

# *Contamination in the Rare-Earth Element Orthophosphate Reference Samples*

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Several of the fourteen rare-earth element (plus Sc and Y) orthophosphate standards grown at Oak Ridge National Laboratory in the 1980s and widely distributed by the Smithsonian Institution's Department of Mineral Sciences, are significantly contaminated by Pb. The origin of this impurity is the  $\text{Pb}_2\text{P}_2\text{O}_7$  flux that is derived from the thermal decomposition of  $\text{PbHPO}_4$ . The lead pyrophosphate flux is used to dissolve the oxide starting materials at elevated temperatures ( $\approx 1360^\circ\text{C}$ ) prior to the crystal synthesis. Because these rare-earth element standards are extremely stable under the electron beam and considered homogenous, they have been of enormous value to electron probe micro-

analysis (EPMA). The monoclinic, monazite structure, orthophosphates show a higher degree of Pb incorporation than the tetragonal xenotime structure, orthophosphates. This paper will attempt to describe and rationalize the extent of the Pb contamination in these otherwise excellent materials.

**Key words:** EPMA; microanalysis; orthophosphates; quantitative analysis; rare earth elements; rare earth phosphates; REE; standards.

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## 1. Introduction

Highly accurate analyses from the electron microprobe analyzer (EMPA) are only (but not solely) obtainable through the use of well-characterized and stable standards containing a major and/or known concentration of the element in question. For the rare earth elements (REE) this goal has, until recently, been elusive

due to the lack of specimens exhibiting these vital properties.

The lanthanide orthophosphates, consisting of compounds with the stoichiometry  $\text{LnPO}_4$  where Ln represents any of the REE in the series extending from La to Lu (plus the related compounds  $\text{YPO}_4$  and  $\text{ScPO}_4$ ), are

chemically durable and radiation resistant refractory materials. During the early 1980s a variety of single crystal rare earth orthophosphate samples were synthesized at Oak Ridge National Laboratory and the structures determined from x-ray refinements [1, 2, 3, 4, 5, and 6]. The primary purposes of these studies were varied, but they included nuclear and actinide waste disposal and scintillator material research as well as fundamental materials characterization investigations. The crystals were synthesized using a high-temperature solvent (flux-growth) technique, the details of which are available from the original papers, and a good overview of the development of these orthophosphates is discussed in Boatner and Sales [7], and references therein.

One interesting fact is that although the starting materials were carefully selected to be free from REE impurities, they were grown in a lead pyrophosphate ( $\text{PbHPO}_4$ ) flux. Pb contamination was not a concern for the original purposes of those experiments, however its presence was detected early on, and the solid state chemistry (but not the concentration) of Pb in the orthophosphate was characterized by means of electron paramagnetic resonance spectroscopy (EPR) [8]. Subsequently, these materials were investigated for possible use as standards for EPMA by the Smithsonian Institution [9], and put through a series of tests. These included homogeneity testing and a comparison to the commonly used REE doped aluminum silicate glass standards of Drake and Weill [10] using the EPMA, and a check of 10 selected REE contaminants on 7 of the compounds using instrumental neutron activation analysis. The materials appeared to be robust under electron bombardment, did not oxidize or seem hygroscopic, and no serious contamination or inhomogeneities were noted at the time and these efforts were followed by a general distribution of the material to interested parties.

In the late 1990s it was reported to one of us (JJD) that at least one investigator (E. J. Essene, University of Michigan, personal communication) had raised the issue of the role of the Pb impurity in some of the REE phosphate standards. The Pb impurity is especially significant in the  $\text{CePO}_4$  crystals whose black coloration is consistent with possible mixed valence ( $\text{Ce}^{3+} - \text{Ce}^{4+}$ ) effects—the presence of which could alter the high-temperature solid-state chemical properties and lead to an enhanced incorporation of Pb during the crystal-growth process. Subsequent investigations of the materials revealed Pb ranging in concentration from less than 0.01 mass fraction to more than 0.04 mass fraction in the  $\text{CePO}_4$ , depending on the specific grains analyzed. It is the intent of this paper to characterize the extent of the Pb contamination in these otherwise extremely useful standards for EPMA.

## 2. Experimental Methods

Quantitative wavelength dispersive spectrometry (WDS) analyses for the REEs Sc, Y, and Pb in each of the 16 orthophosphate samples were done using a Cameca SX-51<sup>1</sup> electron microprobe at 20 keV, 20 nA ( $2.0 \times 10^{-8}$  A), using a 10  $\mu\text{m}$  beam diameter at UC Berkeley. In addition, one of the Drake and Weill REE glasses [10], and two other REE doped calcium aluminum silicate discussed in Roeder [11] and Roeder et al. [12] were analyzed. For quantitative analyses, the  $K_{\alpha}$  x-ray line was used for Sc,  $L_{\alpha}$  lines for Y and the other REE elements, and the  $M_{\alpha}$  line was used for Pb. Count times were 20 s on peak and 10 s on each off-peak position except for Pb where the count times were doubled, respectively.

A complete description of the analytical setup and secondary standard accuracy for the analyzed elements (the composition of the REE phosphate primary standards in these cases had been previously adjusted for average Pb concentrations) is presented in Table 1. Secondary standards included synthetic yttrium-aluminum garnet (YAG) and alamosite ( $\text{PbSiO}_3$ ) from Tsumeb, Namibia and were assumed to be stoichiometric for Y and Pb, respectively. The Roeder REE glass S-254 [12] was assumed to have a nominal concentration ( $1.04 \times 10^{-2}$  mass fraction) for La, Ce, Pr, Nd, Sm, Dy, Ho, Er, Yb, and Lu, and the Drake and Weill REE-1 glass was used based on published concentrations for Eu, Gd, Tb, and Tm [10]. For all rare-earth elements, the relative differences obtained when comparing the secondary standards to the primary standard is better than 10 % at the 0.01 mass fraction to 0.04 mass fraction concentration levels and better than 6 % in all but three cases (Pr, Sm and Lu).

The difficulty of dealing with interfering elements for REE analyses using the  $L_{\alpha}$  x-ray lines is painfully evident in even cursory WDS spectral scans on these samples and can only be overcome by careful and consistent application of an automatic correction scheme. Table 2 shows the REEs that interfere with the analyzed elements. These were interferences quantitatively corrected for using the iteration method of Donovan et al. [13], that is especially well suited for using large magnitude interferences for trace element determinations. For the Pb analyses, the  $M_{\alpha}$  line was used with a quantitative interference correction for Y (possible high order interferences from La and Tb were not observed). Standard

<sup>1</sup> NIST disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

**Table 1.** Analytical setup and measured differences between the secondary standards and the primary standard for REE quantitative analysis<sup>a</sup>

Element Sc K <sub>α</sub>	Spect. setup LiF (FPC-2)	Primary standard ScPO <sub>4</sub> (syn.)	Secondary standard Conc in mass fraction × 10 <sup>2</sup>	Relative diff.
YI <sub>α</sub>	PIET (FPC-1)	YPO <sub>4</sub> (syn.)	YAG (stoic.)	+0.368, +0.82 %
LaI <sub>α</sub>	LiF (FPC-2)	LaPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.020, −1.92 %
CeI <sub>α</sub>	LiF (FPC-2)	CePO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.010, −0.95 %
PrI <sub>α</sub>	LiF (FPC-2)	PrPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.103, −9.95 %
NdI <sub>α</sub>	LiF (FPC-2)	NdPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.007, −0.70 %
SmI <sub>α</sub>	LiF (FPC-2)	SmPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.055, −5.27 %
EuI <sub>α</sub>	LiF (FPC-2)	EuPO <sub>4</sub> (syn.)	REE-1 (3.63 pub.)	+0.069, +1.90 %
GdI <sub>α</sub>	LiF (FPC-2)	GdPO <sub>4</sub> (syn.)	REE-1 (3.87 pub.)	−0.012, −0.31 %
TbI <sub>α</sub>	LiF (FPC-2)	TbPO <sub>4</sub> (syn.)	REE-1 (3.78 pub.)	−0.116, −3.08 %
DyI <sub>α</sub>	LiF (FPC-2)	DyPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.035, −3.35 %
HoI <sub>α</sub>	LiF (FPC-2)	HoPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.041, −3.92 %
ErI <sub>α</sub>	LiF (FPC-2)	ErPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.047, −4.51 %
TmI <sub>α</sub>	LiF (FPC-2)	TmPO <sub>4</sub> (syn.)	REE-1 (3.81 pub.)	−0.127, −3.33 %
YbI <sub>α</sub>	LiF (FPC-2)	YbPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.047, −4.53 %
LuI <sub>α</sub>	LiF (FPC-2)	LuPO <sub>4</sub> (syn.)	S-254 (1.04 nom.)	−0.103, −9.94 %
PbM <sub>α</sub>	PIET (FPC-1)	PbCO <sub>3</sub> (Tsumeb)	PbSiO <sub>3</sub> (stoic.)	+0.550, +0.75 %

<sup>a</sup> Analytical spectrometer setup (flow proportional detectors: FPC-1 indicates 1 atm P-10 and FPC-2 indicates 2 atm P-10) for REE elements (plus Sc, Y, and Pb) and results of secondary standard measurements (algebraic difference and relative difference) performed at UC Berkeley. All elements were measured at 20 keV, 20 nA (150 nA for the four grain map), 10 μm beam diameter, 20 s on-peak integration time and 10 s on each off-peak except for Pb which was counted for 40 s on-peak and 20 s on each off-peak position (240 s on-peak and 120 s on each off-peak position for the four grain map in Fig. 5). Each result shown is the average of 10 measurements.

and background intensities along with the calculated  $P/B$  (peak to background) for each line in its associated primary standard are shown in Table 3.

Under the analytical conditions which were utilized at Berkeley, the minimum detection limits for both single analyses calculated from Love and Scott [14], and for the average of 10 replicate analyses based on Goldstein et al. [15], are shown in Table 4. Minimum detection limits for 10 replicate analyses based on the actual measured standard deviation are about  $3.0 \times 10^{-4}$  mass fraction to  $6.0 \times 10^{-4}$  mass fraction for all elements in all matrices although only values for CePO<sub>4</sub> or GdPO<sub>4</sub> are shown in Table 4. A measured detection limit of  $3 \times 10^{-4}$  mass fraction to  $6 \times 10^{-4}$  mass fraction for the average of 10 replicates at 99 % a confidence level was typical for the REE analyses under these conditions. The Pb detection limit at a 99 % confidence level was about  $4.5 \times 10^{-4}$  mass fraction.

Another set of measurements, for the analysis of Pb homogeneity only, were also done on the same grains, but in a different area from the REE and Pb measurements done at UC Berkeley. These measurements were made for each REE orthophosphate using a JEOL 8900 Superprobe at the University of Maryland-College Park. X-ray intensities of Pb were obtained using an accelerating voltage of 20 keV, and a beam current of 150 nA. Count times were 60 s on peak, and 30 s for backgrounds on each side of the peak. Pb was analyzed using a PETH (which utilizes a smaller diameter Rowland Circle allowing for higher count rates, but has poorer

wavelength resolution) crystal, and background positions of +4 mm ( $L = 173.307$  mm or  $5.4013$  Å) and −3 mm ( $L = 166.307$  mm or  $5.1828$  Å). Natural cerussite (PbCO<sub>3</sub>) from Tsumeb, Namibia, was used as a standard for Pb (0.8393 mass fraction PbO). It should be noted that although cerussite is a carbonate mineral it did not appear to degrade under the electron beam during the analyses. The Pb M<sub>α</sub> x-ray line was used for all analyses, with the exception of YPO<sub>4</sub>, where M<sub>β</sub> was used due to an interference from Y<sub>173</sub> on Pb M<sub>α</sub>. For these Pb homogeneity measurements, the REE and phosphate concentrations were not measured but were incorporated as stoichiometric proportions into the ZAF algorithm in order to approximately account for matrix effects. The single analysis detection limit at a 99 % confidence level for Pb under these analytical conditions was about  $1.4 \times 10^{-4}$  mass fraction Pb based on a standard count rate of 263.9 cps/nA and a background of 0.8 cps/nA measured on CePO<sub>4</sub>.

Measurements were done on two different sets of REE orthophosphate samples. The first set consists of material for 16 orthophosphates, including Sc and Y obtained from one of us (JMH) and mounted along with primary and secondary standards for analysis and interference corrections. These materials were mounted in a 25 mm diameter acrylic mount approximately 1.5 cm deep using a cold set epoxy and circulated to both laboratories. This sample will be referred to as the “Round Robin” mount in the discussion that follows.