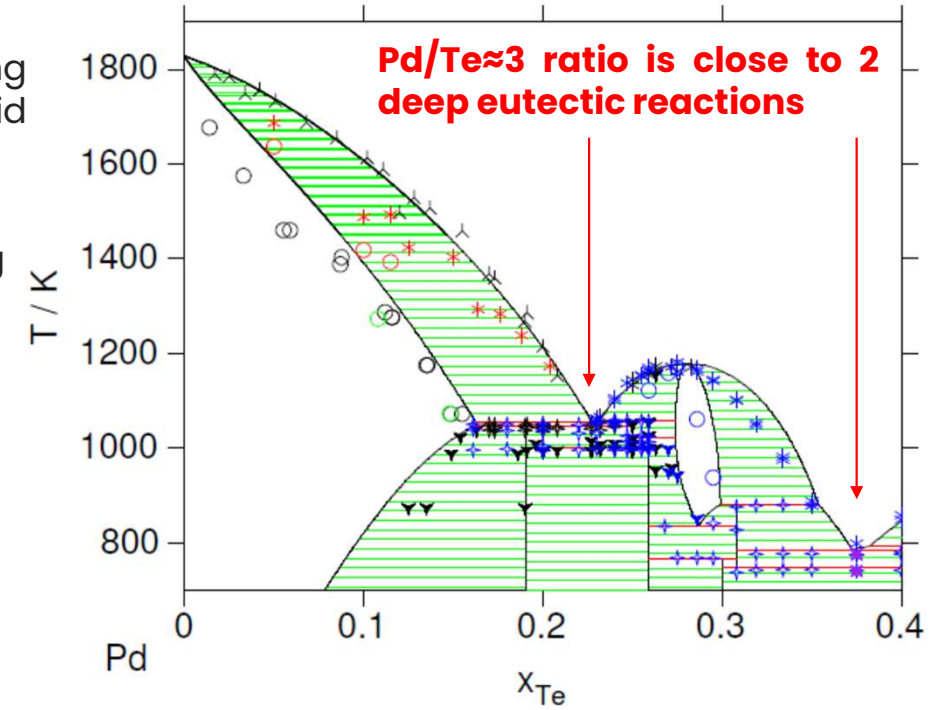
The Pd-Te phase diagrams

The formation of Pd-Te precipitates is linked to the strong interaction between Pd and Te (No Te → no metallic liquid droplets)

Pd-Te alloys are characterized by their relatively low melting points:

- 1st reaction: @ 1053 K & x_{Te}=0.228 in at. fr.
- 2nd reaction: @ 768 K & x_{Te}=0.375 in at. fr.

The Pd-Te binary system was the first one to be published in the framework of PGMs interactions in HL nuclear waste



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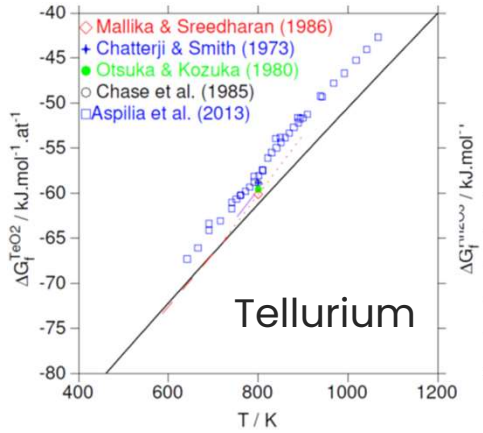
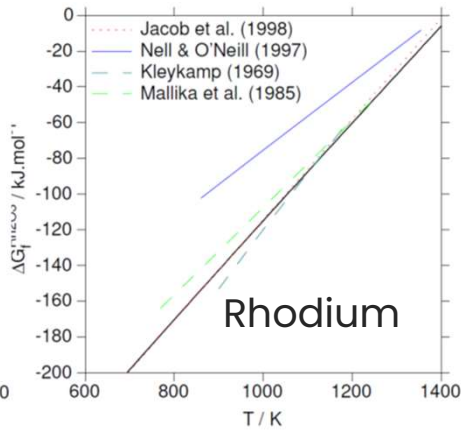
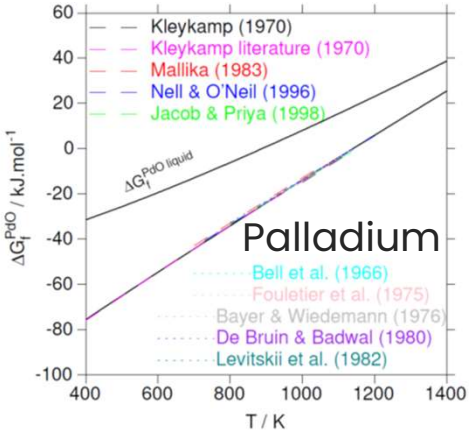
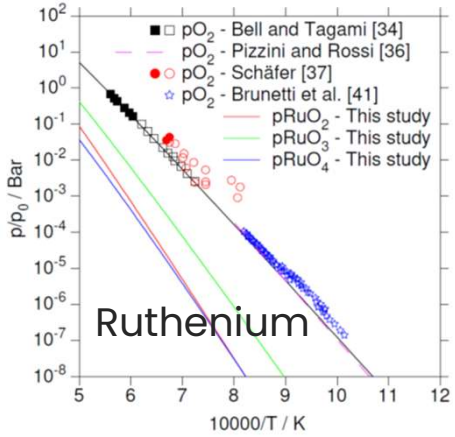
Some relevant data on PGM & chalcogen oxide phases

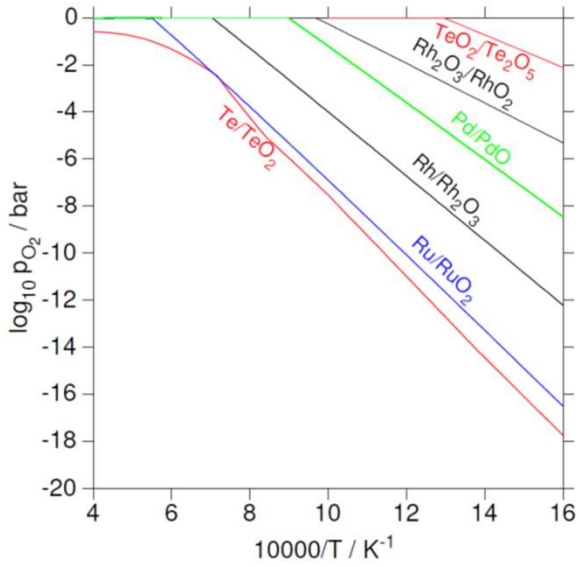
Thermodynamic properties: Gibbs energies of oxide phases











Controlling the RedOx of the elements involved in the interactions at the origin of precipitation phenomena is a key point in this thermodynamic approach. In the specific case of PGMs, it enables us to predict speciation between the metallic or oxide phases.

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Calculations of PGMs thermodynamic properties
Focus on Ruthenium speciation

Because PGMs are poorly soluble, their thermodynamic properties can be calculated without considering the glass chemistry → The interaction with the melt is only taken into account through its oxygen potential

Case of an UOX waste composition after reprocessing:

TeO_2=0.3, RuO_2=1.3, Rh=0.2, Pd=0.64 (in g/l in the solution)

Temperature is fixed to 1473 K, calculations are performed as a function of $p(O_2)$

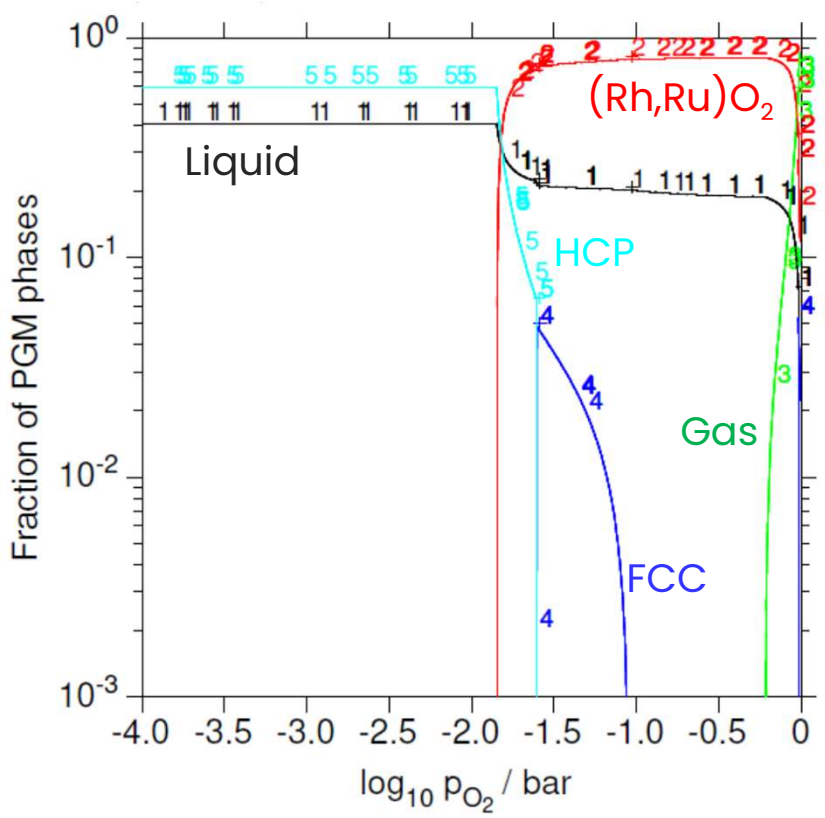
Calculations of PGMs thermodynamic properties
Focus on Ruthenium speciation

Question 1: In which phases are the PGMs elements?

If log $p(O_2)$ < -1.8:
All the elements are reduced in the metallic liquid and the HCP alloy

If -1.8 < log $p(O_2)$ < -1.1:
$(Rh,Ru)O_2$ forms, the amount of metallic alloys decreases rapidly

If -1.1 < log $p(O_2)$:
$(Rh,Ru)O_2$ and metallic liquid are the only phases until gas forms at high O_2 pressure



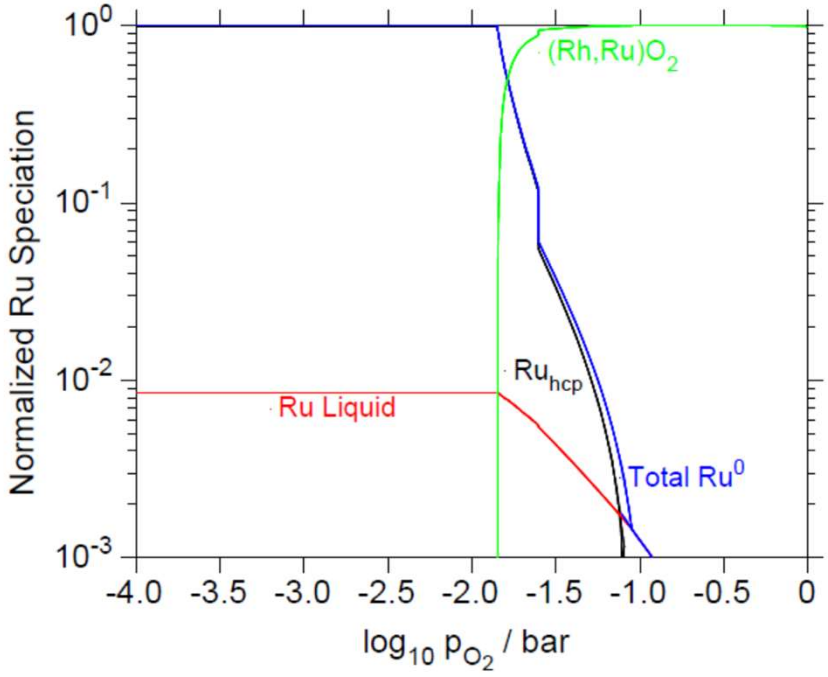
Calculations of PGMs thermodynamic properties
Focus on Ruthenium speciation

Question 2: What is ruthenium speciation?

If log p(O_2) < -1.8:
Nearly all the Ru is alloyed in the HCP solid solution, about 1% in the metallic liquid

If -1.8 < log p(O_2) < -1.1:
(Rh,Ru)O_2 forms, the amount of Ru^{+IV} skyrockets, the amount of alloys (HCP+FCC) decreases rapidly

If -1.1 < log p(O_2):
Ru is oxidized in (Rh,Ru)O_2 rutile phase
Only a few amount of Ru remains in the metallic liquid…
This limit is still badly known
(The gas phase is not represented)



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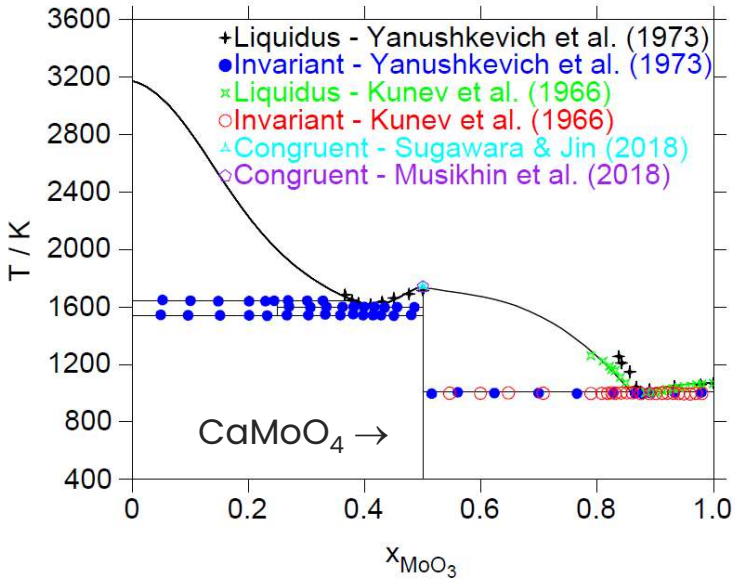
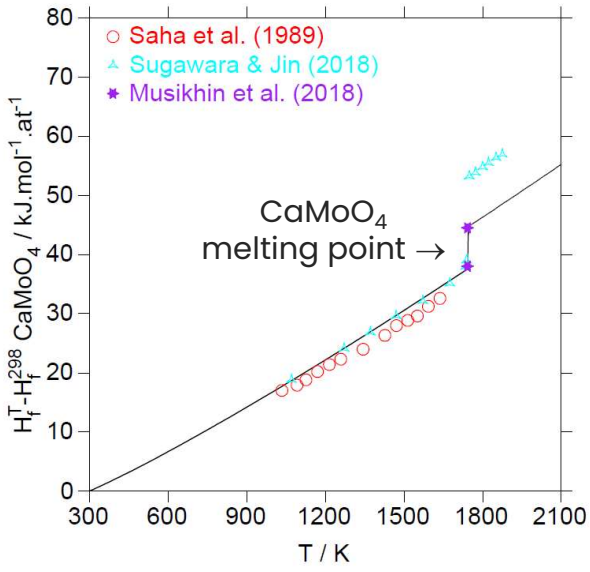
Some relevant data on calcium molybdates
Thermodynamic properties & phase diagrams

Enthalpy calculation for intermediary compounds formed during glass melting: $CaMoO_4$

These data can be useful to be implemented in glass melting modeling to optimize the vitrification processes (knowledge of the latent heat of fusion)

- Calculation of transition temperatures
- Prediction of heat contents





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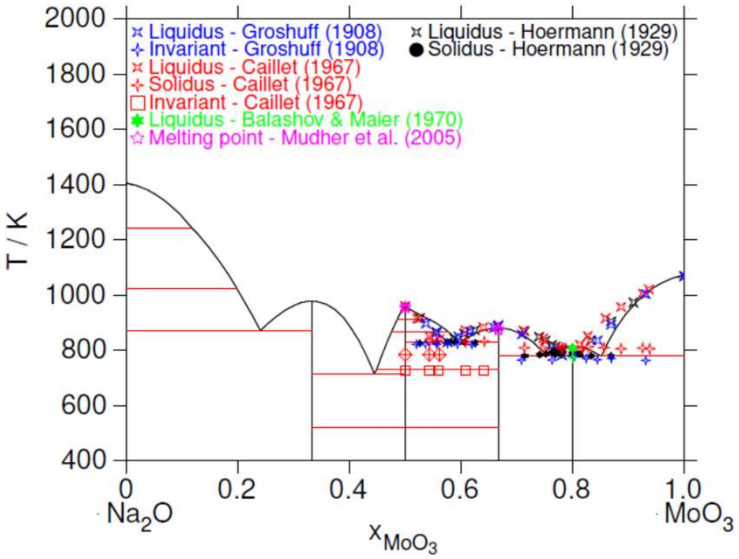
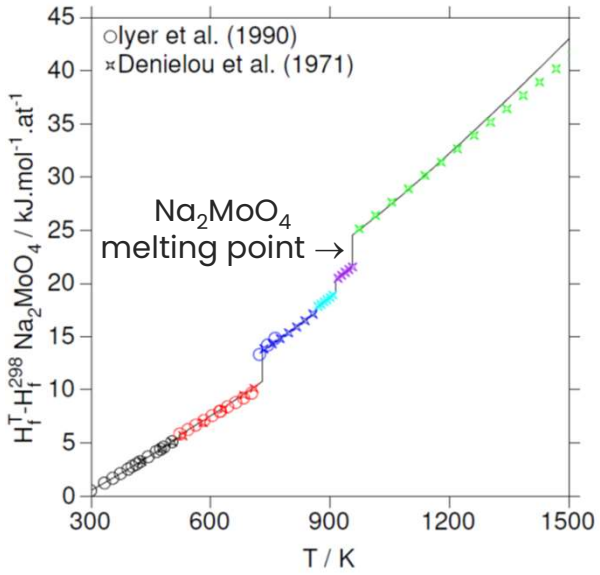
Some relevant data on sodium molybdates
Thermodynamic properties & phase diagrams

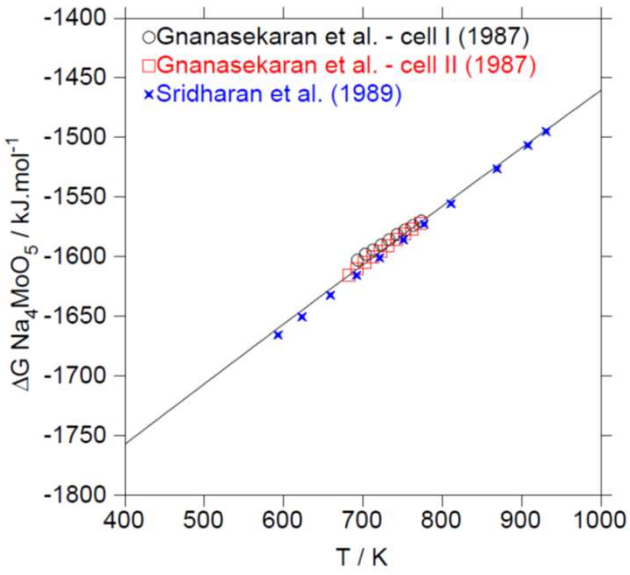
Enthalpy calculation for intermediary compounds formed during glass melting: Na_2MoO_4 allotrops

These data can be useful to be implemented in glass melting modeling to optimize the vitrification processes (knowledge of the latent heat of fusion)

- Calculation of transition temperatures
- Prediction of heat contents







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Some relevant data on Na_2O–SiO_2 system
Thermodynamic properties & phase diagrams


Computational Materials Science 66 (2013) 20–27

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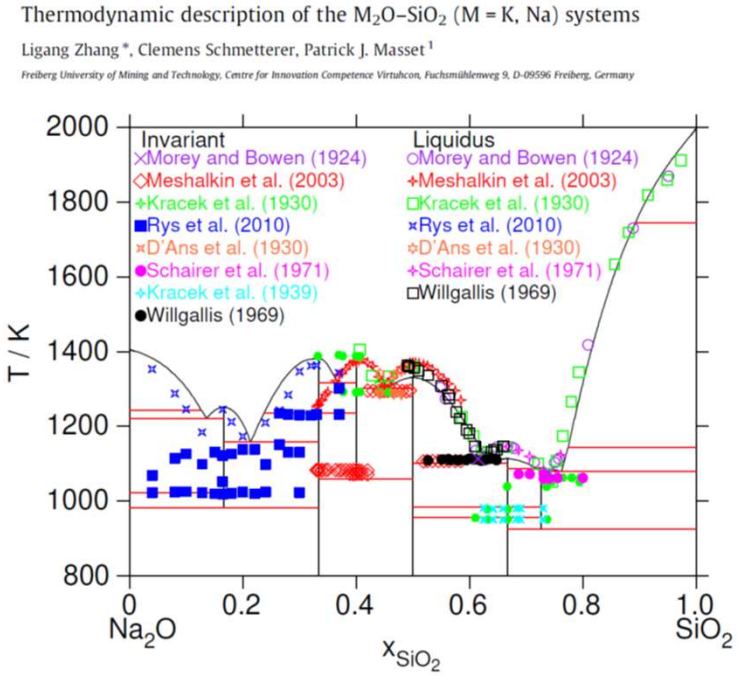
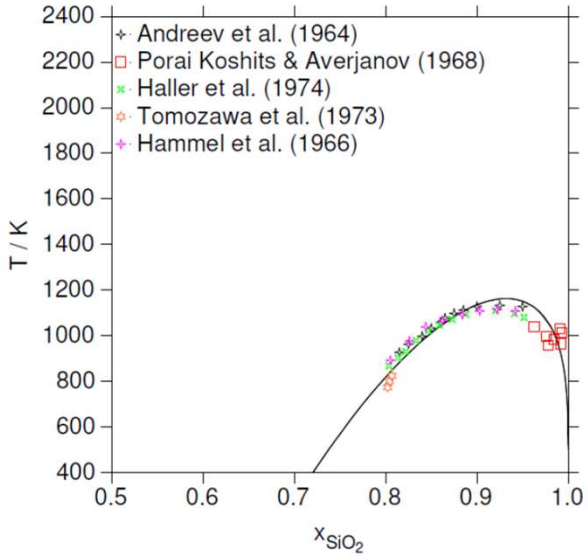
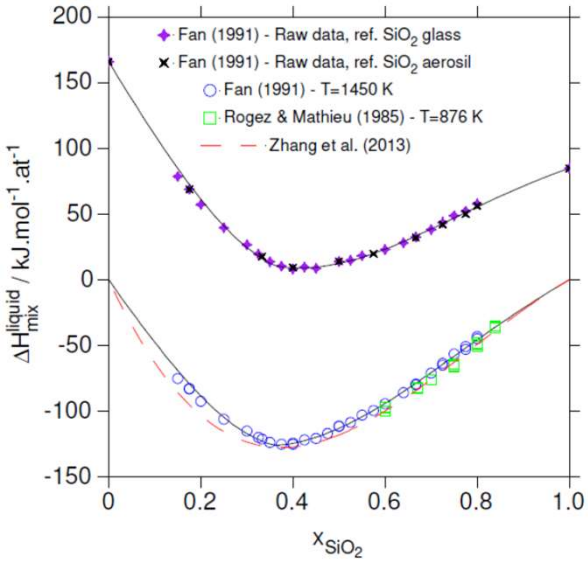
The Na_2O–SiO_2 system is a key binary for predicting glass chemistry

The model from Zhang et al. has been reassessed, with particular emphasis on modelling miscibility gaps







The aim of this modelling is to obtain a complete description of the NBS ternary in order to couple the behavior of the insoluble phases to the thermochemistry of glass melt

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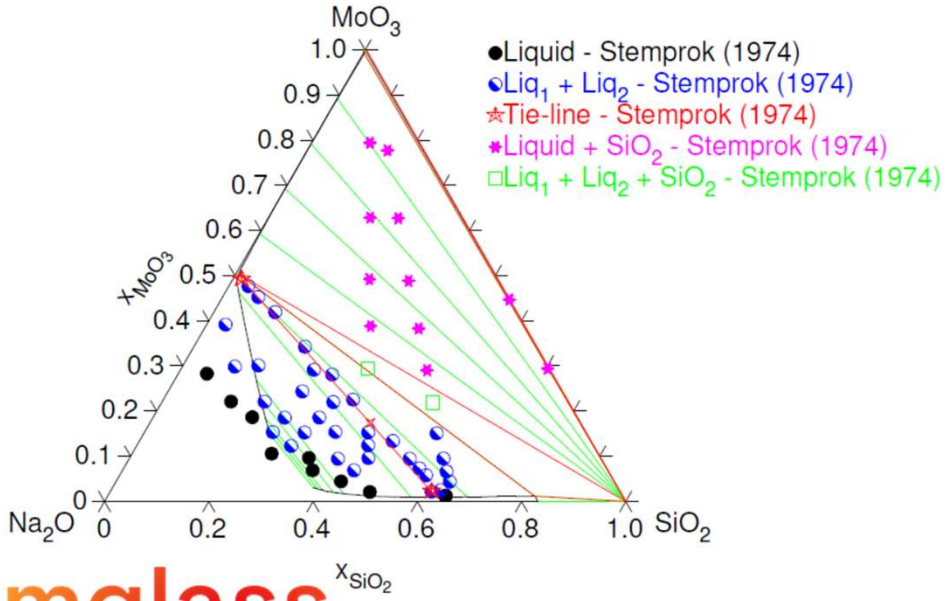
Some relevant data on sodium molybdates

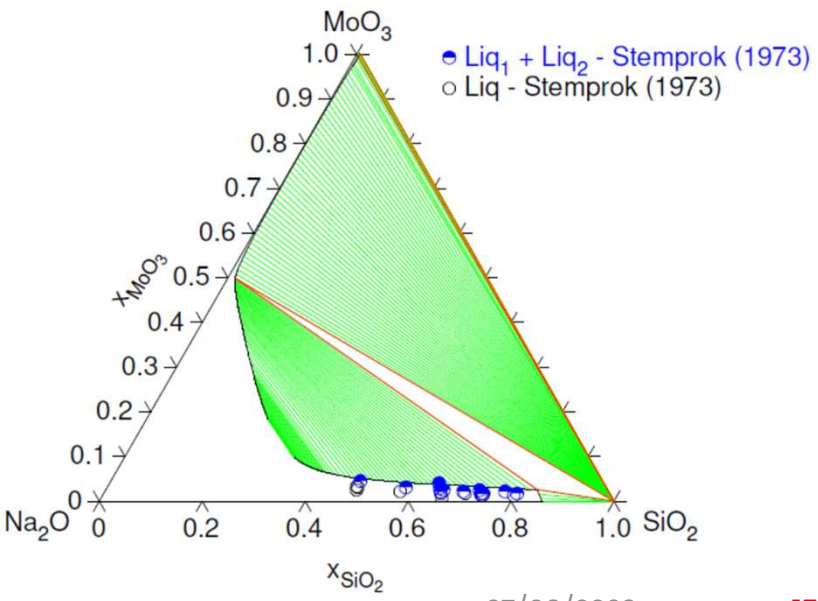
Extrapolated Na_2O-MoO_3-SiO_2 phase diagram

The calculation of the ternary Na_2O-MoO_3-SiO_2 system reveals the extent of the miscibility gap between Silica rich and molybdate rich liquids

These data are used to predict the solubility limit of molybdates in the melt and the precipitation temperatures. Calculations are compared with experimental results from:

- Fig. 1: Stemprok at 1473 K
- Fig. 2:Stemprok at 1673 K

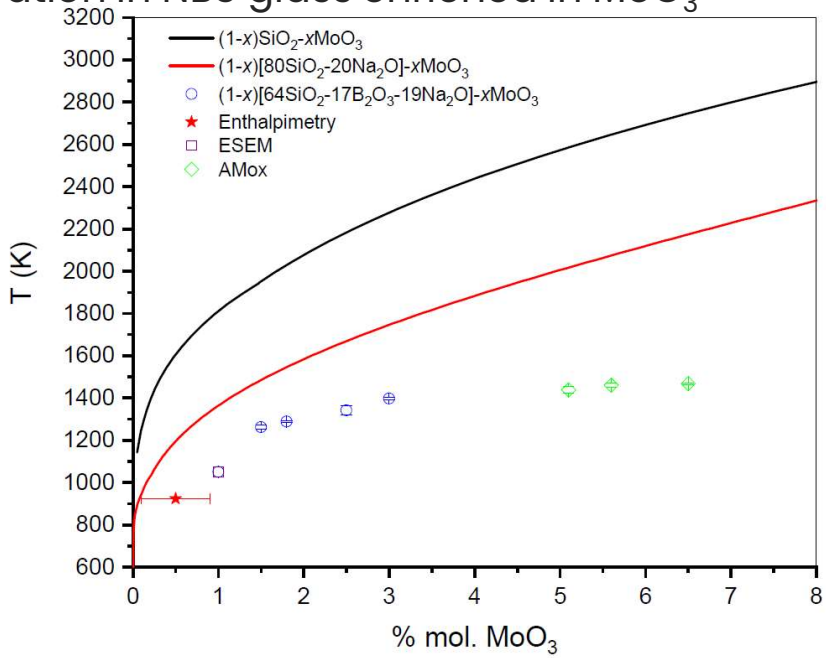




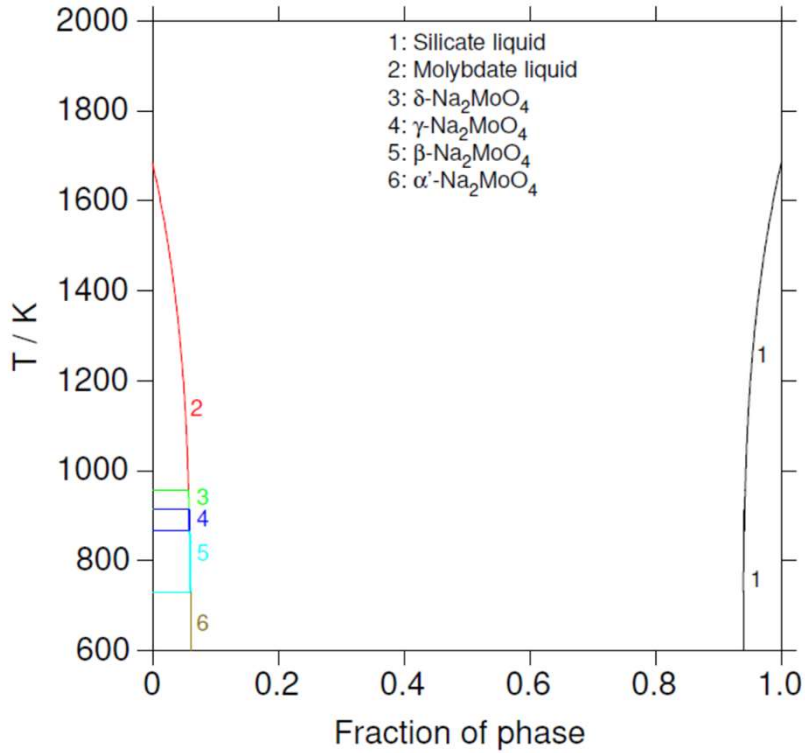
Calculation of sodium molybdate thermodynamic properties

Focus on Na_2MoO_4 formation temperature

Objective: Comparison between experimental investigations and thermodynamic calculations about liquid-liquid phase separation in NBS glass enriched in MoO_3



Phase separation temperatures as a function of MoO_3 for SiO_2-MoO_3 & SiO_2-Na_2O-MoO_3. Comparison with SiO_2-Na_2O-B_2O_3-MoO_3 glasses and in previous study on complex AMox glass compositions



Calculated solidification path of a MoO_3-Na_2O-SiO_2 glass having a ratio $SiO_2/Na_2O \approx 4$ and containing 3 mol.% MoO_3.

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In: Schuller, S., Benigni, P., Gossé, S., ...Podor, R., Rogez, J. *Journal of Non-Crystalline Solids, 2023, 600, 121997*

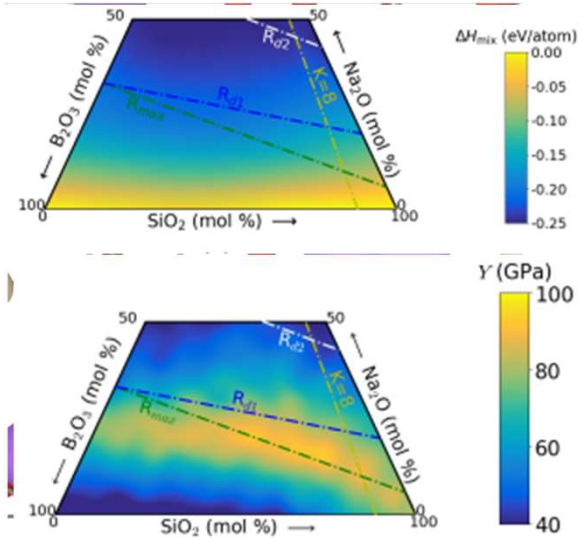
Complementary of multiscale approaches of phase separation

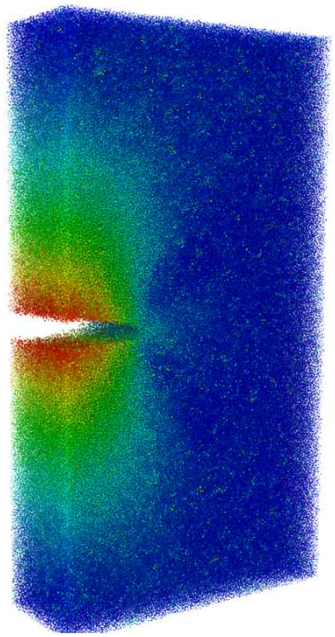
From molecular dynamics to phase-field modeling

The Calphad method complements atomistic approaches, enabling atomistic calculations to be validated and providing input data for diffusion/precipitation calculations.

Molecular dynamics

Mixing enthalpy & Young modulus of SBNO glass
(M. Mama Toulou *et al.*, 2023)

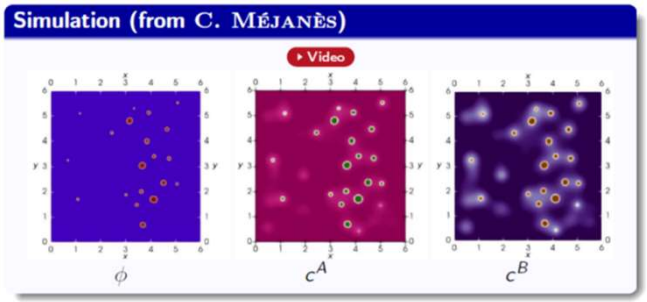


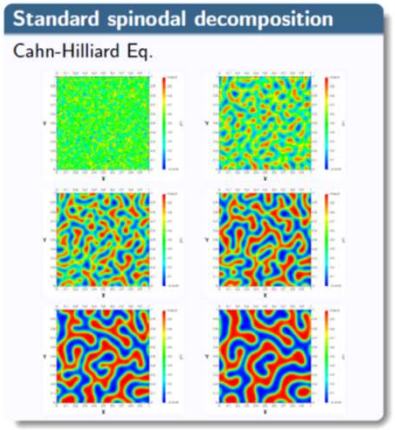


Fissure in SBNO glass
(Ph.D. M. Mama Toulou)

Phase-field simulations

Modeling Ostwald ripening





See:
Poster of C. Mejanes

Presentation of A. Cartalade.
At 11:45

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Conclusion

To optimise vitrification processes, a Calphad database is under development – since 2007 – to obtain reliable fundamental data on low-solubility elements in nuclear glass. The thermodynamic results predict the stable phases and their thermodynamic properties for all compositions and temperatures

Many thermodynamic properties of PGMs & molybdate phases can be calculated $f(T,x_i)$:

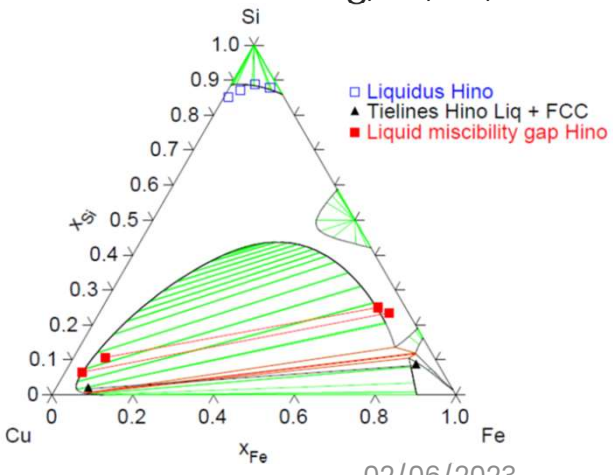
- PGMs & molybdates phase stability domains
- Redox and speciation of Pd/Rh/Ru
- Help to understand the origin of the different morphologies involving Ru^0

The results from this database are now coupled with modelling tools dedicated to the phase separation of molybdates

The database is still under development, NBS ternary & other elements are considered: Ag, Se, Re, Tc…

Comment

The same methodology was applied – with relevant results – to the PIVIC process to model the formation of Al-Cu-Fe-Si-U alloys in a Al_2O_3-CaO-SiO_2 matrix



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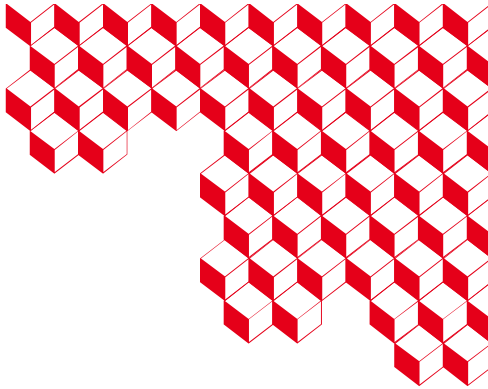

Merci de votre attention

Thanks to: Pierre Bénigni, Sébastien Bordier, Annabelle Laplace, Cloé Laurin, Luiz Pereira, Damien Perret, Renaud Podor, Elise Régnier

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