



20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
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BLED - SLOVENIA

THE $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ SYSTEM: EXPERIMENTAL STUDY AND THERMODYNAMIC MODELLING

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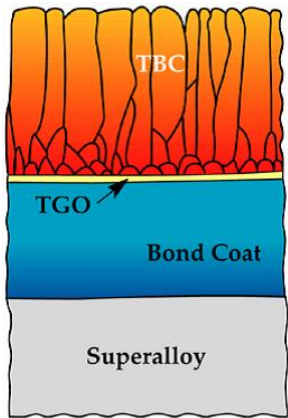
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Seit 1765.

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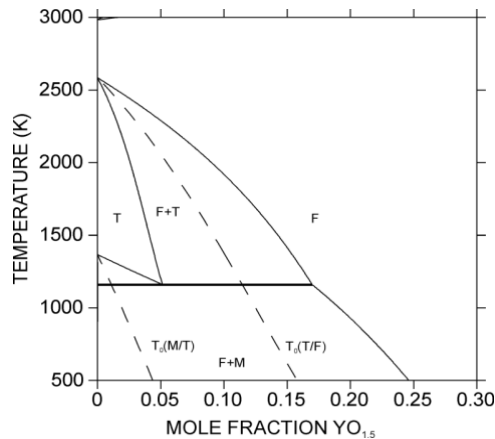
Motivation



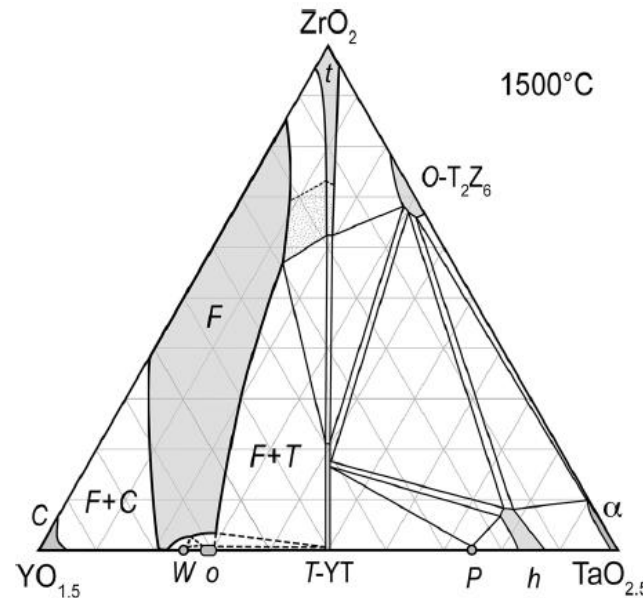
The aim of the project is thermodynamic database development for the $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system for thermal barrier coating application.

1. The $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ is sub-system of the system $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$.
2. HfO_2 is always present in ZrO_2 materials as impurity
3. HfO_2 is stable up to higher melting temperature than ZrO_2 and it has lower thermal expansion than ZrO_2 .
4. Cubic HfO_2 has higher ionic conductivity than ZrO_2 that makes it promising materials for solid oxide fuel cell application and as oxygen sensors and other applications

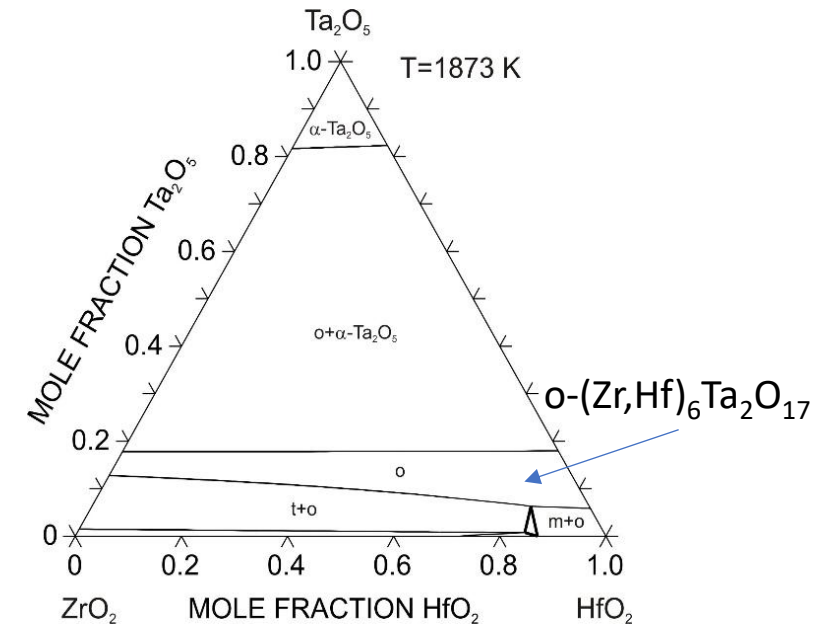
Scheme of TBC system



Part of the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ phase diagram together with T^0 -lines for F-T and T-M diffusion-less transformations

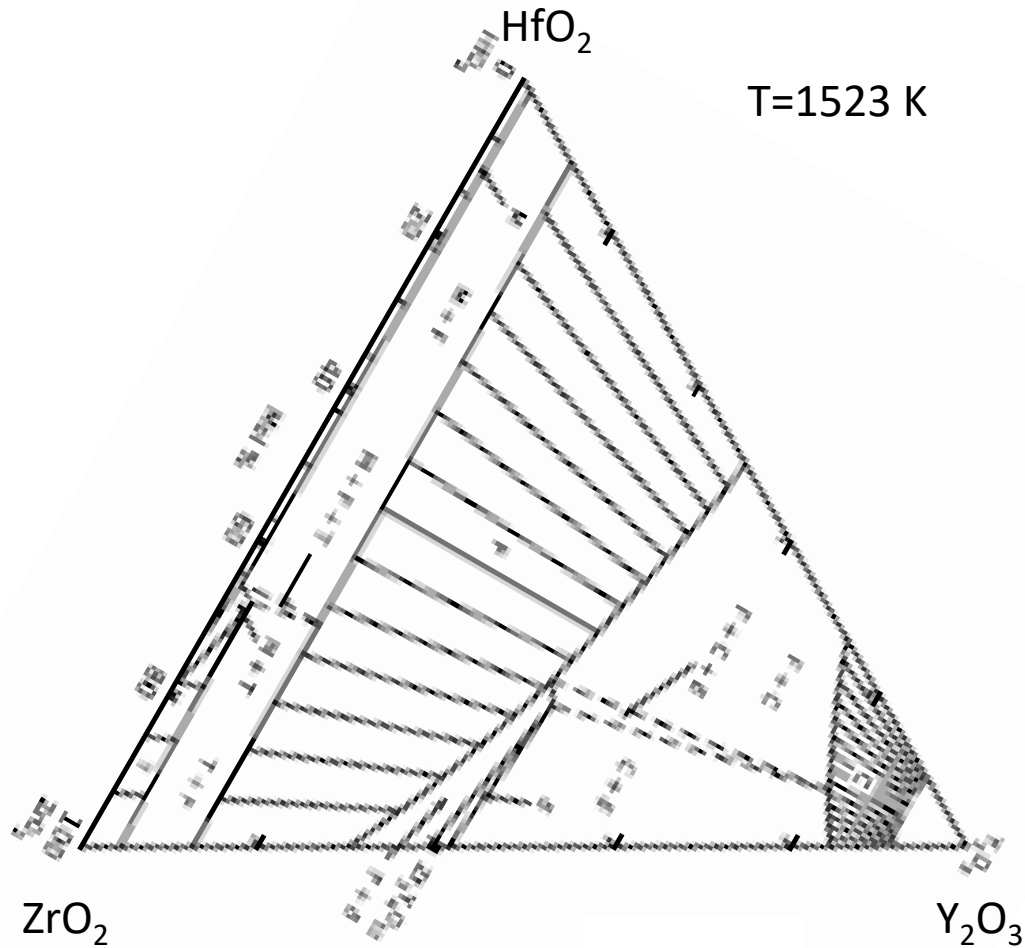


Phase diagram of the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system according to Macauley et al (2017)

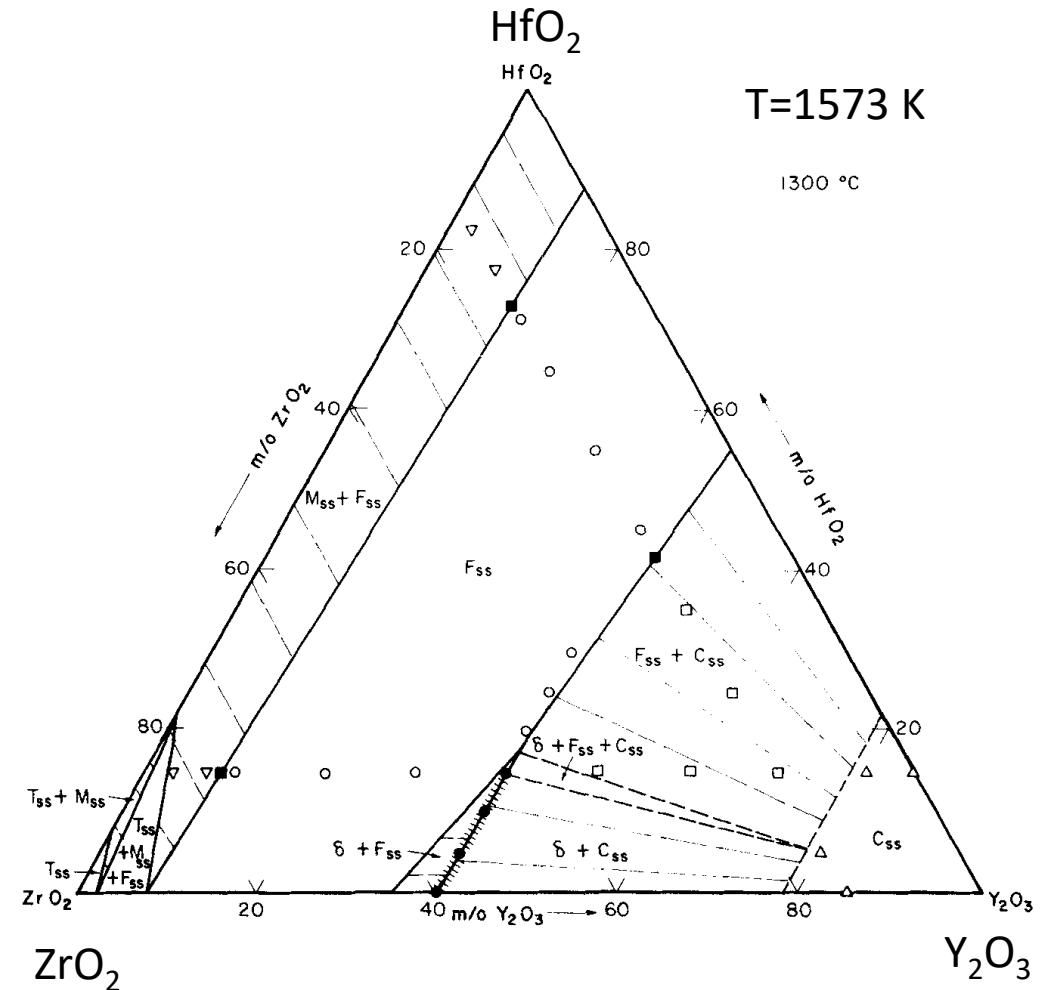


Phase diagram of the $\text{ZrO}_2\text{-HfO}_2\text{-Ta}_2\text{O}_5$ system according to Löffler and Fabrichnaya (2025)

Review of literature data

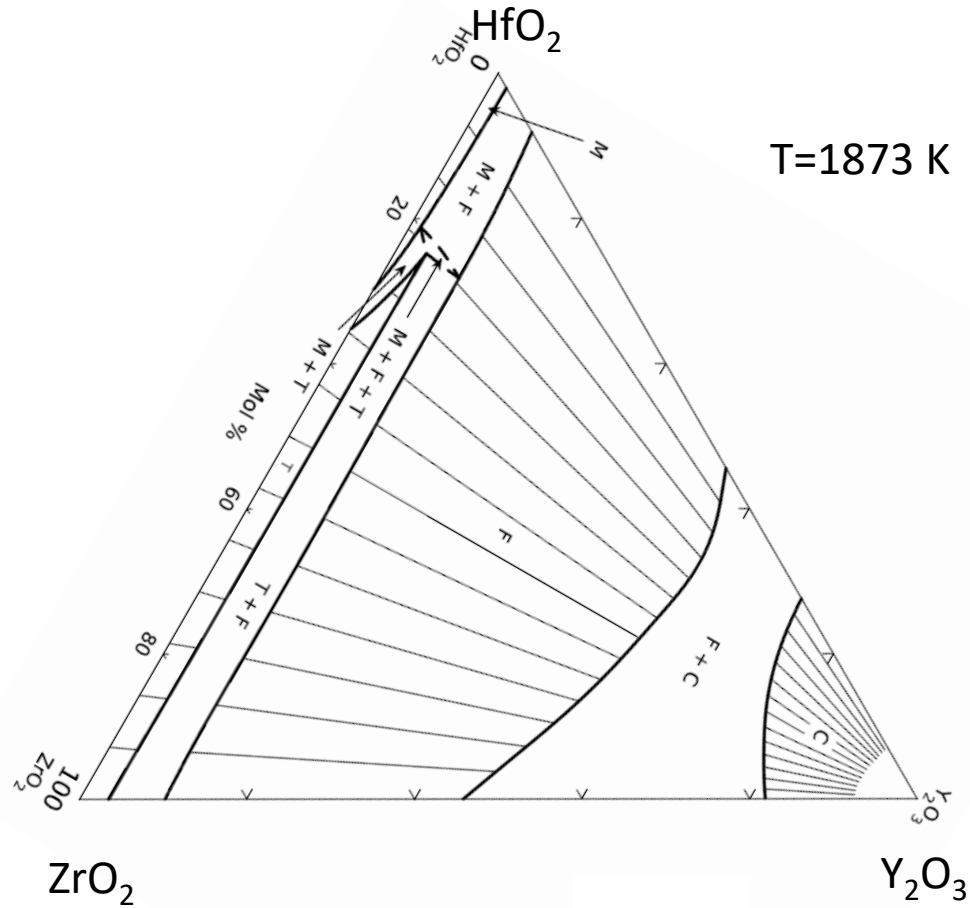


Isothermal section at 1523 K by Obolonchik et al. [1991Obo]

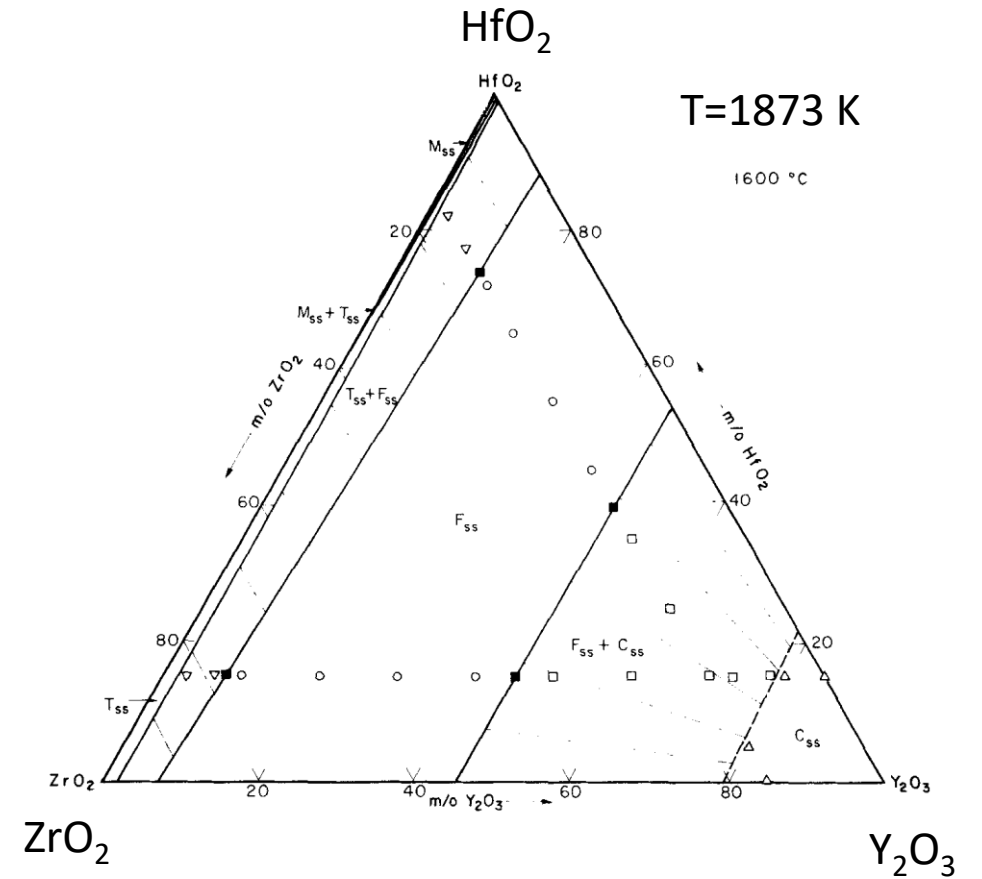


Isothermal section at 1573 K by Trubelja and Stubican [1988Tru]

Review of literature data

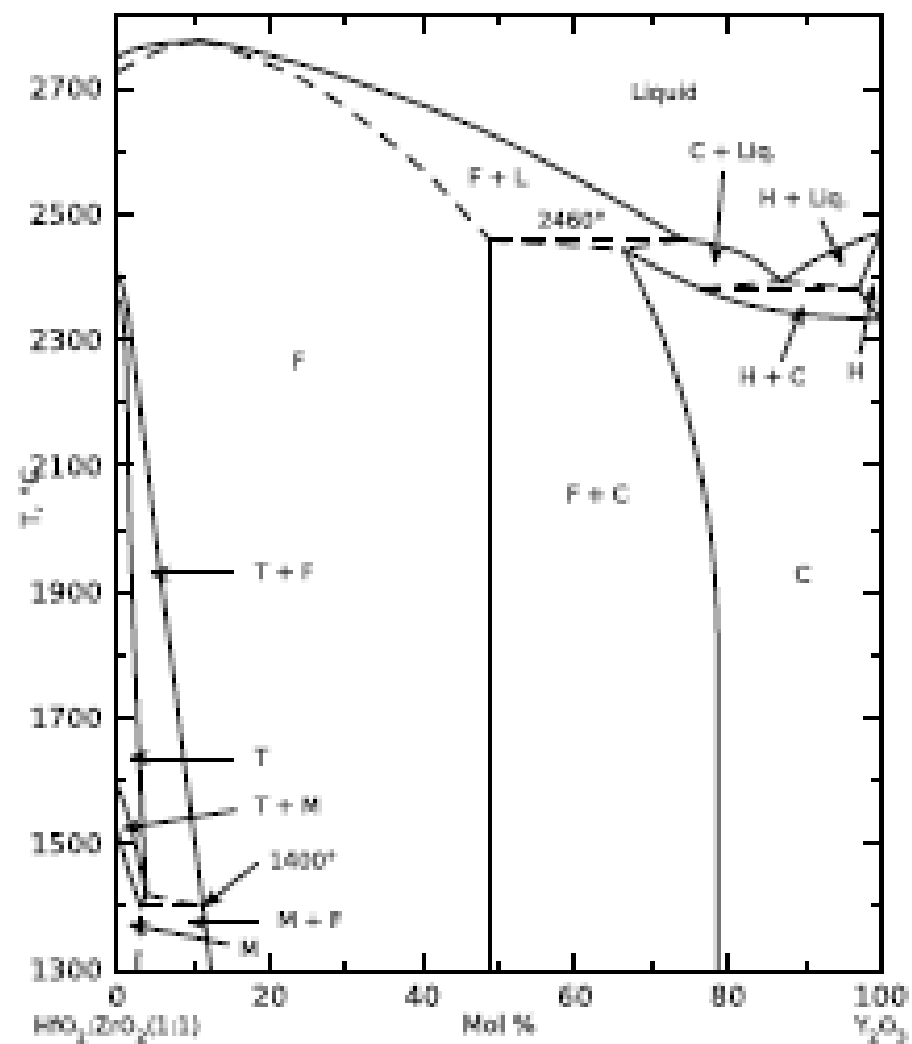


Isothermal section at 1873 K [1991Obo]

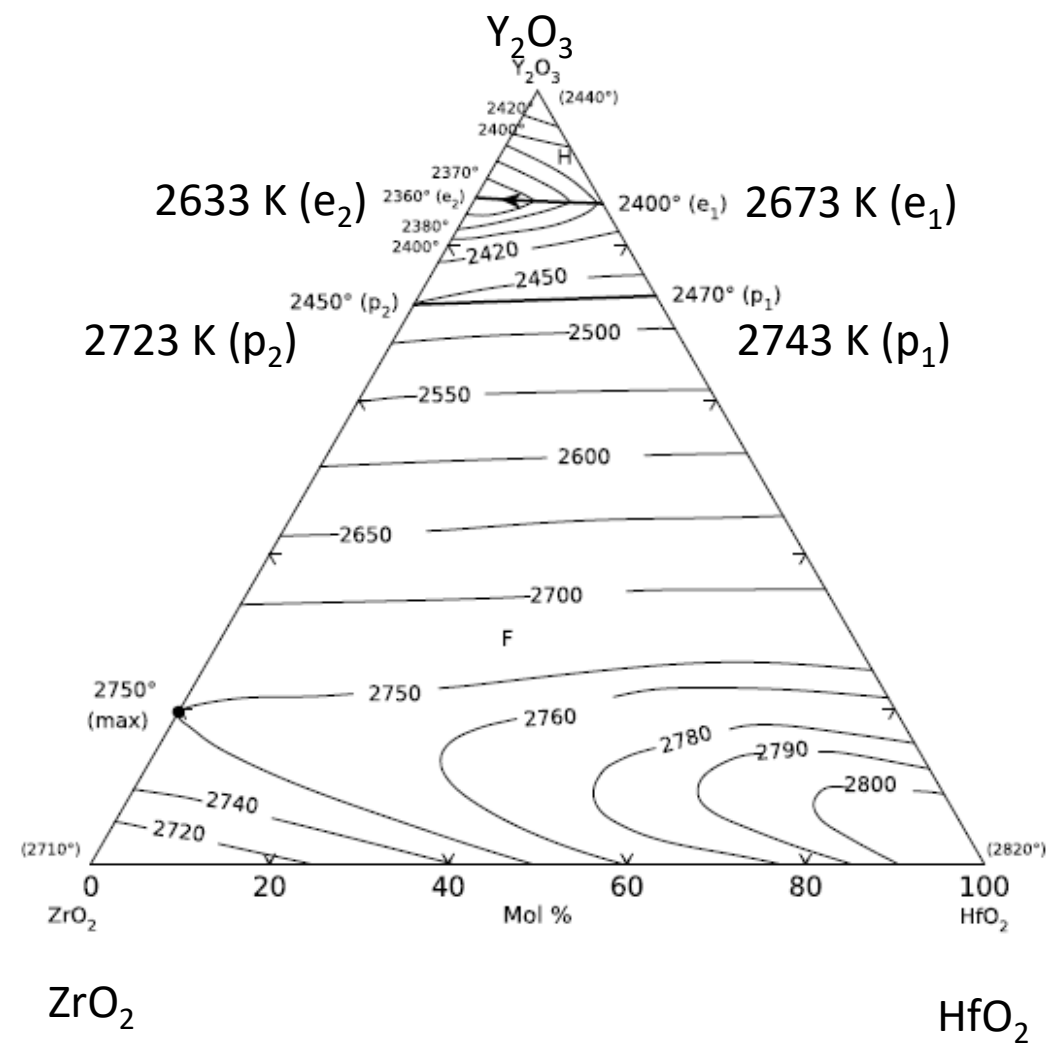


Isothermal section at 1873 K [1988Tru]

Review of literature data



Vertical section $(\text{Hf}_{0.5}\text{Zr}_{0.5})\text{O}_2$ - Y_2O_3 [1991Obo]



Liquidus surface according to [1987She]

The aims of this study

1. To synthesize samples of the $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ system and characterize them using XRD and SEM/EDX;
2. To measure heat capacity of $\delta\text{-Y}_4\text{Zr}_3\text{O}_{12}$ using DSC;
3. To re-assess thermodynamic parameters of $\delta\text{-Y}_4\text{Zr}_3\text{O}_{12}$ phase using new data on heat capacity as well as available experimental phase equilibrium data and calorimetric measurements;
4. To re-assess thermodynamic data for the $\text{HfO}_2\text{-Y}_2\text{O}_3$ system using new thermodynamic data for the HfO_2 and Y_2O_3 polymorphs;
5. To combine thermodynamic data for binary systems into the $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ system and compare calculated results with literature data and own experimental data.

Sample preparation and characterization

Precursor materials:

$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ dissolved in H_2O
 HfCl_4 dissolved in $\text{C}_2\text{H}_5\text{OH}$

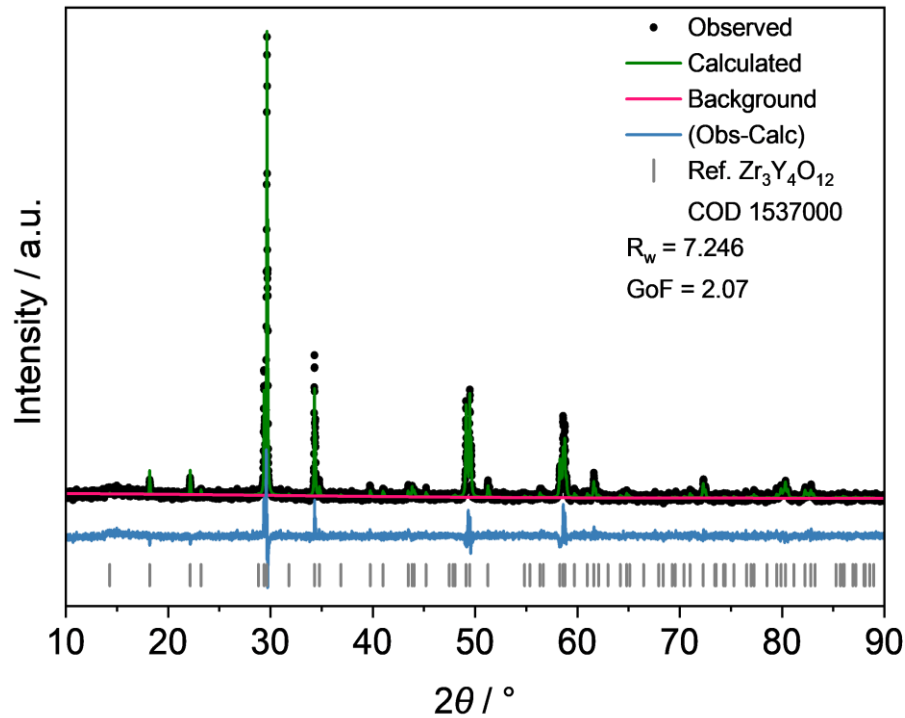
Co-precipitation in NH_3OH pH=10

Washing, drying, calcination at 1073 K

Heat treatment at 1573 K for 2160 h

Characterization : XRD, SEM/EDX
DSC (Cp measurements)

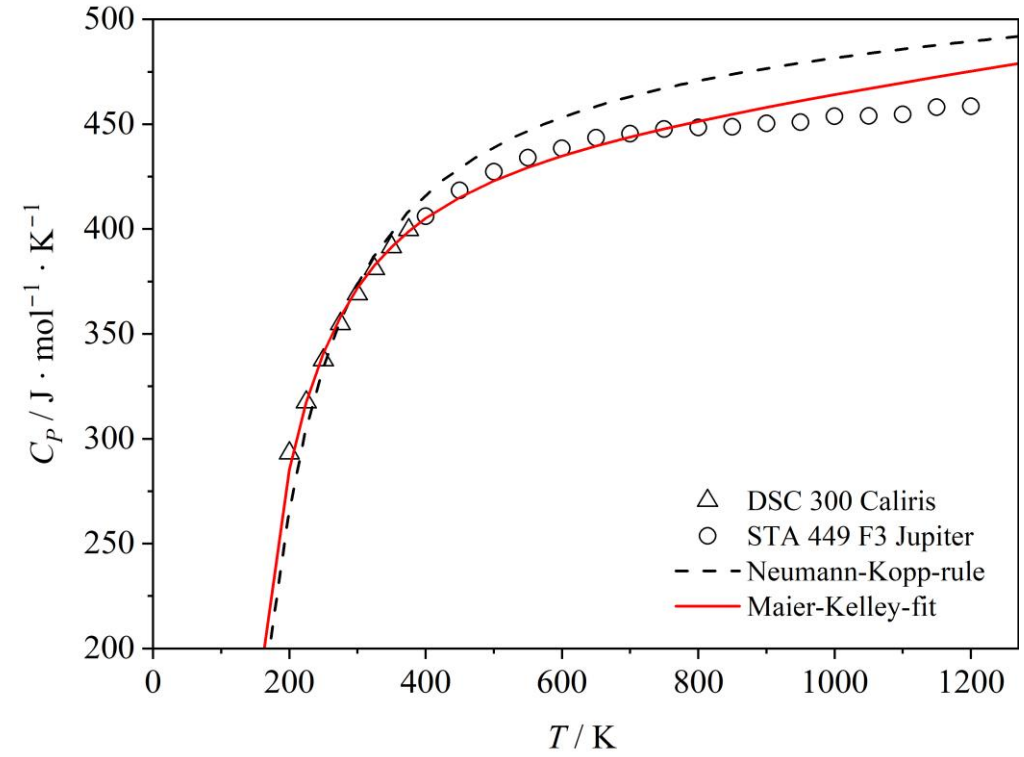
Heat capacity measurements $\delta\text{-Y}_4\text{Zr}_3\text{O}_{12}$



XRD pattern for sample $\delta\text{-Y}_4\text{Zr}_3\text{O}_{12}$

The results of heat capacity measurements using DSC compared with calculation using Neumann-Kopp rule and fitting using Maier – Kelley equation

Table presents calculated enthalpy increment compared with experimental data [2003Lee]

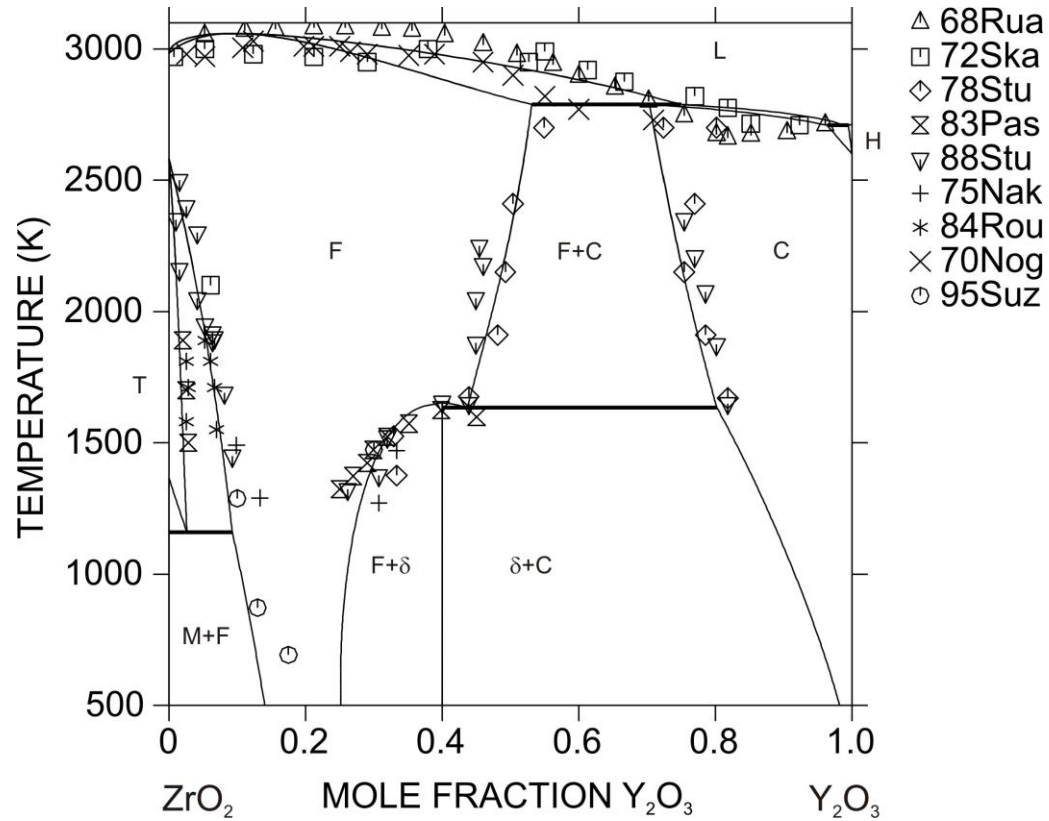


$$C_p(T) = 422.97997 + 0.04692 \cdot T - 5873307.175 \cdot T^{-2}$$

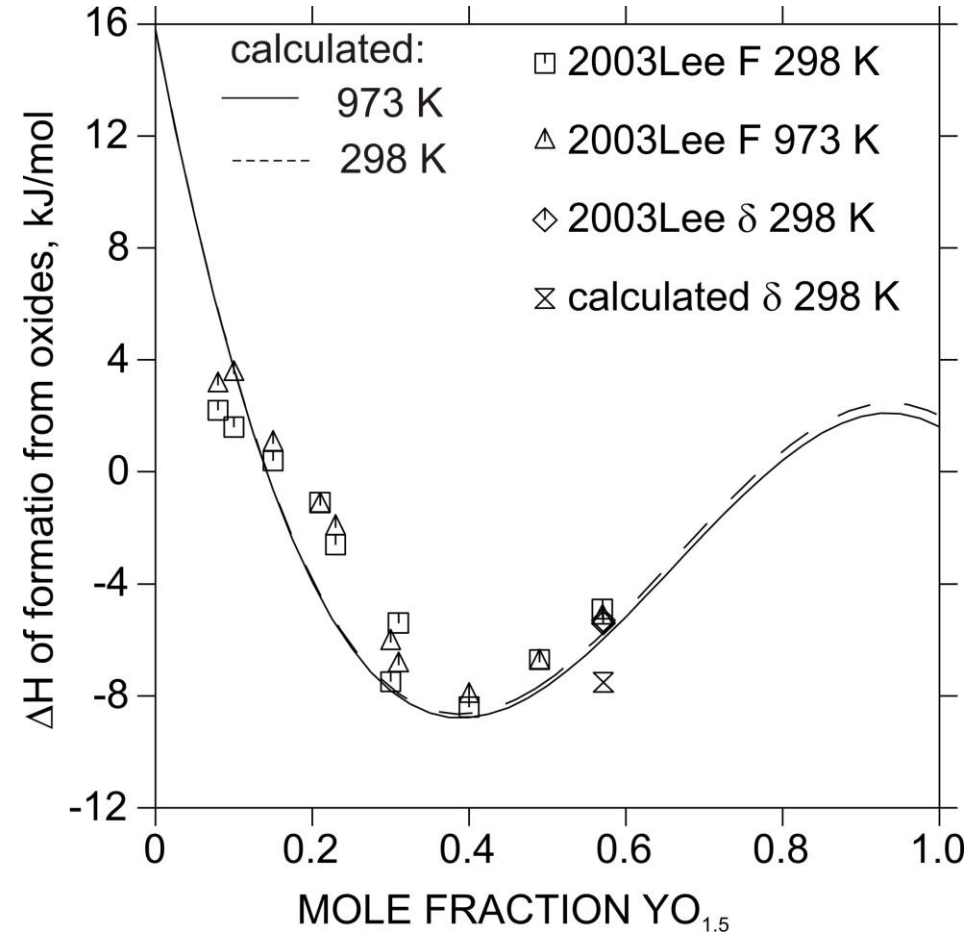
Heat content, kJ/mol	This work	[2003Lee]
$H_{298.15}^{973.15}$	41.711	41.44
$H_{298.15}^{1073.15}$	48.358	46.93
$H_{298.15}^{1473.15}$	75.73	73.00
$H_{298.15}^{1673.15}$	89.86	85.95

Thermodynamic description of the ZrO₂-Y₂O₃ system

$$G(\text{Zr}_3\text{Y}_4\text{O}_{12}) = -7367795 + 2488.83 \cdot T - 422.97997 \cdot T \cdot \ln(T) - 0.02346 \cdot T^2 + 2936653.587/T$$



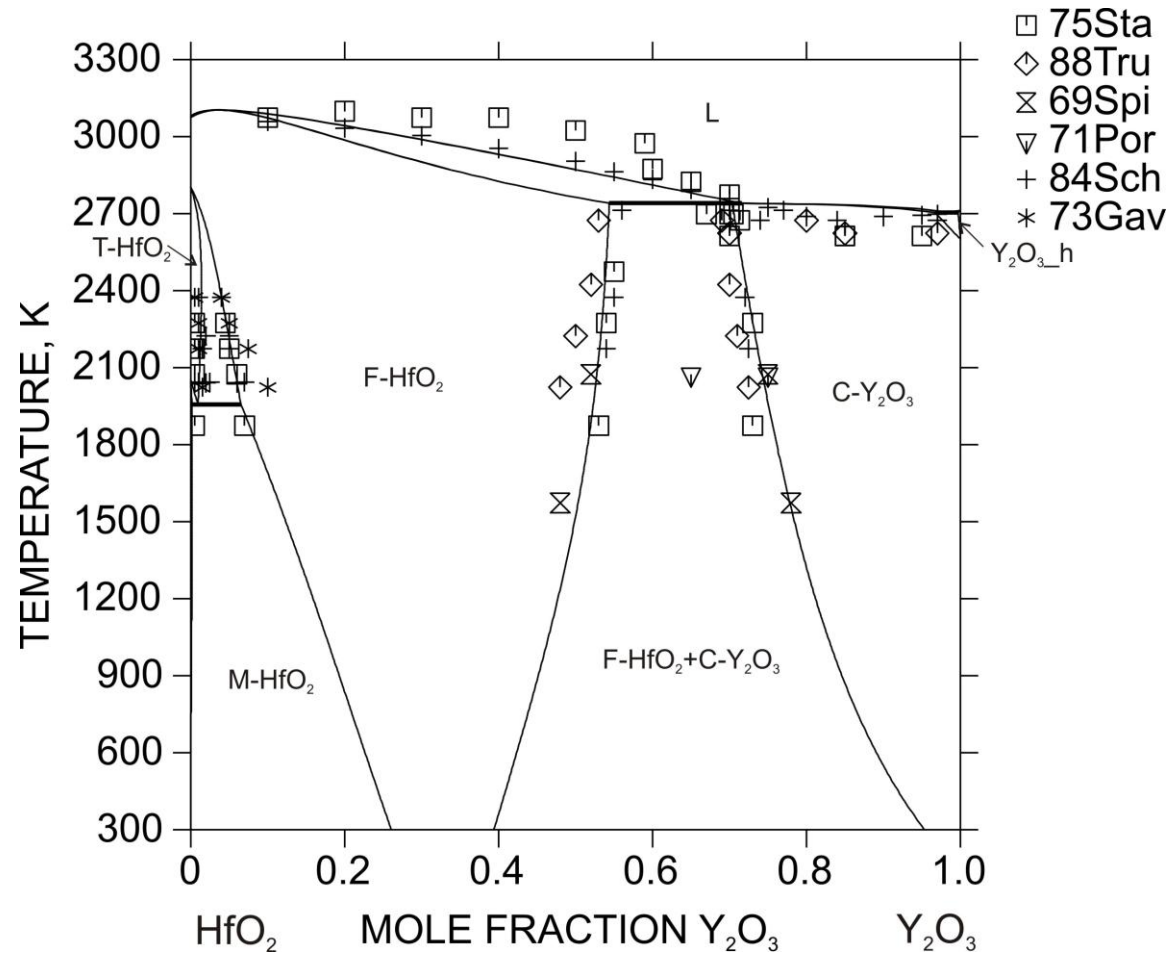
Calculated phase diagram of the ZrO₂-Y₂O₃ system using new Gibbs energy for δ-phase



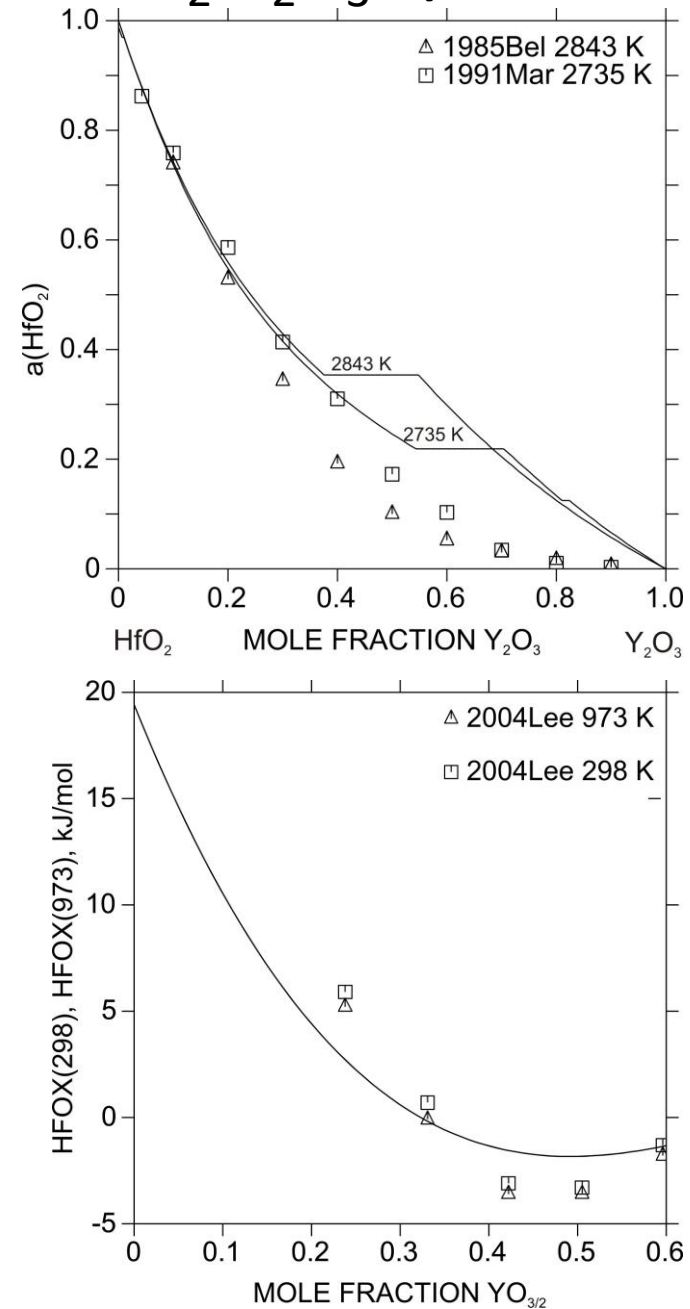
Enthalpy of formation of oxides of fluorite solid solution and δ-phase

$\Delta H_{298.15}^{0\text{oxide}}(\delta\text{-Zr}_4\text{Y}_3\text{O}_{12})$	-7.517 kJ/mol	-5.4 kJ/mol [2003Lee]
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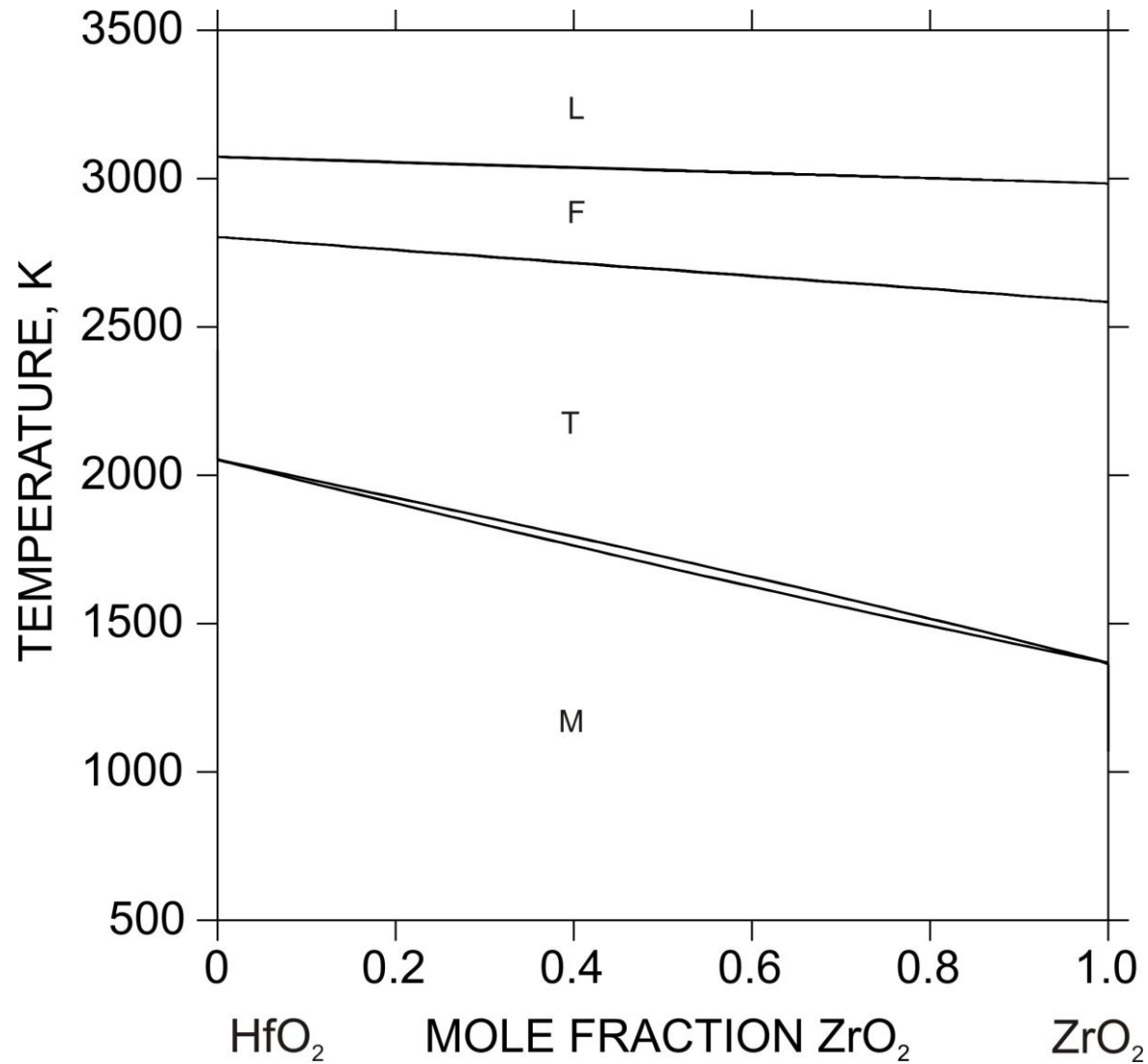
Thermodynamic description of the $\text{HfO}_2\text{-Y}_2\text{O}_3$ system



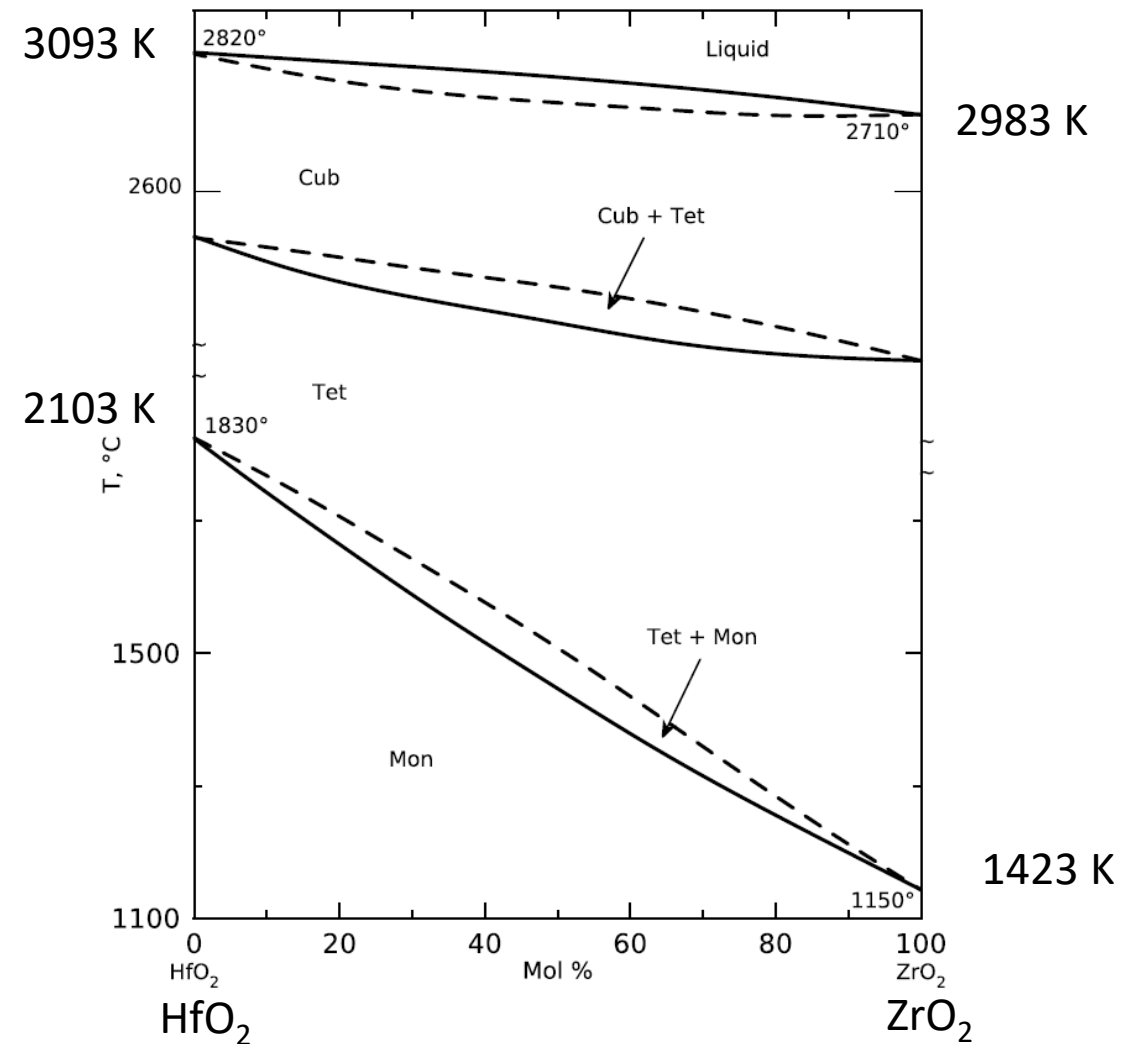
Calculated phase diagram and thermodynamic properties of fluorite phase compared with experimental results



Thermodynamic description of the $\text{ZrO}_2\text{-HfO}_2$ system

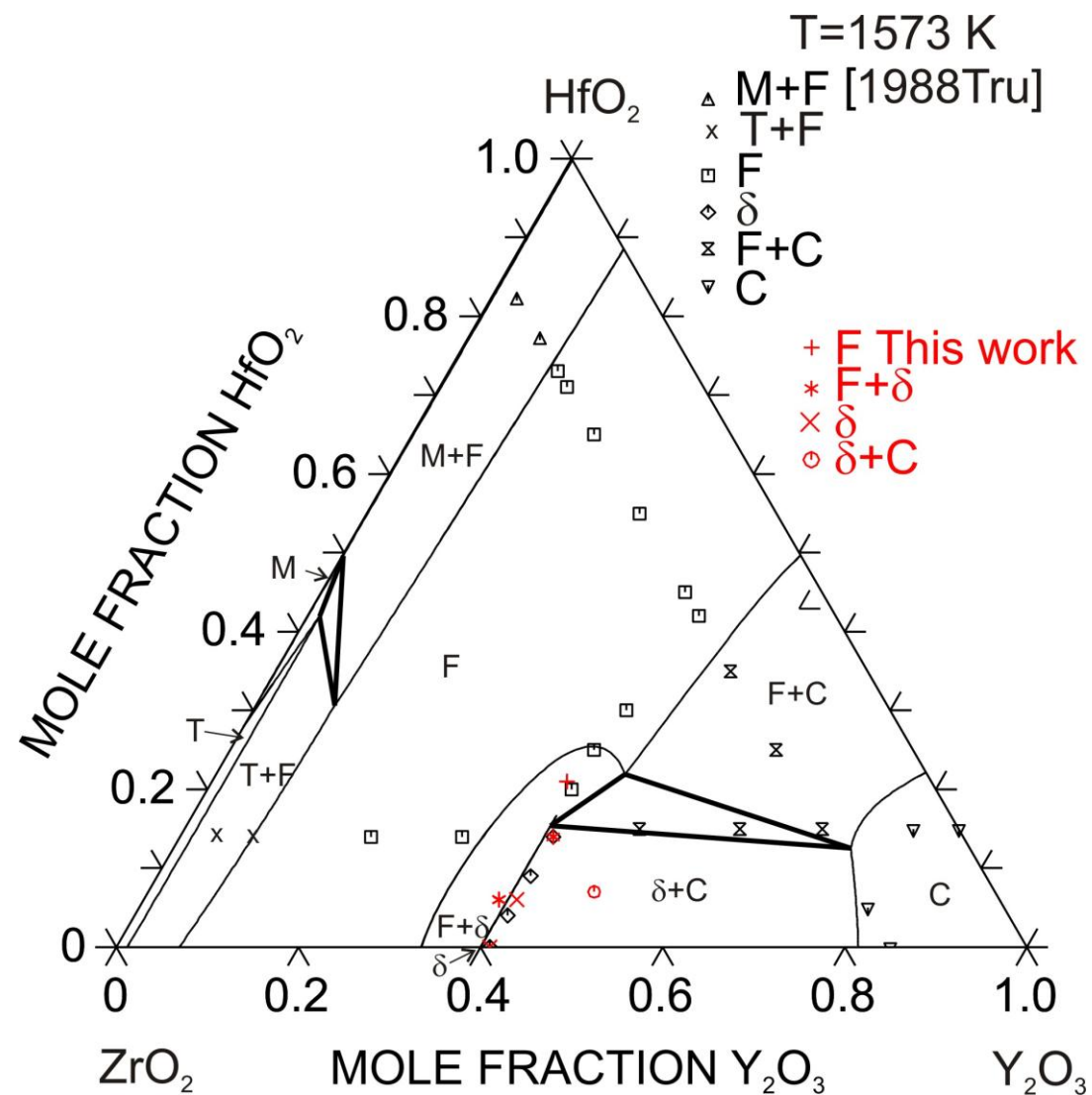
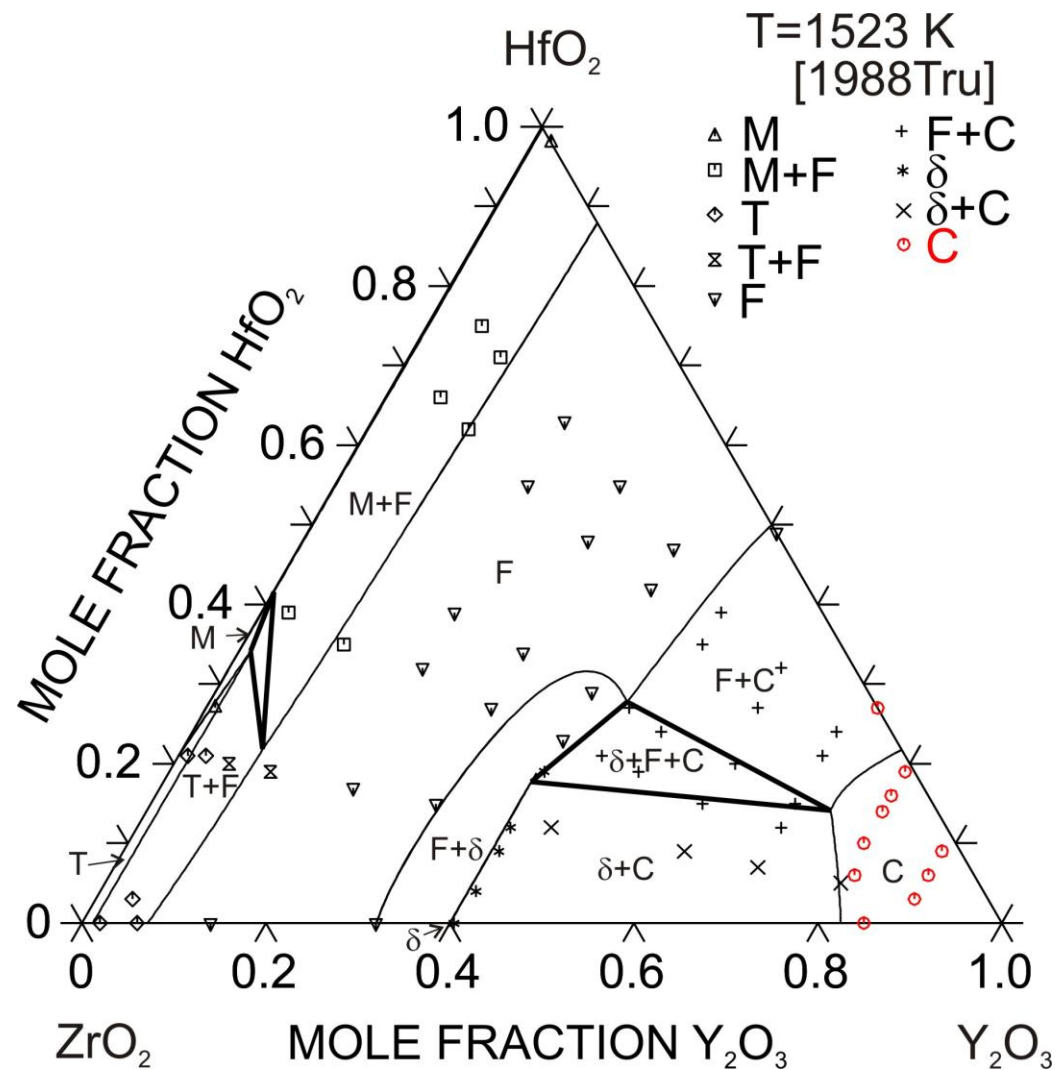


Calculated phase diagram using data of Wang et al. [2006Wan] for pure ZrO_2 and HfO_2 and ideal model for solutions

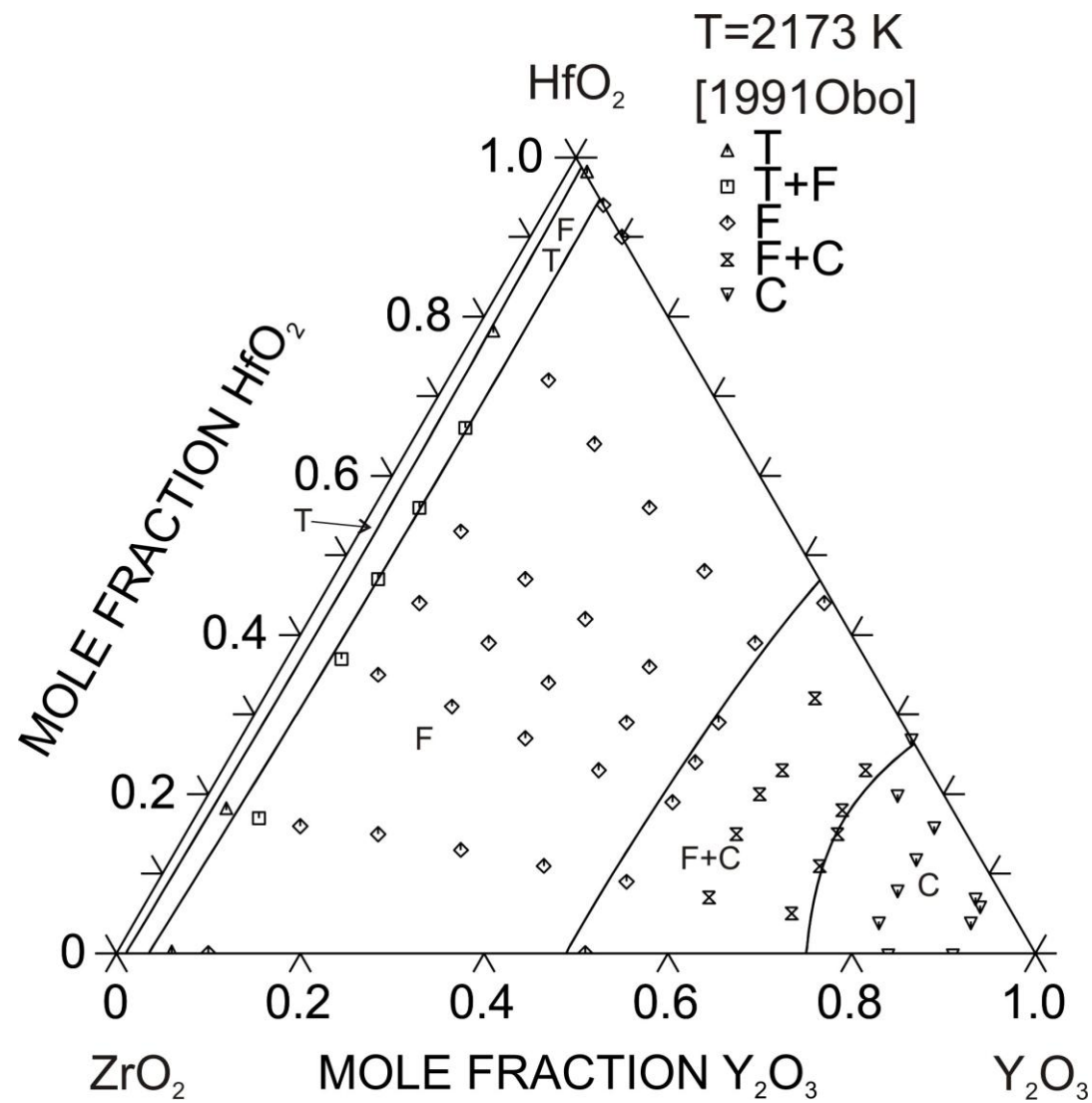
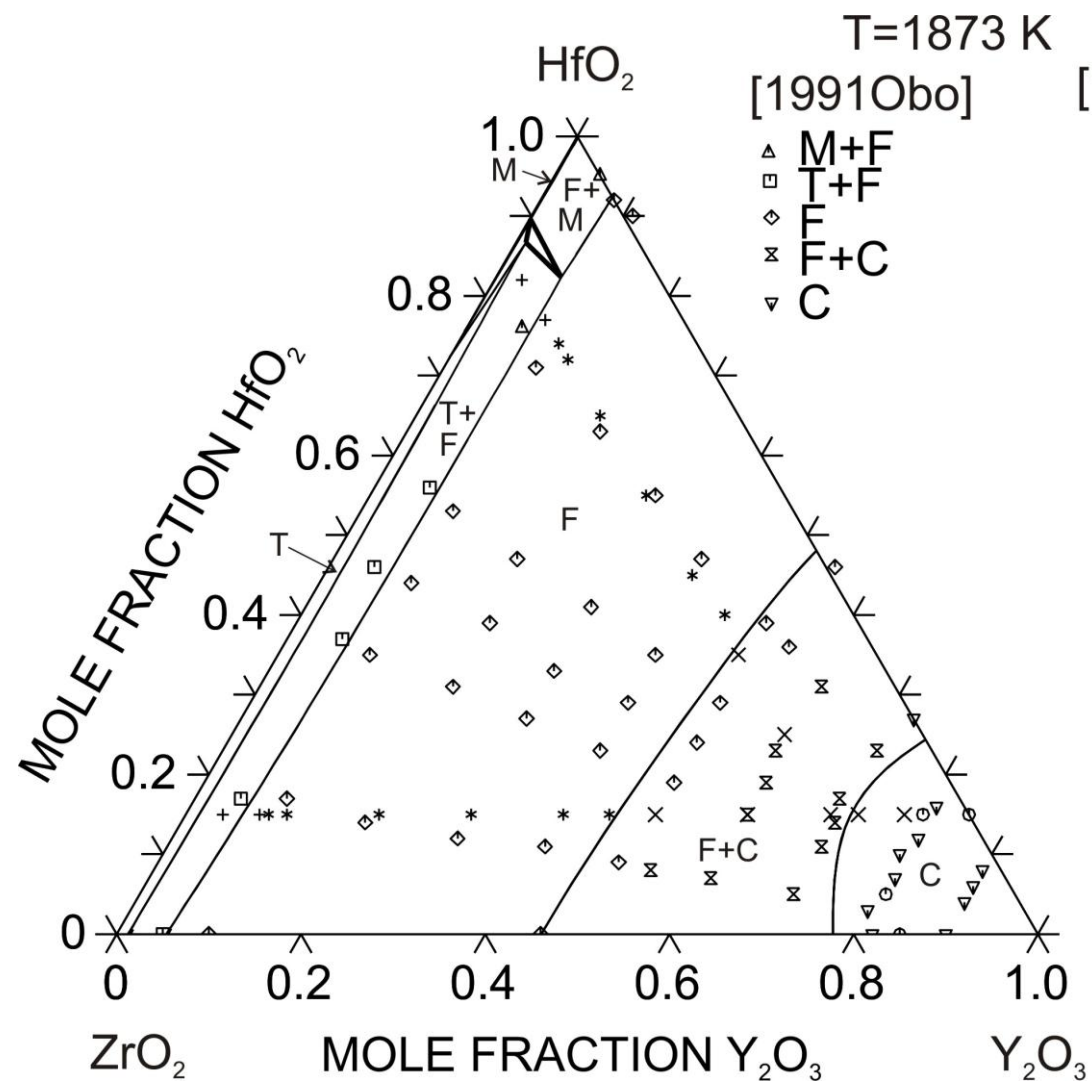


Experimental phase diagram of Shevchenko et al. (1987)

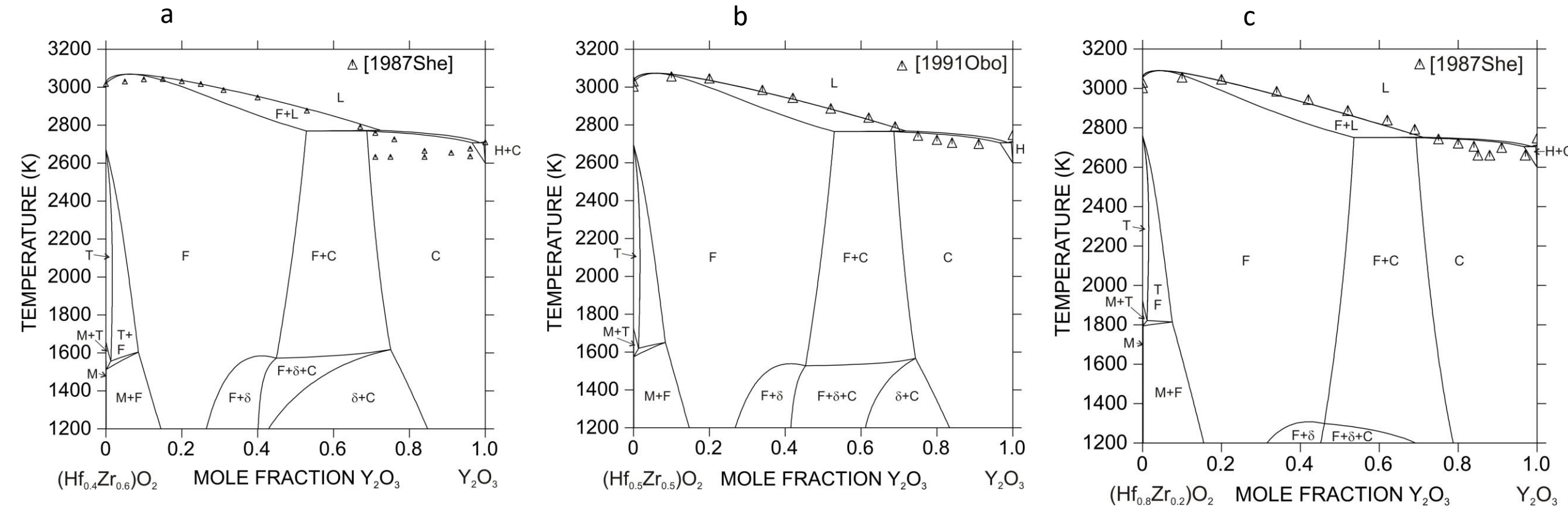
Isothermal sections of the ZrO_2 - HfO_2 - Y_2O_3 system



Isothermal sections of the $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ system

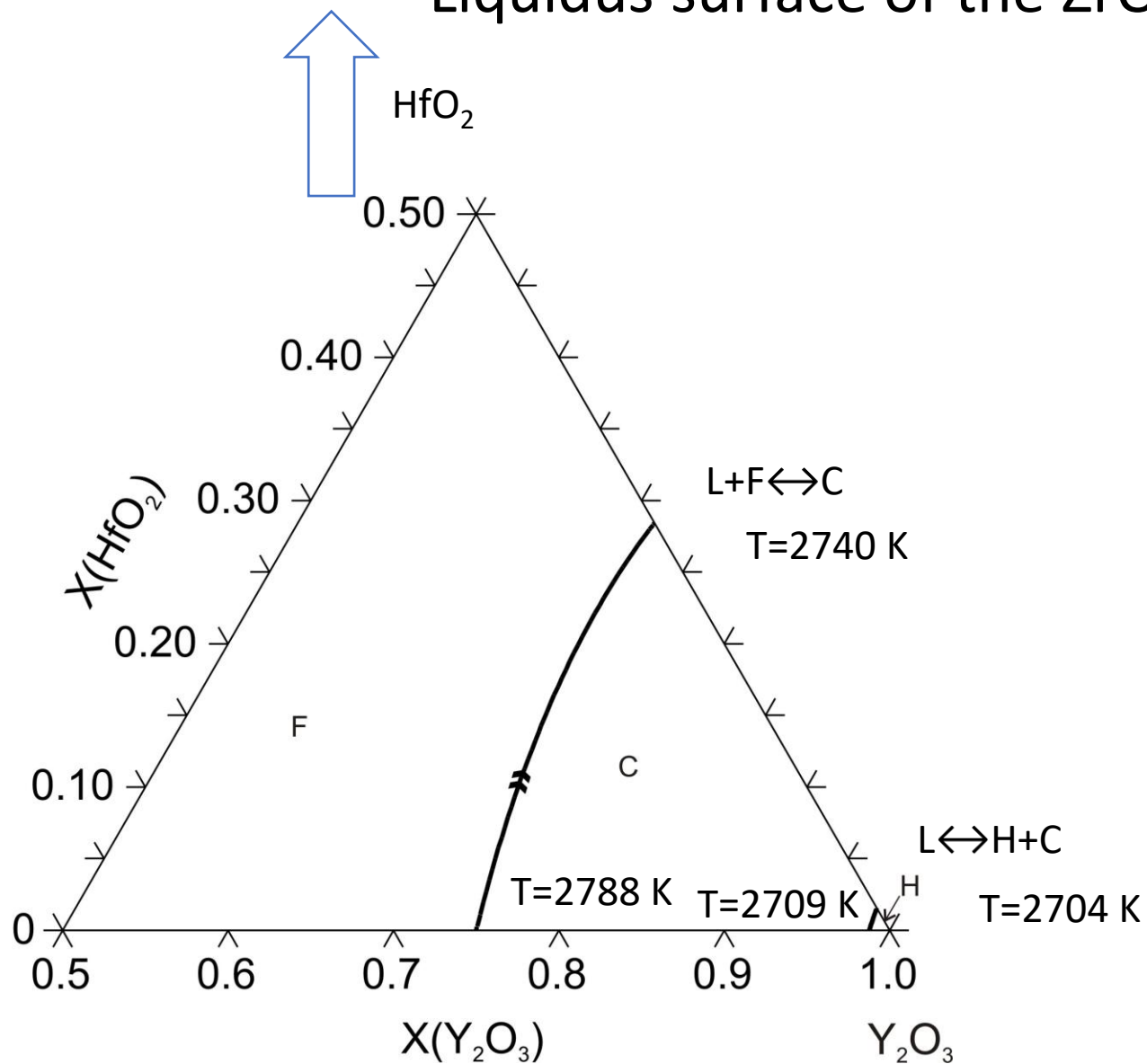


Vertical sections $(\text{Hf}_{1-x}\text{Zr}_x)\text{O}_2\text{-Y}_2\text{O}_3$

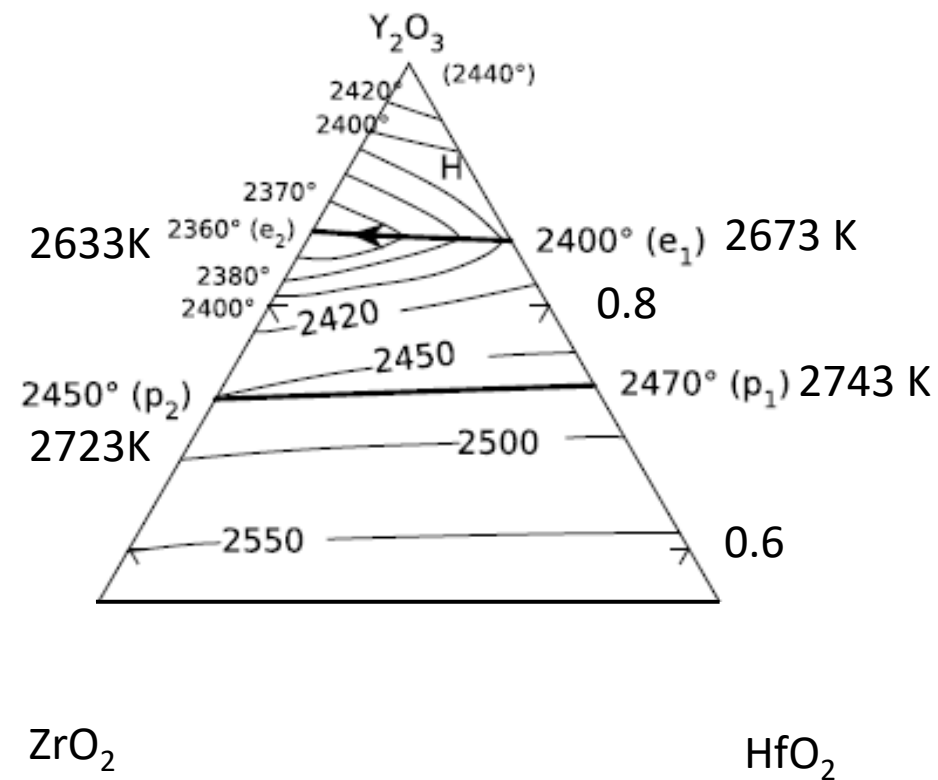


Calculated vertical sections for $x=0.6$ (a), 0.5 (b) and 0.2 (c) compared with experimental data

Liquidus surface of the $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ system



Calculated liquidus surface



Liquidus surface from Shevchenko et al. (1987)

Conclusions

1. The $\delta\text{-Y}_4\text{Zr}_3\text{O}_{12}$ was successfully synthesized and heat capacity in the temperature range between 200 and 1200 K was measured using two different DSC devices;
2. Thermodynamic parameters of the $\delta\text{-Y}_4\text{Zr}_3\text{O}_{12}$ were re-optimized using phase equilibrium data and calorimetric data;
3. Thermodynamic parameters of the $\text{HfO}_2\text{-Y}_2\text{O}_3$ system were re-assessed using data from literature;
4. The binary descriptions were combined into the ternary description of $\text{ZrO}_2\text{-HfO}_2\text{-Y}_2\text{O}_3$ system and phase diagrams were calculated and compared with experimental data (isothermal sections, vertical sections and liquidus surface);
5. The calculated phase diagrams reproduces experimental data within uncertainty.

Thank you for your attention!

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