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Thermodynamic assessments of the $LiF-ZrF_4-BaF_2$, $NaF-ZrF_4-BaF_2$, $KF-ZrF_4-BaF_2$ systems

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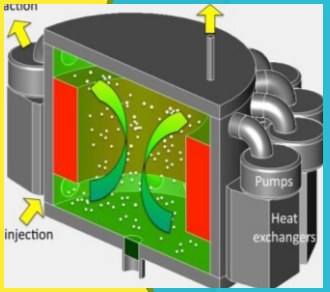
Background and context of research

TRANSPORT
- Low viscosity
- High thermal conductivity

NEUTRONIC
- Small neutron capture cross section

Generation IV

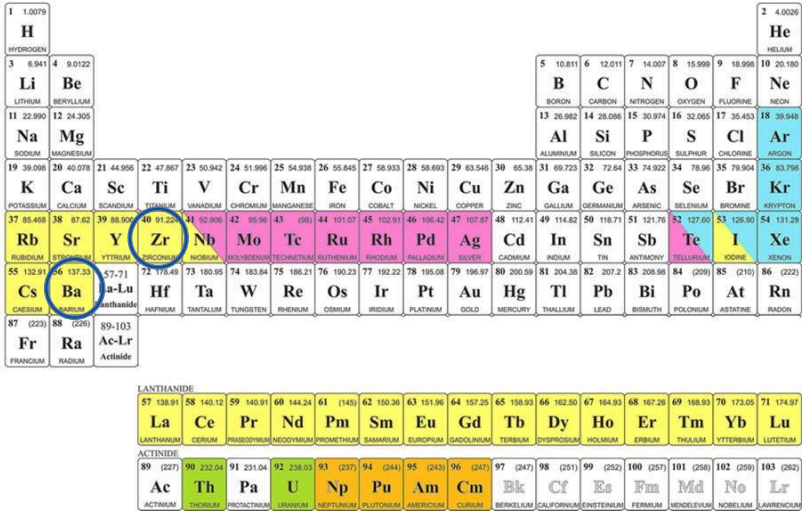


Molten Salt Reactor

CHEMICAL & THERMAL
- High solubility of actinides
- Compatibility with structural materials
- Low melting point & vapour pressure
- High heat capacity

Fuel reference: fluorides

- REFERENCE fuel for the MSFR
  - ^{7}LiF-ThF_4-$^{233}UF_4$ (77.5-20.0-2.5 mol %)
  - ^{7}LiF-ThF_4-$^{enr}UF_4$-PuF_3 (77.5-6.6-12.3-3.6 mol %)
- REFERENCE salt carrier
  - **LiF/NaF/KF**
- CORROSION PRODUCTS
  - Ni-based alloy as structural material
  - Soluble CrF_x (no passivation)
- FISSION PRODUCTS
  - Salt soluble fission products
  - Metallic precipitates
  - Gas



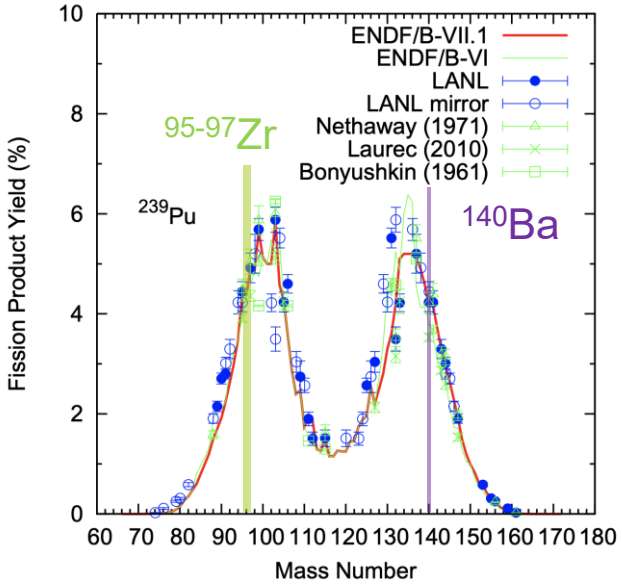
- Complex multi-component system
- Non-ideal thermodynamic behaviour

Barium and zirconium properties

- Major fission products

  For ^{235}U and ^{238}U fission products:

  - ^{140}Ba: 4.7-5.4 % yield
  - ^{95}Zr: 5.0-6.1 % yield
  - ^{97}Zr: 5.3-5.8 % yield
- Short-lived radionuclides
- High potential for complexation

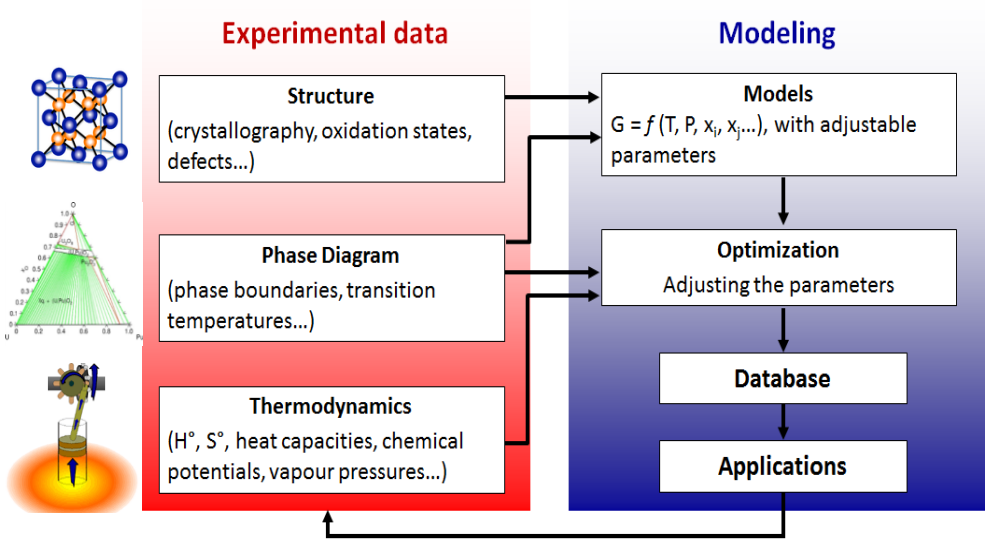


Chadwick, M. B. et al. ENDF/B-VII.1 Nuclear Data for Science and Technology: Cross Sections, Covariances, Fission Product Yields and Decay Data *Nuclear Data Sheets, Elsevier BV,* **2011**, *112*, 2887-2996

Modeling method – CALPHAD (CALculation of PHAse Diagrams)

- Least-square minimization of the total Gibbs energy G of the system to find the thermodynamic equilibrium at given conditions (T, P, x_i).
  - G is expressed as a linear combination of the G for all phases:

$$G(T, P, x_i) = \sum N^{\alpha} \, G_m^{\alpha}(T, P, x_i^{\alpha})$$

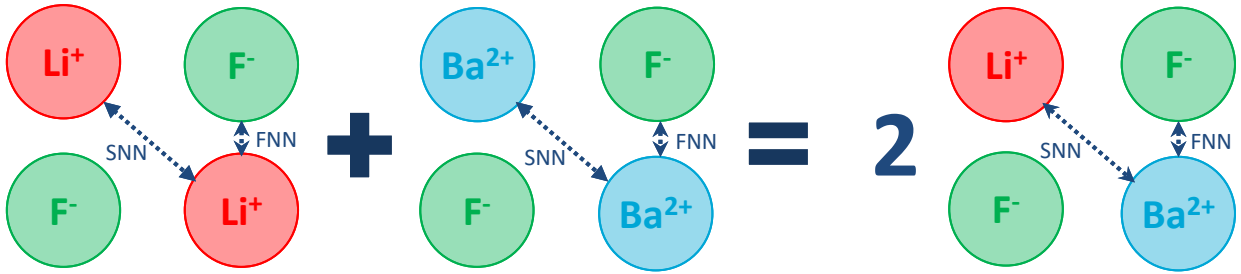


Modeling method – The quasichemical model

- **Modified quasichemical model in quadruplet approximation**
  - Formalism well-adapted to ionic liquids
  - Two sub-lattices

(Li^{+}, Ba^{3+}, cations, …) (F^{-}, Cl^{-}, anions)

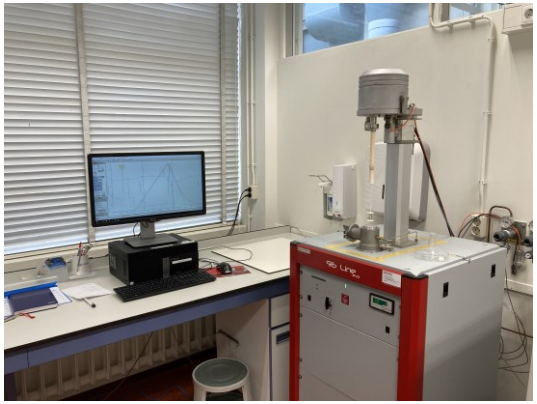
  - Basic unit = quadruplet composed of 2 anions and 2 cations



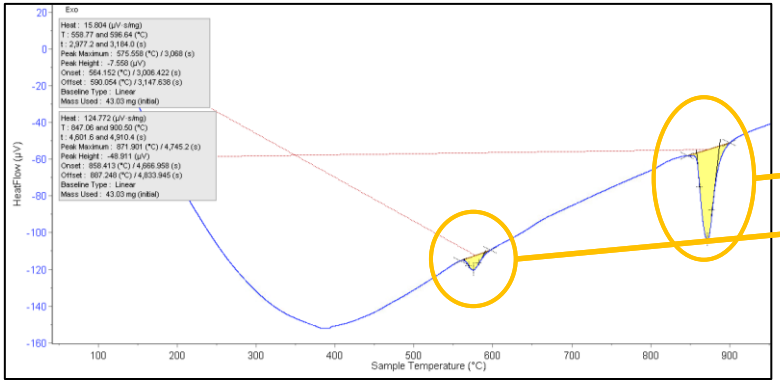
- Optimized excess parameters linked to SNN exchange reaction

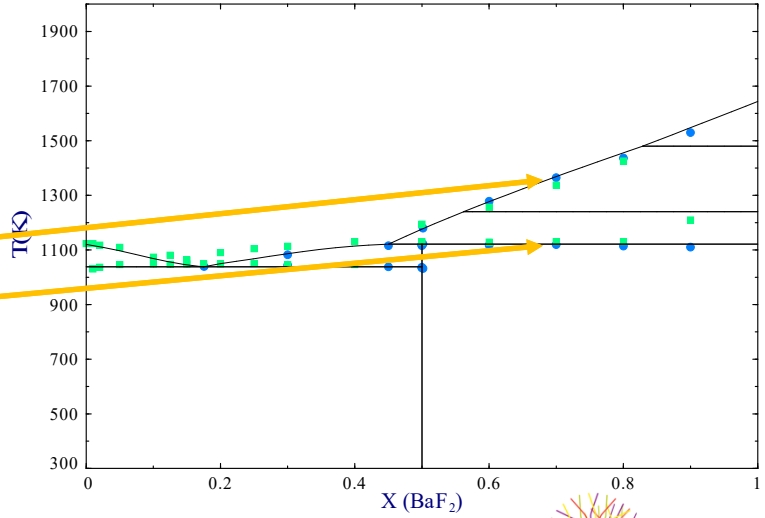
$$\Delta g_{AB/Cl} = \Delta g^{0}_{AB/Cl} + \sum_{i\geq 1} g^{i0}_{AB/F}\, \chi^{i}_{AB/F} + \sum_{j\geq 1} g^{j0}_{AB/F}\, \chi^{j}_{AB/F}$$

Determination of thermodynamic data

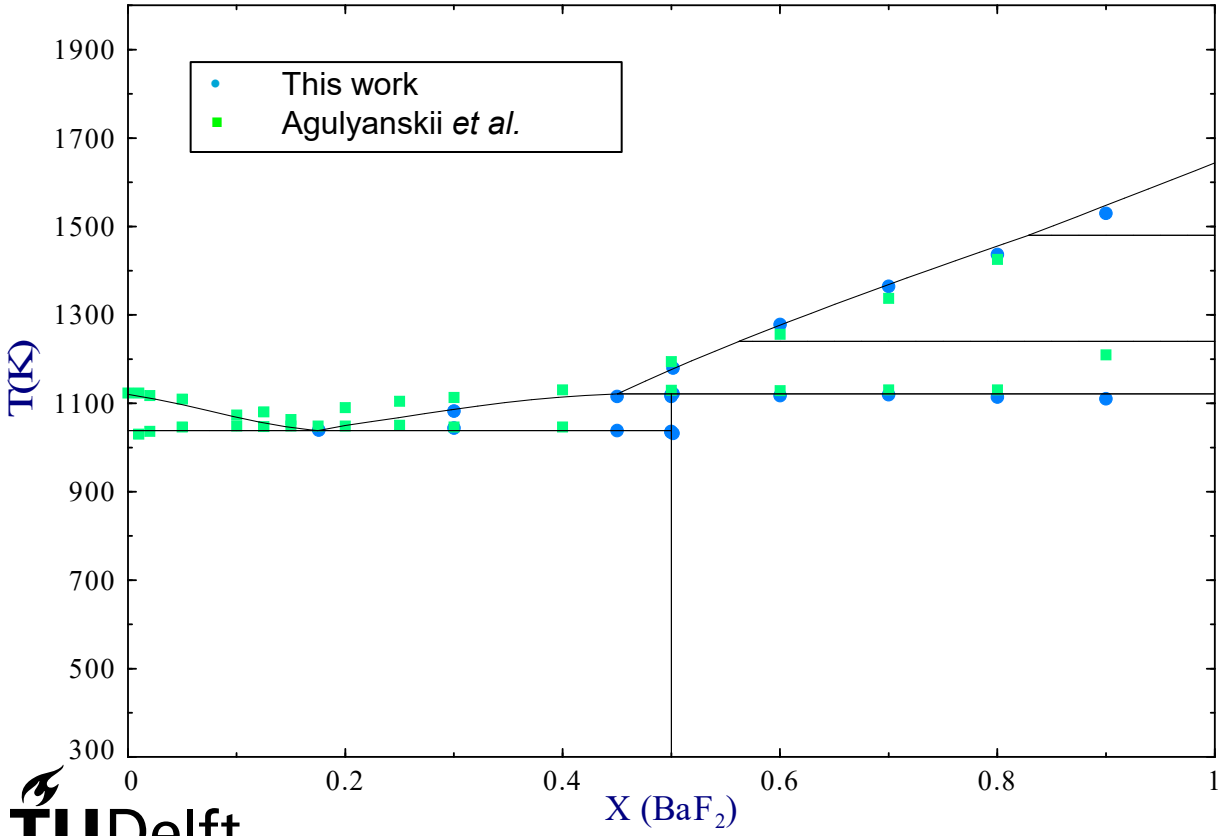


- Synthesis by solid state route from pure compounds
- Determination of phases transitions along the composition range by DSC-TGA
- Determination of phase diagram data





Thermodynamic assessment of LiF-BaF_2



- Based on updated experimental data
- Good agreement of the model with the exp. data

A. I. Agulyanskii and V. A. Bessonova, Meltability of salt mixtures containing fluorides of lithium, barium and lanthanum *Zhurnal neorganicheskd khimii*, **1982** *27*(4), 1029–1032.

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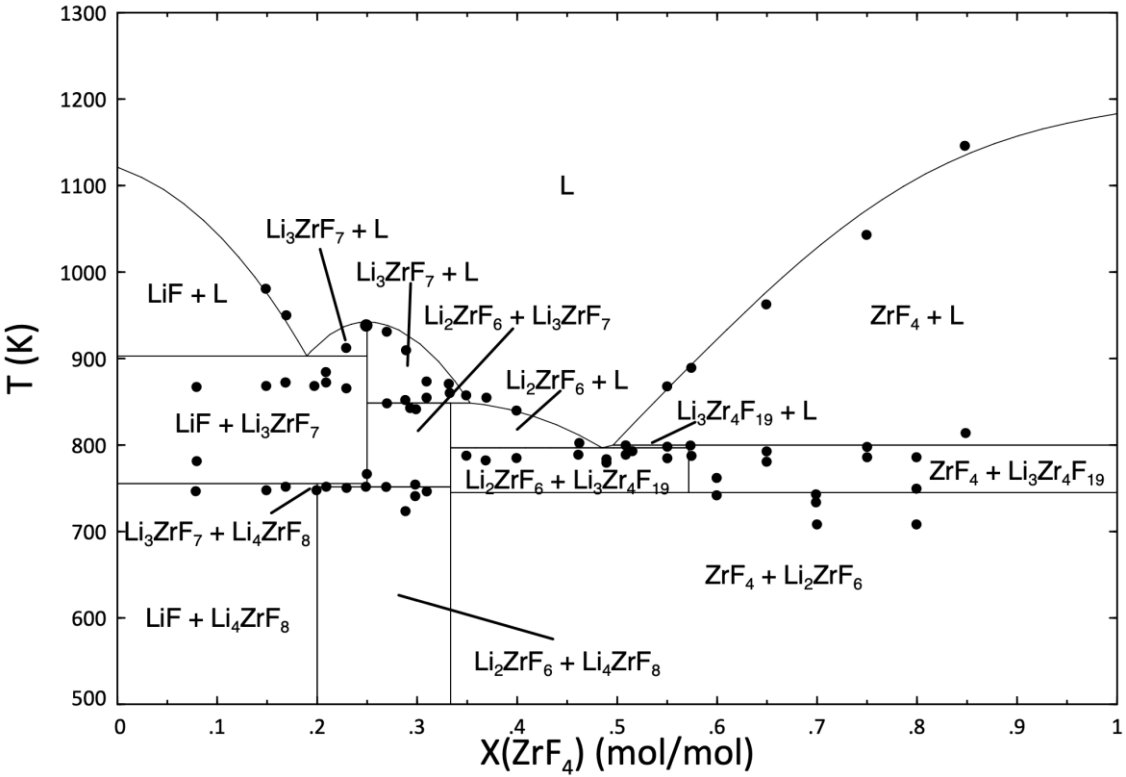
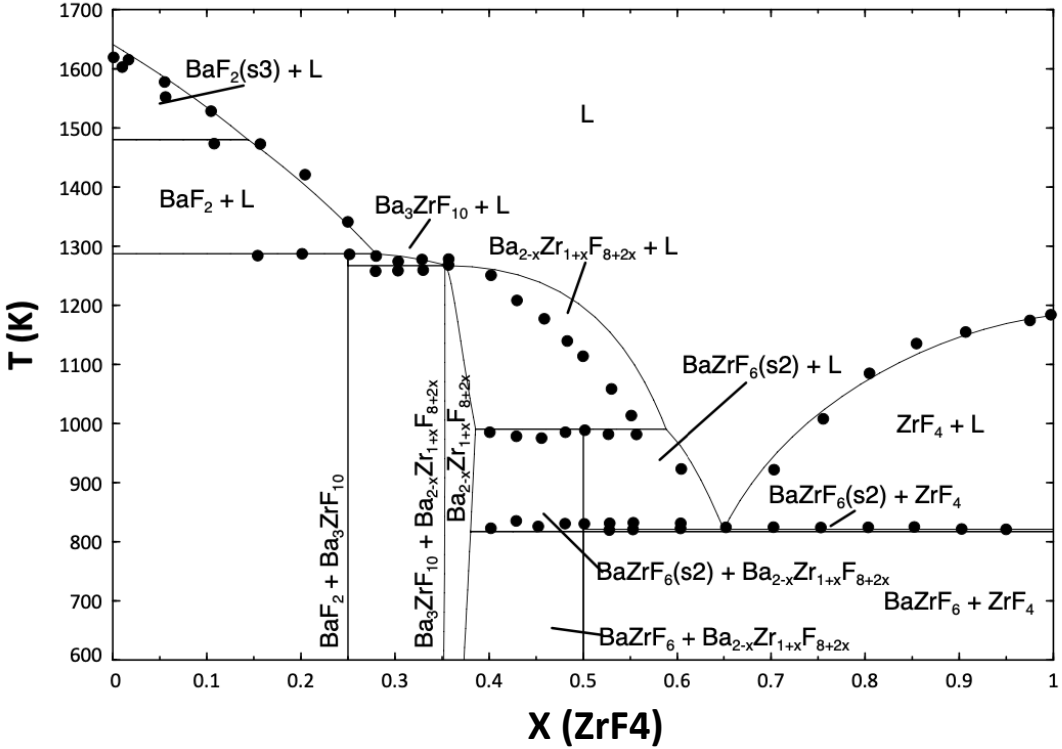
Thermodynamic assessment of LiF-ZrF_4



- Based on the data of Thomas *et al.*
- Correct agreement but still some discrepancies with respect to eutectics
- Experimental validation would be needed but challenge of high volatility of ZrF_4

R. E. Thoma et al., Condensed system LiF-NaF-ZrF_4 phase equilibria and crystallographic data. *Journal of Chemical and Engineering Data*, **1965**, *10*(3), 219–230.

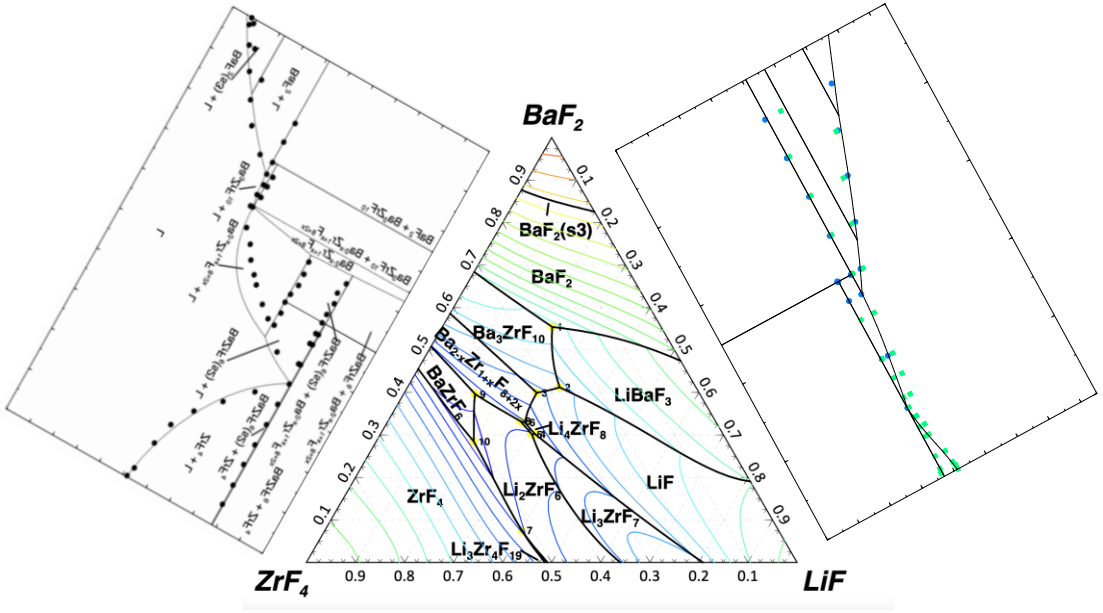
Thermodynamic assessment of BaF_2-ZrF_4

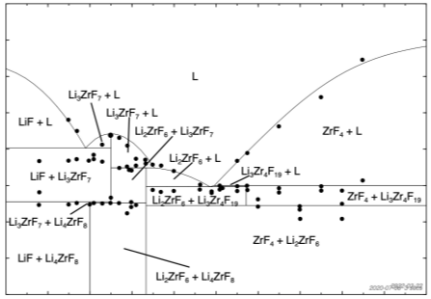


- Based on the data of Patkinova *et al.*
- Good agreement of the model with the exp. data

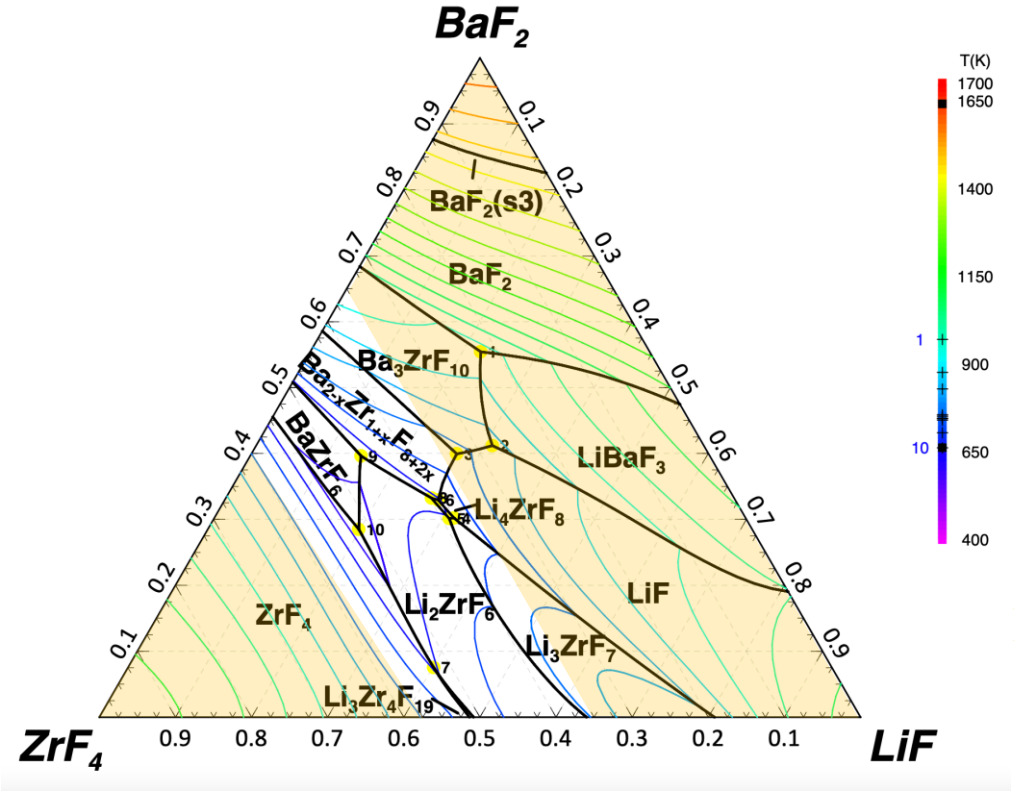
I. D. Patnikova, Y. M. Korenev, and P. P. Fedorov, Phase Diagrams of BaF_2 – RF_4 Systems (R = Zr, Hf) *Journal of Inorganic Chemistry*, **1997**, *42*(2), 302–307.

Thermodynamic assessment of $LiF\text{-}BaF_2\text{-}ZrF_4$





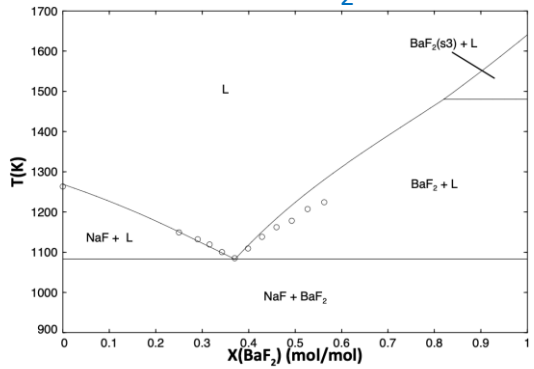
Thermodynamic assessment of LiF-BaF_2-ZrF_4



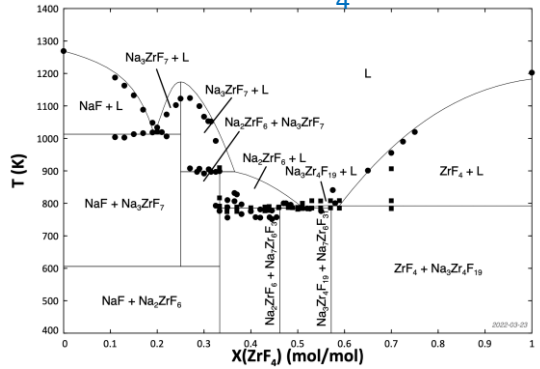
- Area above the operating safety temperature (873 K)

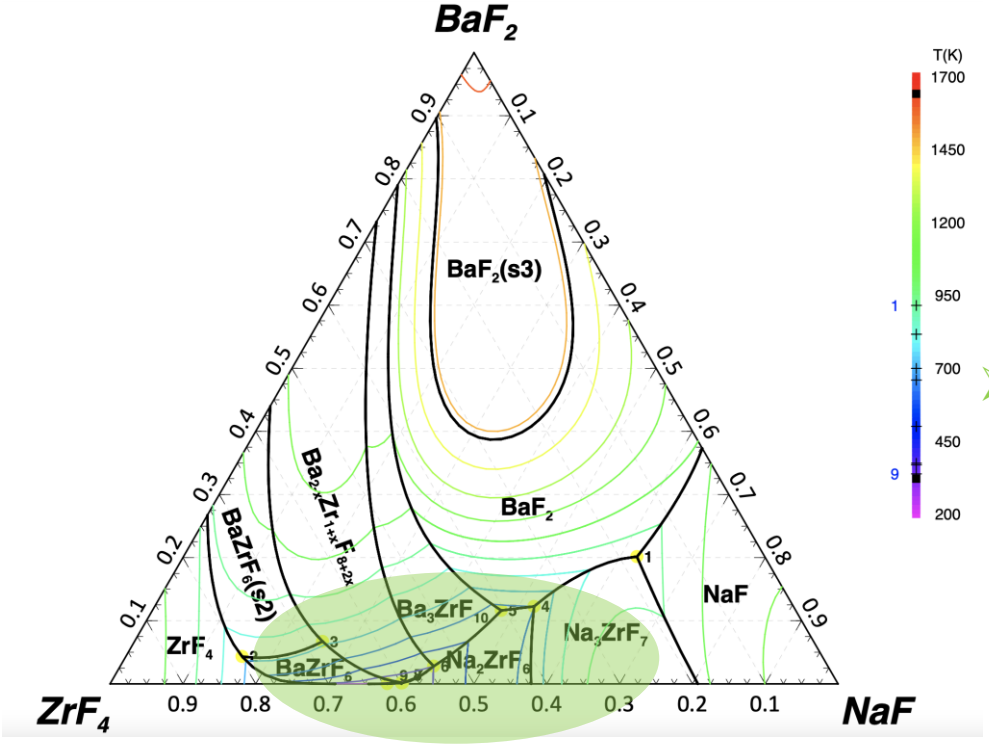
Thermodynamic assessment of the $NaF-BaF_2-ZrF_4$ system

$NaF-BaF_2$



$NaF-ZrF_4$





- Area below the operating safety temperature (873 K)

- Experimental data validation necessary

Conclusion

- Barium and zirconium fission products present a high potential of solid intermediate compounds formation in the MSR

  ➔ Risks of: - Precipitation during reactor operation?

  - Contamination of the fuel salt with highly active isotopes that need to be considered in case of accidental release

- The systems demonstrated high stability above the operating temperature for a large range of compositions

Thank you for your attention!
Any questions?