



# Thermochemical Study of the Relations of the Monazite and Zircon Structures in the Rare-earth Orthophosphates

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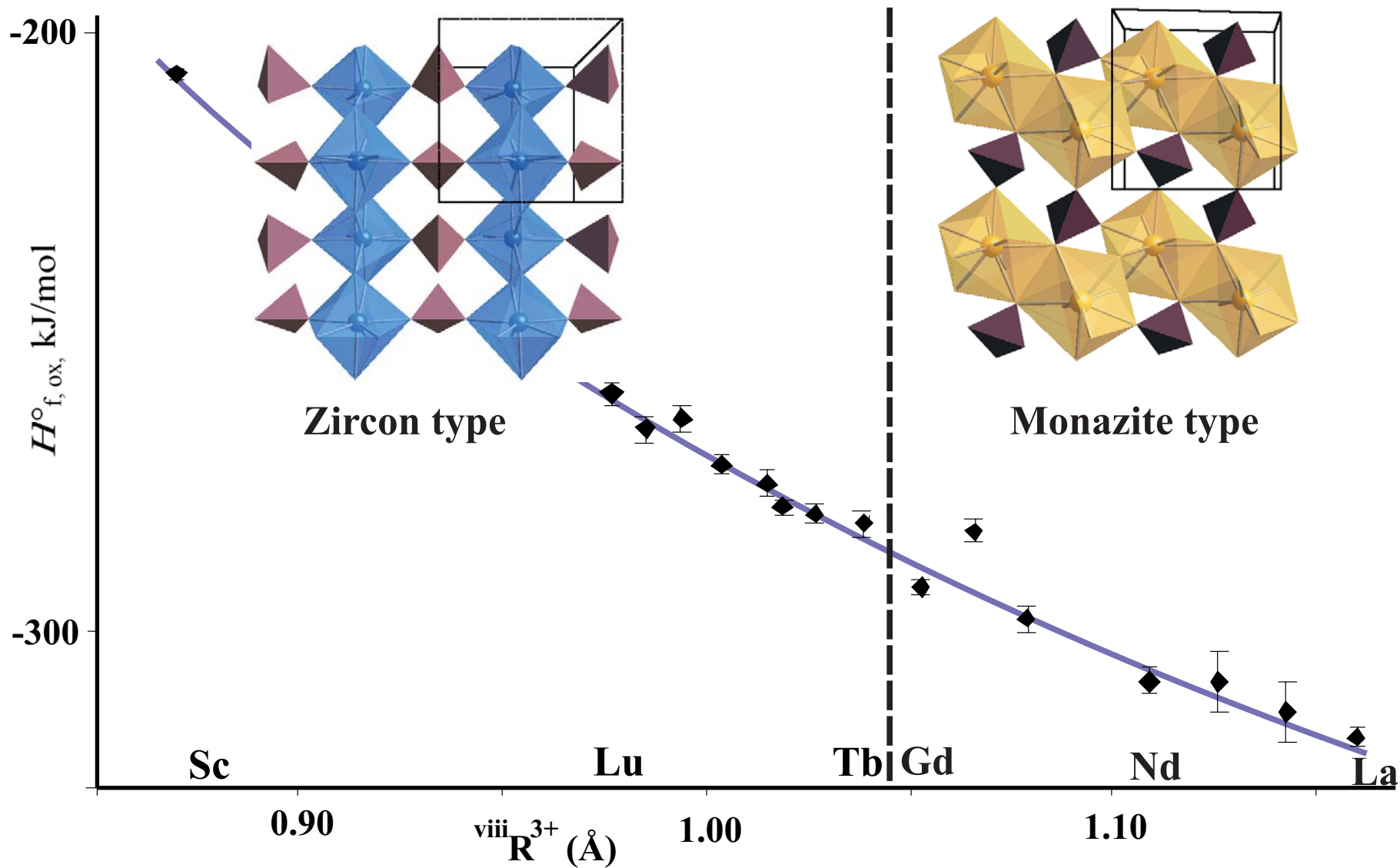
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# Introduction

- RE orthophosphates are of importance as actinide hosts in glass and ceramic radioactive waste forms and their alteration products.
- REE orthophosphates are under development as inert matrices for Pu fuel and as multilayered (with  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ) weak-bonded ceramic composites.
- Pure anhydrous  $(\text{RE})\text{PO}_4$  compounds change structure with increasing RE radius: i.e., orthophosphates from Lu to Ho as well as Sc and Y exist only in the tetragonal zircon (xenotime) structure, while the orthophosphates from Eu to La exist only in the monoclinic monazite structure.
- The enthalpies of formations from oxides for zircon-type (Lu-Gd) and monazite-type (Gd-La) orthophosphates show an almost linear dependence on the RE radius. There was no significant discontinuity observed upon changing the structure type from xenotime to monazite.
- Existence of both zircon- and monazite-type polymorphs for Dy, Tb and Gd orthophosphates has been previously reported, however, available structural and thermodynamic data are scarce. The goal of this work was to evaluate the energetics of structural changes in these compounds.



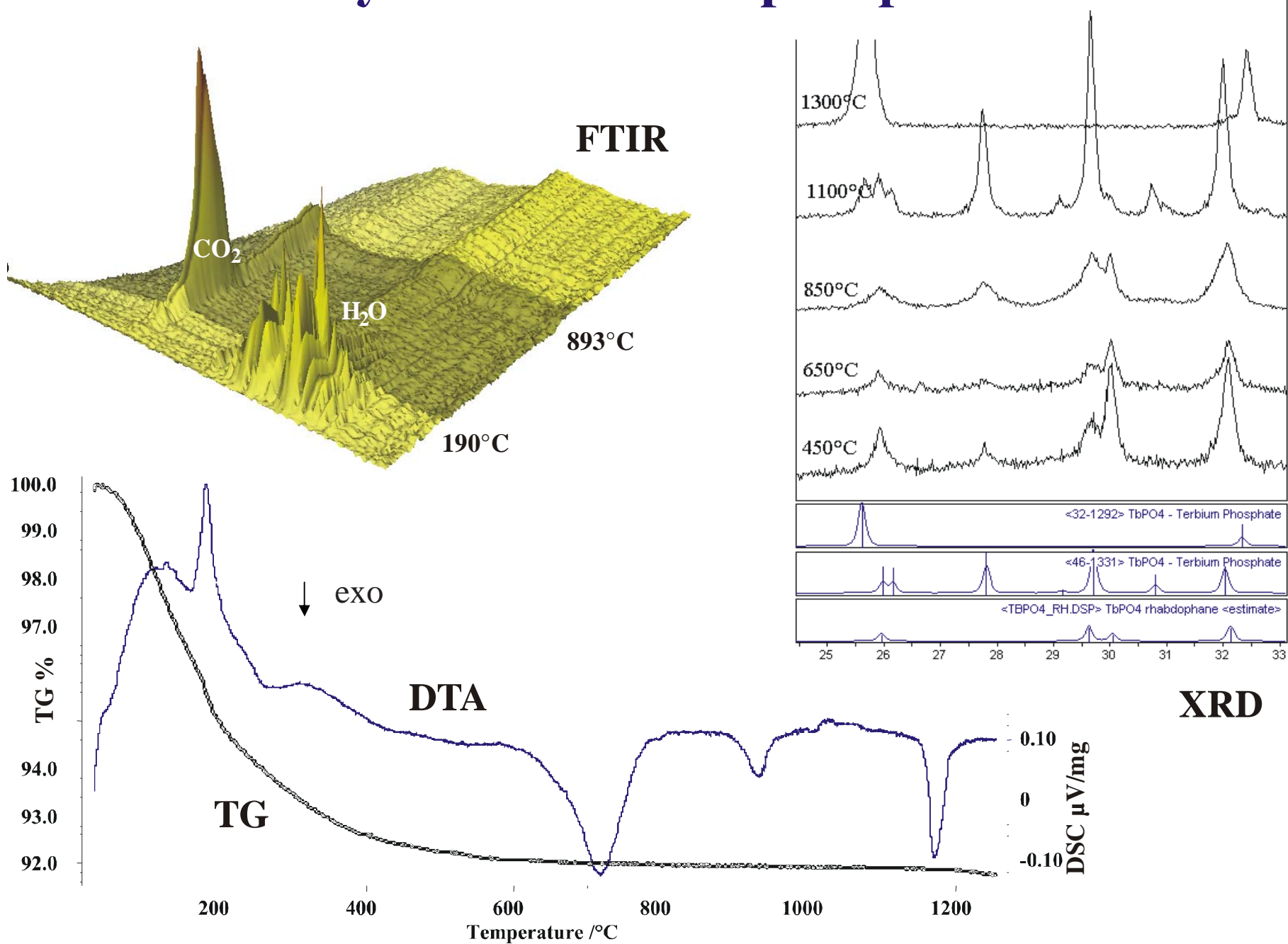
Enthalpies of formation from oxides at 298 K for (RE)PO<sub>4</sub> compounds

(S.V. Ushakov, K.B. Helean, L.A. Boatner, A. Navrotsky, JMR, (2001), 16(9), 2623-33)

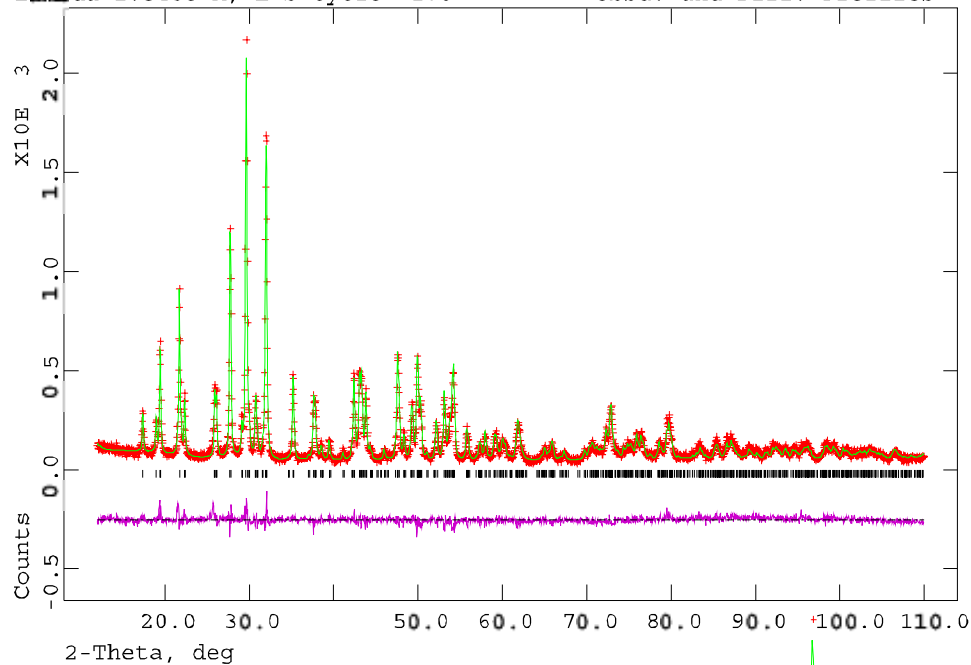
# Experimental

- Hydrous phosphates of Tb and Dy were synthesized by precipitation at pH 3 from the corresponding chlorides and  $\text{H}_3\text{PO}_4$ . Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were performed using a Netzsch 449 apparatus. The composition of evolved gas was monitored using a Bruker Equinox 55 IR spectrometer. Heating rate was  $10^\circ/\text{min}$ , sample chamber was purged with Ar at 40 ml/min. Samples were heated to desired temperature, then quickly cooled by turning off the heater. Crystalline phases were identified by powder X-ray diffraction (XRD) using PAD V Scintag diffractometer.
- Monazite-type  $\text{GdPO}_4$  was synthesized by precipitation in molten urea. Samples were annealed in air at  $900\text{-}1700^\circ$  and analyzed by XRD for presence of zircon-type modification.
- Pure monazite-type  $\text{TbPO}_4$  was synthesized by annealing of rhabdophane-type Tb phosphate at  $900^\circ\text{C}$  in air for 10 hours. Enthalpy of monazite to zircon-type phase transition and enthalpy of formation  $\text{TbPO}_4$  from oxides were determined by high temperature oxide melt solution calorimetry. Lattice parameters for  $\text{TbPO}_4$  and  $\text{GdPO}_4$  polymorphs were refined by Rietveld method using GSAS software.

# Thermal analyses of Tb orthophosphate



Lambda 1.5405 A, L-S cycle 178 Obsd. and Diff. Profiles



monazite type

P21/n

a = 6.6189(3)

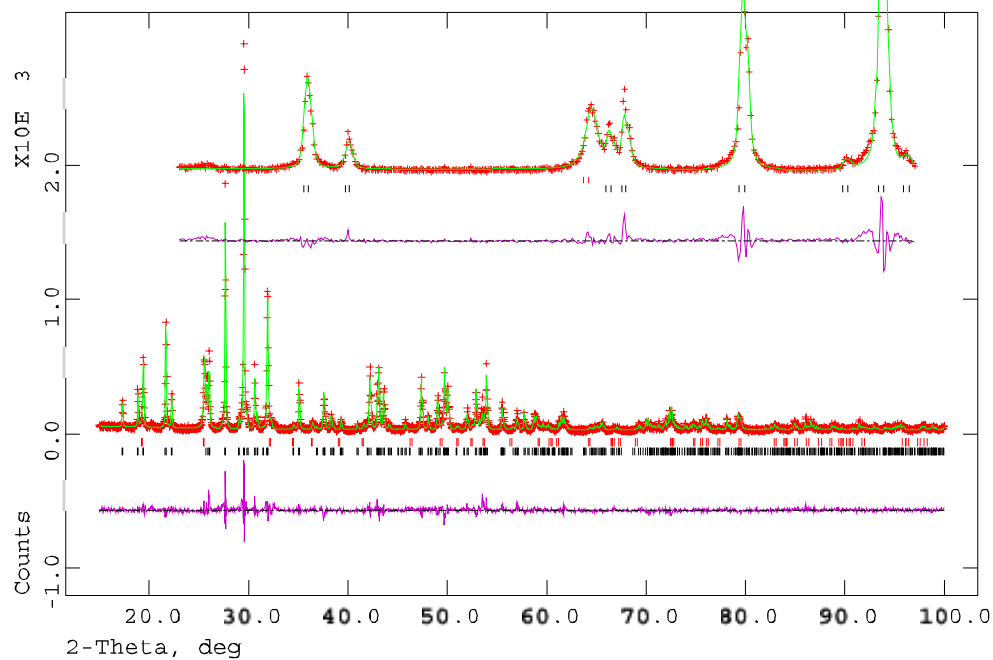
b = 6.8103(2)

c = 6.3173(2)

V = 276.16 (2)

$\chi^2 = 1.687$

Rwp = 9.62%



monazite type

zircon type (~14 wt%)

P21/n

I 41/amd

a = 6.6519(5)

a = 6.9817(8)

b = 6.8471(5)

c = 6.1253(7)

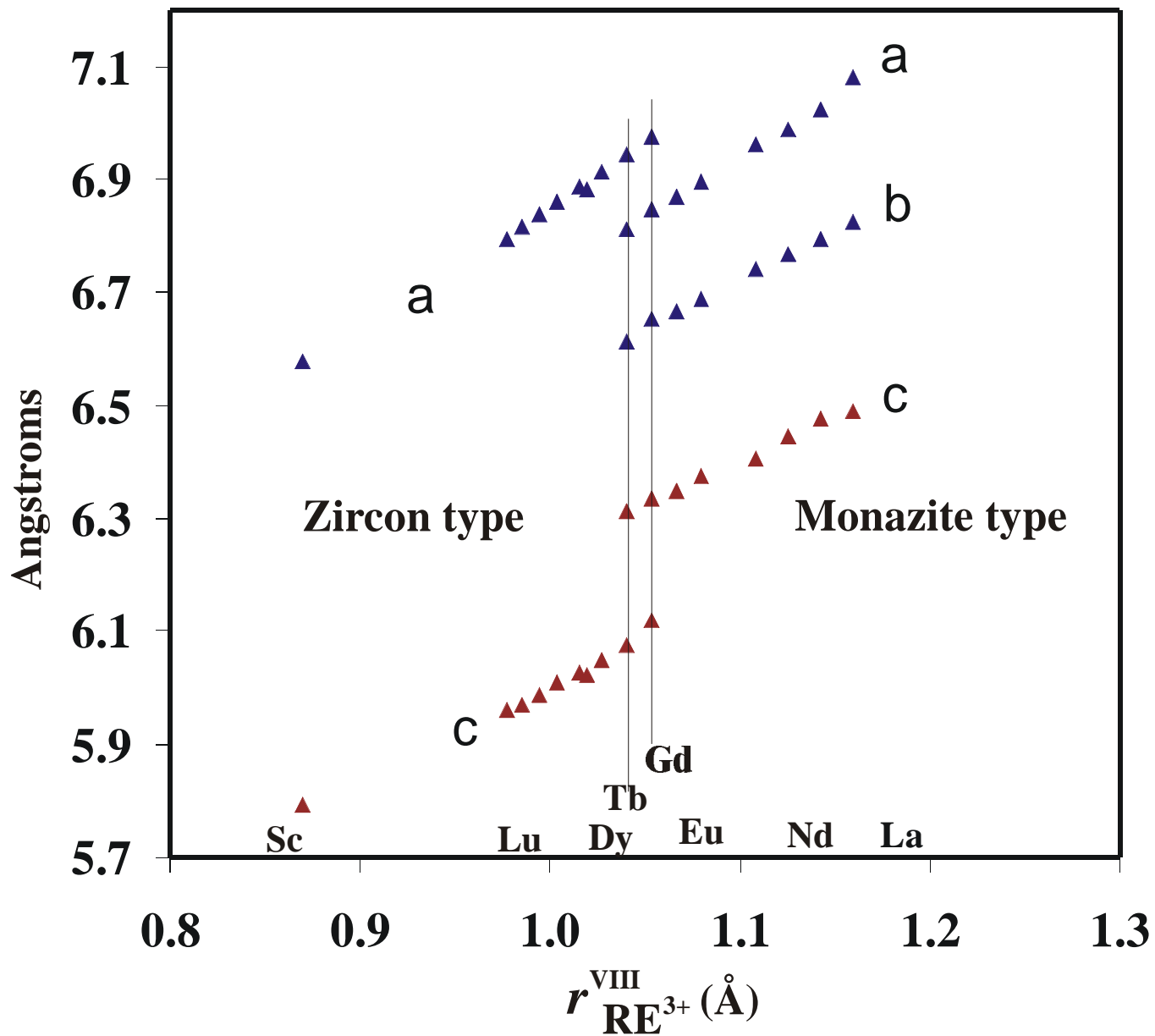
c = 6.3361(5)

V = 6.298.6(9)

V = 280.00(6)

$\chi^2 = 2.201$

Rwp = 15.74



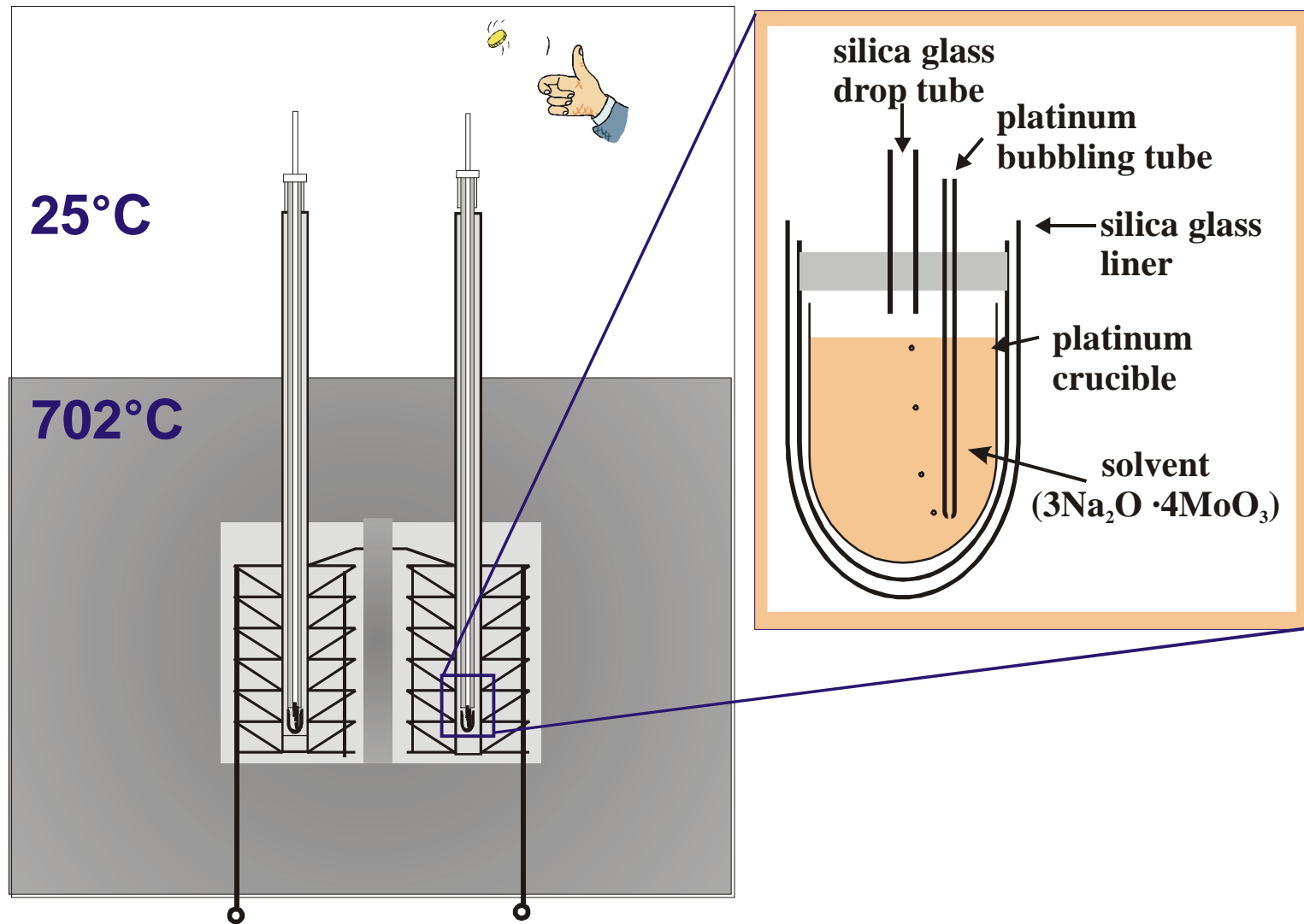
**The lattice parameters for TbPO<sub>4</sub> and GdPO<sub>4</sub> polymorphs. The data for other RE orthophosphates are for flux-grown crystals.**

# Solution Calorimetry

- Experiments were accomplished using isoperibol Tian-Calvet type twin microcalorimeter, operated at 702°C.
- Pelletized samples of  $\text{TbPO}_4$  polymorphs, were dropped from 25°C into sodium molybdate ( $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ ) melt at 700°C. Heat effect (enthalpy of drop solution) was calculated from calorimeter trace, applying calibration factor. In order to obtain enthalpy of formation from oxide, drop solution experiments were also performed on  $\text{Tb}_2\text{O}_3$  (synthesized by reduction of  $\text{Tb}_4\text{O}_7$  in vacuum at 950°C) and  $\text{P}_2\text{O}_5$ .
- Transition enthalpy for monazite to zircon transformation of  $\text{TbPO}_4$  and enthalpies of formation from oxides were calculated from drop solution enthalpies, applying appropriate thermochemical cycles.



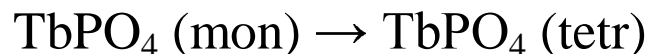
# High temperature oxide melt drop-solution calorimetry



Differential Thermopiles

## Thermochemical cycle for calculation of enthalpy of formation and enthalpy of monazite to zircon phase transition for TbPO<sub>4</sub>

Reaction	$\Delta H$ kJ/mol
(1) TbPO <sub>4</sub> (monazite, 298 K) $\rightarrow$ solution (975 K)	138.43 $\pm$ 1.23 (10)*
(2) TbPO <sub>4</sub> (zircon, 298 K) $\rightarrow$ solution (975 K)	140.98 $\pm$ 1.39 (9)
(3) P <sub>2</sub> O <sub>5</sub> (hex., 298 K) $\rightarrow$ solution (975 K)	-164.60 $\pm$ 0.85 (12)
(4) Tb <sub>2</sub> O <sub>3</sub> (cub., 298 K) $\rightarrow$ solution (975 K)	-125.58 $\pm$ 2.40 (11)



$$\Delta H \text{ mon. to zircon transiton} = \Delta H(1) - \Delta H(2) = \mathbf{-2.6 \pm 1.9}$$

(vs.  $-4\text{-}6$  kJ/mol from DTA trace )



$$\Delta H \text{ form. from oxides at } \mathbf{298 \text{ K}} = \frac{1}{2}\Delta H(3) + \frac{1}{2}\Delta H(4) - \Delta H(1) = \mathbf{-283.5 \pm 1.8}$$

\*Error is indicated by two standard deviations of the mean, number in ( ) is the number of experiments performed.

# Results

- Monazite-type  $\text{DyPO}_4$  phase was formed in minor amounts at 750-850°C upon crystallization of amorphous hydrous  $\text{DyPO}_4$  precipitate into zircon-type structure.
- Monazite-type  $\text{TbPO}_4$  was formed at 450-1100°C upon thermal annealing of rhabdophane-type  $\text{TbPO}_4$  hydrate. At higher temperature it transforms exothermically into zircon-type structure.
- Zircon-type  $\text{GdPO}_4$  polymorph formed in minor amounts upon thermal annealing of monazite-type  $\text{GdPO}_4$  above 1400°C.
- Refined lattice parameters for the monazite-type  $\text{TbPO}_4$  and zircon-type  $\text{GdPO}_4$  are consistent with the trends for isostructural RE orthophosphates. The unit cell dimensions for the zircon-type  $\text{GdPO}_4$  are reported for the first time.

# Conclusion

- Both monazite- and zircon-type polymorphs exist for the Dy, Tb and Gd orthophosphates. The apparent transition temperatures increase in the order DyPO<sub>4</sub> (< 900 °C), TbPO<sub>4</sub> (~900-1100°C), and GdPO<sub>4</sub> (>1100°C).
- The monazite-to-zircon phase transformation for DyPO<sub>4</sub> and TbPO<sub>4</sub> is irreversible and exothermic. This exothermic nature proves that the monazite structure is thermodynamically metastable for Dy and Tb phosphates.
- The enthalpy of the monazite-to-zircon phase transformation for TbPO<sub>4</sub> was estimated from DTA and solution calorimetry as  $-4 \pm 3$  kJ/mole. This small difference in energetics reflects close relations between the two structure types.

# Acknowledgement

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