

## **Synthesis of REE and Y phosphates by Pb-free flux methods and their utilization as standards for electron microprobe analysis and in design of monazite chemical U-Th-Pb dating protocol**

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### **ABSTRACT**

(REE,Y) phosphates were synthesized in a 1 atm furnace by flux-growth methods involving Pb-free fluxes. Microcrystalline (REE,Y) phosphate was precipitated from a solution of (REE,Y) chlorides or nitrates plus ammonium dihydrogen phosphate, and mixed with a  $M_2CO_3$  ( $M = Li$  or  $Na$ )- $MoO_3$  flux (75:25:2 molar ratio  $M_2CO_3:MoO_3:REEPO_4$ ). Crystal growth was achieved over the temperature range 1350–870 °C, with extended (15 h) high- $T$  soaking, and cooling rates of 3 °C/h. Crystals grown by this method are clear, generally inclusion-free, up to several mm in length, and are easily extracted from the water-soluble flux. Crystal size and habit are influenced by the alkali component of the flux. Successful LREE phosphate synthesis is favored by both Li- and Na-bearing fluxes, whereas better results for Y and MREE-HREE phosphates were achieved with Na-bearing fluxes. Li-bearing fluxes produced LREE phosphates with an overall platy habit, in contrast to more prismatic-to-equant LREE-MREE phosphates produced with Na-bearing fluxes.

Structural refinements of single-crystal X-ray diffraction data show that  $LREEPO_4$  (La-Gd) crystallize with the monoclinic monazite structure, and  $HREEPO_4$  (Tb-Lu) plus  $YPO_4$  crystallize with the tetragonal xenotime structure. Element distribution maps of synthetic  $REEPO_4$  reveal homogeneous distribution of REE and P at grain-size scale and below, and both wavelength-dispersive (WD) spectral scans and quantitative electron microprobe analyses show no other elements (e.g., flux inclusions) present at significant levels.

The synthetic phosphates grown with this method are suitable for use as electron microprobe standards and as compositionally simplified monazite analogs for use in the design of U-Th-Pb chemical dating protocols. WD scans of synthetic unary and ternary (La-Ce-Nd) phosphates reveal that Ar X-ray detectors produce non-filterable LREE escape peaks with pulse-height analyzers optimized for Pb analysis. Such LREE escape peaks complicate collection of both U and Pb peak and background counts. Due to the larger energy difference between LREE peaks and Xe (relative to Ar), LREE escape peaks produced in Xe detectors are filterable with pulse height analyzers, resulting in LREE-free spectra over the wavelength range sampled for Pb peak and background collection.