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

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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 Al$_2$O$_3$ and ZrO$_2$) weak-bonded ceramic composites.

- Pure anhydrous (RE)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)PO₄ 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 H$_3$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°/min, sample chamber was purged with Ar at 40 ml/min. Samples were heated to desired temperature, than quickly cooled by turning off the heater. Crystalline phases were identified by powder X-ray diffraction (XRD) using PAD V Scintag diffractometer.

- Monazite-type GdPO$_4$ was synthesized by precipitation in molten urea. Samples were annealed in air at 900-1700° and analyzed by XRD for presence of zircon-type modification.

- Pure monazite-type TbPO$_4$ was synthesized by annealing of rhabdophane-type Tb phosphate at 900°C in air for 10 hours. Enthalpy of monazite to zircon-type phase transition and enthalpy of formation TbPO$_4$ from oxides were determined by high temperature oxide melt solution calorimetry. Lattice parameters for TbPO$_4$ and GdPO$_4$ polymorphs were refined by Rietveld method using GSAS software.
Thermal analyses of Tb orthophosphate

- DTA
- TG
- XRD

FTIR

893°C

190°C

CO₂

H₂O

1300°C
1100°C
850°C
650°C
450°C

<82-1252> TbPO₄ - Terbium Phosphate
<86-321> TbPO₄ - Terbium Phosphate
<1BPO₄_RHDSF> TbPO₄ rhodochrosite <estimato>

TG %

DSC µV/mg

Temperature /°C

TG

DTA

exo

100.0
99.0
98.0
97.0
96.0
95.0
94.0
93.0
92.0

200
400
600
800
1000
1200

0.10
0.0
-0.10
**TbPO$_4$**
- monazite type
- P21/n
- $a = 6.6189(3)$
- $b = 6.8103(2)$
- $c = 6.3173(2)$
- $V = 276.16(2)$

$\chi^2 = 1.687$
$\text{Rwp} = 9.62\%$

**GdPO$_4$**
- monazite type
- P21/n
- $a = 6.6519(5)$
- $b = 6.8471(5)$
- $c = 6.3361(5)$
- $V = 280.00(6)$

$\chi^2 = 2.201$
$\text{Rwp} = 15.74\%$
The lattice parameters for TbPO$_4$ and GdPO$_4$ 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 TbPO₄ polymorphs, were dropped from 25°C into sodium molybdate (3Na₂O·4MoO₃) 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 Tb₂O₃ (synthesized by reduction of Tb₄O₇ in vacuum at 950°C) and P₂O₅.

- Transition enthalpy for monazite to zircon transformation of TbPO₄ and enthalpies of formation from oxides were calculated from drop solution enthalpies, applying appropriate thermochemical cycles.
High temperature oxide melt drop-solution calorimetry

25°C

702°C

Differential Thermopiles
Thermochemical cycle for calculation of enthalpy of formation and enthalpy of monazite to zircon phase transition for TbPO$_4$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) TbPO$_4$ (monazite, 298 K) $\rightarrow$ solution (975 K)</td>
<td>$138.43 \pm 1.23$ (10)*</td>
</tr>
<tr>
<td>(2) TbPO$_4$ (zircon, 298 K) $\rightarrow$ solution (975 K)</td>
<td>$140.98 \pm 1.39$ (9)</td>
</tr>
<tr>
<td>(3) P$_2$O$_5$ (hex., 298 K) $\rightarrow$ solution (975 K)</td>
<td>$-164.60 \pm 0.85$ (12)</td>
</tr>
<tr>
<td>(4) Tb$_2$O$_3$ (cub., 298 K) $\rightarrow$ solution (975 K)</td>
<td>$-125.58 \pm 2.40$ (11)</td>
</tr>
</tbody>
</table>

TbPO$_4$ (mon) $\rightarrow$ TbPO$_4$ (tetr)

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

(vs. $-4$-6 kJ/mol from DTA trace)

$\frac{1}{2}$ Tb$_2$O$_3$ (cub., 298 K) + $\frac{1}{2}$ P$_2$O$_5$ (hex., 298 K) $\rightarrow$ TbPO$_4$ (mon., 298 K)

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

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

- Monazite-type DyPO$_4$ phase was formed in minor amounts at 750-850°C upon crystallization of amorphous hydrous DyPO$_4$ precipitate into zircon-type structure.

- Monazite-type TbPO$_4$ was formed at 450-1100°C upon thermal annealing of rhabdophane-type TbPO$_4$ hydrate. At higher temperature it transforms exothermically into zircon-type structure.

- Zircon-type GdPO$_4$ polymorph formed in minor amounts upon thermal annealing of monazite-type GdPO$_4$ above 1400°C.

- Refined lattice parameters for the monazite-type TbPO$_4$ and zircon-type GdPO$_4$ are consistent with the trends for isostructural RE orthophosphates. The unit cell dimensions for the zircon-type 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$_4$ (< 900 °C), TbPO$_4$ (~900-1100°C), and GdPO$_4$ (>1100°C).

- The monazite-to-zircon phase transformation for DyPO$_4$ and TbPO$_4$ 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$_4$ was estimated from DTA and solution calorimetry as -4 ± 3 kJ/mole. This small difference in energetics reflects close relations between the two structure types.
Acknowledgement

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