High temperature oxide melt solution calorimetry of PrO_2 and Pr_6O_{11}

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Introduction

□ Thermodynamic data on Pr^{4+} - containing compounds are of interest because of their development as ionic conductors, superconductors, and alternative gate dielectrics.

□ Both PrO_2 and Pr_6O_{11} have fluorite-type Fm3m structure with a = 5.392 and 5.467, respectively, ($Pr^{4+}O_2$ and $Pr_{0.66}^{4+}Pr_{0.34}^{3+}O_{1.83}\,\square_{0.17}$).

□ The goal of this work was to synthesize praseodymium dioxide and obtain its drop solution enthalpy to use for calculation of formation enthalpies of Pr^{4+} compounds from high temperature oxide melt solution calorimetry.

Experimental

- **PrO_2 was synthesized by oxidation of Pr_6O_{11} at 280 °C for 10 days in oxygen flow.**

- **Cell parameters and oxygen occupancies were refined by the Rietveld method using GSAS and ExpGUI software from X-ray diffraction data. Scintag PAD V diffractometer (CuKα radiation) with a diffracted beam monochromator was used.**

- **Samples were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Transposed temperature drop and drop solution experiments were performed using isoperibol calorimeter at 702 °C and sodium molybdate solvent.**

Rietveld refinements on PrO_2 and Pr_6O_{11}

	a, Å	Frac O	WRp	χ^2
PrO_2 after preparation	5.3931(1)	1.01(2)	0.2262	1.96
PrO_2 aged 14d in air	5.3928(1)	1.04(2)	0.2036	1.70
Pr_6O_{11} (PrO_2 -post TTD 702 °C)	5.4706(1)	0.93(1)	0.1861	1.88
Pr_6O_{11} (post DSC 500 °C)	5.4656(1)	0.97(2)	0.2177	2.43
Standards				
LaB_6 660A (4.15691(1))	4.15704(1)		0.2300	1.85
LaB_6 660 (4.15695(6))	4.15691(7)		0.1697	2.87
Si 640b (5.43094(4))	5.43137(5)		0.1062	1.65

PrO2 batch #5   Hist   1
Lambda 1.5406 A, L-S cycle 140   Obsd. and Diff. Profiles

Pr6O11 (from PrO2 after 700 °C in air (furnace))
Pr6O11 (PrO2 after DTA 500 °C in oxygen)
Pr6O11 (from PrO2 TTD 702 °C in oxygen)
PrO2 (Pr6O11 after 14d at 280 °C in oxygen flow)
Pr6O11 as received from AlphaAesar

75-0152> PrO2 - Praseodymium Oxide
06-0329> PrO1.83 - Praseodymium Oxide
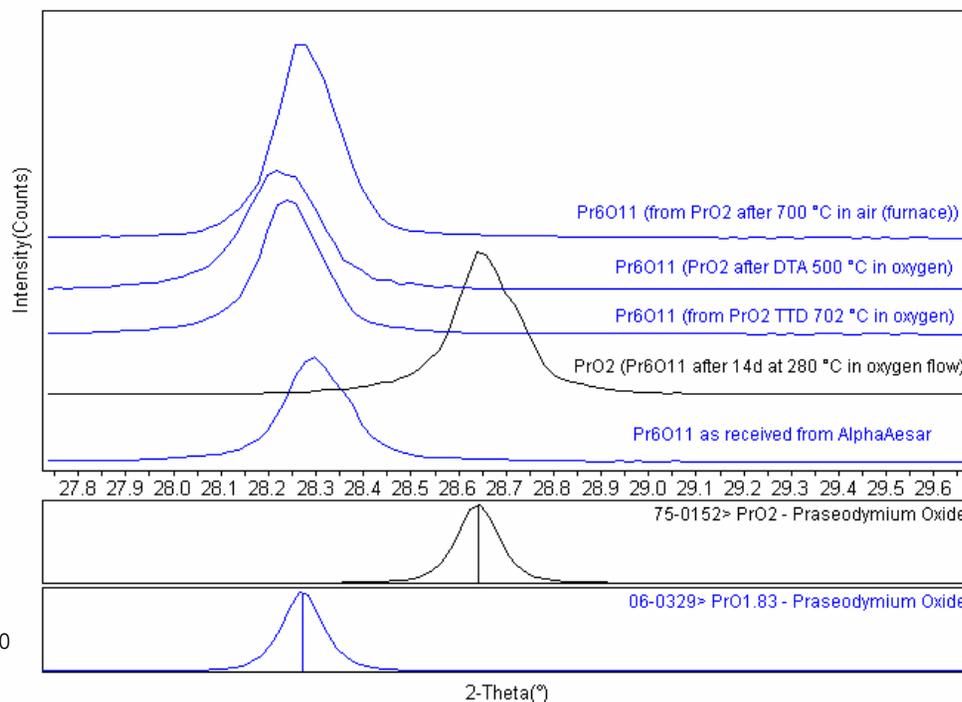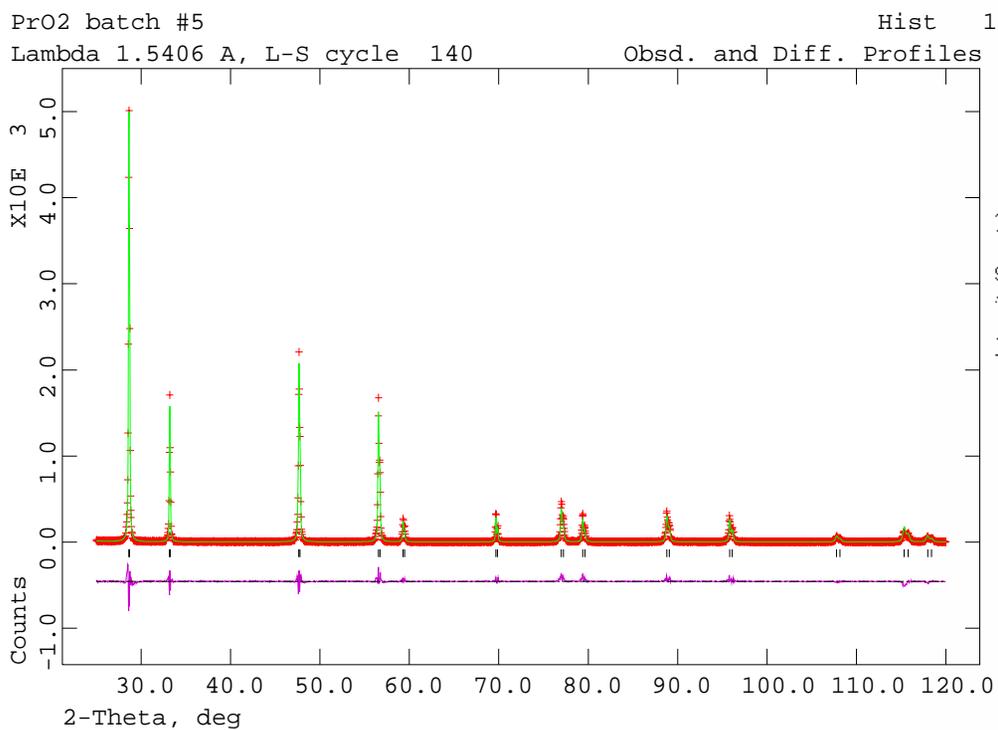
Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG)

- ❑ **Netzsch Simultaneous Thermal Analyzer (STA) 449 was used for PrO_2 analyses. Sample temperature was calibrated by melting pure metal standards. Sensitivity was calibrated by C_p-method using sapphire standard.**

- ❑ **Samples of PrO_2 were heated at 10 °C/min in platinum crucibles in flow of pure oxygen (40 ml/min). An endothermic peak in the DSC trace was observed at about 390 °C and was accompanied by a steep weight loss.**

- ❑ **The cell parameter of the sample quenched from 500 °C (a = 5.4656(1) Å) indicated Pr_6O_{11} stoichiometry (a = 5.467 Å [PDF #241006]). The observed weight loss, 1.56 ±0.05 wt.%, is in good agreement with that calculated from oxygen loss in the $PrO_2 = {}^1/_6 Pr_6 O_{11} + {}^1/_{12} O_2$ reaction (1.545 wt.%).**
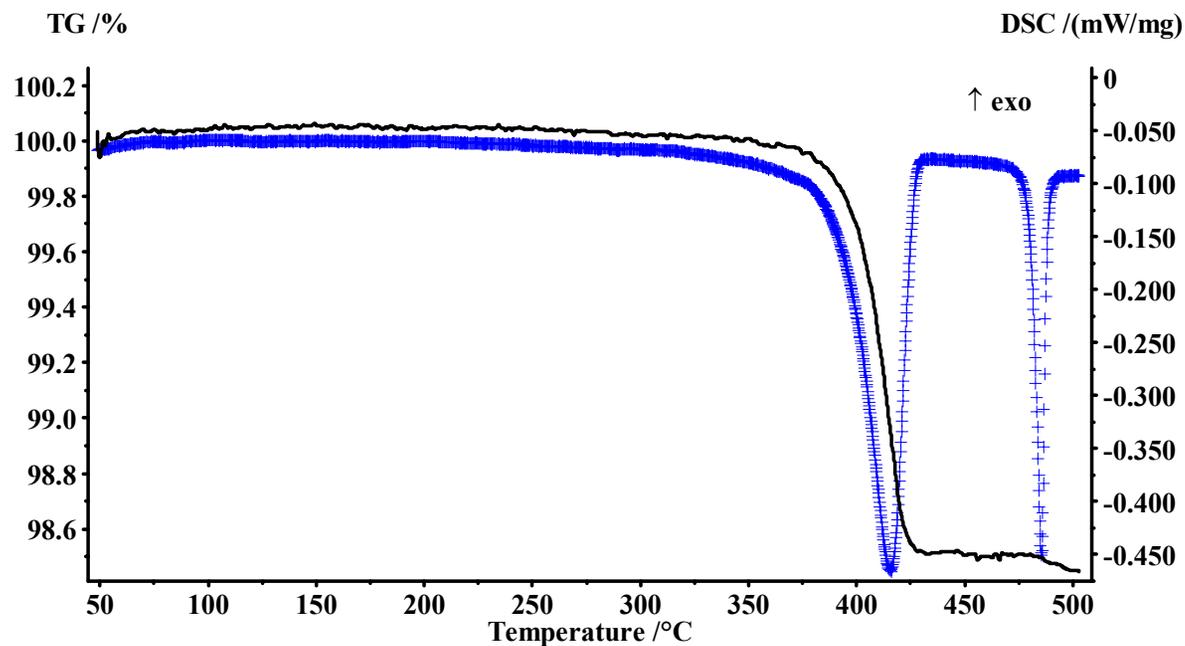
Thermal analyses of PrO$_2$ in oxygen flow. (DSC - blue trace, TG-black trace). Second endothermic peak corresponds to a reversible transition to the alpha phase of Pr$_6$O$_{11}$.

Isoperibol Calorimetry

❑ **Experiments used isoperibol Tian-Calvet type twin microcalorimeter, operated at 702 °C.**

❑ **In transposed temperature drop experiments samples dropped from ambient temperature into empty calorimeter flushed with oxygen. Heat effect (ΔH_{ttd}) was calculated from calorimeter trace, applying calibration factor.**

❑ **In drop solution experiments (ΔH_{ds}) PrO_2 and Pr_6O_{11} samples dropped from ambient into sodium molybdate ($3Na_2O \cdot 4MoO_3$) melt bubbled with oxygen.**

High temperature oxide melt drop-solution calorimetry

25°C

702°C

silica glass drop tube

platinum bubbling tube

silica glass liner

platinum crucible

solvent ($3Na_2O \cdot 4MoO_3$)
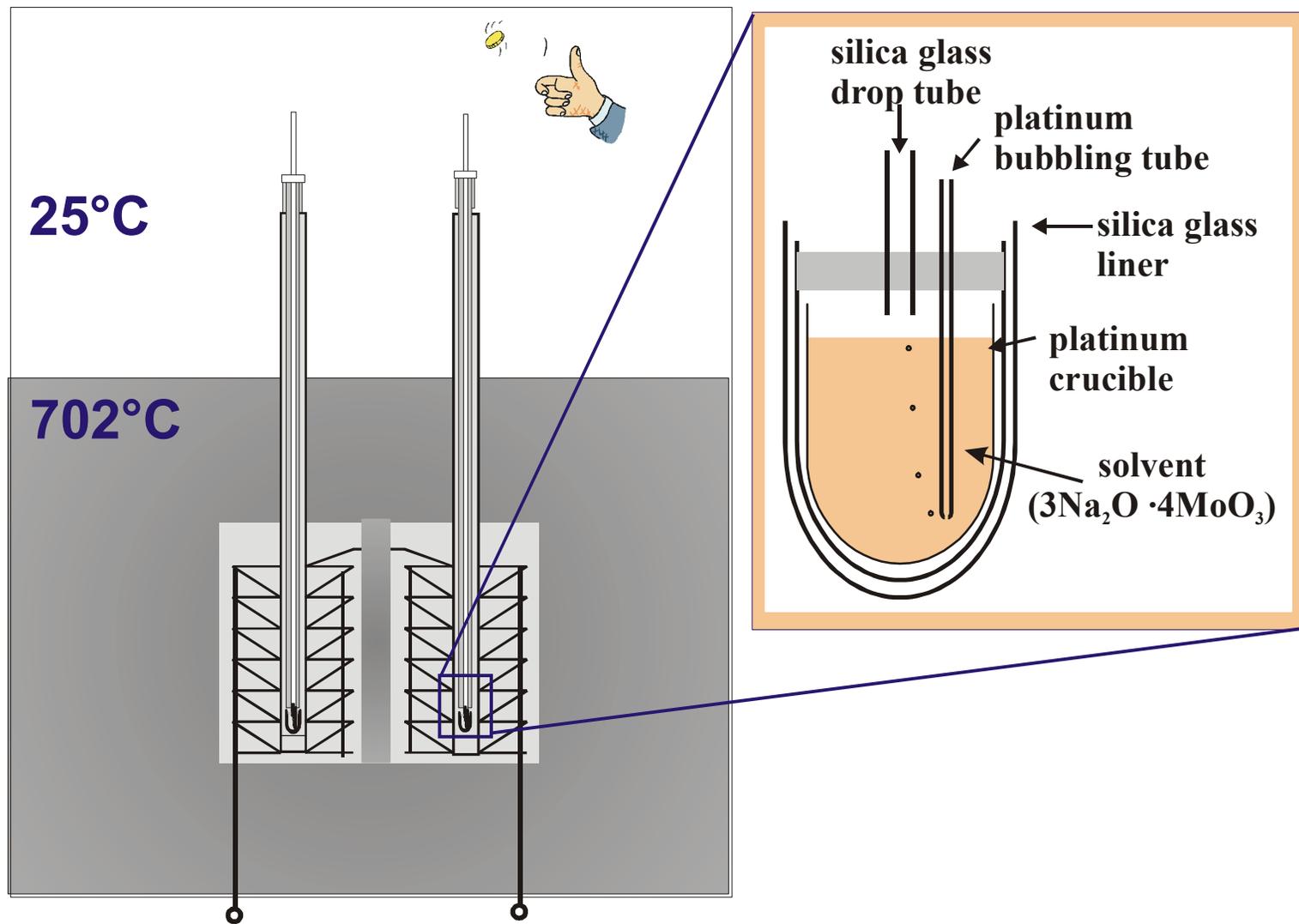
Twinned Thermopiles

Calculation of enthalpy of the reaction

$$(^1/_6)Pr_6O_{11(s,298)} + (^1/_{12})O_{2(g,298)} = PrO_{2(s,298)}$$
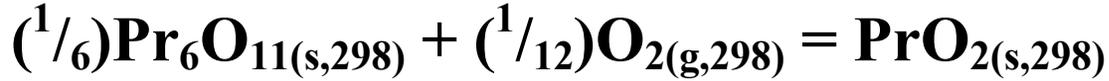
from drop solution (ΔH_{ds}) transposed temperature drop (ΔH_{ttd}), and DSC experiments.

Reaction		ΔH kJ/mol
$PrO_{2(s,298)} = (^1/_6)Pr_6O_{11(s,975)} + (^1/_{12})O_{2\ (g,975)}$	(1) ΔH_{ttd} PrO_2	72.73 ± 1.45 (11)
$(^1/_6)Pr_6O_{11(s,298)} = (^1/_6)Pr_6O_{11(s,975)}$	(2) ΔH_{ttd} $PrO_{1.83}$	60.22 ±0.86 (9)
$O_{2(g,298)} = O_{2(g,975)}$	(3) $\Delta H_{(975-298)}$ O_2	21.74
$PrO_{2(s,298)} = (^1/_6)Pr_6O_{11\ (sln,975)} + (^1/_{12})O_{2(g,975)}$	(4) ΔH_{ds} PrO_2	-29.71 ± 1.35 (9)
$(^1/_6)Pr_6O_{11(s,298)} = (^1/_6)Pr_6O_{11(sln,975)}$	(5) ΔH_{ds} $PrO_{1.83}$	-38.84 ± 0.75 (12)
$(^1/_6)Pr_6O_{11(s,298)} + (^1/_{12})O_{2(g,298)} = PrO_{2(s,298)}$	(6)	

From TTD drops $\Delta H_6 = -\Delta H_1 + \Delta H_2 + (^1/_{12})\Delta H_3$ **-10.7 ±1.69**

From drop solution $\Delta H_6 = -\Delta H_4 + \Delta H_5 + (^1/_{12})\Delta H_3$ **-10.94 ±1.54**

From PrO$_2$ DSC

$(^1/_6)Pr_6O_{11(s,667)} + (^1/_{12})O_{2\ (g,667)} = PrO_{2(s,667)}$ **-9.57±0.11 (3)**

BaPrO$_3$ example

The implication of the drop solution data for PrO$_2$ for determination of formation enthalpies of Pr^{4+} compound.

S.V. Ushakov, J. Cheng, A. Navrotsky, J. R. Wu, S.M. Haile, Mat. Res. Soc. Symp. Proc. Vol. 718

- ❑ **Tetravalent lanthanide perovskites, MLnO$_3$, where M = Ba, Sr and La = Ce, Pr, Tb represent an unusual case of lanthanide stabilization in octahedral coordination. These materials are of interest due to their ionic and proton conducting properties.**

- ❑ **While enthalpies of formation of MLnO$_3$ from oxides follow the usual trend for perovskites, namely decreasing stability with increasing structural distortion (Navrotsky 1981), BaPrO$_3$ was reported to be anomalously stable (Morss and Menzi 1982).**

- ❑ **Drop solution experiments were performed on BaPrO$_3$ and its enthalpy of formation from oxides was calculated.**

Thermochemical cycle for calculation of formation enthalpies from oxides for $Ba_xPr_yO_3$

Reaction		ΔH, kJ/mol
(1) $BaO_{(s,298)} \rightarrow$ solution$_{(975\ K)}$	$\Delta H_{ds}\ BaO$	$-184.61 \pm 3.12^{(1}$
(2) $PrO_{2(s,298)} \rightarrow$ solution$_{(975\ K)}$	$\Delta H_{ds}\ PrO_2$	$-29.71 \pm 1.35 (9)$
(3) $Ba_xPr_yO_{3\ (s,298)} \rightarrow$ solution$_{(975\ K)}$	$\Delta H_{ds}\ Ba_xPr_yO_3$	$-154.01 \pm 3.46\ (9)$
(4) $xBaO_{(s,298)} + yPrO_{2\ (s,298)} = Ba_xPr_yO_{3\ (s,298)}$	$\Delta H_{f,ox}\ Ba_xPr_yO_3$ $^{(2}$	
$\Delta H(4) = x\Delta H(1) + y\Delta H(2) - \Delta H(3)$		-65.4 ± 4.8

[1] Calculated from $BaCO_3$ (witherite) drop solution, (116.74 ± 0.70) (Majzlan et.al. 2002) and formation $(\Delta H_{f,ox} = -269.30 \pm 3.04)$ (Robie and Hamingway, 1995).

[2] Exact composition of $BaPrO_3$ samples was analyzed by microprobe.
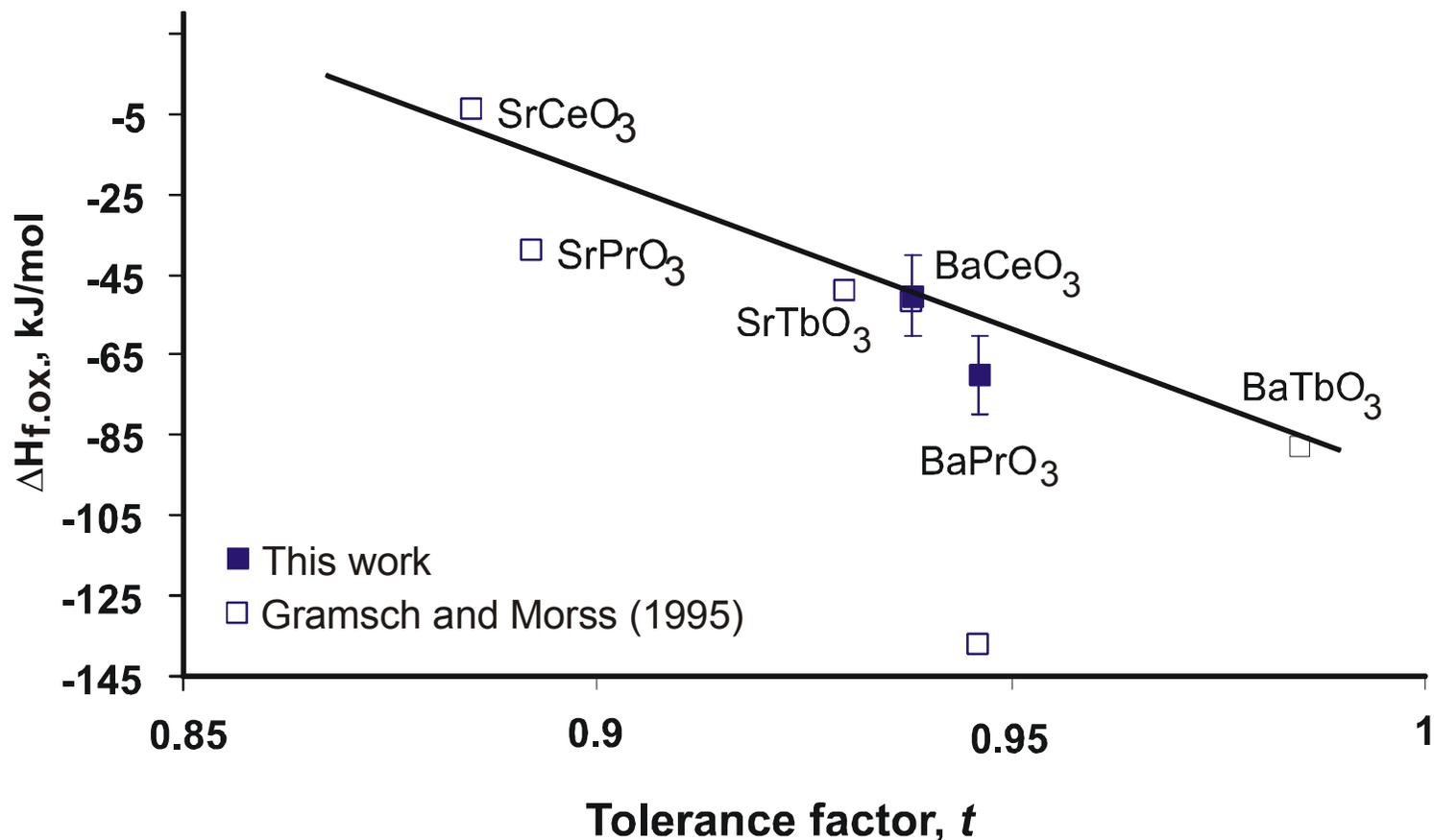
Formation enthalpies of tetravalent lanthanide perovskites $ALnO_3$ (where A = Ba, Sr and Ln = Ce, Pr, Tb) from AO and LnO_2 at 25 °C versus tolerance factor, $t = (Ro+R_A)/1.414(Ro+R_{Ln})$.

Conclusions

- Enthalpy of the reaction $PrO_{2(s,298)} = (^1/_6)Pr_6O_{11(s,298)} + (^1/_{12})O_{2(g,298)}$ derived from transposed temperature drop and drop solution experiments on PrO_2 and Pr_6O_{11} is -10 ±2 kJ/mol. That is in agreement with thermal analysis results on PrO_2.

- Using obtained value for drop solution enthalpy for PrO_2, formation enthalpy of $BaPrO_3$ from oxides was calculated as −70 ±10 k/mol. It falls on the normal trend of energetics versus Goldschmidt tolerance factor and do not show any special stabilization of $BaPrO_3$ relative to other $MLnO_3$ perovskites.