

Rare Earth Orthophosphate Reference Materials From Na₂CO₃-MoO₃ Flux: New Synthetic Procedures and Trace Element Determinations

Jared Wesley Singer¹ and Daniele J. Cherniak¹.

¹ Earth and Environmental Science/Rensselaer Polytechnic Institute, Troy, NY USA.

There are several types of reference materials for rare earth elements (REE), including REE-orthophosphates (REE-PO₄) grown from either Mo-based or Pb-based fluxes, REE-ultraphosphates (REE-P₅O₁₄), and multi-element glasses. Of the REE-PO₄ variety, Cherniak et al. (2004) developed a method of synthesis based on Na₂CO₃-MoO₃ flux [1] to avoid the X-ray spectral interferences from Pb contamination [2]. This contribution describes recent modifications to the original synthetic procedures of Cherniak et al. and presents LA-ICPMS and EPMA trace element measurements of the REE-PO₄ materials grown at Rensselaer Polytechnic Institute.

Fifteen orthophosphates, including LaPO₄ to LuPO₄ and YPO₄, are grown from microcrystalline precursors in a MoO₃-Na₂CO₃ flux mixture by ramping up to 1280°C in platinum crucibles, followed by slow cooling [1]. Methodological variants since 2016 include use of REE-carbonate rather than nitrate in synthesizing the microcrystalline precursors, increasing Na₂CO₃ content of the flux, decreasing of the hold temperature from 1280°C to 1260°C, and lowering the cooling ramp rate from 3°C/minute to 2.5°C/minute. The REE-carbonate starting material is decarbonated using ultra-pure HNO₃ (in-house, triple-distilled), and the microcrystalline REE-phosphate is precipitated with ammonium phosphate according to the original methods of Cherniak and others. Increasing Na₂CO₃ content of the flux has grown large crystals which are broadly free of flux inclusion, perhaps due to a lower flux viscosity. The lower hold temperature at 1260°C was intended to suppress Na volatility during the hold at maximum temperature. The slower descending ramp rate of 2.5°C/minute is intended to slow the crystal growth rate, and thereby mitigate massive flux inclusion and reduce non-equilibrium incorporation of molybdenum traces.

Trace REEs were measured by laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) using a Photon Machines G1 Analyte.193, 40 micron spot, 30 second ablations, at 6Hz repetition rate, coupled to a Varian 820MS ICPMS. Average values for REE (n=3) are reported for all REE and Y (table 1). The total REE trace element contaminants are typically between 0.01 and 0.1 wt%, consistent with 99.9% purity of REE starting materials. Notably there is a 0.6 wt% contamination of Gd in historical batches of PrPO₄. Other trace elements were measured by LA-ICPMS including Si (BDL), Na (BDL), Ca (BDL), Sc (<1ppm), Ti (<0.1ppm), Hf (<1ppm), and Pb (<0.2ppm).

Molybdenum was measured at 15keV (table 1) and mapped at 10keV (figure 1) by electron probe microanalysis (EPMA) with a 100nA beam using a 5 micron beam size and 4 LPET spectrometers. Average concentrations of Mo >0.1 wt% are observed for middle REE (Tb, Dy) and >0.05 wt% for moderately heavy REE (Ho-Yb, Y). As shown in the EPMA Mo maps (figure 1), heavy REE-PO₄ minerals show radial and sectoral zoning of Mo. Other REE-PO₄ were mapped and do not show sectoral zoning. EPMA measurements of well-polished domains give minimum Mo concentrations. Molybdenum L-lines (~2.5keV) do not overlap with REE L-lines (4<KeV<10) and are also sufficiently removed from Y L-lines (~2keV). Overall, the REE-PO₄ as synthesized at RPI in the past and present are ~99.8% pure or better—accounting for both REE impurities and Mo incorporation [3].

References:

- [1] DJ Cherniak, J Pyle and J Rakovan, *American Mineralogist* **89** (2004) p. 1533.
- [2] J Donovan *et al.*, *J. Res. Natl. Inst. Stand. Technol.* **107** (2002) p. 693.
- [3] The authors acknowledge NSF grant EAR-0230019 to DJ Cherniak, the Electron Microprobe Laboratory at Rensselaer Polytechnic Institute for continued synthesis, and your contribution.

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	REE	Mo
*YPO ₄		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06
LaPO ₄	0.00		0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.04
CePO ₄	0.00	0.01		0.00	0.02	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.04
PrPO ₄	0.01	0.00	0.00		0.00	0.00	0.00	0.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.62	0.01
NdPO ₄	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.03	0.02
SmPO ₄	0.00	0.00	0.00	0.00	0.00		0.00	0.04	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.07	0.01
EuPO ₄	0.00	0.00	0.00	0.00	0.00	0.00		0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01
GdPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.03	0.02	0.06	0.01
TbPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.01	0.00	0.00	0.00	0.00	0.04	0.07	0.11
DyPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01		0.01	0.00	0.00	0.00	0.00	0.02	0.12
HoPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01		0.05	0.00	0.01	0.00	0.07	0.08
ErPO ₄	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02		0.01	0.00	0.00	0.04	0.08
TmPO ₄	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.03		0.02	0.00	0.08	0.05
YbPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01		0.05	0.07	0.05
*YbPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.02	0.02	0.06
*YbPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.04	0.04	0.06
LuPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02		0.02	0.02
*LuPO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.01

Table 1. Trace elements in REE-PO₄ determined by LA-ICPMS (REE, n=3), and by EPMA (Mo, n=5). Asterisk (*) indicates recent batches with modified synthesis. Red indicates grain to grain variability.

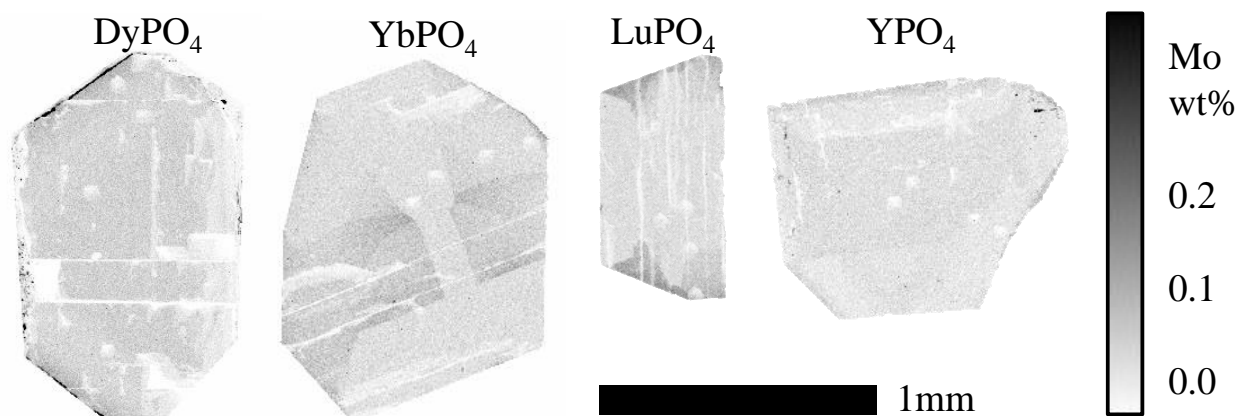


Figure 1. EPMA mapping of molybdenum concentrations for Dy-, Yb-, Lu-, and Y-orthophosphates. DyPO₄ shows the highest average Mo content (0.12 wt%), while heavy REE and Y have zoned Mo contents. Other REE-PO₄ are do not show Mo sector zoning, but typically have higher values on rims.