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Synthesis and characterisation of PuPO₄ - a potential analytical standard for EPMA actinide quantification

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Abstract. Transmutation nuclear fuels contain weight percentage quantities of actinide elements, including Pu, Am and Np. Because of the complex spectra presented by actinide elements using electron probe microanalysis (EPMA), it is necessary to have relatively pure actinide element standards to facilitate overlap correction and accurate quantitation. Synthesis of actinide oxide standards is complicated by their multiple oxidation states, which can result in inhomogeneous standards or standards that are not stable at atmospheric conditions. Synthesis of PuPO₄ results in a specimen that exhibits stable oxidation-reduction chemistry and is sufficiently homogenous to serve as an EPMA standard. This approach shows promise as a method for producing viable actinide standards for microanalysis.

1. Introduction

Nuclear fuels are being developed for next-generation nuclear reactors (GEN-IV) that have the ability to burn Pu, Am, and Np from spent nuclear fuels. Upon irradiation, these so-called transmutation fuels convert long-lived minor actinide elements (MA) to shorter-lived fission products, thereby decreasing the radiotoxicity and heat load of spent nuclear fuel.

The thermodynamic behaviour of MA is unlike that of uranium in conventional nuclear fuels. Moreover there is much greater variation in the chemical and isotopic composition of transmutation fuels, such that they cannot be considered to be a simple extension of extant fuels [1].

Because of these features, considerable research and development is required for both fabrication and analysis of transmutation fuels. Integral to the fabrication and analysis of irradiated fuel is electron probe microanalysis (EPMA). This technique has been used since at least 1961 [2] for the analysis of nuclear fuels because wavelength dispersive spectrometers permit better separation of complex peaks, such as those exhibited by the actinide metals group, than is possible with energy dispersive detectors.

Reference materials are necessary to calibrate the instrument in order to obtain an accurate MA measurement. While some progress has been made with regard to creating models for standardless analysis [3], such efforts are still in their infancy. Therefore, nuclear fuels researchers still rely on the use of physical standards for the analysis of MA. Unfortunately, fabrication and use of such standards is fraught with difficulty. All fabrication and polishing must be done in special nuclear-grade facilities. Such facilities typically include glove boxes with prescribed atmospheres, and remote handling tools. Metal specimens are relatively easy to handle, but when exposed to oxygen, will oxidise very rapidly.
This causes a large dimensional change to the specimen, and it will begin to spall, resulting in radioactive contamination. Oxides have been commonly employed because they are more stable under atmospheric conditions; however, they are difficult to fabricate. Actinide elements can exist in many oxidation states [4], therefore the atmosphere and temperature control during fabrication is crucial for creating stable oxide compounds [5, 6]. Incorrect atmosphere or temperature control during synthesis can result in an oxide compound that is not homogeneously oxidised and/or will not remain at that oxidation state when removed from the glove box atmosphere.

Lanthanide orthophosphates can crystallise in two different forms. The lighter lanthanides, LaPO₄ - GdPO₄ precipitate as a monoclinic structure analogous to monazite (a naturally occurring light rare earth mineral) while the heavier lanthanides, TbPO₄ - LuPO₄ precipitate as a tetragonal structure, analogous to zircon [7]. Experiments with Pu, Am, Cm, Bk, Cf and Es show that these elements precipitate with a monoclinic structure [7].

Several methods exist to make monoclinic orthophosphates. Begun [8] described dissolving and reacting lanthanide (Ln) oxides with molten lead orthophosphate at high temperature and then separating the crystals from the lead phosphate matrix by dissolving the matrix in boiling nitric acid. Cherniak et al. [9] created Ln-phosphates by dissolving Ln-nitrates in distilled water, adding NH₄H₂PO₄ and heating the solution on a hot plate. The ensuing precipitate was then mixed with a flux consisting of MoO₃ and either Li₂CO₃ or Na₂CO₃ and heated to at least 1,280 °C. Bjorklund [10] created monoclinic PuPO₄ via the precipitation and high temperature dehydration of hexagonal PuPO₄(0.5 H₂O), and Jardin et al. [11] prepared PuPO₄ by sol-gel reaction starting with a Pu (+4) solution that was mixed with (NH₄)₂HPO₄ to create PuP₂O₇. This compound was then reduced with H₂ to create PuPO₄.

While actinides sometimes do behave like lanthanides, Pu is known to decompose above 1,000 °C [11], thus the Begun [8] and Cherniak et al. [9] methods were not likely to create a homogeneous PuPO₄ specimen. A solid state method based on Bregiroux et al. [12] was chosen because PuO₂ was available as a starting material and this method demonstrated that single phase monoclinic PuPO₄ could be fabricated relatively easily via sintering in an argon atmosphere. While this method has been employed for structural investigations [13], it has not been tested for its ability to make crystals that are homogeneous on a micrometre spatial scale.

Herein we describe a method for fabricating stable, highly homogeneous actinide phosphate specimens for use as EPMA standards.

2. Methods

2.1. PuPO₄ synthesis
PuO₂ with ~2 % AmO₂ resulting from beta decay of ²⁴¹Pu was ground and mixed with (NH₄)₂HPO₄, placed into an alumina crucible, and heated slowly to 1,000 °C in an argon glove box (99.96 % purity with < 7 ppm H₂O). Heating and cooling ramps of 100 °C/h were employed with a 12 hour dwell at the target temperature. A dark violet powder was produced at the conclusion of the heating cycle.

X-ray diffraction of the powder shows that the material is a pure phase and has a monoclinic structure (figure 1), with valence states of Pu, P, and O atoms approximating +3, +5, and -2, respectively [13]. This was confirmed with X-ray absorption near edge structure (XANES) spectra [13]. This structure is similar to that of monoclinic monazite.

2.2. Preparation of the standard
A 7-mm disk of PuPO₄ was prepared by pressing. A second thermal treatment was applied wherein the pressed disk was sintered at 1,000 °C for 72 hours in an argon atmosphere. The sintered disk was then sectioned and a small piece was selected, mounted in epoxy, and polished to 1 µm (figure 2a). The sample was coated with approximately 20 nm aluminium prior to electron probe examination. While an aluminium coating is not a traditional choice for microprobe analysis, it is useful for nuclear applications for several reasons. Carbon coatings are known to be inadequate under high beam currents.
used in trace element acquisition [14], therefore, a more robust coating (one that has higher thermal and electrical conductivity) is required. While gold would be adequately robust, the porous nature of nuclear materials sometimes necessitates the use of thicker coatings (e.g., 20 nm or more) to ensure adequate conductivity across the entire surface. Such thick gold coatings would highly absorb lower energy X-rays, therefore aluminium is a more suitable choice. Since nuclear specimens are often coated and handled in an inert gas environment, the coating is not expected to oxidise during the analysis. Nuclear materials also have the benefit of not usually having aluminium as a constituent, therefore aluminium is a feasible choice for nuclear scientists, whereas it would be more problematic for geologists.

2.3. Analysis of the Standard
A Cameca SX100R EPMA was used to analyse the sample. Five 120 µm x 50 µm regions were selected for quantitative point analysis (figure 2a), with 30 points measured in each region. An accelerating voltage of 25 kV and current of 50 nA was used on each point, and the beam was focussed. Pu-Mα and Am-Mα were measured at each point. The Pu-peak was measured for 40 seconds while the Am-peak was measured for 200 seconds. P and O were not measured, but were included in the analysis as specified constituents. Probe for EPMA v. 11.7.1 with full PAP [15] phi-rho-z correction was used. Analysis locations were not chosen randomly, but rather were selected based on the size of the crystal and proximity to obvious defects (e.g., pores) (figure 2b). Despite the fact the P and O were not measured, the average deviation (N = 150) from perfect charge balance was 0.16 %.
Figure 2. a) Secondary electron image of the mounted, polished specimen showing five regions selected for analysis. Each region (A-E) contained 30 analysis points. Some epoxy remains on the surface. b) Shows region D from figure 2a, with specific locations for the 30 selected points. Note the presence of relatively large grains, which provide numerous locations for reliable analysis.

3. Results
Table 1 shows a summary of statistics for the measured points. The level of homogeneity, \( H \) in weight percent is calculated from equation (1)

\[
(H) = \pm \frac{100(t_{n-1}^{1-\alpha})Sc}{\sqrt{nN}} \%
\]  

where \( t_{n-1}^{1-\alpha} \) is the student’s \( t \)-value for a 1-\( \alpha \) confidence level and \( n-1 \) degrees of freedom, \( n \) is the number of measurements, \( Sc \) is the standard deviation of the number of counts, and \( \bar{N} \) is the average number of counts for the set of measurements. A homogeneous sample should have a level of homogeneity <1 [16], which is true for Pu-Ma in this sample. In addition, under 50 nA of current for 200 seconds, the sample demonstrated no visible damage, unlike LnP_{3}O_{14} specimens, which exhibit obvious pitting with a 20 nA, 30 second, diffuse beam.
Table 1. Shows the average number of counts, standard deviation, average weight percent, a comparison of measured to predicted concentrations, and level of homogeneity for Pu-Mα and Am-Mα.

| Parameter                        | Pu Mα  | Am Mα |
|----------------------------------|--------|-------|
| Mean Counts (150 points)         | 130565 | 10271 |
| Standard Deviation               | 1665   | 738   |
| Mean Weight Percent (150 points) | 70.20  | 1.50  |
| Measured Concentration/Predicted Concentration | 0.9952 | 1.042 |
| Standard Deviation               | 0.85   | 0.11  |
| Level of Homogeneity             | 0.21   | 1.15  |

While the PuPO₄ is slightly less homogeneous than the PuO₂ previously prepared and analysed by the Institute for Transuranium Elements (level of homogeneity of 0.12 [17]), the Pu oxidation state in PuPO₄ is extremely stable at temperatures < 1,000 °C and in oxygen atmospheres. In addition, oxide standards often have small grains and are more porous than PuPO₄, which makes finding suitable analysis locations difficult.

4. Implications and future work

While the standard produced is sufficiently homogeneous to serve as a Pu reference material, there is opportunity to improve the quality of the crystals. Many researchers (e.g., Bregiroux et al. [12]; Cherniak et al. [9]) suggest cooling rates on the order of 3 - 4 °C per hour, rather than the 100 °C per hour that was used in this study. Unfortunately the latter rate was the slowest possible using the available furnace. We do think that a slower cooling rate could produce significantly larger crystals, thus improving the quality of the specimen.

Given the success in creating homogeneous PuPO₄, naturally the question arises as to whether other MA standards can be fabricated in this manner. Bregiroux et al. [12] showed that ²⁴¹AmPO₄ could indeed be made by this route. However, ²⁴¹Am, which has a half-life of 432.2 years, caused the crystal to become amorphous within 300 days. If the crystal remains reasonably homogeneous and robust despite the lack of crystallinity and ingrowth of decay products, this method could be viable. Tetravalent actinides, such as Np and Th can be synthesized as a cheralite analogue (M²⁺M⁴⁺)(PO₄)₂ [18]. Testing is required to determine if the cheralite analogue is sufficiently homogeneous to serve as a microprobe reference material.

5. Conclusions

- The plutonium concentration is homogeneously distributed in this standard; however, care needs to be taken to select large, non-porous regions in which to make measurements.
- Americium’s level of homogeneity was >1, suggesting that the element is not homogeneously distributed. However, significantly more counts are required to draw a robust conclusion.
- The grains are larger, and the porosity lower than that of actinide oxide standards that are typically used. Using actinide phosphates like the present example is a promising new method to obtain high-quality standards for difficult-to-prepare actinide materials.

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References
[1] Carmack J and Pasamehmetoglu K 2008 Review of transmutation fuel studies. Idaho National Laboratory Report, INL/EXT-08-13779
[2] Lévy V, Kirianenko A, Brebec G and Adda Y 1961 Contribution à l’étude de la précipitation des gaz rares dans les métaux. C.R. Acad. Sci. Paris 252 876-878
[3] Moy A, Merlet C and Dugue O 2015 Standardless quantification of heavy elements by electron probe microanalysis. Anal. Chem. 87 7779-7786
[4] Lieser K 2000 Nuclear and radiochemistry. Second edition. (Darmstadt, Germany: Wiley-VCH) 462
[5] Tanaka K, Yoshimocki H, Obayaski H and Koyama S 2015 Oxidation behavior of Am-containing MOX fuel pellets in air. Energy Procedia 71 282-292
[6] Vaucy R, Belin R, Robisson A, Lebreton F, Aufore L, Scheinost A and Martin P 2016 Actinide oxidation state and O/M ratio in hypostoichiometric uranium-plutonium-americiun U_{0.75}Pu_{0.24}Am_{0.004}O_{2-x} mixed oxides. Inorg. Chem. 55 2123-2132
[7] Hobart D, Begun G, Haire R, and Helliwege H 1983 Raman spectra of the transplutonium orthophosphates and trimetaphosphates. J. Raman Spectrosc. 14 59-62
[8] Begun G, Beall G, Boatner L, and Gregor W 1981 Raman spectra of the rare earth orthophosphates. J. Raman Spectrosc. 11 273-278.
[9] Cherniak D, Pyle J, and Rakovan J 2004 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. Am. Mineral. 89 6347-6350
[10] Bjorklund C 1957 The preparation of PuP2O7 and PuPO4. J. Am. Chem. Soc. 79 6347-6350
[11] Jardin R, Pavel C, Raison P, Bouëxiére D, Santa-Cruz H, Konings R and Popa K 2008 The high-temperature behaviour of PuPO4 monazite and some other related compounds. J. Nuc. Mater. 378 167-171
[12] Bregiroux D, Belin R, Valenza P, Audubert F and Bernache-Assollant D 2007 Plutonium and americium monazite materials: solid state synthesis and X-ray diffraction study. J. Nuc. Mater. 366 52-57
[13] Popa K, Raison P, Martel L, Martin P, Priuer D, Solari P, Bouëxiére D, Konings R and Somers J 2015 Structural investigations of PuIII phosphate by X-ray diffraction, MAS-NMR and XANES spectroscopy. J. Solid State Chem. 230 169-174
[14] Jercinovic M and Williams M 2005 Analytical perils (and progress) in electron microprobe trace element analysis applied to geochronology: background acquisition, interferences, and beam irradiation effects. Am. Mineral. 90 526-546
[15] Pouchou J and Pichoir F 1991 in: Electron probe quantitation. (Heinrich K F J and Newbury D E; Eds.) (New York, NY: Plenum Press) 31-76
[16] Goldstein J, Newbury D, Echlin P, Joy D, Romig Jr. A, Lyman C, Fiori C and Lifshin E 1992 Scanning electron microscopy and X-ray microanalysis, 2nd edition. (New York and London: Plenum Press)
[17] Ritter X 2015 Micro-analytical investigations on actinide reference materials. Master’s Thesis. (Münster, Germany: Westfälische Wilhelms Universität)
[18] Bregiroux D, Popa K and Wallez G 2015 Crystal chemistry of MIII\textsubscript{IV}(PO\textsubscript{4})\textsubscript{2} double monophosphates. J. Solid State Chem. 230 26-33.