This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 661891

SAMOFAR Final Meeting

4 July 2019

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European Commission

Thermodynamic properties of MSFR fuel

by Ondrej Benes
on behalf of Alberto Tosolin

Initial materials

Properties	Techniques	Analysed systems
Phase equilibria	Encapsulation, DSC, XRD, CALPHAD	PuF_3-LiF ThF_4-PuF_3
Heat capacity	Laser welding, DSC, Drop calorimetry	solid and liquid ThF_4
Vaporiz. behaviour	KEMS	MSFR fuel options
Thermal conductivity	Laser welding, LFA, FEM, tomography	FLiNaK (validation)

Goal → Fill the gap affecting investigation of actinide fluorides!

Challenging issues

Well-established techniques + Adjustments & Improvements

Reliable safety-related properties of molten salts

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Synthesis

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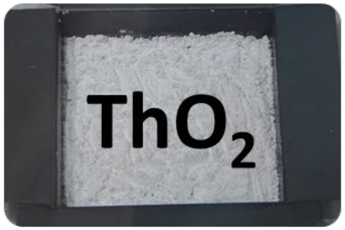
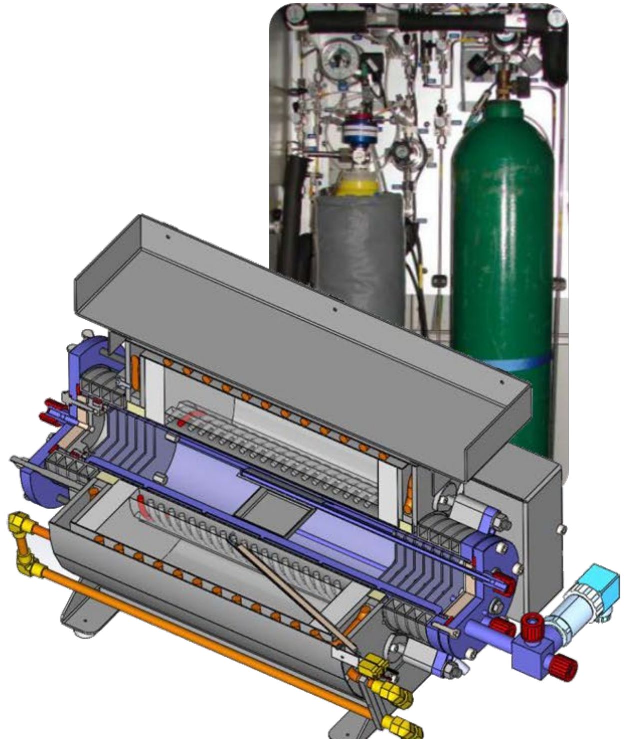
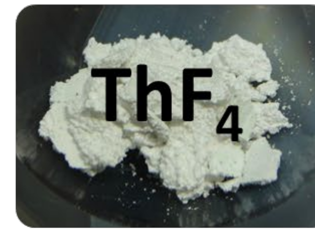
Synthesis & Purificaton of the Actinide fluorides







P. Souček, O. Beneš, A. Tosolin, R.J.M. Konings, *Chemistry of Molten Salt Reactor Fuel Salt Candidates*, Trans. Am. Nucl. Soc., 118 (2018) 114-117.

Phase Equilibria

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Phase diagrams knowledge

	LiF	ThF_4	UF_4	PuF_3
LiF		[59THO]	[58BAR]	[61BAR]
ThF_4	[13CAP]		[60WEA]	This work
UF_4	✗	✗		✗
PuF_3	This work	✗	✗	

First measurement

Second independent measurement

[59THO] R.E. Thoma et al., J. Phys. Chem. 63 (1959)

[58BAR] C.J. Barton et al., J. Am. Ceram. Soc. 41 (1958)

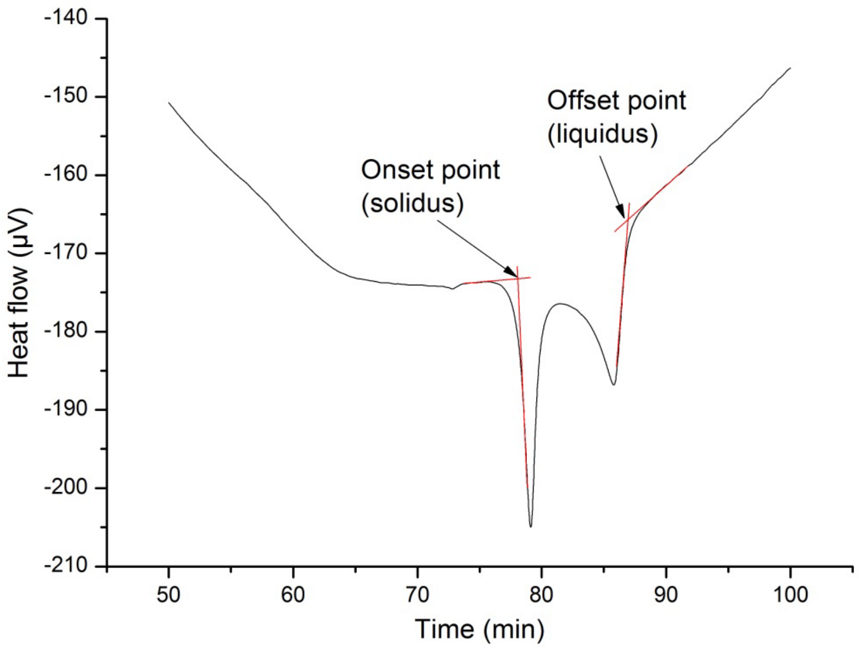
[61BAR] C.J. Barton and R.A. Strehlow, J. Inorg. Nucl. Chem. 18 (1961)

[60WEA] C.F. Weaver et al., J. Am. Ceram. Soc. 43 (1960)

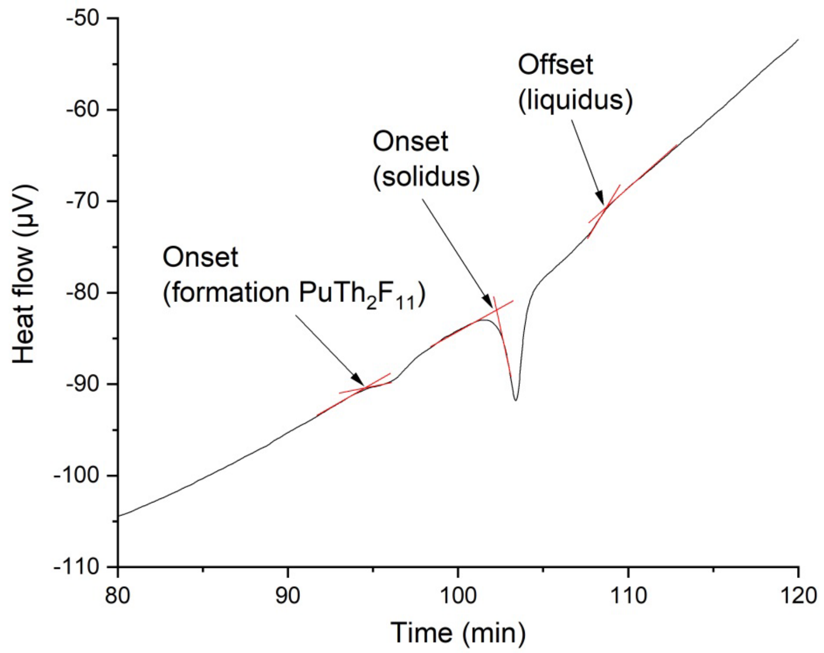
[13CAP] E. Capelli et al., J. Chem. Thermodyn. 58 (2013)

Phase diagram studies

LiF-PuF_3 (92.5-7.5 mol%)



ThF_4-PuF_3 (82-18 mol%)



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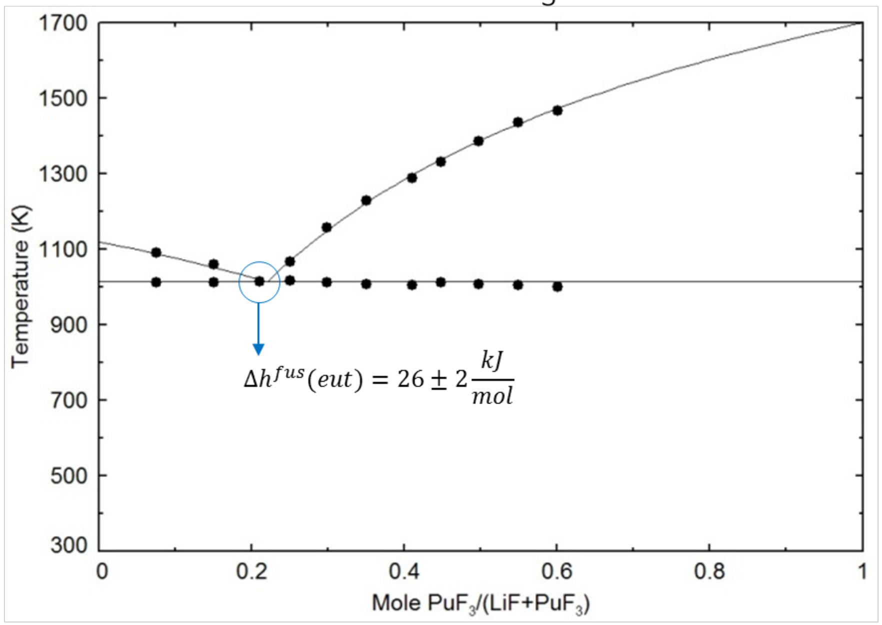
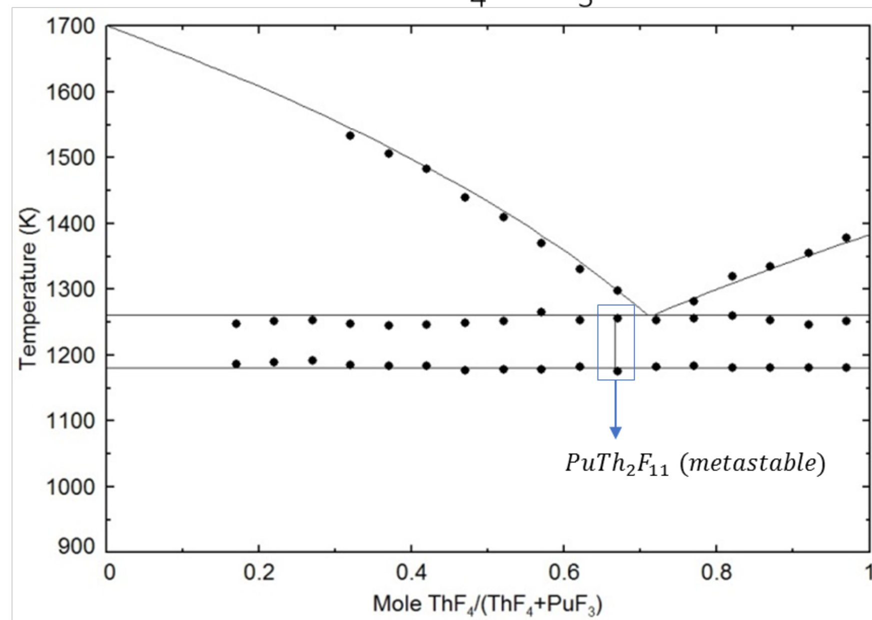
Phase diagrams assessed

LiF-PuF_3



A. Tosolin, P. Souček, O. Beneš, J.-F. Vigier, L. Luzzi, R.J.M. Konings, *Synthesis of plutonium trifluoride by hydro-fluorination and novel thermodynamic data for the PuF_3-LiF system*, J. Nucl. Mat. 503 (2018) 171-177.

ThF_4-PuF_3



A. Tosolin, S. Mastromarino, J.-F. Vigier, L. Luzzi, R.J.M. Konings, O. Beneš, *Phase transitions in the ThF_4-PuF_3 system*, in preparation.

Extension of JRCMSD

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Heat Capacity

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Heat capacity: Data for end–members

	LT	HT
LiF	[49CLU] [56CLU]	[54DOU] [56VOR] [73MAC]
ThF_4	[54LOH]	This work
UF_4	[48BRI] [55OSB] [60BUR]	[61KIN] [72DWO]
PuF_3	[74OSB]	✗

[49CLU] K. Clusius et al., Z. Naturforsch. 49 (1949)

[56CLU] K. Clusius and W. Eisenhauer, Z. Naturforsch. 2a (1956)

[54DOU] T. B. Douglas and J. L. Dever, J. Amer. Chem. Soc. 76 (1954)

[56VOR] N. K. Voskresenskaya et al., Izvest. Sect. Fiz. Khim. Anal. 27

[73MAC] A. Macleod, J. Chem. Soc. Faraday Trans I 69 (1973)

[54LOH] H. R. Lohr et al., Jr. J. Am. Chem. Soc. 76 (1954)

[48BRI] F. G. Brickwedde et al., J. Chem. Phys. 16 (1948)

[55OSB] D. W. Osborne et al., J. Am. Chem. Soc. 77 (1955)

[60BUR] J. H. Burns et al., Jr. J. Chem. Phys. 33 (1960)

[61KIN] E. G. King and A. U. Christensen, BMI Report 5709, (1961)

[72DWO] A. S. Dworkin. J. Inorg. Nucl. Chem. 34 (1972)

[74OSB] D. W. Osborne, et al., J. Chem. Phys. 61 (1974) 1463.

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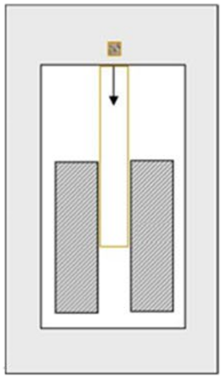
Techniques

Drop calorimetry



A_{tot} A_{ref}

tot → crucible + sample
ref → ref material

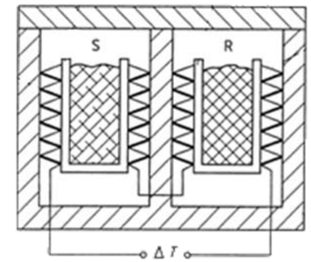
$$\Delta H_{sam} = \frac{A_{sam}}{A_{ref}} \Delta H_{ref} - \Delta H_{cruc}$$

→ $c_p = \left(\frac{\partial h}{\partial T}\right)_p$

Drop sensor ← → DSC sensor

Setaram MHTC 96

Differential Scanning Calorimetry



3 steps method:
A_{sam} A_{bla} A_{ref}

tot → crucible + sample
bla → empty crucible
ref → crucible + ref material

$$C_{p,sam} = \frac{n_{ref}}{n_{sam}} C_{p,ref} \frac{(A_{tot} - A_{bla})}{(A_{ref} - A_{bla})}$$

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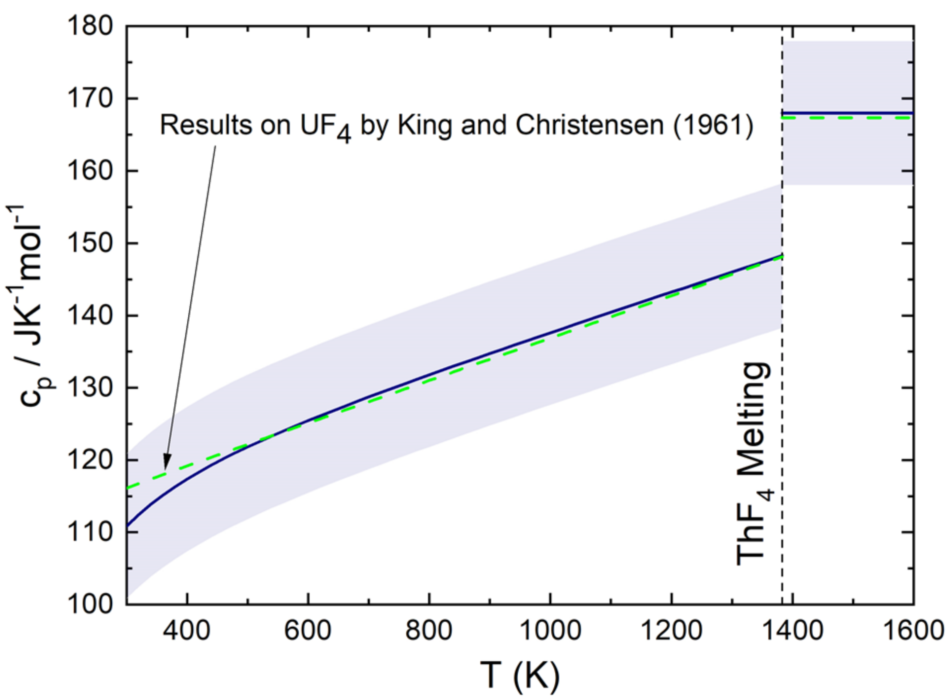
Results: Heat capacity



E.G. King and A.U. Christensen, US Bereau of Mines, Technical Report BMI Report 5709 (1961)

Empirical formula for liquid fluorides by Khokhlov et al., J. Fluor. Chem., 130 (1), (2009)

$$170 \pm 15 \frac{J}{K \cdot mol}$$

Excellent agreement!

A. Tosolin, E. Capelli, R.J.M Konings, L. Luzzi, O. Beneš, *Heat capacity of solid and liquid thorium tetrafluoride*, Submitted to J. Chem. Eng. Data.

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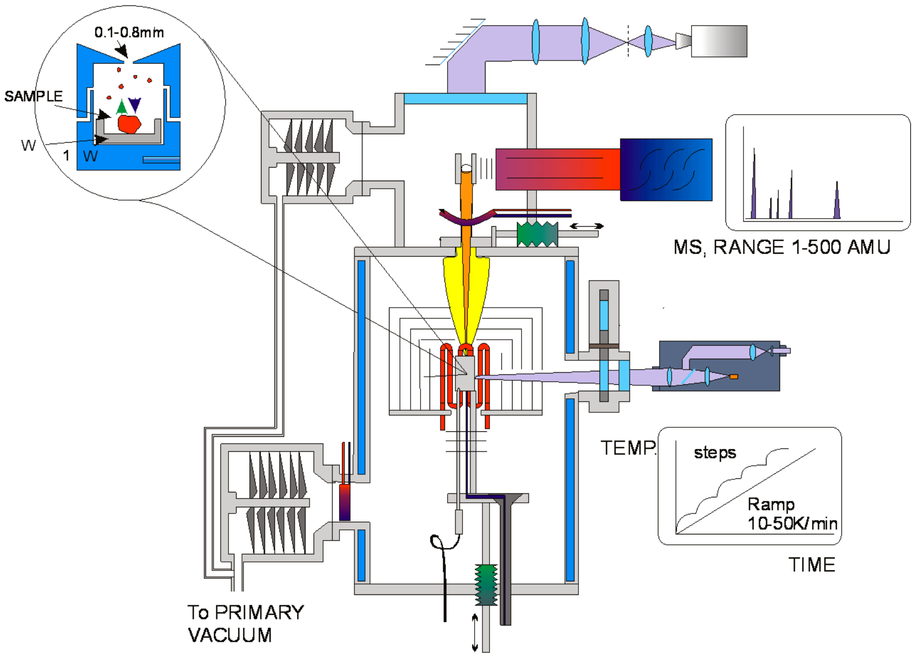
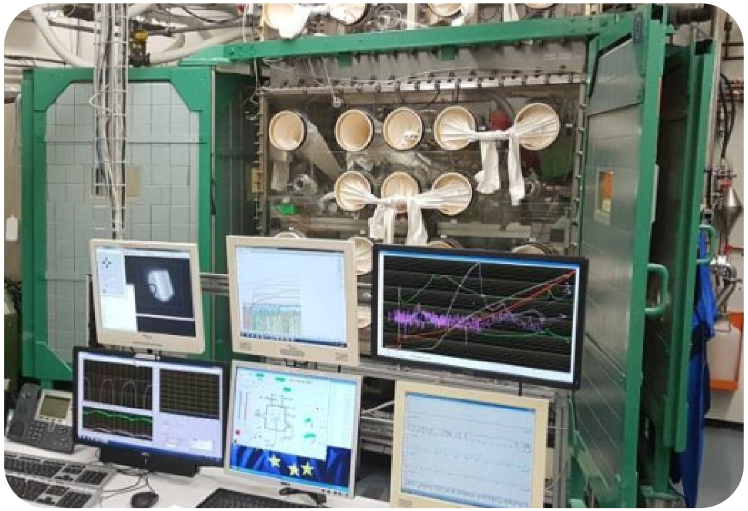
Vaporization behaviour

LiF	✓	✓	**This work** LiF–ThF_4–UF_4 (77.5–20.0–2.5)*	**This work** LiF–ThF_4–UF_4–PuF_3 (77.5–6.6–12.3–3.6 mol%)*
ThF_4	✓	✓	**This work** LiF–ThF_4–UF_4 (77.5–20.0–2.5)*	**This work** LiF–ThF_4–UF_4–PuF_3 (77.5–6.6–12.3–3.6 mol%)*
UF_4	✓		**This work** LiF–ThF_4–UF_4 (77.5–20.0–2.5)*	**This work** LiF–ThF_4–UF_4–PuF_3 (77.5–6.6–12.3–3.6 mol%)*
PuF_3	✓			**This work** LiF–ThF_4–UF_4–PuF_3 (77.5–6.6–12.3–3.6 mol%)*

* Fuel options selected within SAMOFAR European Project

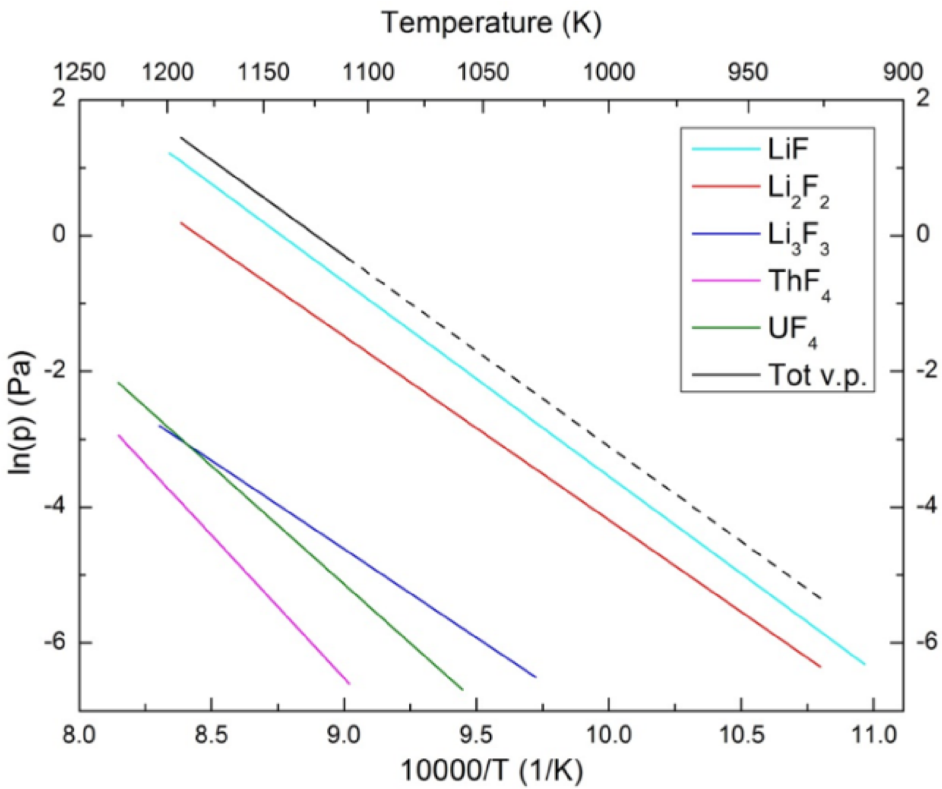
Knudsen Effusion Mass Spectrometry





Colle et al., ECS Transactions, 46 (1) 23-38 (2013)

Results: LiF-ThF_4-UF_4 system



LiF-ThF_4-UF_4
(77.5-20.0-2.5 mol%)

T_m (by DSC) = 828 ± 3 K

T_b = 2019 ± 10 K

v.p. (1000 K) = 0.045 Pa ± 50%

A. Tosolin, O. Beneš, J.-Y. Colle, P. Souček, L. Luzzi, R.J.M. Konings, *Vaporization behaviour of the Molten Salt Fast Reactor fuel: The LiF-ThF_4-UF_4 system*, J. Nucl. Mat. 508 (2018) 319-328.

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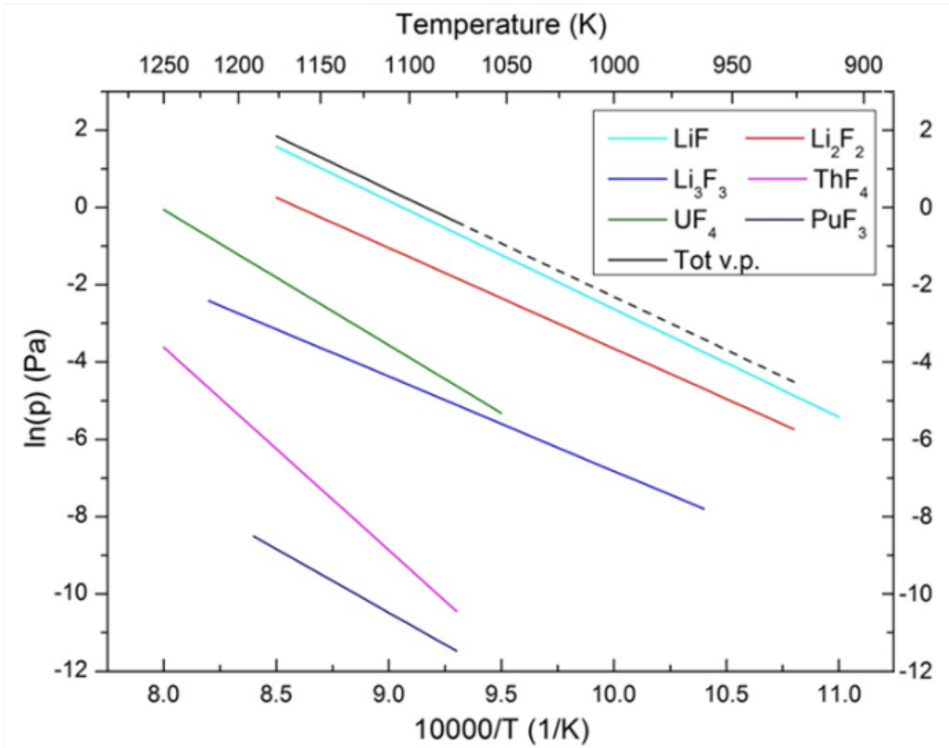
Results: $LiF-ThF_4-UF_4-PuF_3$ system



$LiF-ThF_4-UF_4-PuF_3$
(77.5–6.6–12.3–3.6 mol%)

T_m (by DSC) = 893 ± 5 K

T_b = 1908 ± 10 K

v.p. (1000 K) = 0.099 Pa ± 50%

A. Tosolin, J.-Y. Colle, P. Souček, S. Mastromarino, L. Luzzi, R.J.M. Konings, O. Beneš, *Vaporization behaviour of a PuF_3 containing fuel mixture for the Molten Salt Fast Reactor*, submitted to J. Nucl. Mat.

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Summary

- **Synthesis of PuF_3**
  - Definition of a method for PuF_3 production on a gram scale
- **Phase equilibria**
  - Second independent study on PuF_3-LiF and first results on ThF_4-PuF_3 phase diagram
- **Heat capacity**
  - First experimental results on high temperature heat capacity of ThF_4
  - Improvements in coupling drop calorimetry and DSC with encapsulated samples
- **Vaporization behaviour**
  - First measurements partial vapour pressures MSFR fuel options
- **Thermal conductivity**
  - Development of a novel technique and validation with FLiNaK molten salt