GEN IV International Forum SM

INTERACTIONS BETWEEN SODIUM AND FISSION PRODUCTS IN CASE OF A SEVERE ACCIDENT IN A SODIUM-COOLED FAST REACTOR

Mr. Guilhem Kauric

CEA, France

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NEA Nuclear Energy Agency · UJV · SCK·CEN Studiecentrum voor Kernenergie Centre d'Etude de l'Energie Nucléaire · cea De la recherche à l'industrie · Los Alamos National Laboratory · Department of Energy United States of America · ГНЦ РФ - ФЭИ · Canadian Nuclear Laboratories / Laboratoires Nucléaires Canadiens · Tsinghua University · National Nuclear Laboratory

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Meet the Presenter

Mr Guilhem Kauric is a second year PhD student at CEA Saclay in the "Service de la corrosion et du comportement des matériaux dans leur environnement" (SCCME) in the "Laboratoire de Modelisation de Thermodynamique et de Thermochimie (LM2T)."

His PhD research investigates the chemical interactions between MOX fuel, fission products and sodium for the safety assessment of the Sodium-cooled Fast Reactor in case of a severe accident. As the chemical system contains many elements, the CALPHAD method approach is the most suitable to develop a model for this study.

The first year of his PhD was spent at the TU Delft (Radiation Science & Technology department) to investigate the fission products-sodium interactions. He is currently doing his second year at JRC-Karlsruhe (European Commission) on the experimental study of the sodium-MOX fuel interaction, and the last year will be done in CEA Saclay to build a CALPHAD model of the different systems under study. His research activities, funded by CEA and the ENEN + program, are based on a multidisciplinary approach combining experimental work and modelling. In 2017, he graduated from Chimie Paristech ENSCP (diplome d'ingenieur option chimie des materiaux) and from INSTN with a Master's Degree in Nuclear Engineering option Fuel Cycle.

Mr. Kauric is one of the three students who won the Elevator Pitch Challenge (EPiC) contest at the last GIF Symposium meeting in October 2018, Paris and as a result has been awarded the opportunity to give this presentation.

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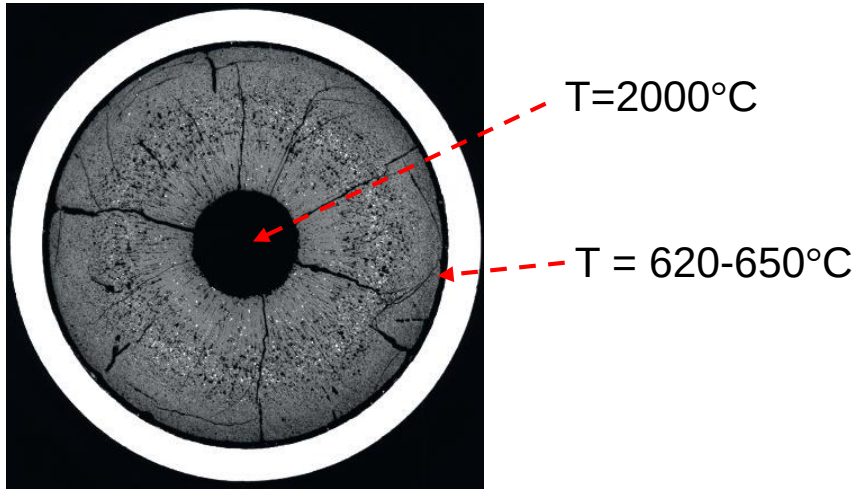
Outline

- Context of the study
- The Calphad Method
- Basics on Gibbs energy models
- How to get input data for the modelling?
  - Structure
  - Phase diagram data
  - Thermodynamic data
- Conclusions

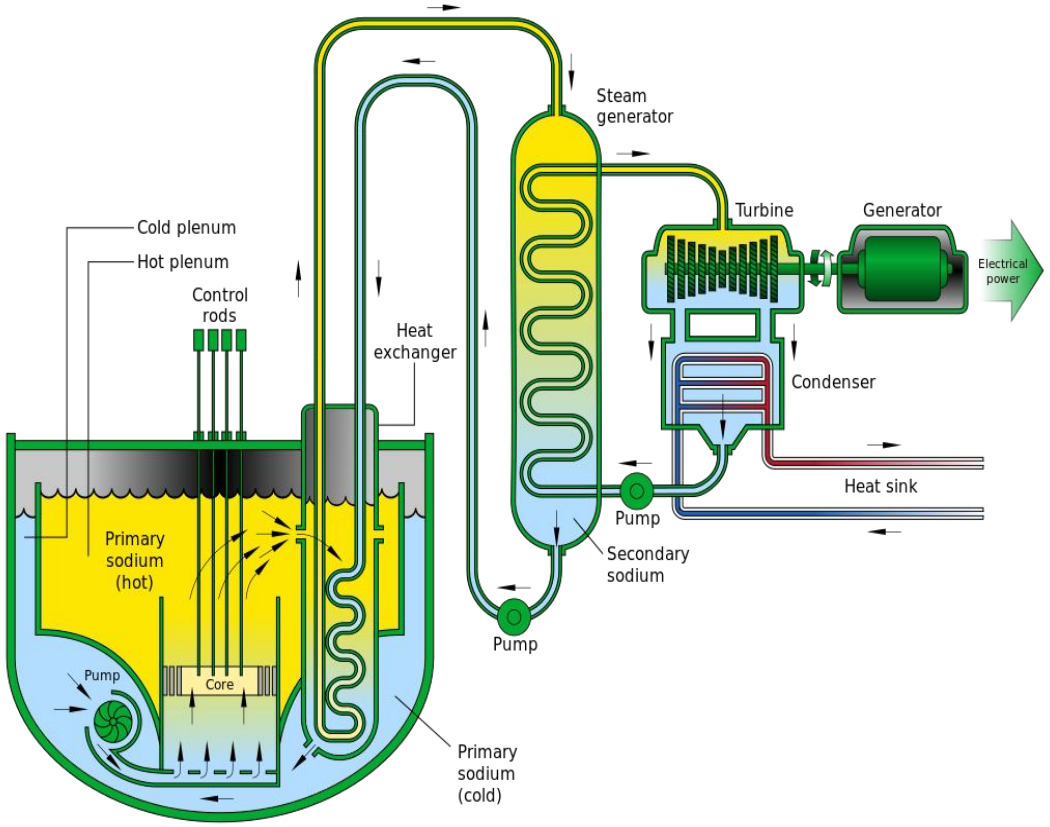
Context of the study

Sodium-cooled Fast Reactors

- Mixed Oxide Fuel $(U_{1-x},Pu_x)O_2$
  - $x > 0.2$
- Pellet restructuring under irradiation



Transversal macrograph of a fuel pin after irradiation in a SFR (2)



Sketch of a Sodium-cooled Fast Reactor (1)

(1) A Technology Roadmap for Generation IV Nuclear Energy Systems, Issued by the U.S. DOE Nuclear Energy Research Advisory Committee and the Generation IV International Forum, (2002)

(2) J. GUIDEZ, B. BONIN, Réacteurs nucléaires à caloporteur sodium, CEA Saclay; Groupe Moniteur, 2014

Irradiation Effects

- Formation of fission products

Location of the fission products ?

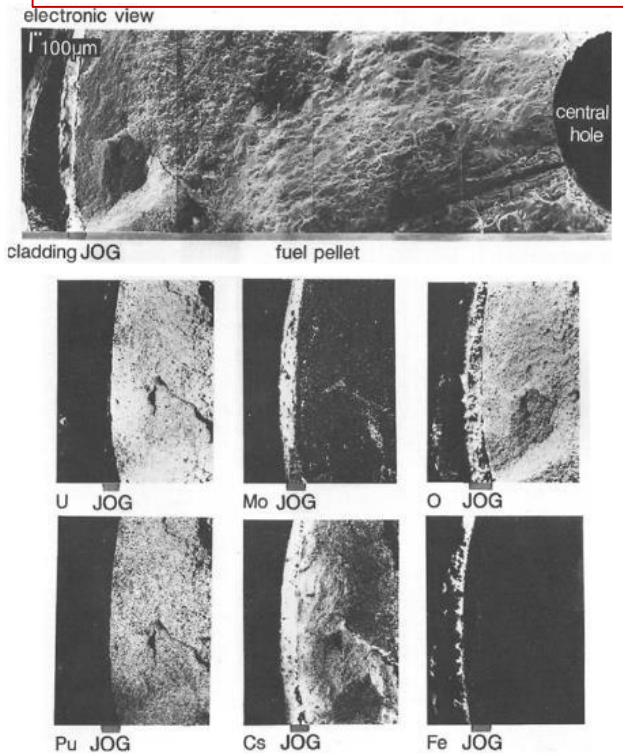
- Fission gases and other volatile fission products: Kr, Xe, Br, I
- Fission products forming metallic precipitates: Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te;
- Fission products dissolved in the fuel matrix: Sr, Zr, Nb
- Fission products forming oxide precipitates: Rb, Cs, Ba, Zr, Nb, Mo, Te;

- Large thermal-gradient:
  - Migration of volatile fission products towards the cold parts of the fuel pellet

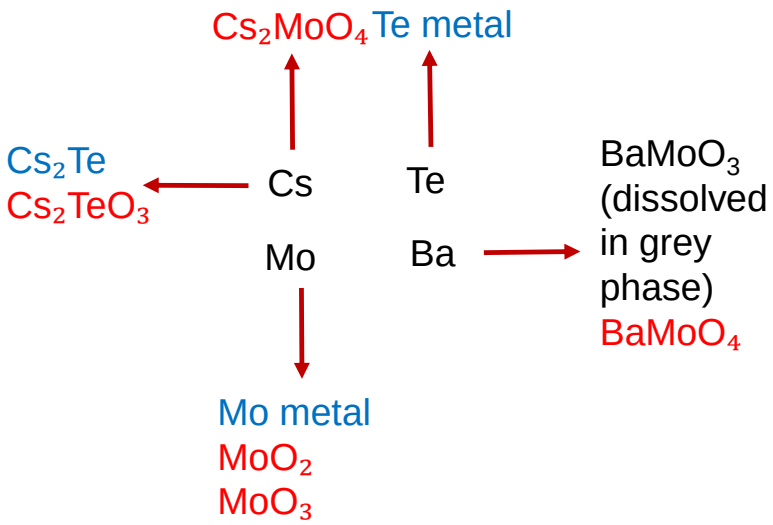
(1) M. Tourasse et al., JNM 188 (1992) 49-57

Fission Products Compounds Formed During Irradiation

Main thermodynamic stable phases in the "Joint Oxyde-Gaine" layer

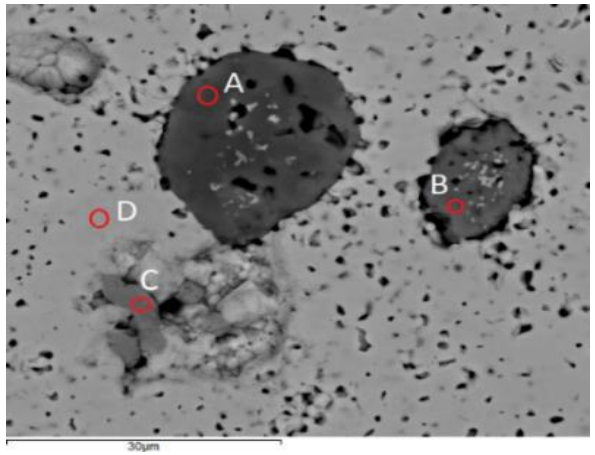


M. Tourasse et al., JNM 188 (1992) 49-57



Main thermodynamic stable phases in the "grey phase"

$(Ba,Sr)(Zr,Mo,U,Pu)O_3$

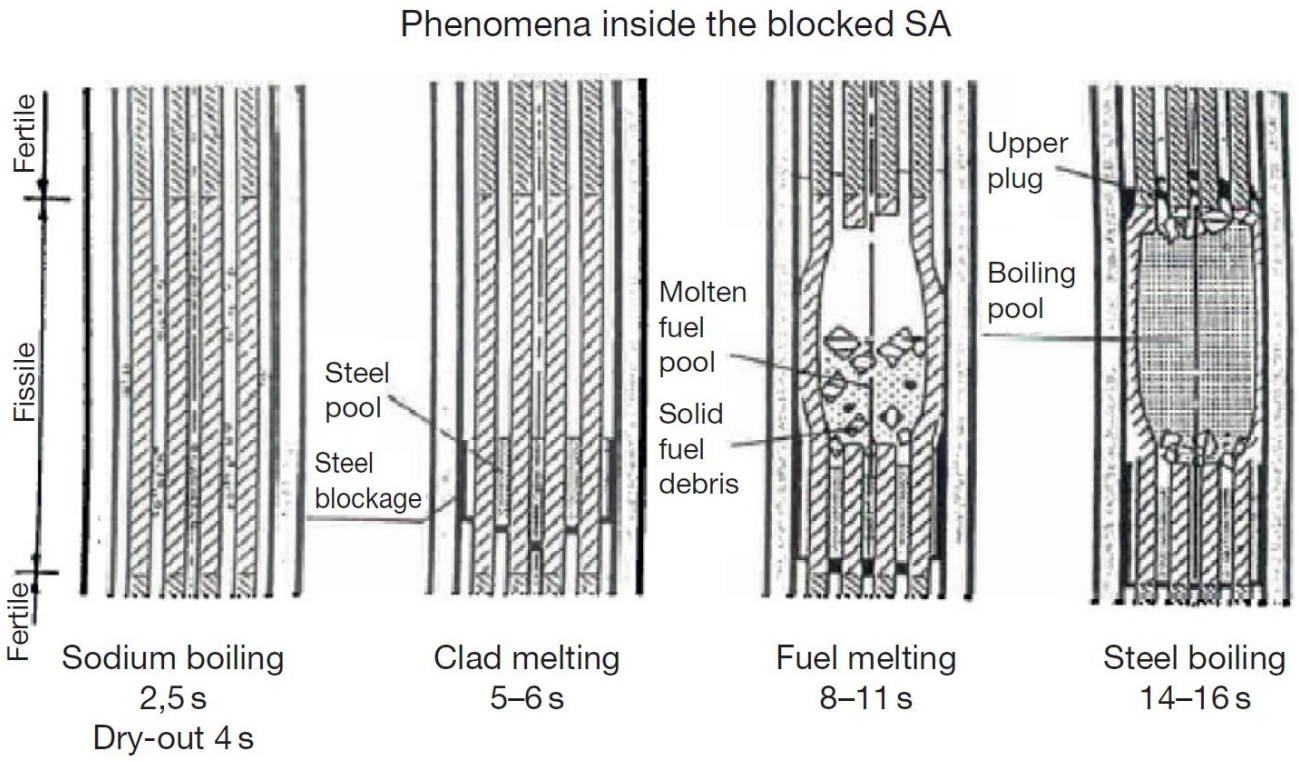


EDX image of the grey phase (A,B), a Mo-Ru-Pd alloy (C) and the fuel (D)

Simfuel Approaches to Understanding Spent Fuel Behaviour, I.Farnan.

Severe Accident: Definition

- The reactor fuel is significantly **damaged** with more or less extensive **melting of the reactor core**



- **Fuel ejection into sodium** or formation of a **local boiling pool** depending on the **scenario**
- Interaction **Na/Fission products compounds**
- Interaction **Na/Mixed Oxide fuel**
- **Volatile fission products** release

J. Papin, Behavior of Fast Reactor Fuel During Transient and Accident Conditions, in: Compr. Nucl. Mater., Elsevier, 2012: pp. 609–634

Severe Accident: Description

- 3 different types of severe accidents:
  - **ULOF:** Unprotected Loss Of Coolant
    Sodium vaporization → Biphasic coolant → Total vaporization
  - **UTOP:** Unprotected Transient Over Power
    Slight increase in the sodium temperature → Liquid sodium
  - **TIB:** Total Inlet Blockage
    Quick sodium vaporization

2 time scales:

Short term effects → Control the energy release during the accident

Long term effects → Management of the core after the accident and risk of re-criticality

Safety Assessment of the SFR

- **Sodium/ Mixed oxide fuel** (and **fission products**) interaction **at all stages of a severe accident**
- Assess the **consequences** **of** a **complete loss of the fuel pin tightness (boiling pool of irradiated materials)**:
  - Fission products released?
  - Interaction with sodium?
- **Management** **of the molten pool** formed after an interaction between **sodium** and the **irradiated fuel** in a **severe accident scenario**.
  - Compounds formed during the **cooling down**?

Need for Thermodynamic Modelling

- **Complex** system and **large range of temperatures and compositions**
  - **(Cs-Sr-Ba-I-Te-Mo)-(U,Pu)-O** + interaction with **Na**
- **Thermodynamic model** of the interaction between **fuel**, **fission products** and **liquid sodium** at the **different stages of a severe accident scenario**

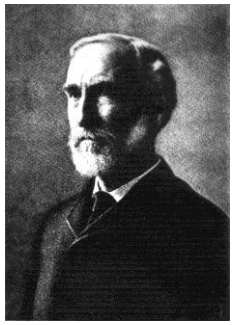
Describe the effect of **temperature** and **oxygen potential** on the interaction between sodium and the different fission product compounds

The Calphad method

The Calphad Method

- Develop a thermodynamic model based on the **Gibbs energy** of the gas, liquid and solid phases as a function of the **temperature**, **composition** and **pressure** of the system
- The Gibbs energy of a system is defined by:

$$G = H - TS = U + PV - TS$$



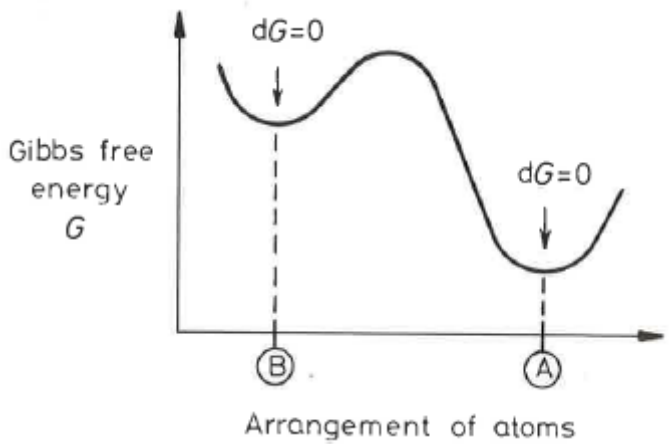
Josiah Willard Gibbs (1839-1903)

H is the **enthalpy** ⇨ heat content of the system
T is the temperature
S is the **entropy** of the system ⇨ randomness of the system
U is the internal energy of the system ⇨ kinetic (vibrations) and potential (bonds) energies of atoms
P is the pressure
V is the volume

The Gibbs Energy

- G is the **key function** in thermodynamics of materials
- At constant temperature and pressure, a closed system (fixed mass and composition) will be in stable equilibrium if it has the lowest value of the Gibbs energy:

$$dG = 0$$



⇨The A configuration is the lowest possible value of G ⇨ Equilibrium
⇨The B configuration is a metastable equilibrium state (local equilibrium)
⇨The intermediate configurations are unstable
⇨The rate at which the system will reach the equilibrium is not provided by thermodynamics

Calphad Modelling

- Linear combination of the Gibbs energies of the phases, G_m^{φ}

$$G = \sum_i m^{\varphi} G_m^{\varphi} \qquad m^{\varphi} : \text{mole fraction of phase } \varphi$$

- The G_m^{φ} functions are optimized by a least square minimization method to match the **experimental data**

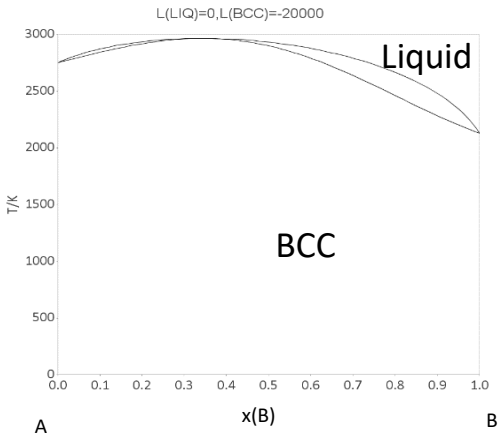
→ Semi-empirical method

Modelling of a Regular Solution (A,B)

- Interaction parameter L_{AB}

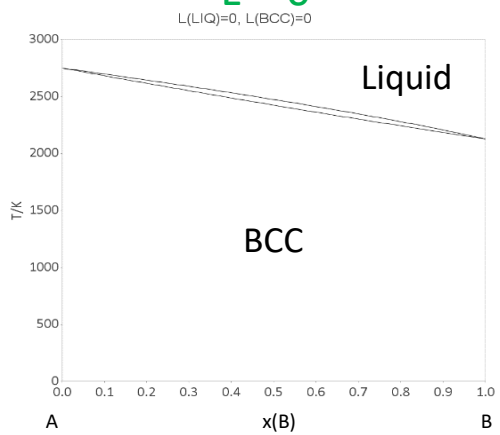
$$G_m^{\alpha} = \underbrace{x_A \, {}^{\circ}G_A + x_B \, {}^{\circ}G_B}_{\text{G reference}} + \underbrace{RT(x_A ln x_A + x_B ln x_B)}_{\text{G ideal}} + \underbrace{x_A x_B \, L_{AB}}_{\text{G excess}}$$

L < 0



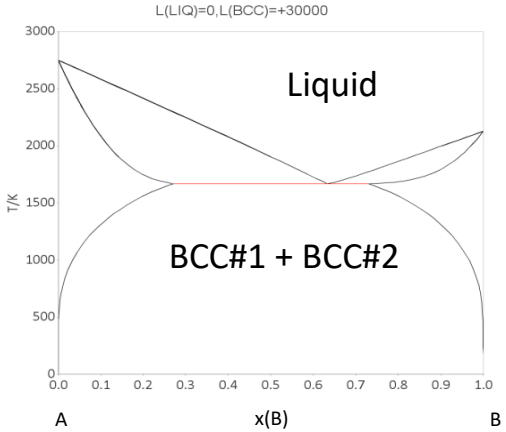
L(BCC) = -20000
Stabilization

L = 0



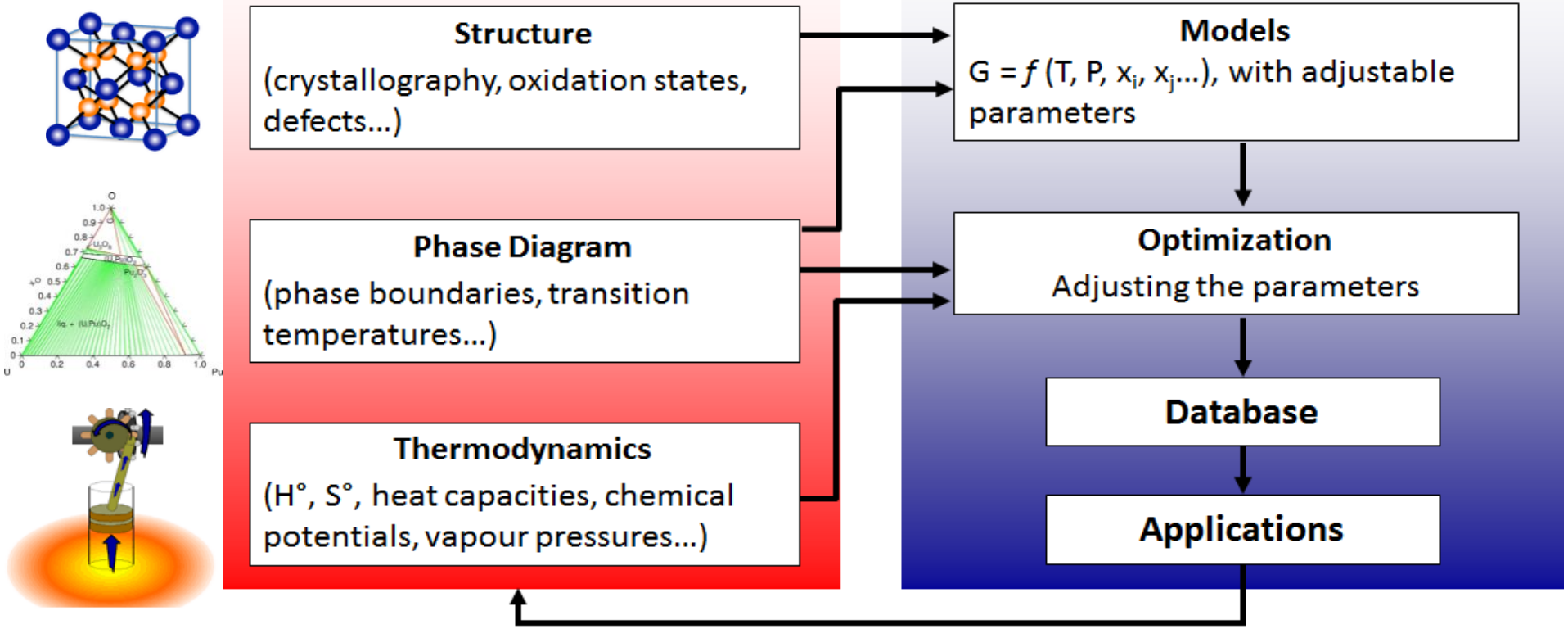
L(BCC) = 0
Ideal solution

L > 0



L(BCC) = +30000
Phase separation
(Miscibility gap)

Calphad Modelling Scheme



→ Need for **experimental thermodynamic measurements**

State of the Art: Calphad Modelling of Systems

Binary phase diagram

Chemical Element	**Na**	O	Cs	Ba	Sr	Mo	Te	I	U
O	Calphad								
Cs	Calphad								
Ba	Diagram								
Sr	Calphad								
Mo	S.Gossé, Private communication								
Te	Calphad			Lyskova not available	Lyskova not available				
I	Calphad								
U	Calphad								
Pu	Calphad						Diagram		

Calphad: Phase diagram modelled in an paper
Diagram: Phase diagram reported in a paper but not modelled

Ternary phase diagram (with oxygen)

System	**Na-O**	Cs-O	Ba-O	Sr-O	Mo-O	Te-O	I-O	U-O
Cs								
Ba								
Sr								
Mo	S.Gossé, Private communication							
Te			Partially known					
I								
U	Calphad							
Pu								

In TAF ID (https://www.oecd-nea.org/science/taf-id/)
No model found

Almost all **binary systems** have been modelled whereas only **ternaries with Mo and U are known**

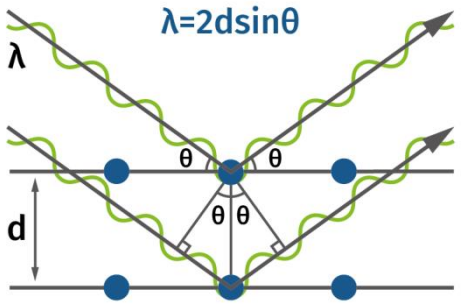
From experimental results to Calphad modelling

The Ba-Na-Mo-O System

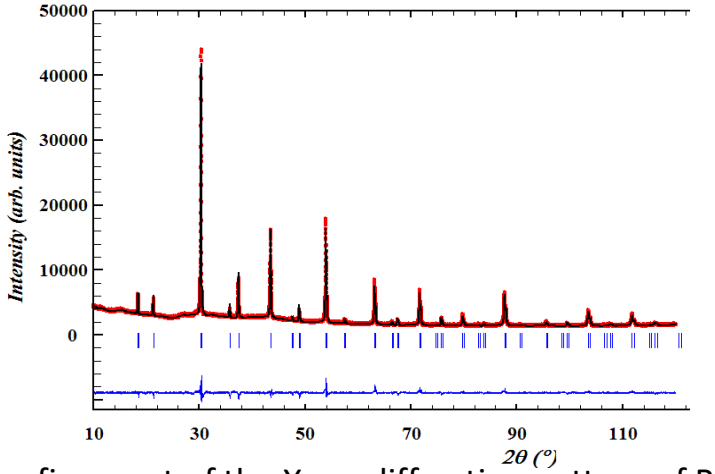
- $BaMoO_3$ and $BaMoO_4$ are found in the irradiated fuel
  - $BaMoO_3$ dissolved in the “grey phase”
  - $BaMoO_4$ in the JOG
- No thermodynamic data on the interaction with sodium
- Ba-Mo-O, Na-Mo-O and Ba-Na → Calphad models available
- One quaternary compound reported: **$Ba_2NaMoO_{5.5}$**
- Only **structural data** reported

Synthesis of $Ba_2NaMoO_{5.5}$

- Solid synthesis at 800°C under dry O_2
  - $BaMoO_{4\,(s)} + BaCO_{3\,(s)} + 0.5\ Na_2CO_{3\,(s)} \rightarrow Ba_2NaMoO_{5.5\,(s)} + CO_{2\,(g)}$
- First control of the purity → **X-Ray diffraction**



X-ray diffraction



Rietveld refinement of the X-ray diffraction pattern of $Ba_2NaMoO_{5.5}$

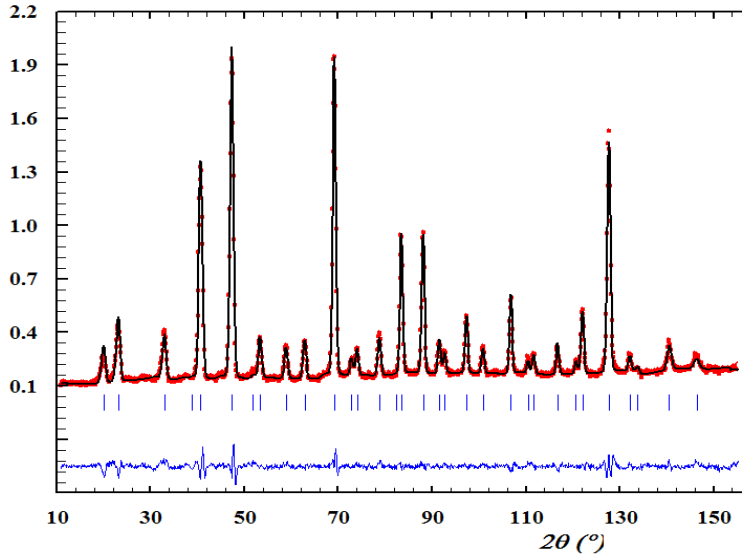
Space group and **lattice parameters**

Determination of Structural Information (1)

- Neutron diffraction:
  - Atomic positions of light atoms can be determined accurately

Neutron diffraction (PEARL beamline, RID, Delft)

L.Van Eijck et al., Appl Crystallogr. 49 (2016) 1398-1401

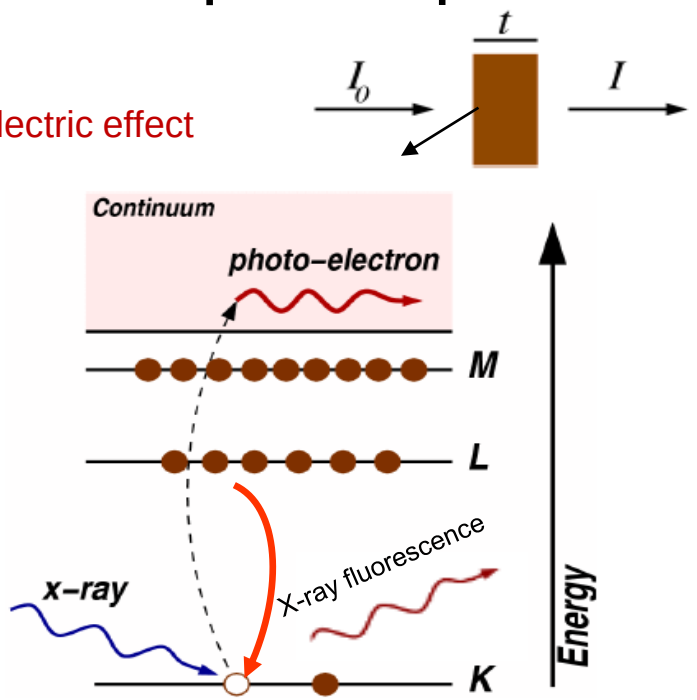


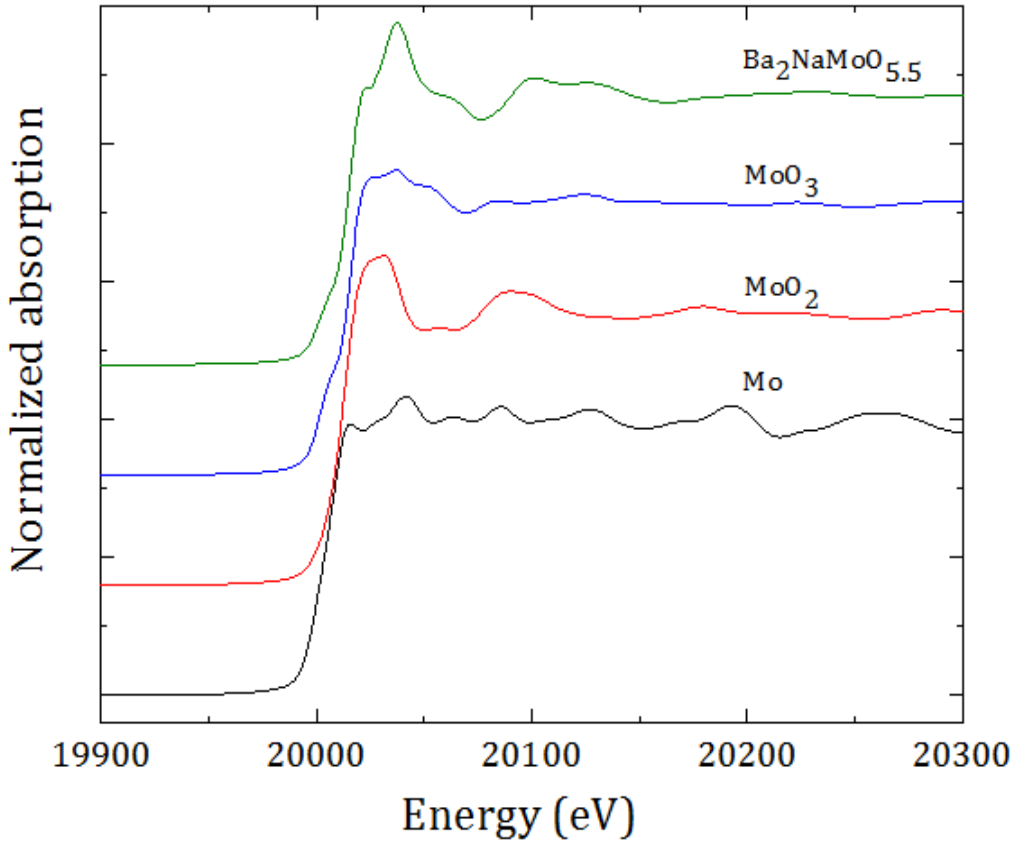
Rietveld refinement of the neutron diffraction pattern of $Ba_2NaMoO_{5.5}$

Determination Structural Information (2)

- X-ray Absorption Spectroscopy

Photoelectric effect



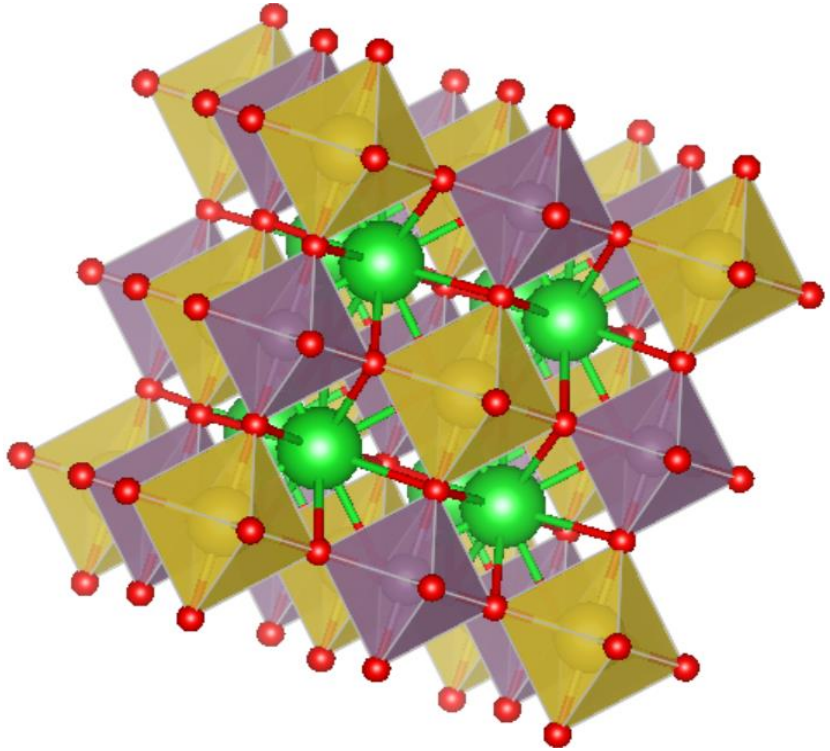


→Oxidation state

→Molybdenum is +VI

Structure Modelling

- XRD + Neutron diffraction + XAS
  → Structure determination
- Choice of an appropriate sublattice model for the Calphad modelling
- The **purity** of the sample is good enough (> 99%) for **thermodynamic measurements**



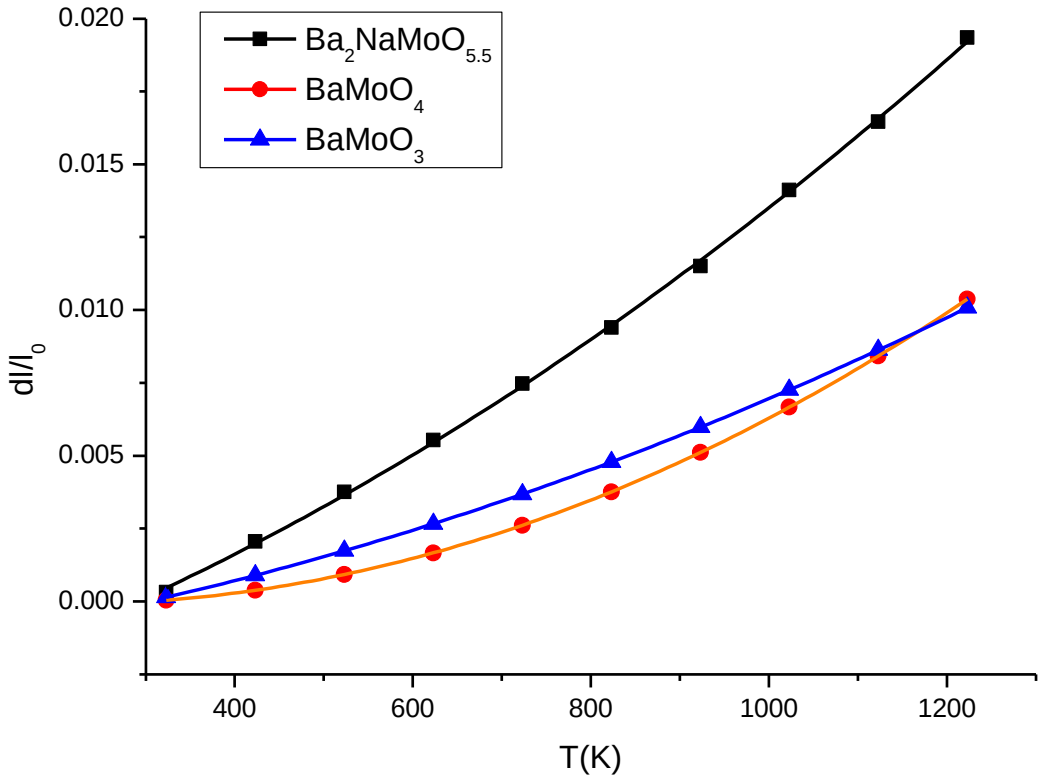
Structure of $Ba_2NaMoO_{5.5}$. The octahedrons around the atoms of molybdenum and sodium are represented in purple and yellow, respectively. The barium atoms are represented in green.

Structural Analysis-HTXRD

- Increase of the temperature during an accident
  - Thermal expansion of the compounds
  - Key thermo-physical property for safety assessment of the SFR

The **mean linear thermal expansion** of $Ba_2NaMoO_{5.5}$ is **higher** than that of the ternary compounds

→ **Safety evaluations** have to take this compound into account !

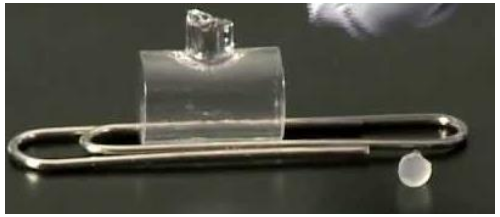


Relative thermal expansion of $Ba_2NaMoO_{5.5}$, $BaMoO_4$ (1) and $BaMoO_3$ (2)

(1) M. Sahu, K. Krishnan, B.K. Nagar, D. Jain, M.K. Saxena, C.G.S. Pillai, S. Dash, Characterization and thermo physical property investigations on Ba1−xSrxMoO4 (x=0, 0.18, 0.38, 0.60, 0.81, 1) solid-solutions, J. Nucl. Mater. 427 (2012) 323–332
(2) M.Sahu, K. Krishnan, M.K. Saxena, S. Dash, Thermophysical properties of Ba1−xSrxMoO3(s), J. Nucl. Mater. 457 (2015) 29–35

Calorimetric Investigations

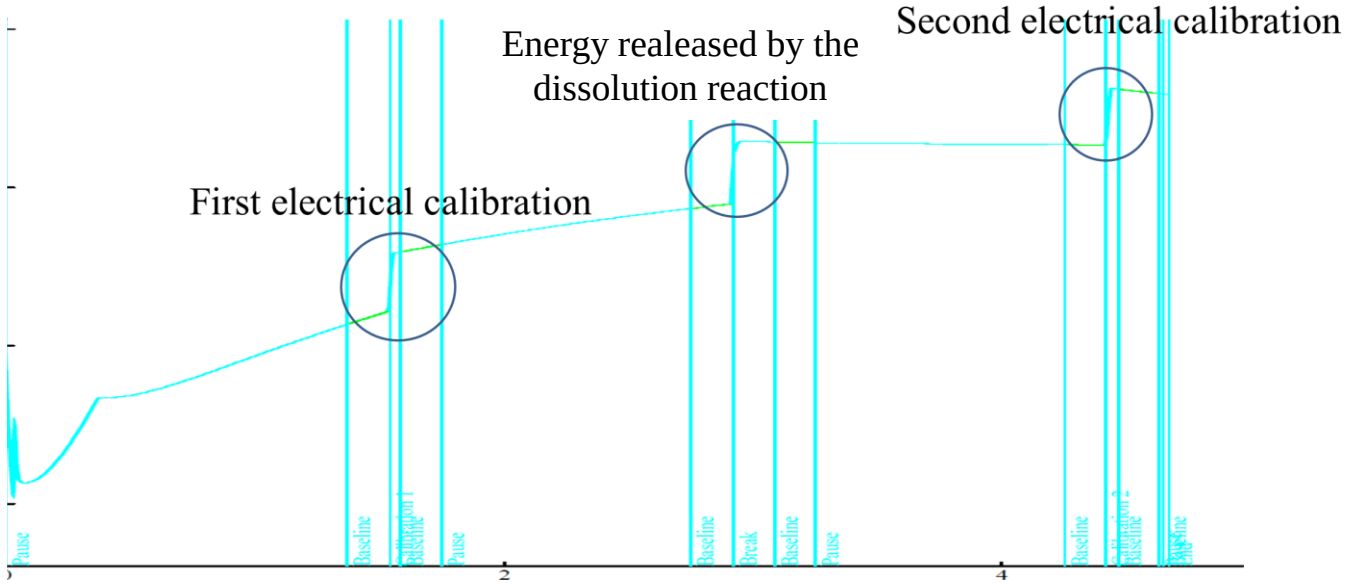
Solution calorimetry to determine the enthalpy of formation of $Ba_2NaMoO_{5.5}$



Crushing ampoule (1)

Reaction vessel

Solution calorimeter thermostat



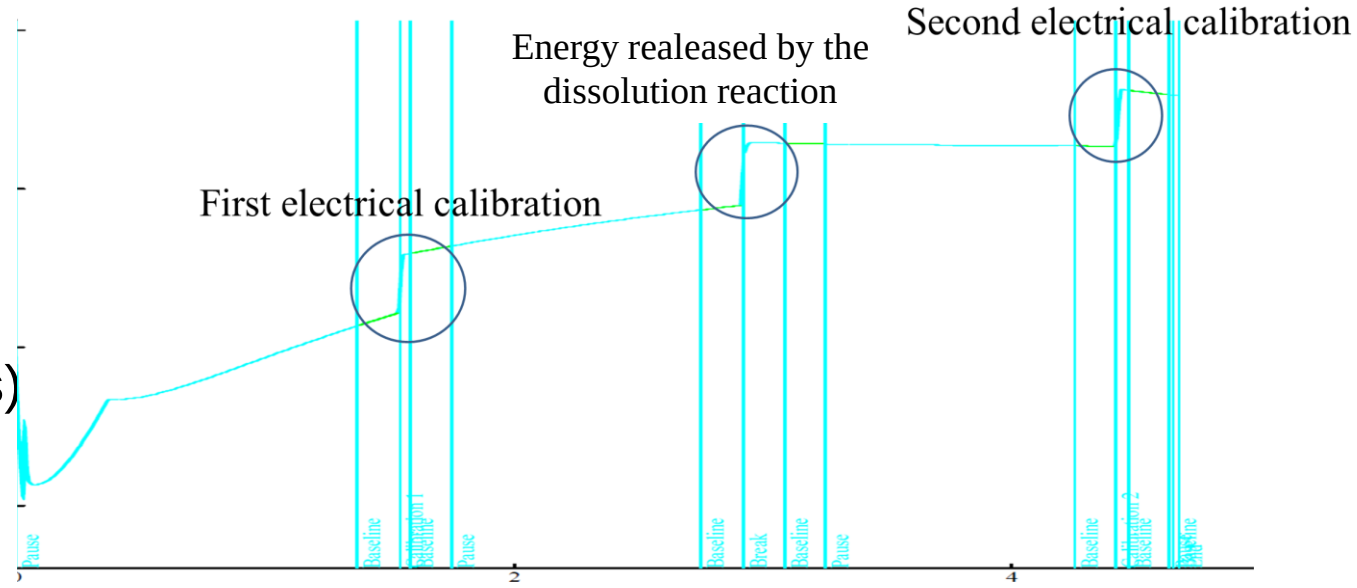
Measurement by solution calorimetry of the reaction of dissolution of $Ba_2NaMoO_{5.5}$ in a solution of 2M HNO_3

(1) www.tainstruments.comwp-contentuploadscrushing-ampoule-preparation-sol

Standard Enthalpy of Formation Measurement

- Thermodynamic cycle used with a 2M HNO_3 solution

(1) $Ba_2NaMoO_{5.5}(s)$= sol. 1
(2) 2 BaO(s) = sol. 2
(3) 1/2 $Na_2Mo_2O_7(s)$ +sol. 2 = sol. 3
(4) Ba(s)+1/2 $O_2(g)$ = BaO(s)
(5) 2 Na(s)+2 Mo(s)+7/2 $O_2(g)$ = $Na_2Mo_2O_7$ (s)



(6)=(2)+(3)-(1)-2*(4)-1/2*(5)

2 Ba(s)+Na(s)+Mo(s)+ 11/4 O_2 (g)= $Ba_2NaMoO_{5.5}$ (s)

Enthalpy of formation of $Ba_2NaMoO_{5.5}$

$\Delta_r H^\circ_m(6) = \Delta_f H^\circ_m(Ba_2NaMoO_{5.5}, cr, 298.15K)$

Recall on Calphad Modelling

$$G_m(T) = \Delta_f H_m^\circ(298.15K) - S_m^\circ(298.15K)\,T + \int_{298}^{T} C_{p,m}(T)\,dT - T\int_{298}^{T} \frac{C_{p,m}}{T}\,dT$$

Standard enthalpy of formation

Standard entropy

$$\int_0^{298K} \frac{C_p}{T}\,dT$$

Heat capacity

$$C_{p,m}(T) = a + bT + cT^2 + dT^{-1} + eT^3 + ..$$

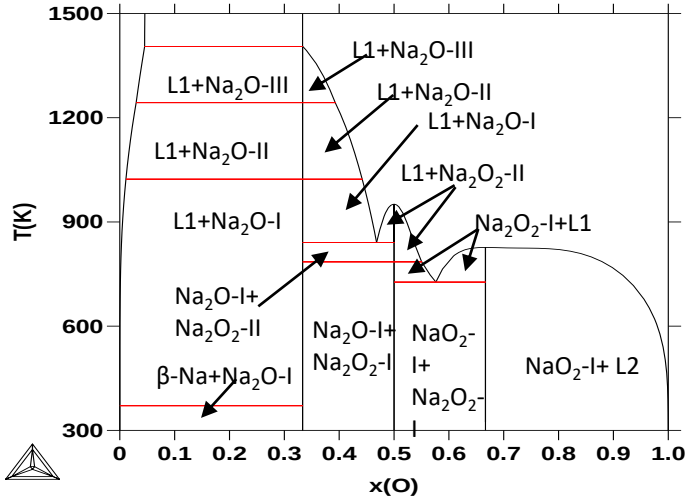
Other measurements are useful: Standard entropy, Heat capacity evolution at high temperatures, Melting temperature, phase diagram data, enthalpy of melting,…

The more experimental data, the more accurate modelling

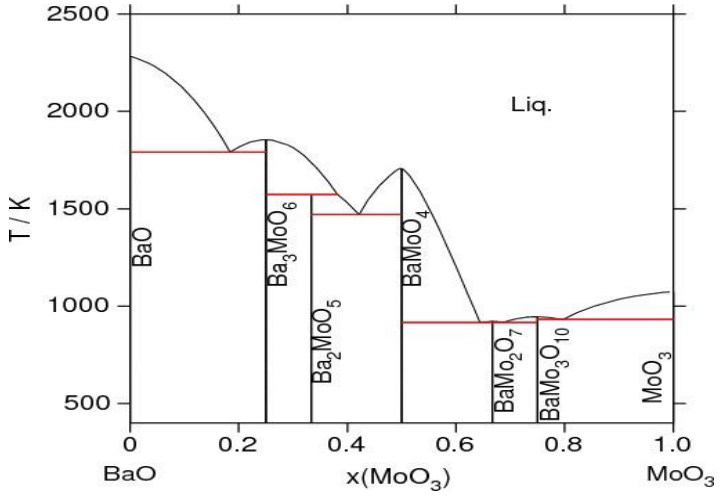
Strategy to Model the Ba-Na-Mo-O System

- 1st step: modelling of Ba-Na, Ba-Mo, Ba-O, Na-Mo, Na-O, Mo-O binary sub-systems
- 2nd step: modelling of Ba-Na-Mo, Ba-Na-O, Ba-Mo-O, Na-Mo-O ternary sub-systems
- 3rd step: modelling of Ba-Na-Mo-O quaternary system

- At each step, determination of :
  - G functions for the compounds
  - Interaction parameters for solutions



A. L. Smith et al.J. Chem. Thermodyn. 114 (2017) 93–115

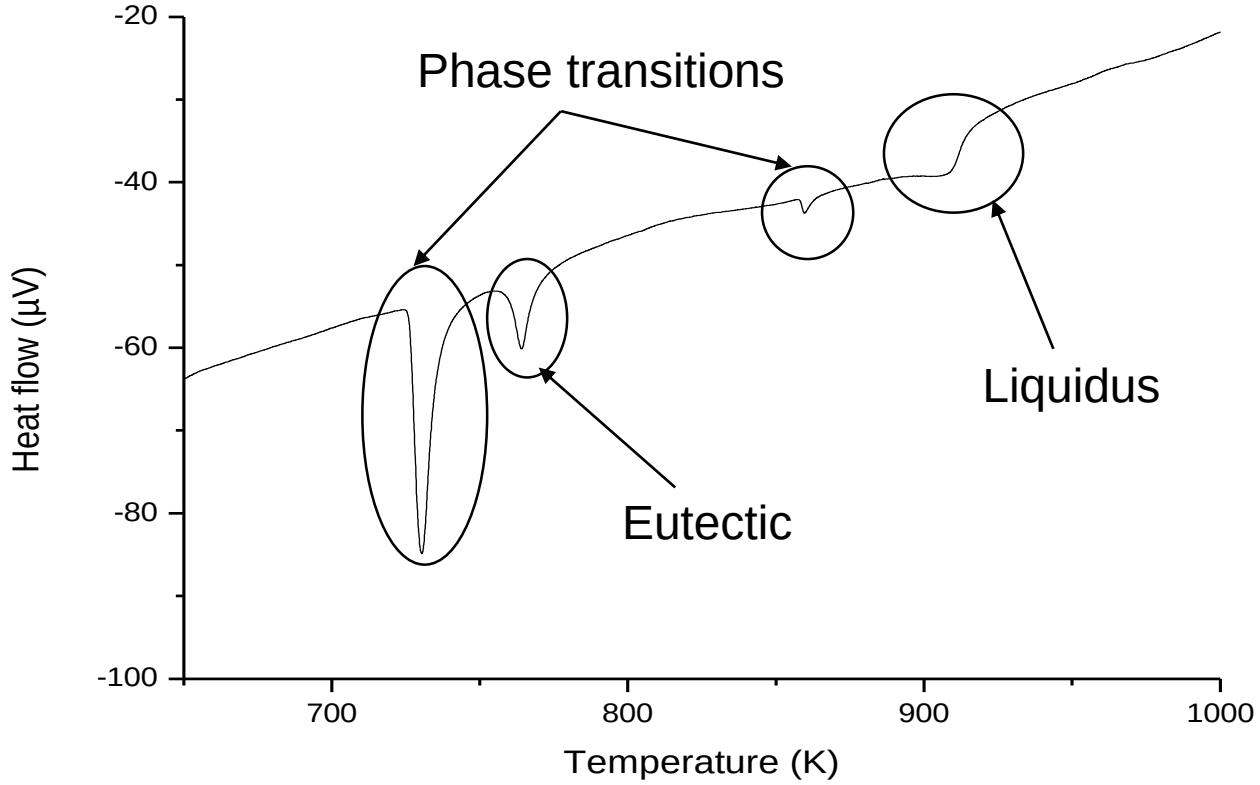


www.oecd-nea.org/science/taf-id/

The Cs-Na-Mo-O System

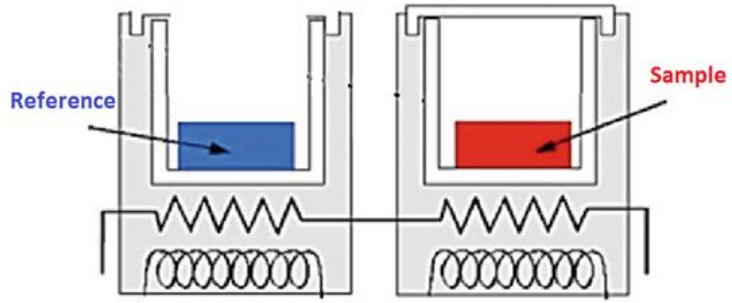
- Cesium? Why?
  - Cesium is very **volatile**
  - **Important radiological impact** on the environment if released
- 2 quaternary compounds:
  - $Cs_3Na(MoO_4)_2$ and $CsNaMo_3O_{10}$
- Study of the pseudo-binary phase diagram Cs_2MoO_4-Na_2MoO_4
  - Cs_2MoO_4 is the main phase expected in the JOG
    - Substitution of sodium into Cs_2MoO_4 ?
  - $Cs_3Na(MoO_4)_2$ is on this pseudo-binary phase diagram

Experimental Study of Pseudo-binary Phase Diagram: Na_2MoO_4-Cs_2MoO_4



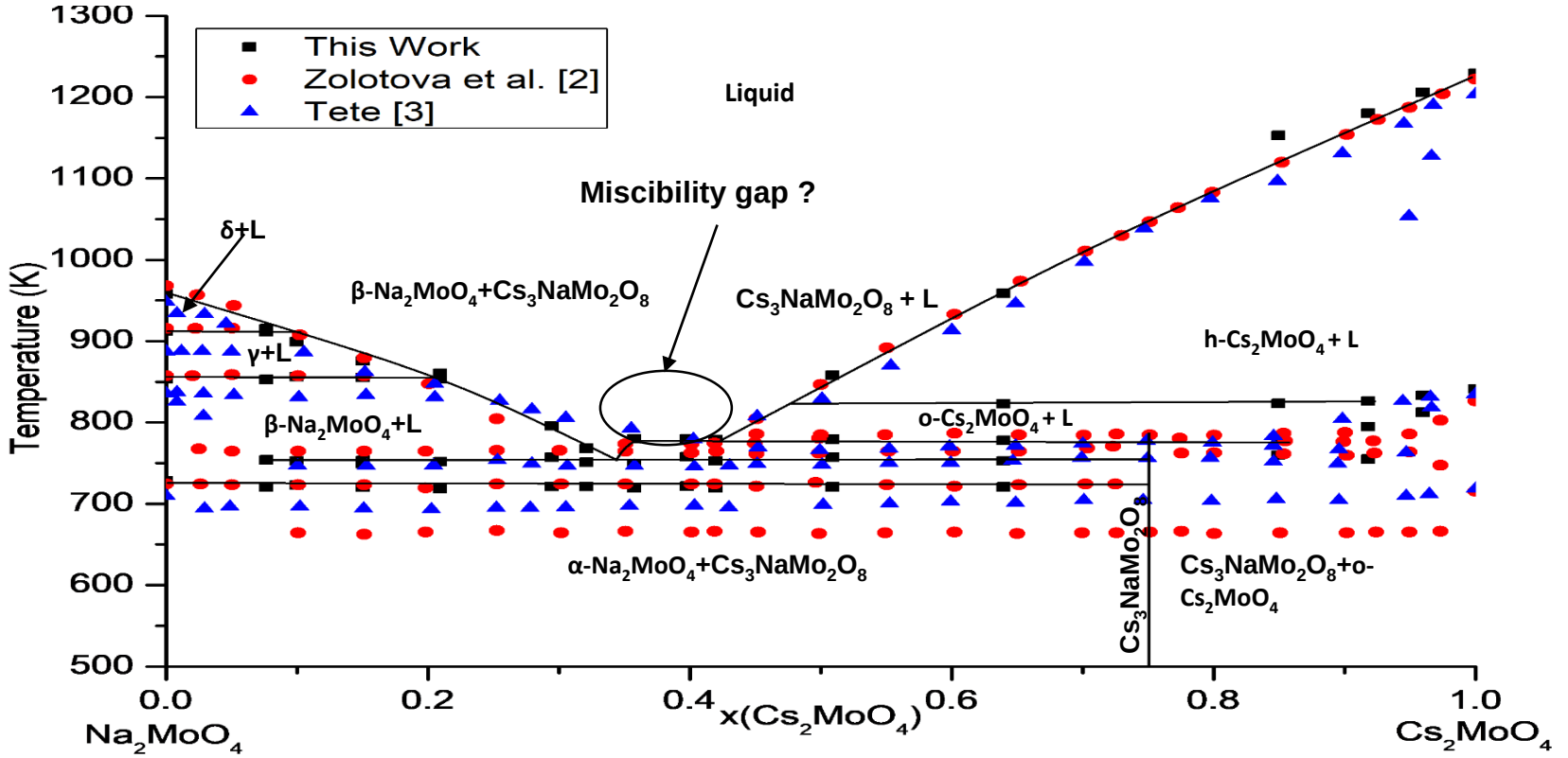
DSC measurement of a mixture of $0.93Na_2MoO_4$-$0.07Cs_2MoO_4$

Differential Scanning Calorimetry (DSC)



DSC

Experimental Study of Pseudo-binary Phase Diagram: Na_2MoO_4-Cs_2MoO_4



[2] E.S. Zolotova, Z.A. Solodovnikova, V.N. Yudin, S.F. Solodovnikov, E.G. Khaikina, O.M. Basovich, I.V. Korolkov, I.Y. Filatova, Phase relations in the Na_2MoO_4 –Cs_2MoO_4 and Na_2MoO_4 –Cs_2MoO_4 –$ZnMoO_4$ systems, crystal structures of $Cs_3Na(MoO_4)_2$ and $Cs_3NaZn_2(MoO_4)_4$, J. Solid State Chem. 233 (2016) 23–29

[3] F. Tête, La réaction Cs_2MoO_4/ Na : Application à l'intéraction combustible / sodium lors d'une rupture de gaine à fort taux de combustion dans un RNR, Université de Provence, 1999.

Examples of applications of the Calphad models

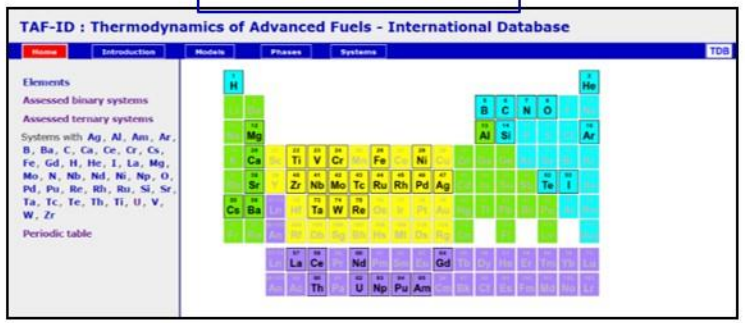
The TAF-ID Database Project

OECD Nuclear Energy Agency NEA

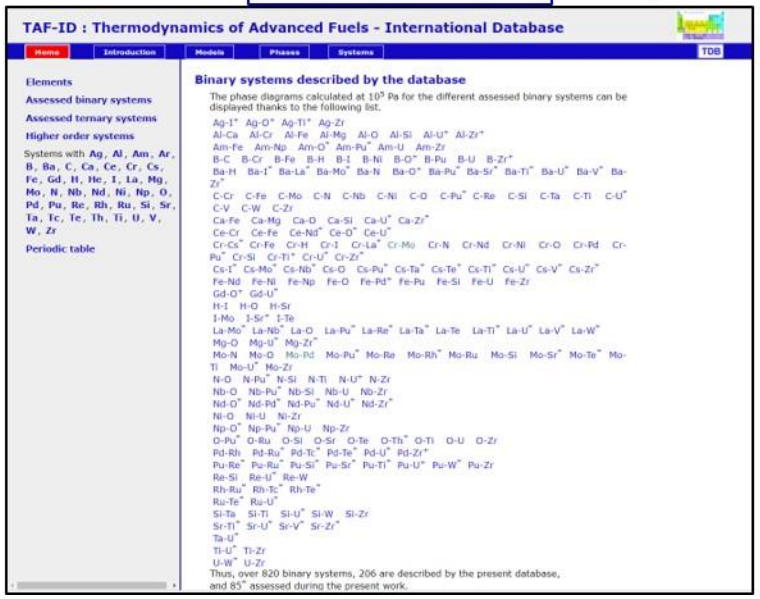
www.oecd-nea.org/science/taf-id/

(Canada, France, Japan, The Netherlands, Korea, UK, USA)

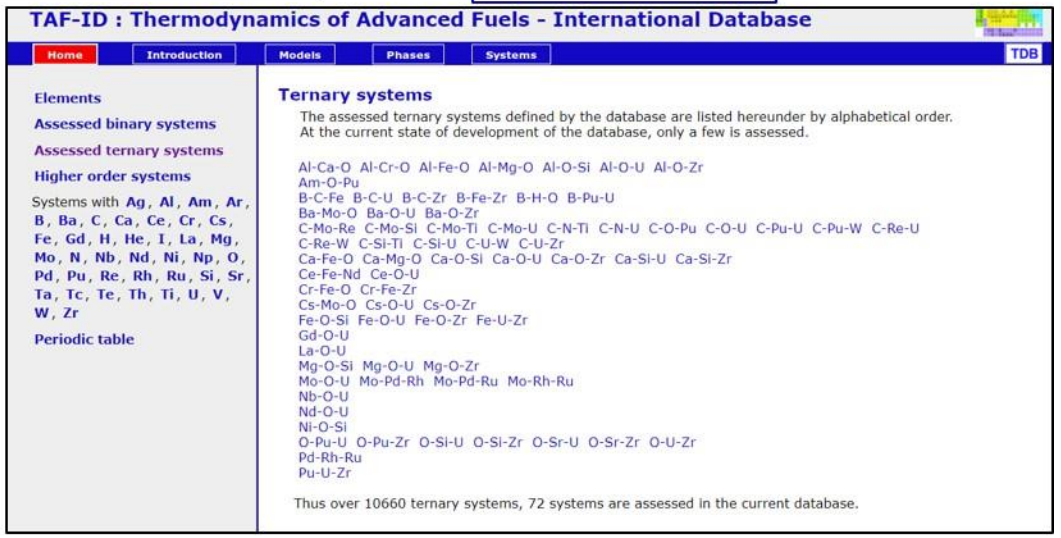
41 Elements



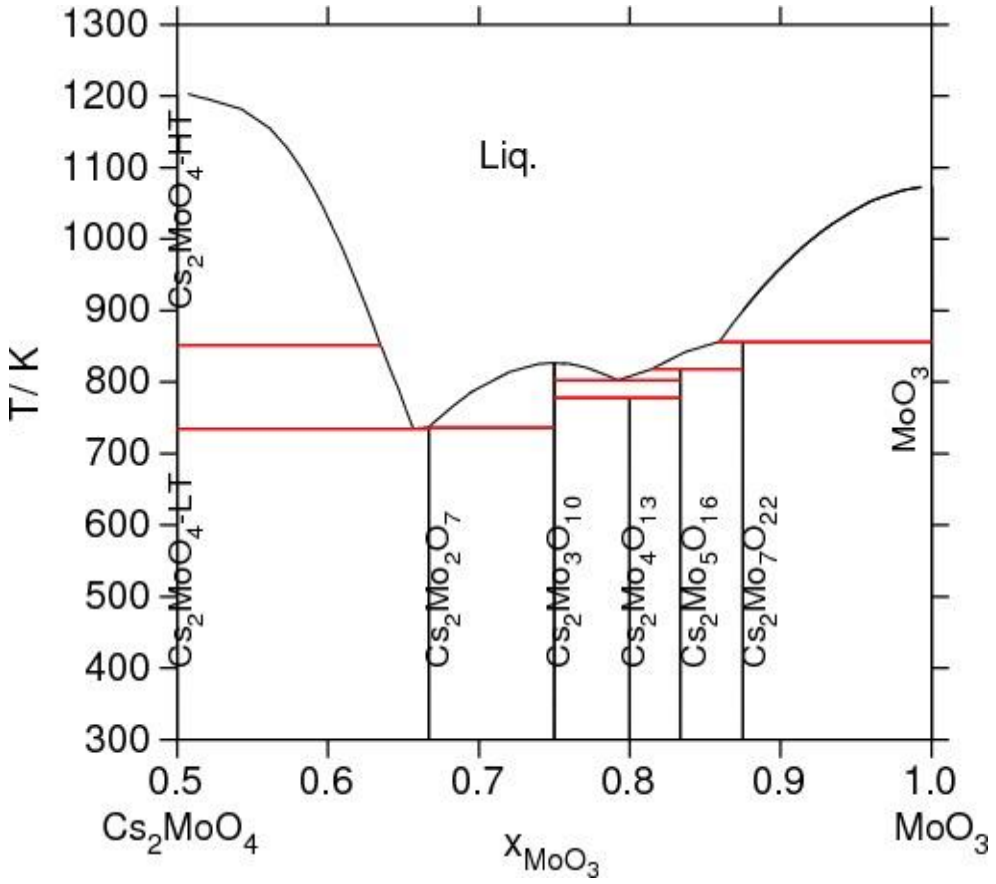
206 Binaries

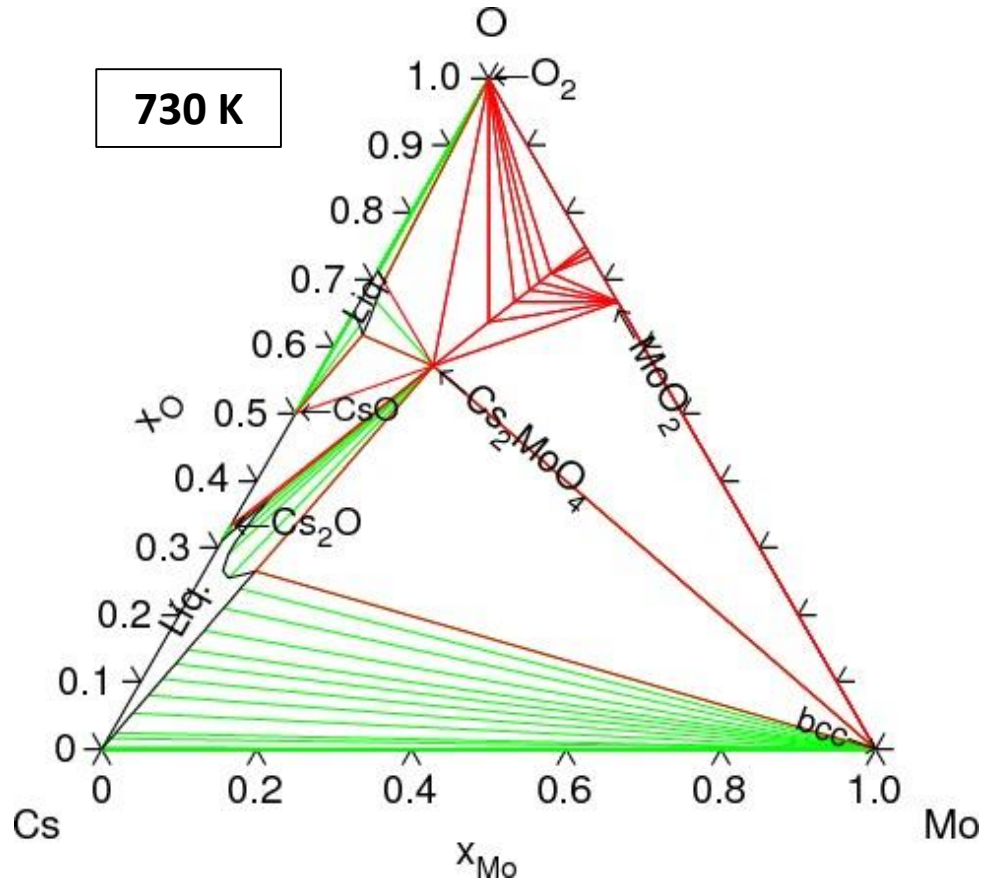


76 Ternaries



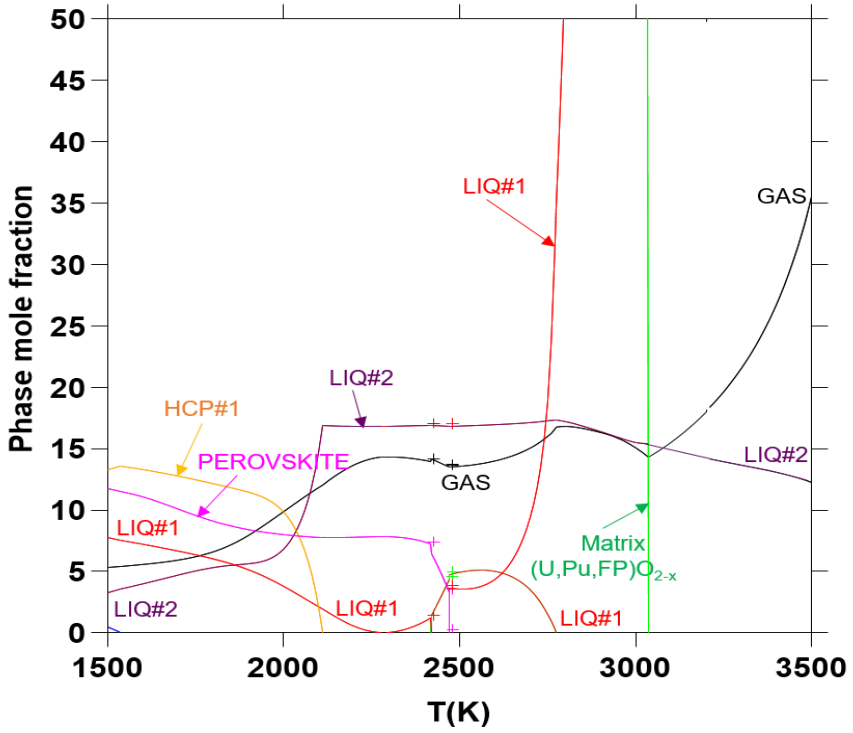
Cs-Mo-O System Modelling





Calculation on Irradiated Fuel: Phase Formation/melting

- Evolution of secondary fission product phases for a 7 at. % burnup fuel from 1500 K to 3500 K



Metallic precipitates (HCP)
Melting
at T=2109 K

Perovskite $(Ba,Sr)(Zr,U)O_3$
Melting
at T=2469 K

Dissolution of the fuel matrix in the molten perovskite

Beginning of the oxide fuel melting

Matrix $(U,Pu,FPs)O_2$ matrix
+ Metallic precipitates (HCP)
+ Perovskite precipitates
+ Liquid phases
+ Gas

Melting of the Fuel Matrix at a lower temperature than expected

Conclusions (1)

- The study of such complex systems and wide physico-chemical conditions requires thermodynamic modelling of nuclear fuels

  ⇨ Oxygen potential, fission product phases, solid/liquid transitions, heat capacity, vaporization ….

- CALPHAD is a suitable method to model multi-component systems by extrapolation from binary and ternary sub-systems;

  ⇨ It is time consuming ⇨ International collaborative projects are good frameworks to develop large databases

  ⇨ Experimental thermodynamic measurements on fuels are challenging but needed to test the validity of the databases

  ⇨ First-principle calculations are useful to calculate thermodynamic data that can be used as input in the models

Conclusions (2)

- In the TAF-ID database many systems are known but **no model** for Na systems

→ Aim of this work: obtain a model for **Na-fission products** systems

- But thermodynamics (alone) cannnot explain the fuel behaviour; it has to be coupled with kinetic and mass transfer models

⇨ In the SIMMER fuel performance code, the coupling using the open source code Open Calphad (developed by Bo Sundman) and the TAF-ID database is foreseen

- Currently at JRC-Karlsruhe (Germany) to study experimentally **Na-U-Pu-O**

→ Develop a thermodynamic model of this quaternary system

Conclusions (3)

- Acknowledgments:
- C. Guéneau (CEA, Nuclear Energy Division, DPC/SCCME/LM2T, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France)
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- E. Epifano (DMAS/LEM, ONERA & CNRS, Chatillon, France)

- Stay in touch?
- TAF-ID project: www.oecd-nea.org/science/taf-id/
- CEA: https://www.cea.fr
- TU-Delft: https://www.tudelft.nl
- JRC-Karlsruhe: ec.europa.eu/jrc

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25 September 2019	Gen-4 Coolants Quality Control	Dr. Christian Latge, CEA, France