A Thermodynamic database for Salts Systems in Nuclear applications

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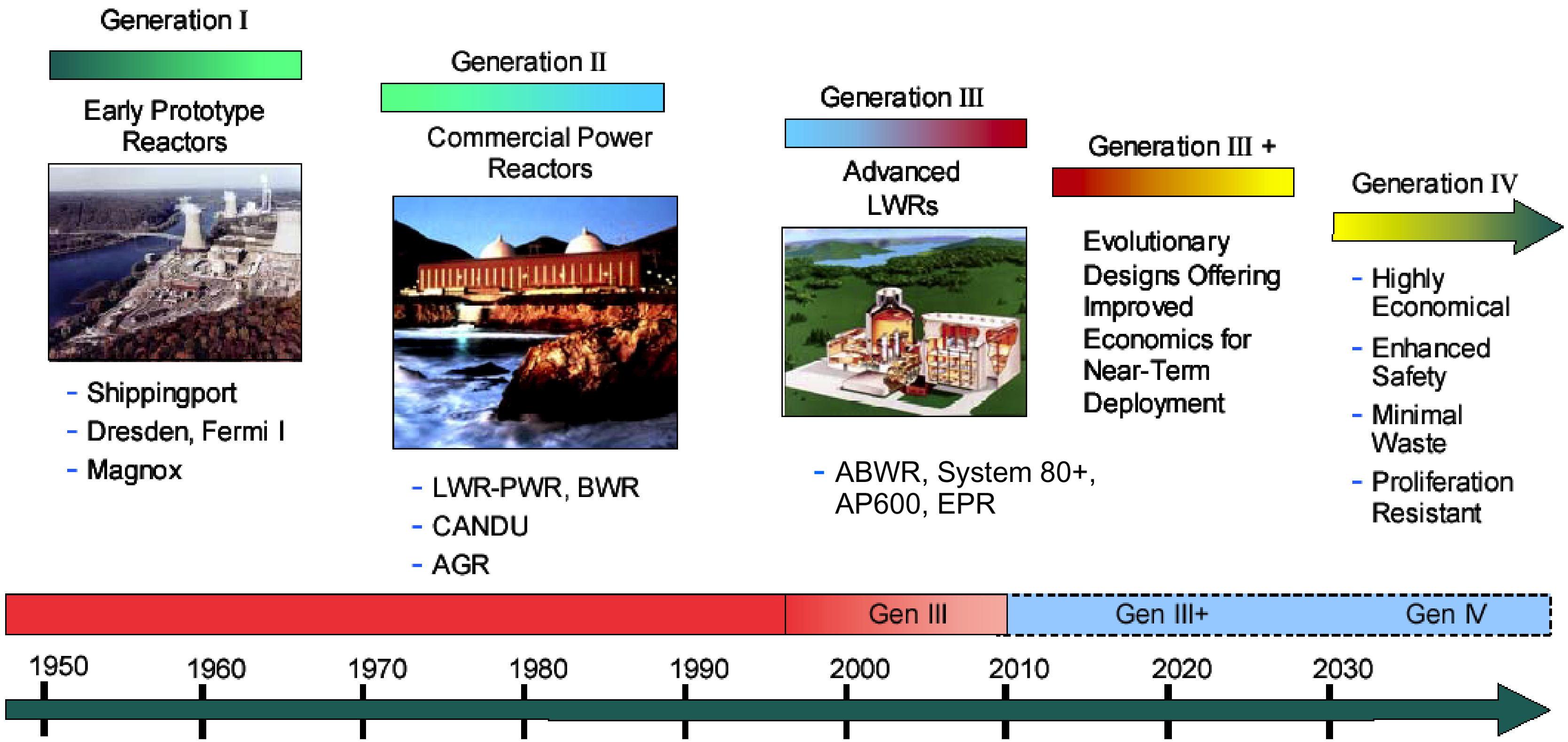


Source: A technological Roadmap for Generation IV Nuclear Energy Systems

The Six GENIV reactor types

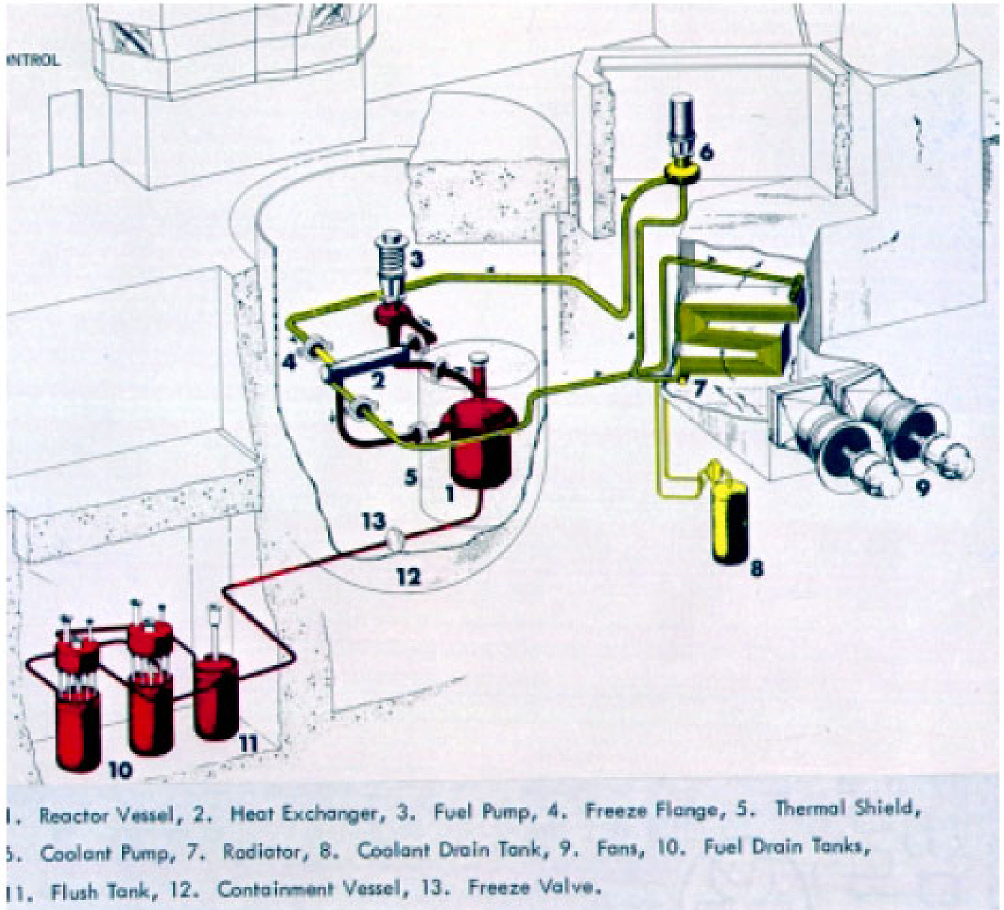
- Gas-cooled Fast Reactor (GFR)
- Very high temperature reactor (VHTR)
- Supercritical-water-cooled reactor (SCWR)
- Sodium-cooled Fast Reactor (SFR)
- Lead-cooled Fast Reactor (LFR)
- Molten Salt Reactor (MSR)

The Molten Salt Reactor - The past

Concept: circulating system with fuel dissolved in molten salt developed at ORNL (USA)

1950's: Aircraft propulsion programme (ARE)

1965-1969: Molten Salt Reactor Experiment (MSRE) & Molten Salt Breeder Reactor (MSBR)



The MSR fuel and its solvent

- ✓ Wide range of solubility for actinides
- ✓ Thermodynamically stable up to high temperatures
- ✓ Stable to radiation (no radiolytic decomposition)
- ✓ Low vapour pressure at the operating temperature of the reactor
- ✓ Compatible with nickel-based structural materials

ARE	$NaF - ZrF_4 - UF_4$
MSR	$^7LiF - BeF_2 - ZrF_4 - ThF_4$
MSBR	$^7LiF - BeF_2 - ThF_4$

The Molten Salt Reactor - The present

- Moderated breeder based on MSBR (thermal)
  $LiF-BeF_2-ThF_4-UF_4$
- Non-moderated breeder (fast)
  $LiF-ThF_4$
- Actinide burner (fast)
  $LiF-BeF_2-NaF-PuF_3$

- AHTR (USA): coated particle fuel with molten salt (fluoride) cooling
  $LiF-BeF_2$

Physical properties needed for design calculations

- Melting point
- Actinide solubility
- Vapour pressure
- Density
- Viscosity
- Heat capacity
- Thermal conductivity

Phase diagram optimisation

Extensive database available from US (ORNL) and USSR research in the period 1950-1970

Databases compiled

- LiF-BeF_2-ThF_4-UF_4
  - QKTO polynomial model in FactSage™
  - Re-assessment in SUBG quasichemical model underway
- LiF-NaF-KF-RbF-CsF-BeF_2-LaF_3-PuF_3
  - SUBG quasichemical model in FactSage™
- $NaCl$-UCl_3-$PuCl_3$
  - SUBG quasichemical model in FactSage™

Quasichemical model by Blander & Pelton

Symmetry group numbers *i* and *j* are attributed to the components A and B, allowing *i* and *j* particles to mix substitutionally on a quasi-lattice. In this formalism, general polynomials can be used to describe the excess Gibbs energy coeffcients.

Excess parameters

$$\Delta_{xs}G = \sum_{p,q} L^{p,q}_{A,B}(T)\,Y_A\left(\frac{\chi_i}{\chi_i+\chi_j}\right)^p Y_B\left(\frac{\chi_j}{\chi_i+\chi_j}\right)^q$$

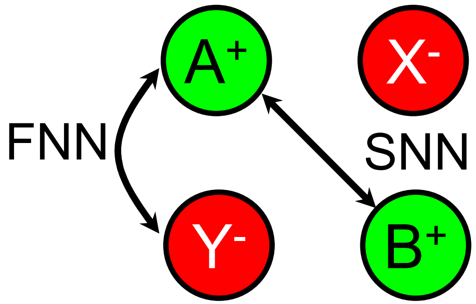
Equivalent fractions

Sum of Equivalent fractions

Quasichemical model with quadruplet approximation by Chartand & Pelton

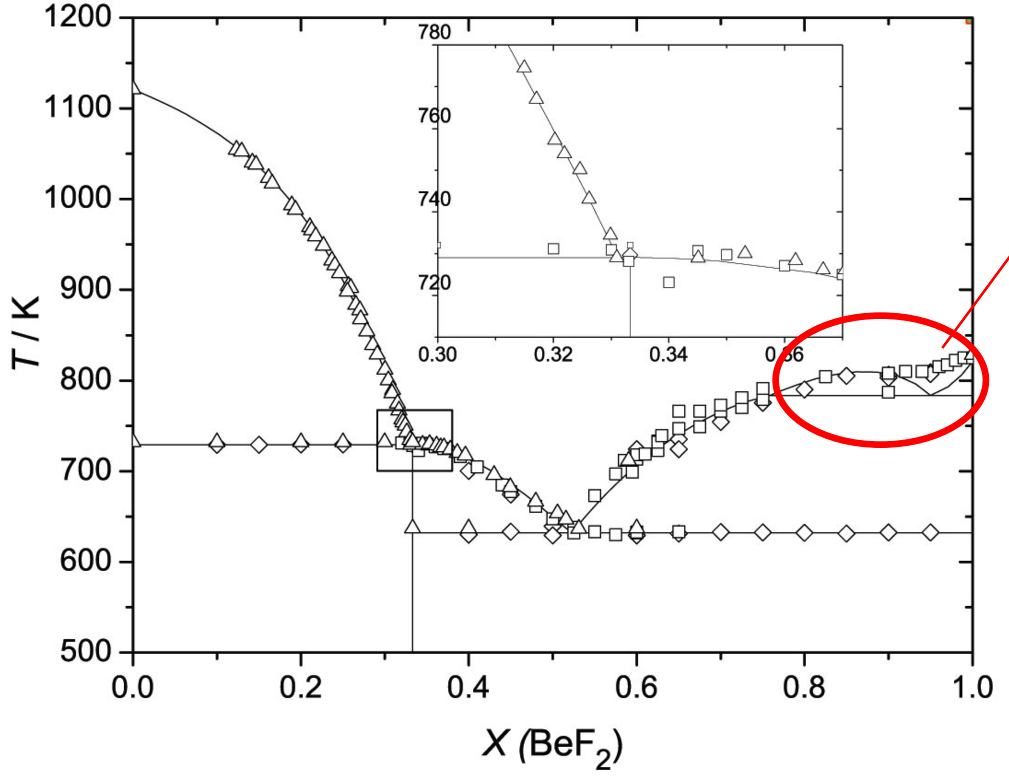
$$(A\cdots X) + (B\cdots Y) = (A\cdots Y) + (B\cdots X) \qquad \Delta g^{exchange}_{AB/XY}$$

$$\Delta g_{AB/X_2} = \Delta g^0_{AB/X_2} + \sum_{(i+j)\geqq 1} \chi^i_{AB/X_2}\chi^j_{BA/X_2} g^{ij}_{AB/X}$$



Two sublattices, which reduces to pair approximation for X = Y = F

The LiF-BeF$_2$ phase diagram (QKTO)

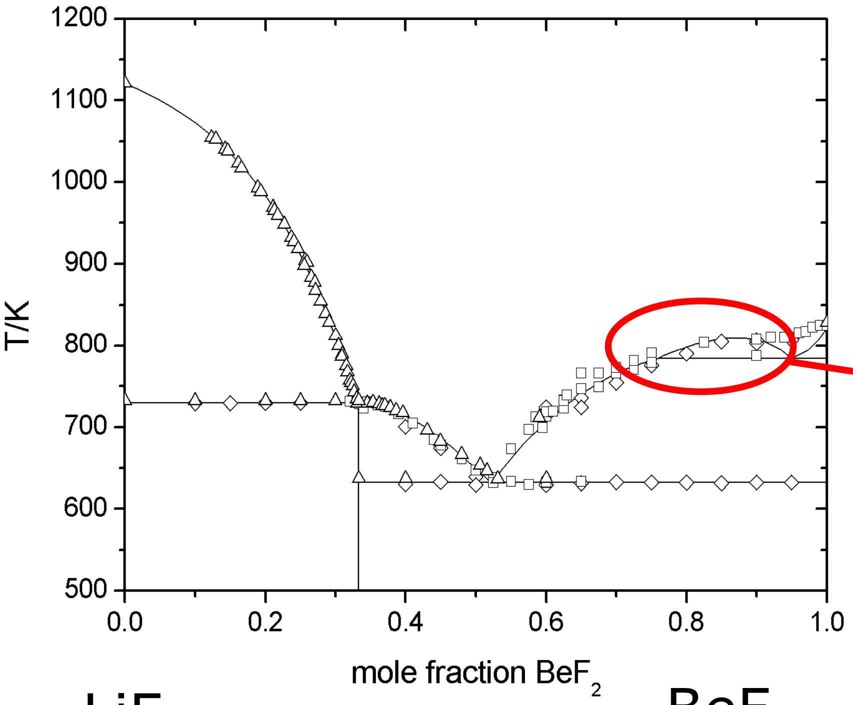


Region of demixing (ROD)

- "Induced" by the small entropy of fusion of BeF$_2$

$$\frac{dT}{dX} = \frac{R\,T_{fus}}{\Delta_{fus}S^0}$$

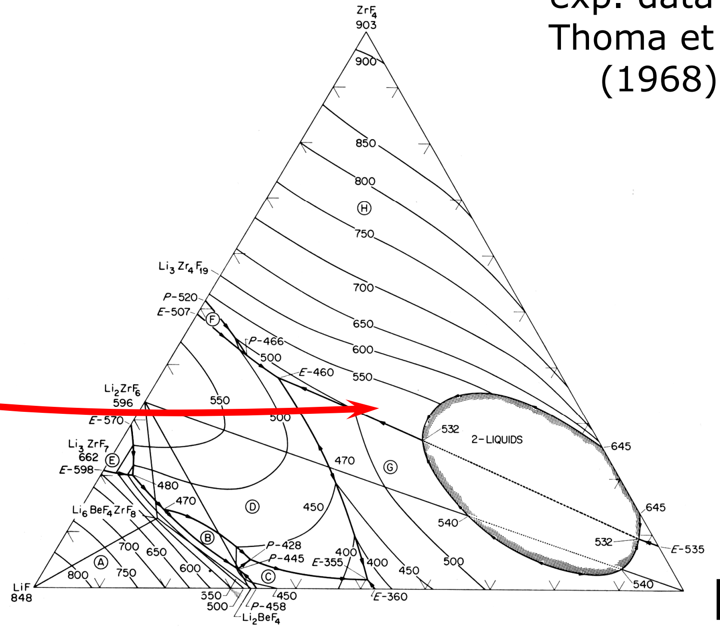
The LiF-BeF_2 phase diagram



LiF BeF_2

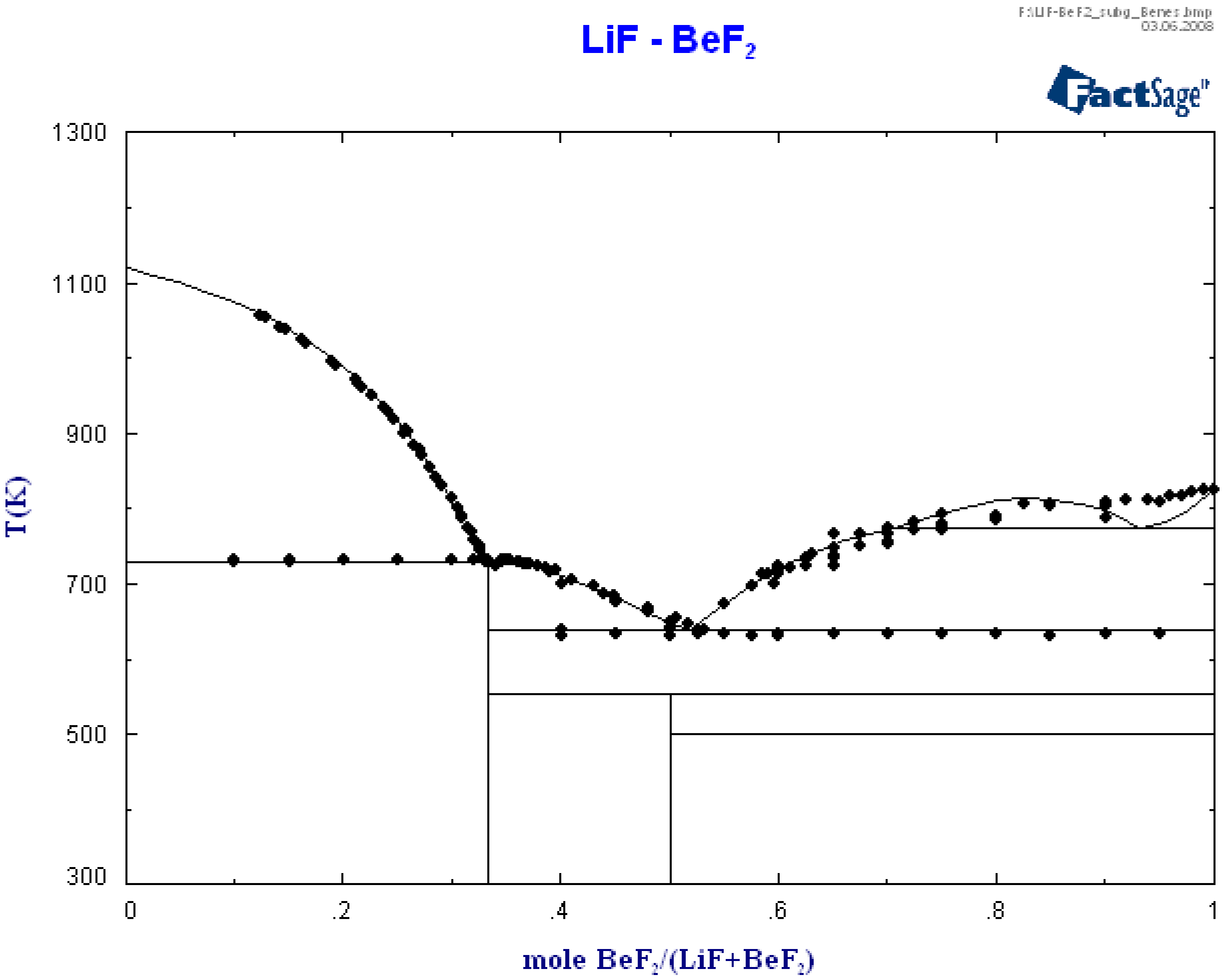
ZrF_4

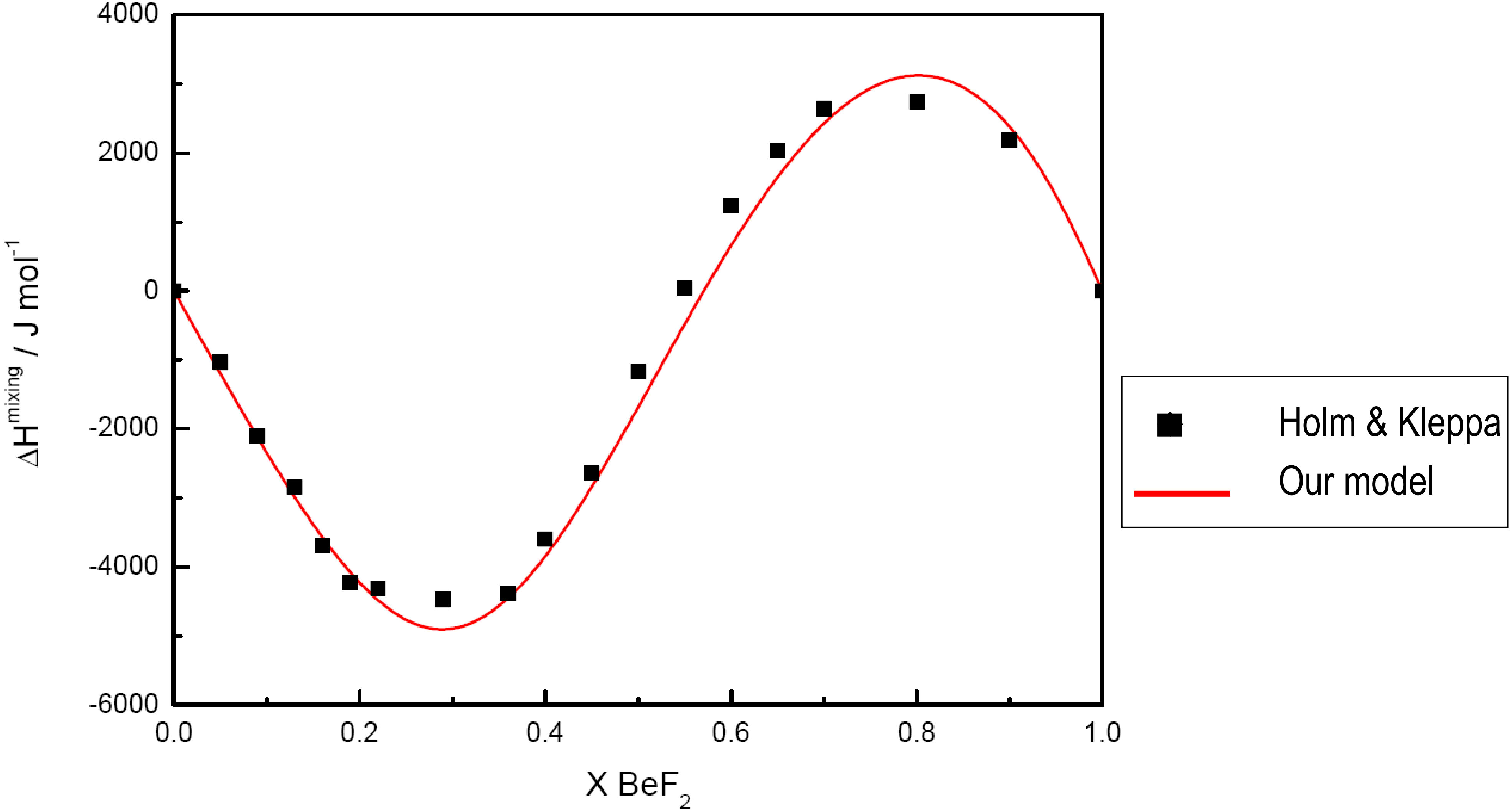
exp. data by Thoma et al. (1968)

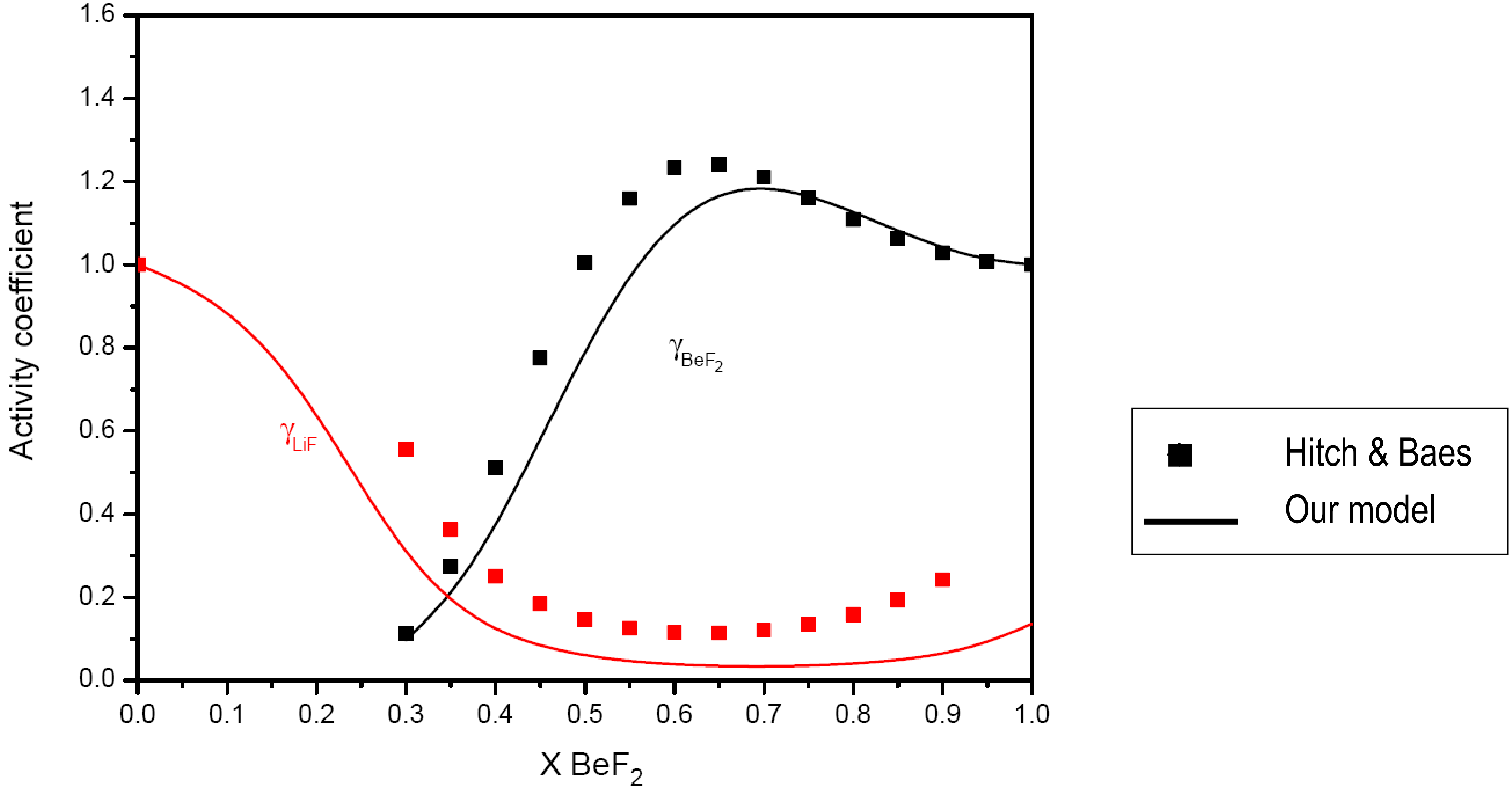


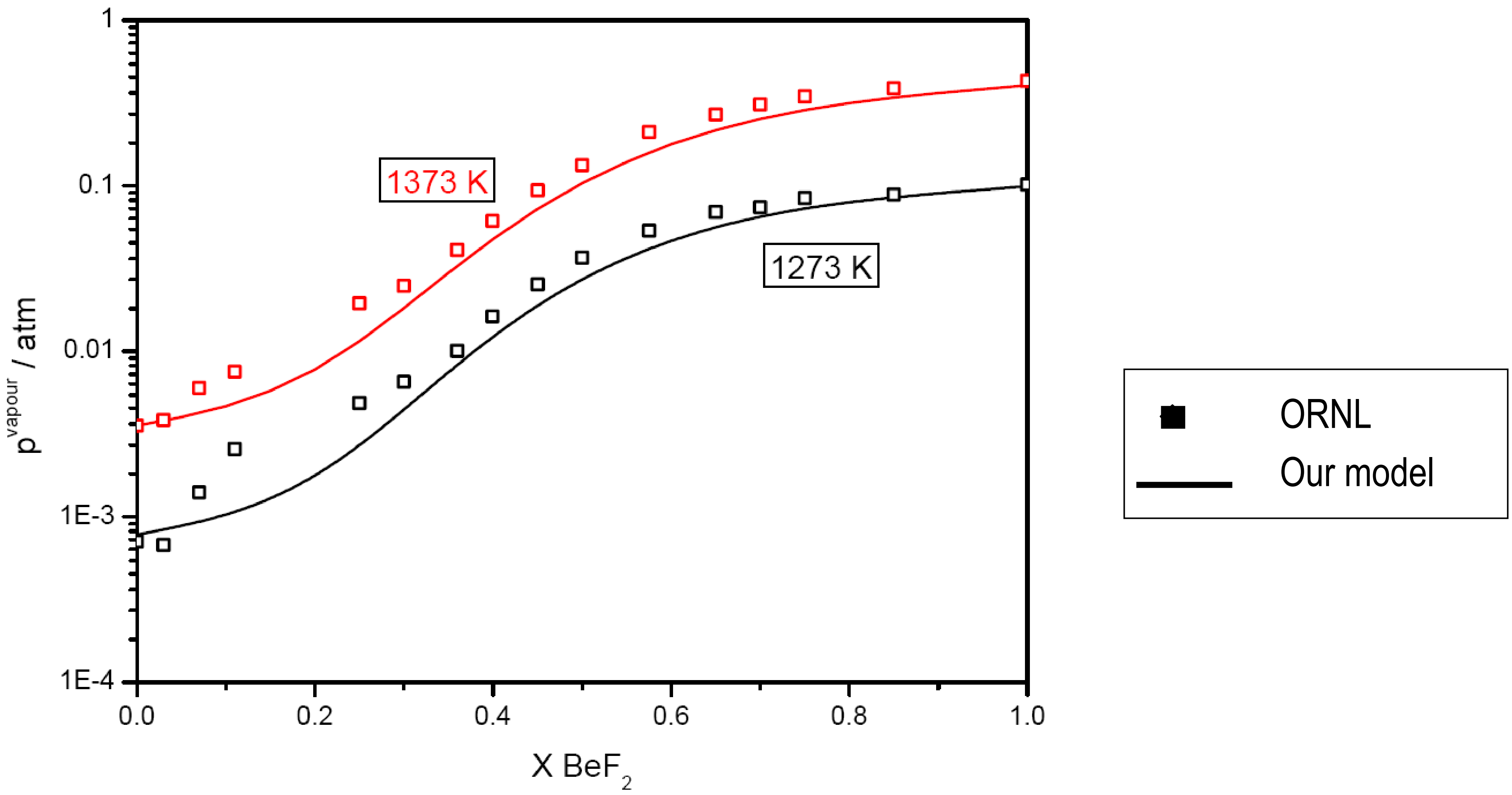
LiF BeF_2

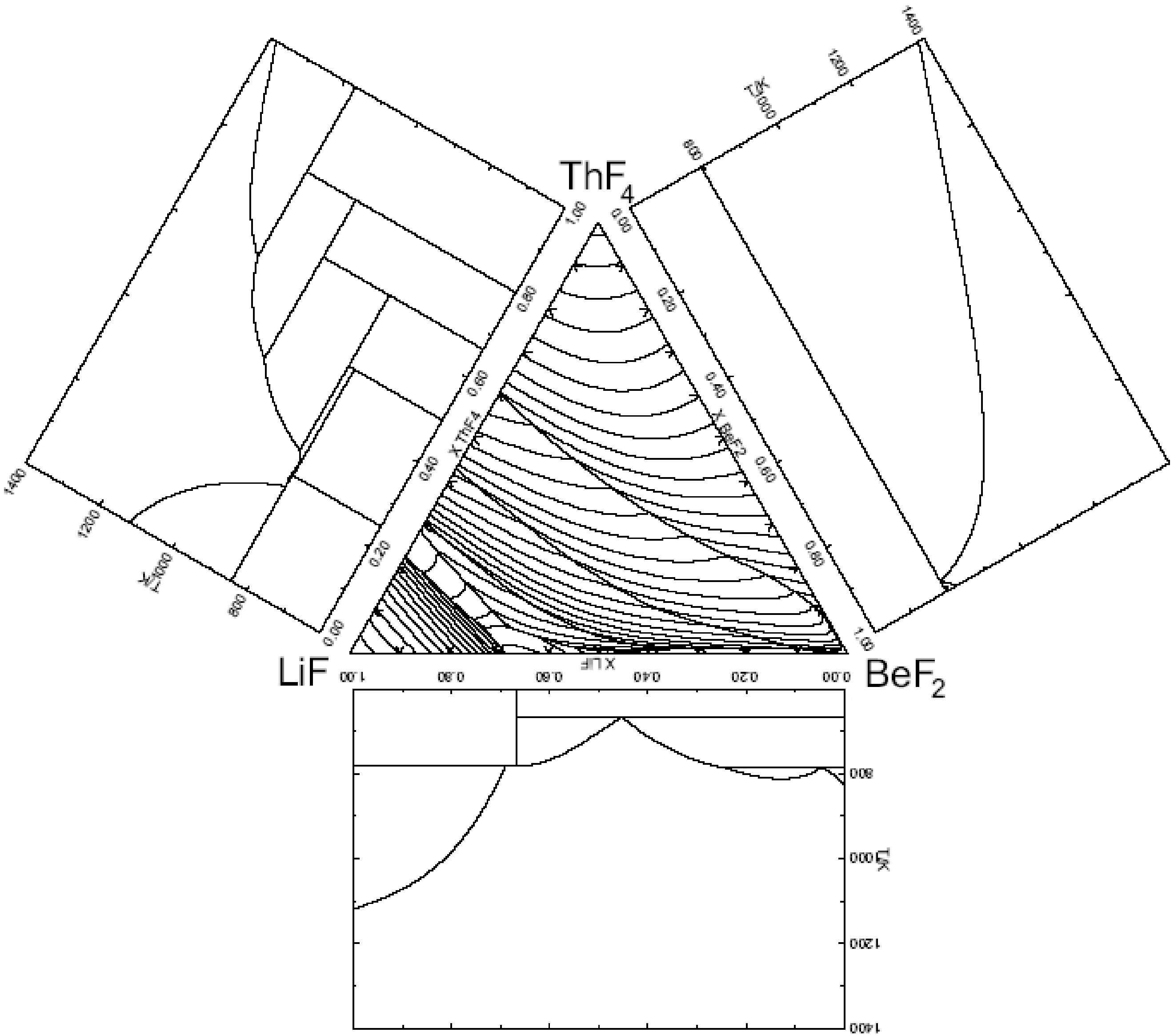
LiF-BeF_2 re-assessed in SUBG

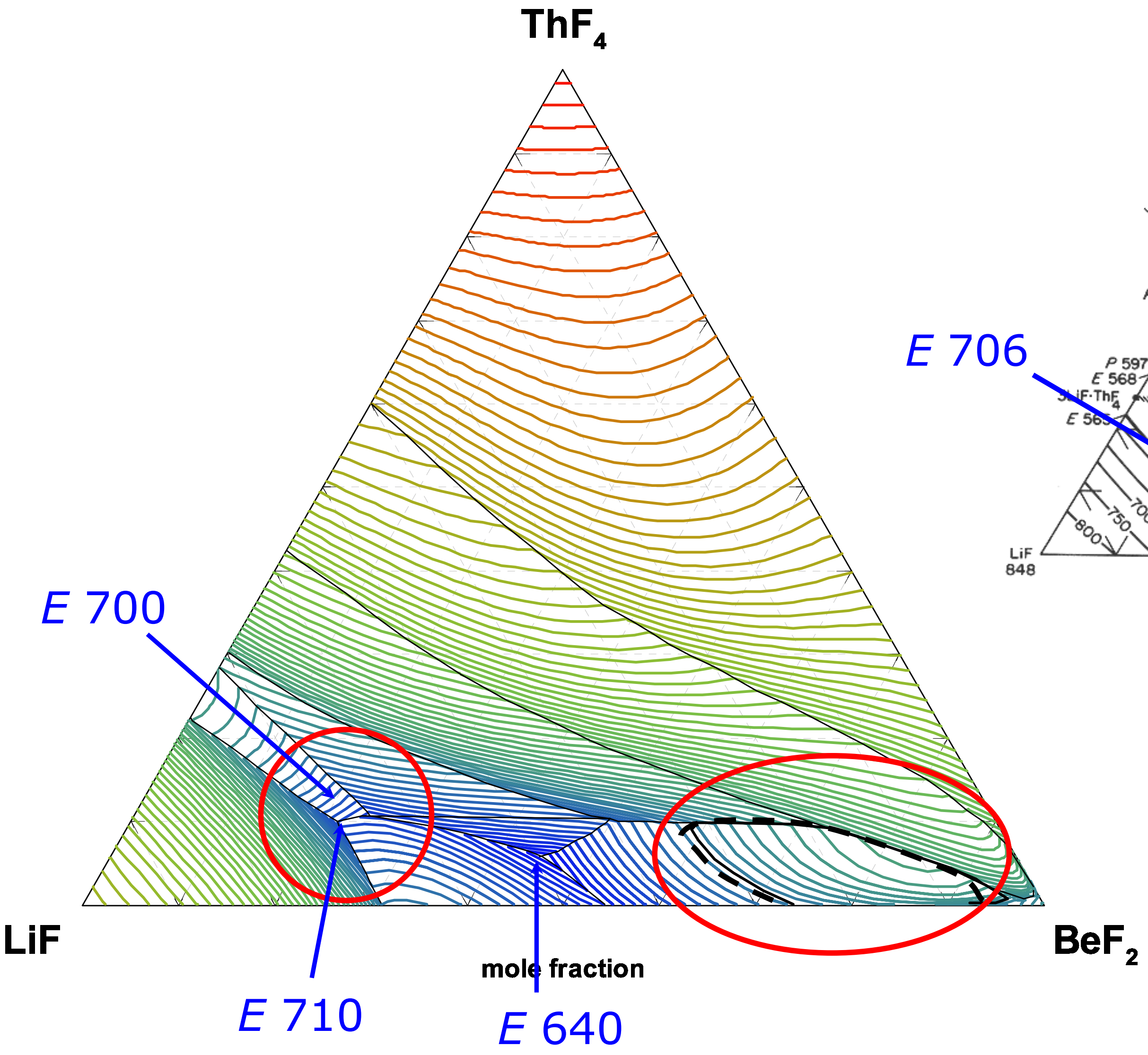


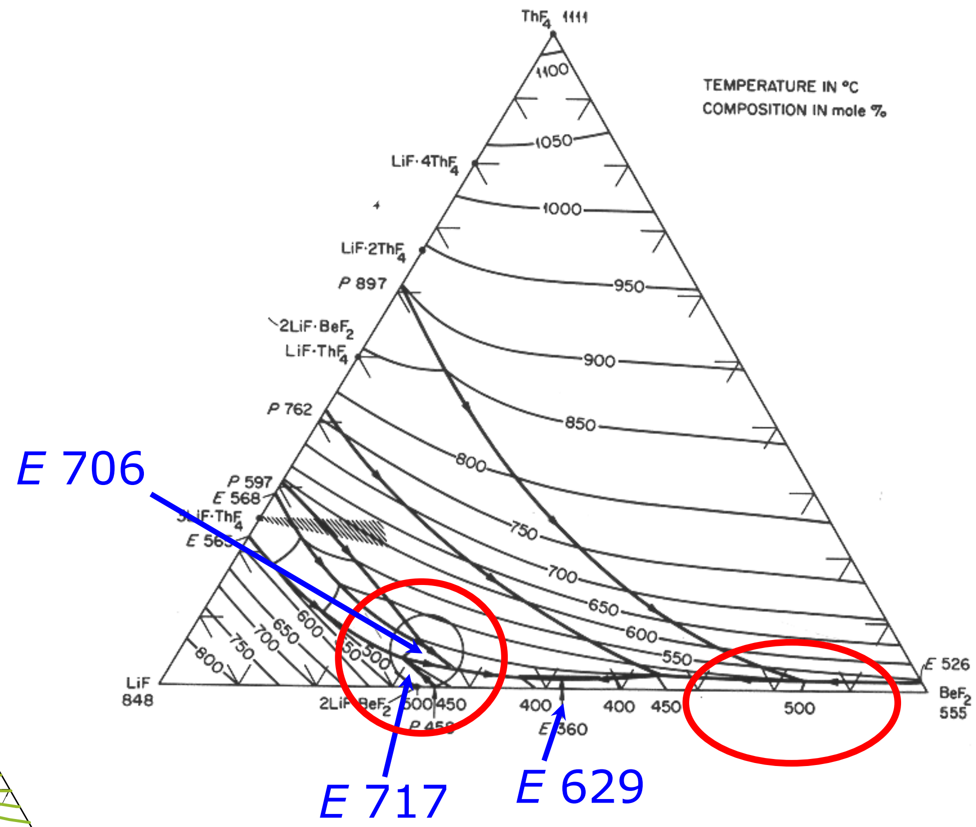

4000
2000
0
-2000
-4000
-6000
0.0
0.2
0.4
0.6
0.8
1.0
X BeF2
ΔH mixing / J mol-1
Holm & Kleppa
Our model


1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Activity coefficient
γLiF
γBeF2
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
X BeF2
Hitch & Baes
Our model

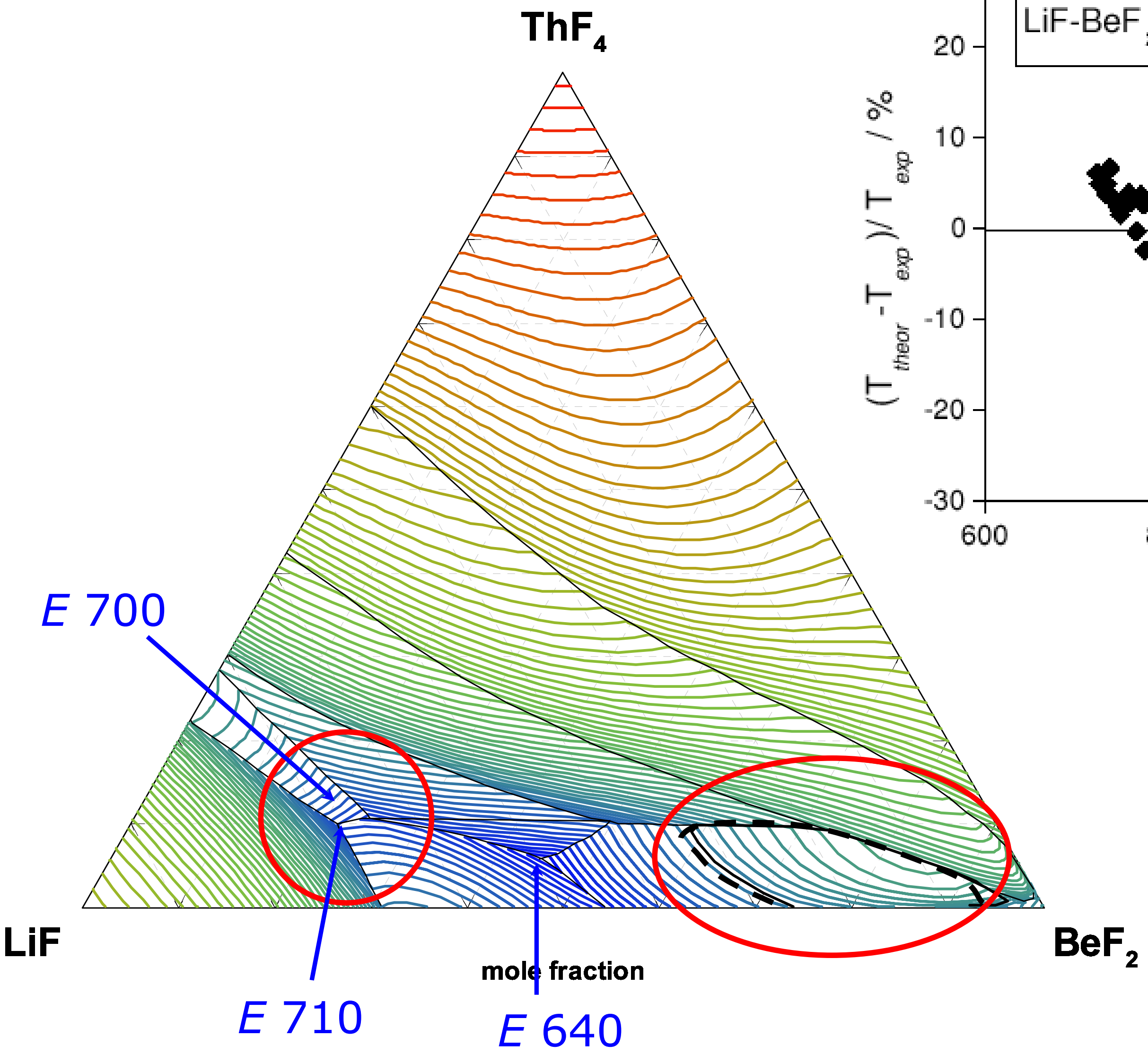

1
0.1
0.01
1E-3
1E-4
p^vapour / atm
0.0
0.2
0.4
0.6
0.8
1.0
X BeF2
1373 K
1273 K
ORNL
Our model

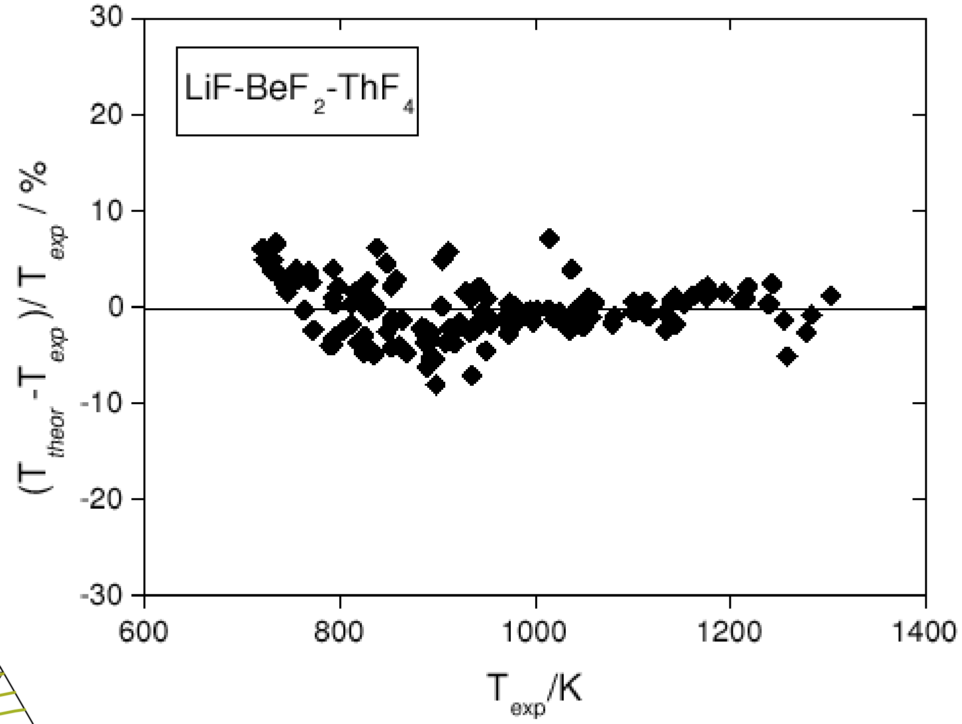

ThF$_4$
LiF
BeF$_2$
X ThF4
X BeF2
X LiF
T/K
0.00
0.20
0.40
0.60
0.80
1.00
800
1000
1200
1400

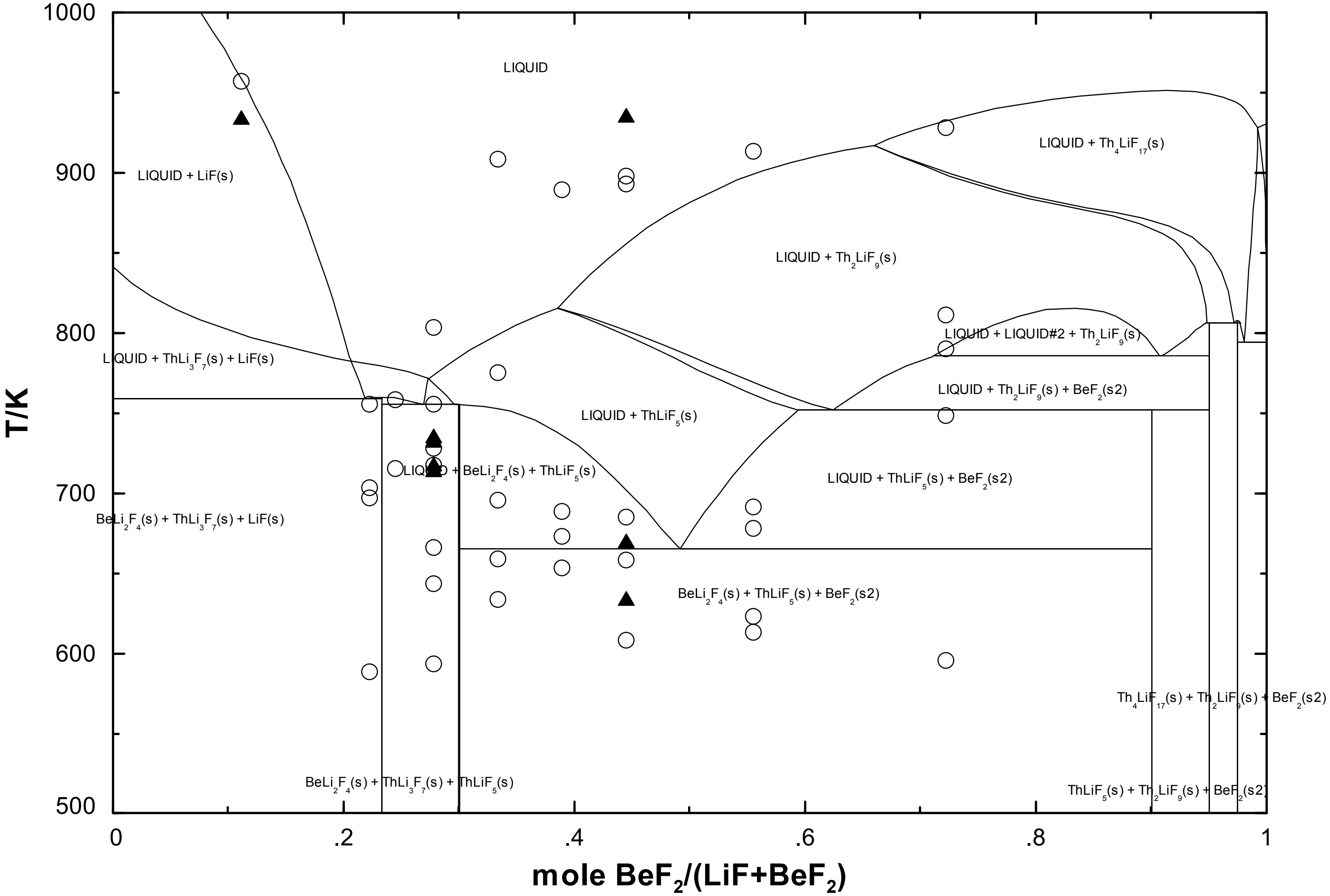




by Thoma et al. (1960)


ThF4
LiF
BeF2
mole fraction
E 700
E 710
E 640


LiF-BeF2-ThF4
(Ttheor-Texp)/ Texp / %
Texp/K
30
20
10
0
-10
-20
-30
600
800
1000
1200
1400



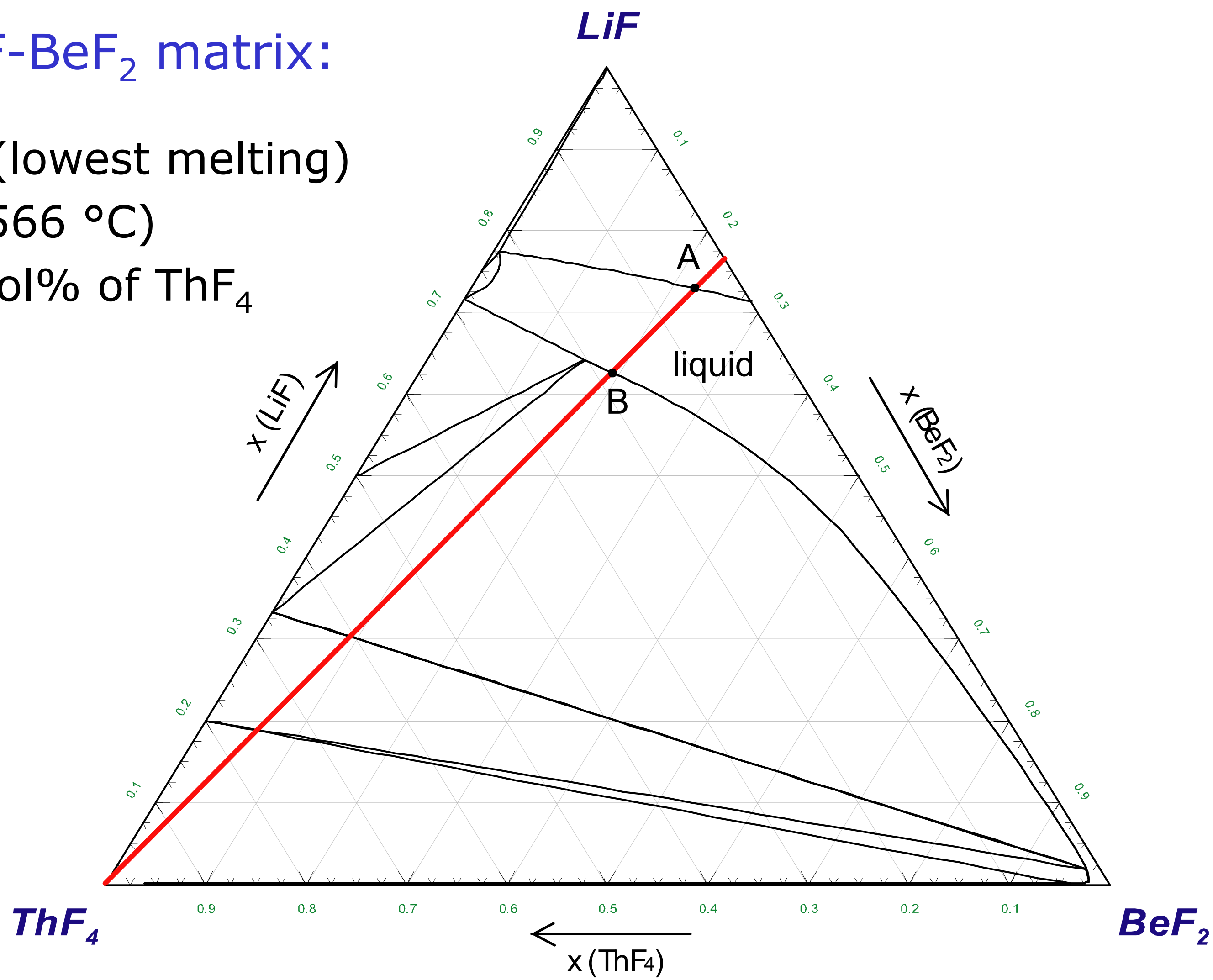
A binary cross-section of LiF-BeF_2-ThF_4 at ThF_4= 10%

Solubility of ThF_4 in LiF-BeF_2 matrix:

LiF / BeF_2 = 76.6 / 23.3 (lowest melting)

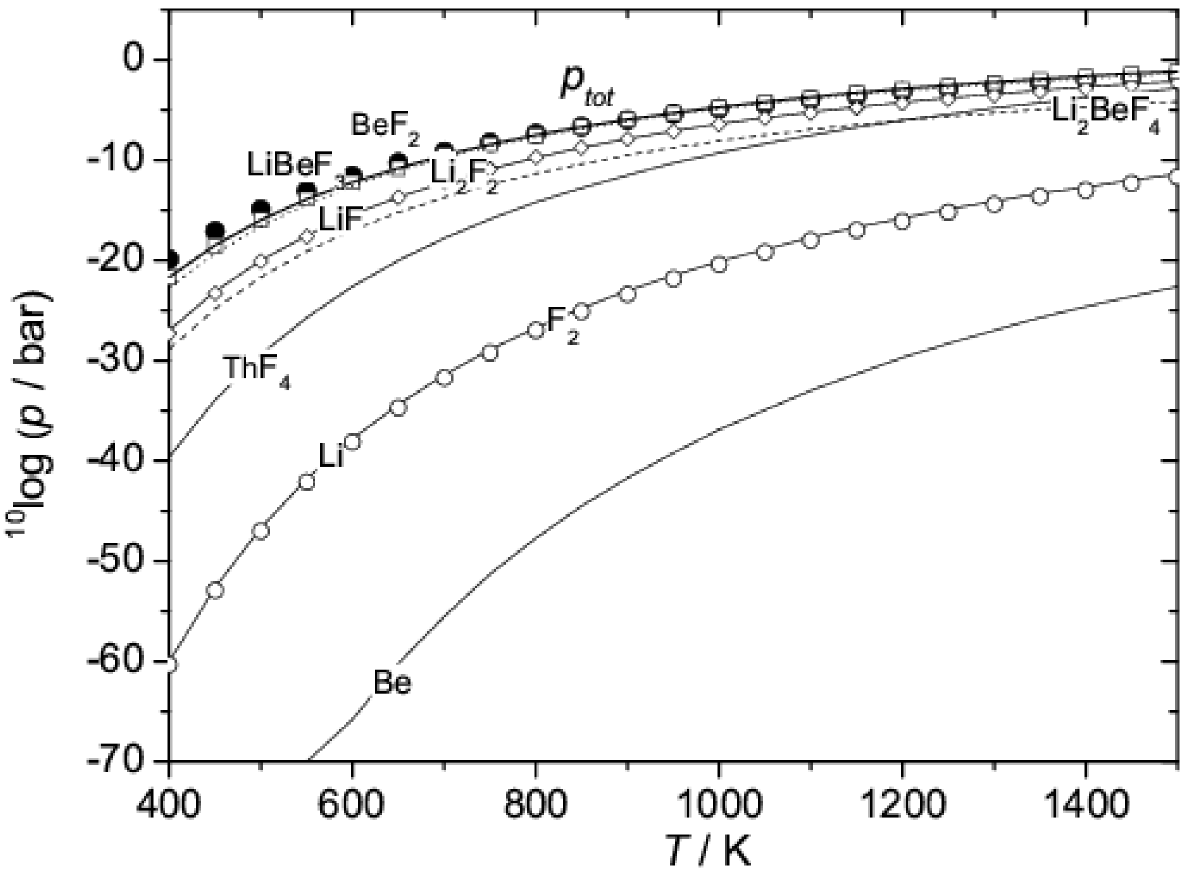
T = $T_{inlet\ (MSBR)}$ = 839 K (566 °C)

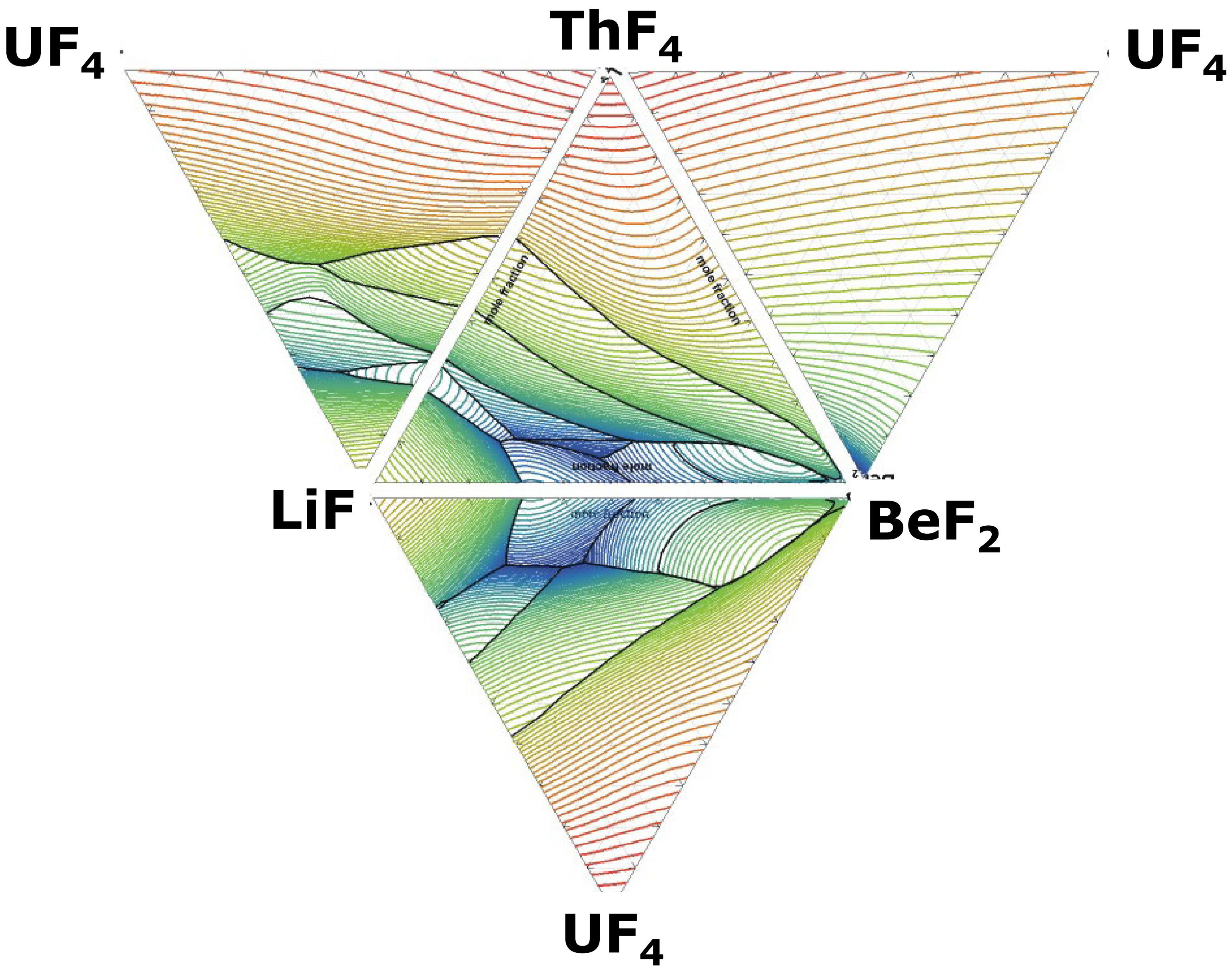
solubility ~ 4.7 – 18.2 mol% of ThF_4



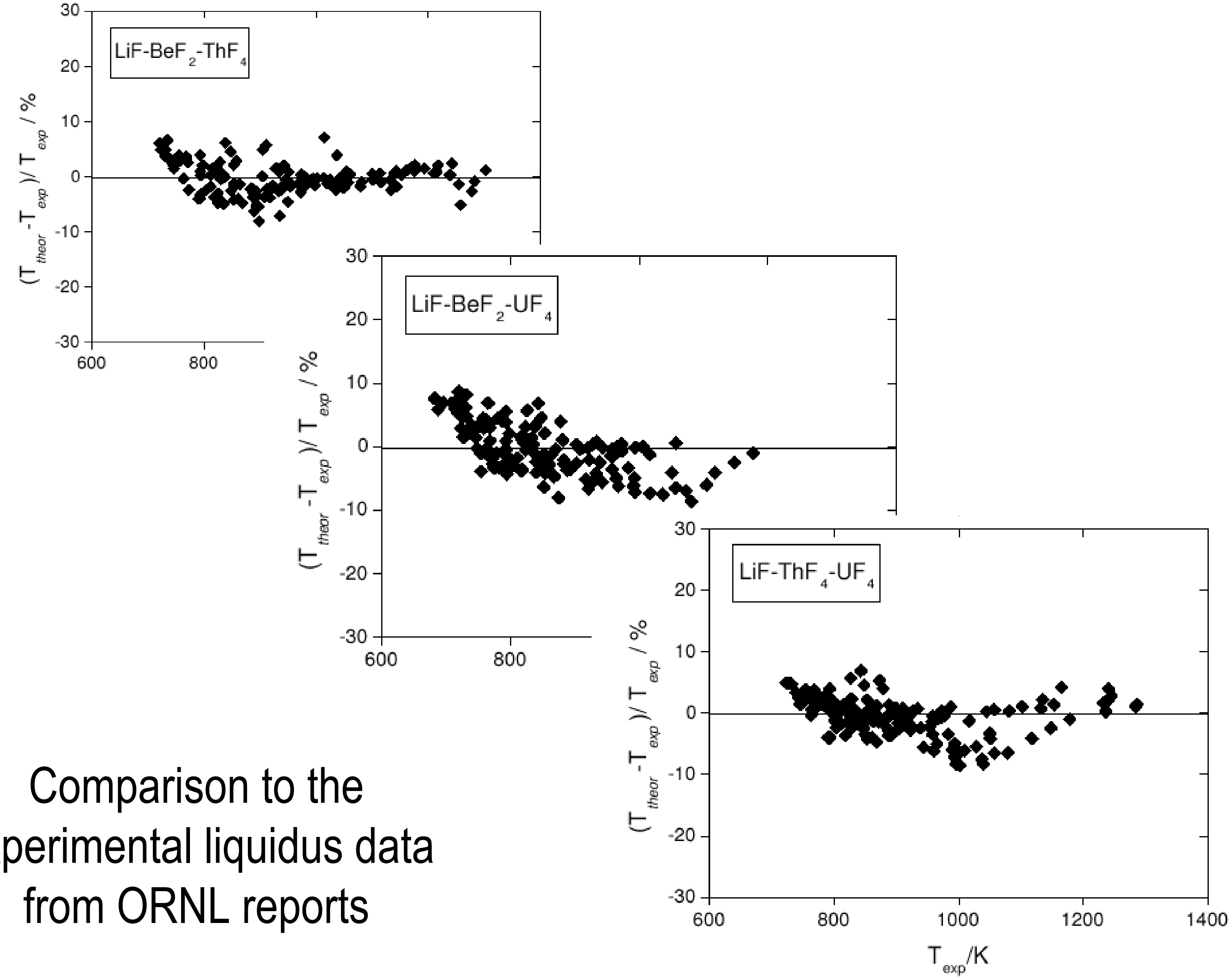
Isothermal section for T = 839K (566 °C)

Vapour pressure of the LiF-BeF_2-ThF_4 system



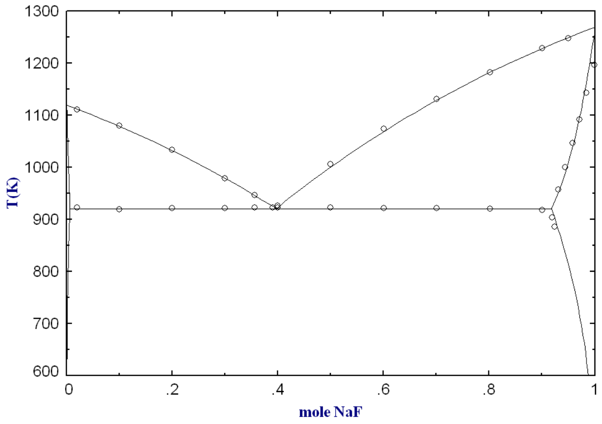


ThF_4
UF_4
UF_4
LiF
BeF_2
UF_4
mole fraction
mole fraction
mole fraction

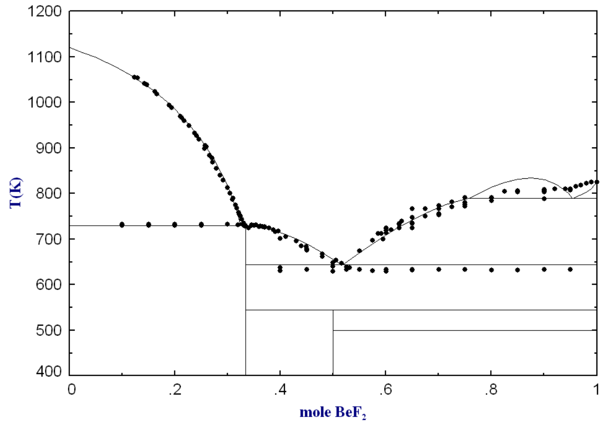


Comparison to the experimental liquidus data from ORNL reports

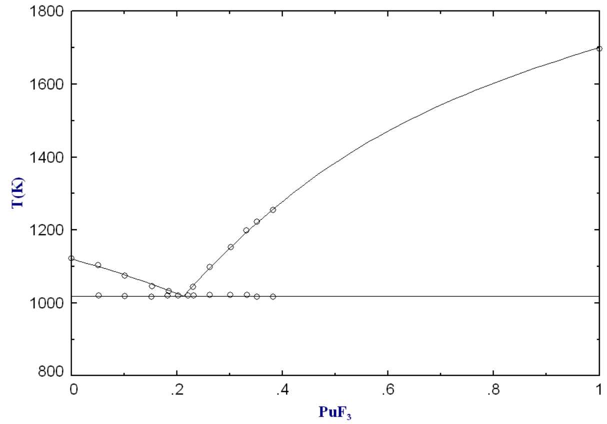
LiF - NaF



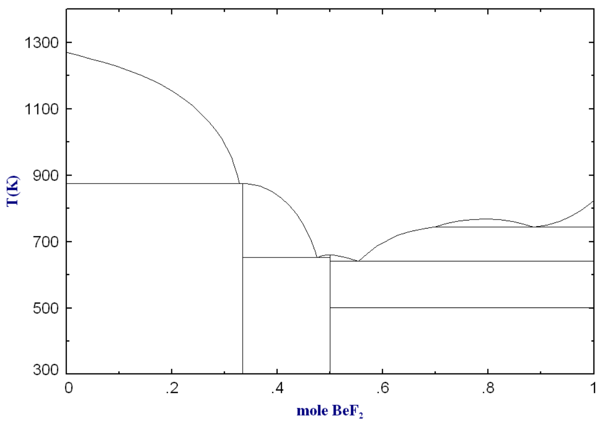
LiF – BeF_2



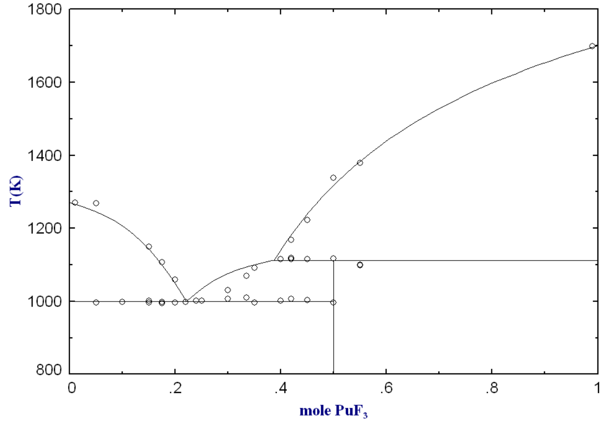
LiF – PuF_3



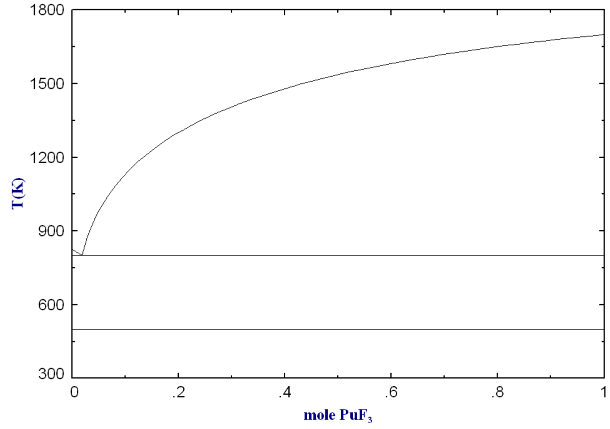
NaF – BeF_2



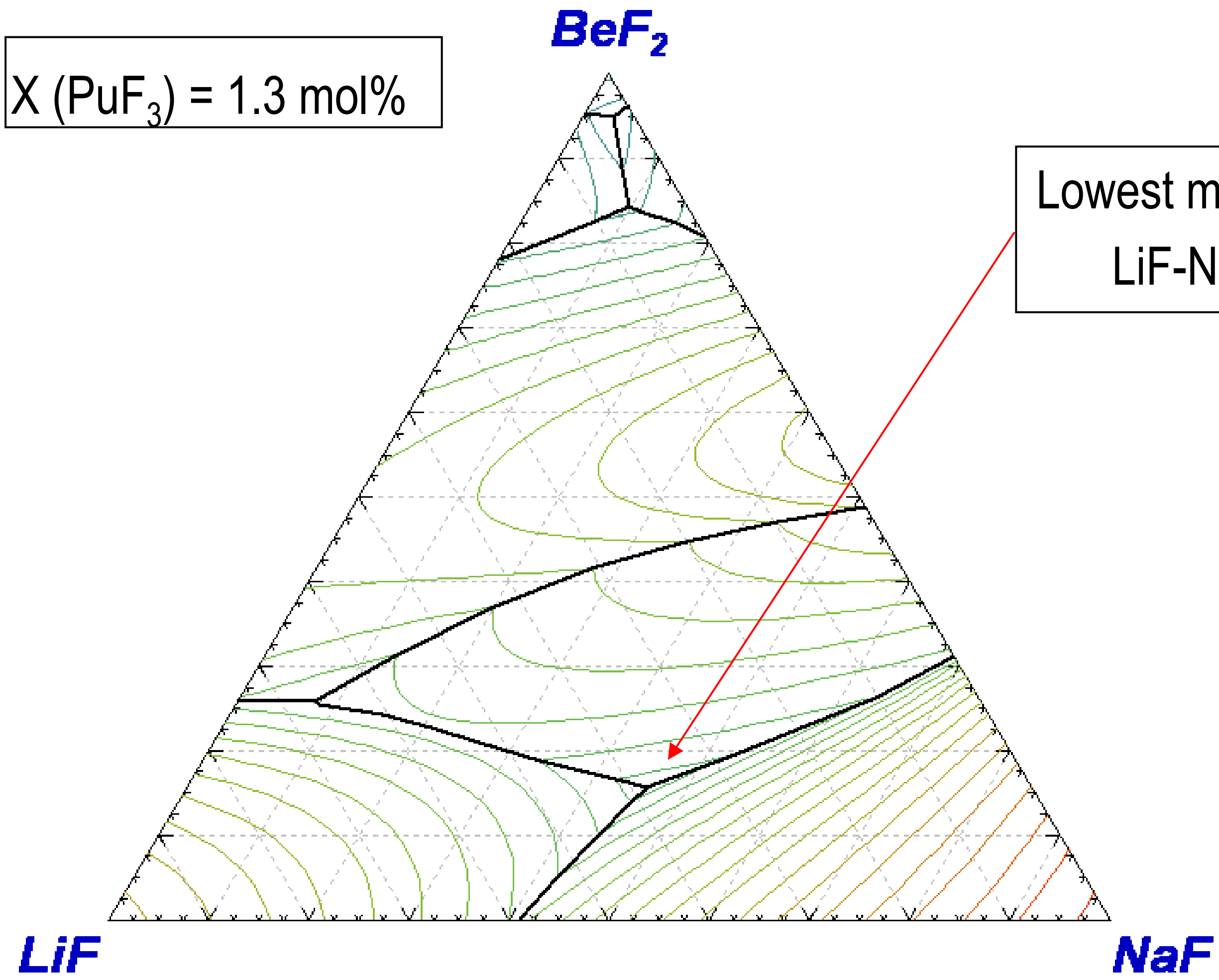
NaF – PuF_3



BeF_2 – PuF_3



X (PuF_3) = 1.3 mol%

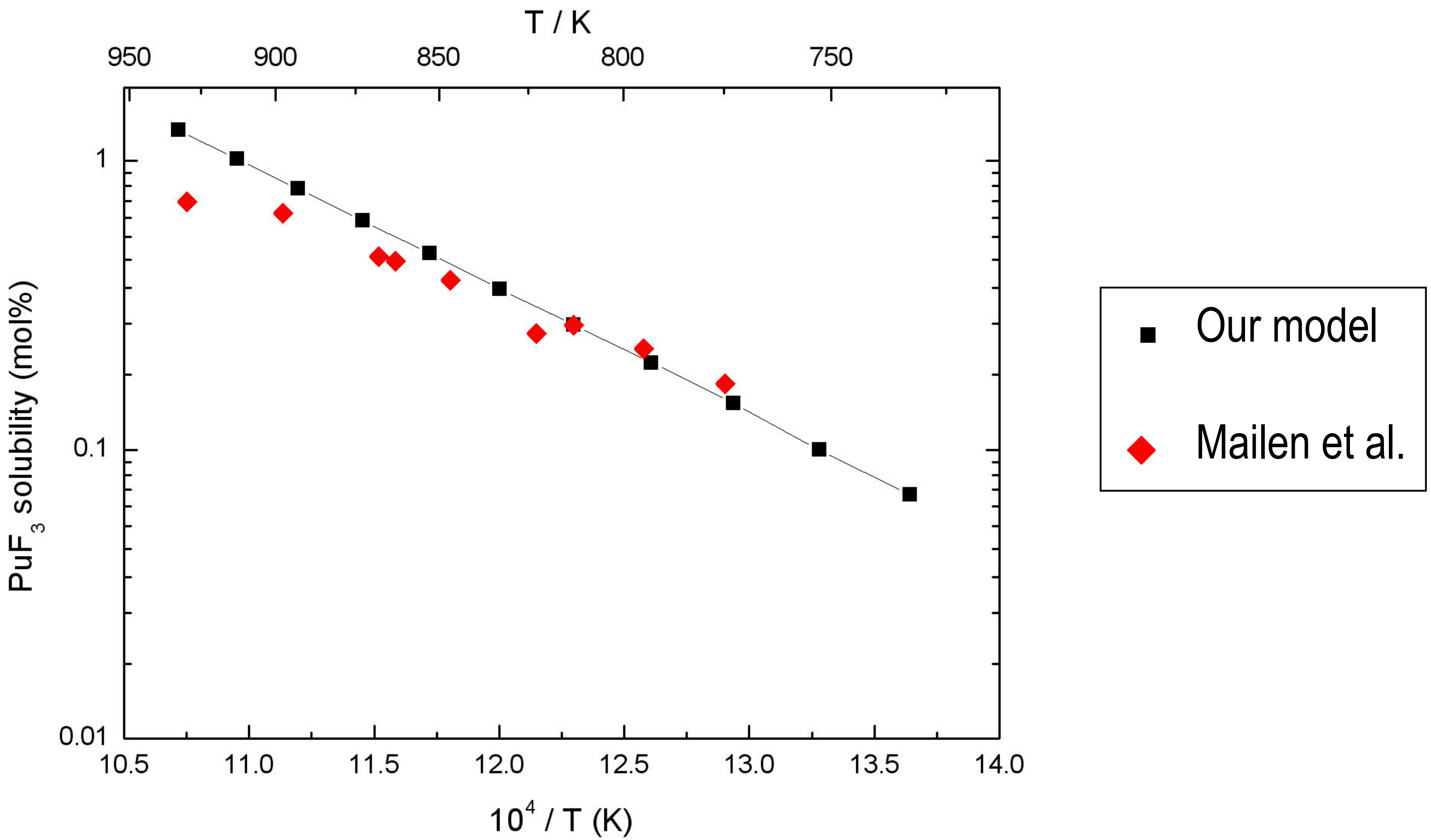


Lowest melting point at: T = 837 K

$LiF-NaF-BeF_2-PuF_3$ (37.9-45.2-15.6-1.3)

- PuF_3 addition has large influence on the melting behaviour
- Inlet temperature at least T=887K
- Relatively low content of BeF_2

Solubility of PuF_3 in $2LiF\text{-}BeF_2$



Summary & Conclusions

- ✓ Two databases for fluoride salts for Molten Salt Reactors have been compiled
- ✓ The Quasichemical model with quadruplet interactions proved to be very useful and versatile
- ✓ The QKTO model also gave reasonable results and is of more universal use as it can be used in other software packages also
- ✓ The models describe melting behaviour, actinide solubility and vapour pressure of the fuel salts well, but some dedicated experiments are needed, especially for plutonium salts