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MONAZITE AND OTHER LANTHANIDE ORTHOPHOSPHATES AS ALTERNATE ACTINIDE
 WASTE FORMS

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INTRODUCTION

The recent results of leach tests performed under hydrothermal conditions have shown that borosilicate glasses are physically and chemically unstable at elevated temperatures and pressures (1). These results emphasize the need for investigations of alternate high level waste forms which offer the potential of both increased resistance to leaching and stability under various possible metamorphic geological conditions. Although many of the previous (and present) studies of high level waste forms emphasize the containment of fission products, in fact, the dominant long term (i.e., after 300 to 500 year) radiation hazard is posed by the α -emitting actinides. Accordingly, the object of the present investigation is to evaluate an alternate means of actinide containment which is potentially superior to encapsulation in borosilicate glass. The mineral monazite, which is a mixed lanthanide-actinide orthophosphate [i.e., (Ce, La, Nd, Th, U)PO₄] of varying composition, is a crystalline material with established chemical and physical stability when subjected to natural geological conditions over extremely long time periods. Additionally, since monazite is a natural source of the actinides Th and U, it

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has been subjected to radiation damage (including α -particle damage) during its natural lifetime, and the continued maintenance of its physical and chemical integrity is evidence of its intrinsic resistance to radiation. In view of these obviously desirable characteristics, a series of investigations of the physical and chemical properties of both natural monazite and the related, synthetically produced lanthanide orthophosphates has been undertaken. These investigations have included the usual applied studies such as leach testing under various conditions and the consolidation of precipitated orthophosphate powders by hot pressing as well as more fundamental determinations of the valence states and site symmetry of the actinide impurities. The details of this work are presented in the following discussion.

LANTHANIDE ORTHOPHOSPHATE CRYSTAL GROWTH

Single crystals of the lanthanide orthophosphates were grown in order to perform X-ray, electron paramagnetic resonance, Mössbauer, radiation damage, and chemical stability studies. In going through the lanthanide series, the orthophosphates from La to Gd are characterized by the monoclinic (monazite) structure while the orthophosphates from Dy to Lu have the tetragonal (zircon) structure. Terbium orthophosphate is dimorphic but crystallization at elevated temperatures produces only the tetragonal form. Orthophosphate crystals of every member of the lanthanide transition series (excepting PmPO_4) have been grown using the flux technique described by Feigelson (2). Crystals of YPO_4 and ScPO_4 (zircon structure) were also grown. Fig. 1a. shows several crystals of LaPO_4 doped with 0.5 wt% americium 241 oxide. These crystals are shown inside the growth crucible and are still entrained by the solidified $\text{Pb}_2\text{P}_2\text{O}_7$ flux which is removed by boiling in nitric acid. Natural monazite ores are known to contain relatively high concentrations of uranium (i.e., up to 15 wt% UO_2), and it was possible to grow single crystals with similar uranium concentrations. Crystals of LaPO_4 with 10 wt% $^{238}\text{UO}_2$ are shown in Fig. 1b. Additionally, plutonium-doped LaPO_4 crystals have been grown from a starting composition of 90 wt% La_2O_3 and 10 wt% $^{242}\text{PuO}_2$. The maximum crystal size obtained for the monoclinic orthophosphates was approximately 4 mm on an edge, but significantly larger crystals of the tetragonal structure materials were obtained. As an example, an exceptionally large crystal of LuPO_4 is shown in Fig. 1c.

LANTHANIDE ORTHOPHOSPHATE PRECIPITATION AND CONSOLIDATION

Although the lead pyrophosphate flux process noted above represents a reliable method for obtaining single crystal specimens for leach tests and more fundamental research investigations, it is not considered to be a practical process for the synthesis of actual waste material. The method of precipitation in molten urea as em-

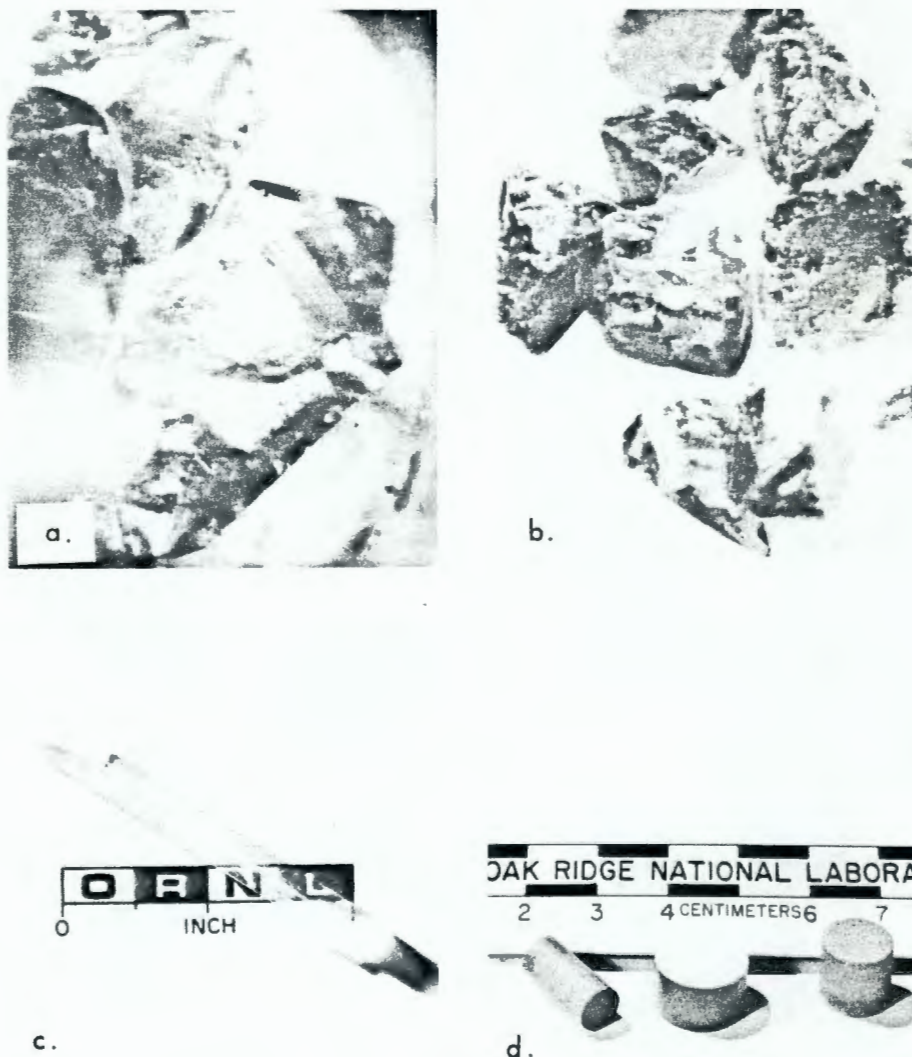


Fig. 1. a. Single Crystals of $\text{La} (^{241}\text{Am})\text{PO}_4$ in the Pt Growth Crucible. Starting composition 99.5 wt% La_2O_3 , 0.5 wt% Am_2O_3 . b. Single crystals of $\text{La} (^{238}\text{U})\text{PO}_4$. Starting composition 90 wt% La_2O_3 , 10 wt% UO_2 . c. Large single crystal of LuPO_4 grown with a cooling rate of $0.5^\circ\text{C}/\text{hr}$ between 1360° and 900°C . d. Hot pressed pellets of CePO_4 formed from precipitated powders.

ployed by W. S. Aaron, T. C. Quinby and E. H. Kobisk in the formation of their cermet material does, however, represent a promising process for the practical synthesis of large quantities of actinide contain-

ing rare-earth orthophosphates (3). Figure 1d. shows several pellets formed by hot pressing CePO_4 powders. The phosphate particle size can be controlled in the urea precipitation process and consolidation via hot pressing of powders with a suitably small particle size has resulted in bodies with 98% of the theoretical density.

SINGLE CRYSTAL X-RAY STRUCTURE ANALYSIS

Earlier single crystal determinations of the monazite structure were conducted using natural materials and were not carried out to the precision obtainable using current crystallographic methods. A redetermination of the structure using pure CePO_4 single crystals yielded more accurate bond distances and indicated nine coordinations rather than the eight found in the earlier measurements. These crystals were monoclinic (space group $P2_1/n$ with lattice constants of $a=6.777(1)$, $b=6.993(1)$, $c=6.445(1)$ and $\beta=103.5^\circ$. Fig. 2. shows a stereo projection of the cerium and phosphorus coordination. Each cerium atom has eight oxygen atoms at a distance of approximately 2.5 Å with a ninth oxygen 2.7 Å away. The polyhedron is irregular and may reflect the ability of this site to accommodate such varied ions as the lanthanides, tetravalent uranium, thorium and plutonium, along with charge compensation ions. The phosphate group is a distorted tetrahedron that links the cerium atoms.

OPTICAL SPECTRA

The visible spectra for LaPO_4 single crystals doped with various actinides are shown in Fig. 3. LaPO_4 was selected as the host orthophosphate since it is totally transparent in the region studied. The ^{238}U -doped crystals whose absorption spectrum is shown at the top of

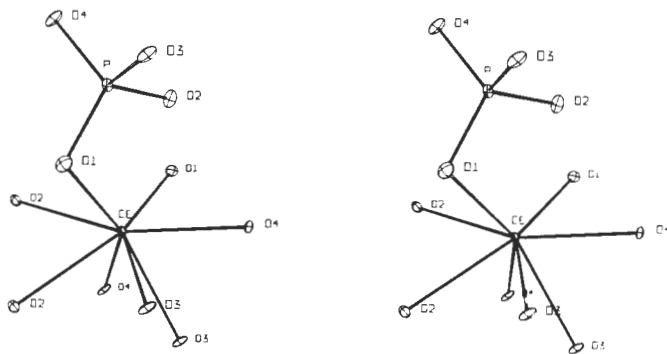


Fig. 2. Stereographic View of the CePO_4 Structure

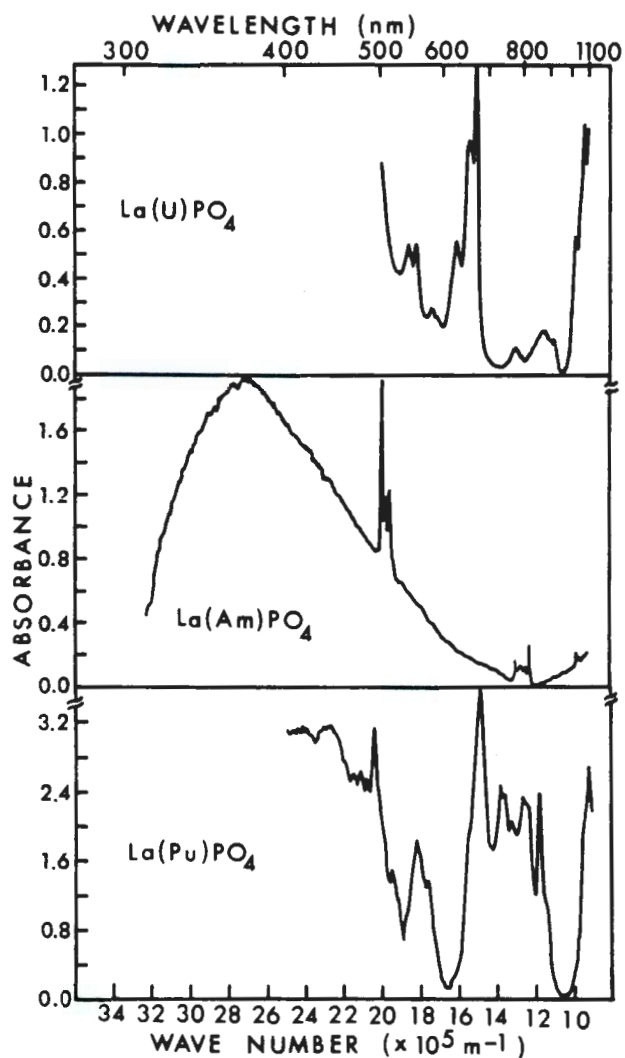


Fig. 3. Top: Optical Absorption Spectrum of LaPO_4 Grown with 10 wt% UO_2 . Middle: Optical spectrum of LaPO_4 doped with 0.5 wt% Am_2O_3 . Bottom: Optical absorption of LaPO_4 grown with the addition of 10 wt% $^{242}\text{PuO}_2$.

Fig. 3. contain 10 wt% uranium dioxide and have a deep green color indicative of tetravalent uranium. When the spectrum is examined in detail, the 4+ state is confirmed (4). Crystals of CePO_4 and (45 at% Sm, 45 at% Ce)(PO_4) have also been grown with a 10 at% uranium dopant. In both of these crystals, the ^{238}U tetravalent state was also confirmed. (The cerium in these crystals appears to be a mixture of Ce^{4+} and Ce^{3+} , with Ce^{3+} representing the predominant species.) These results are in agreement with observations of tetravalent uranium in natural monazite. The middle spectrum in Fig. 3. was obtained for LaPO_4 containing 0.5% americium 241. This spectrum shows that the americium is in the trivalent state, an observation that is consistent with the known redox chemistry of americium (5). These crystals have a pronounced amber color after cooling from the growth process and darken to a deep brown after several days at room temperature. This deepening color appears to be associated with radiation damage due to alpha decay and atom recoil from the americium 241. The color can be annealed out at approximately 500°C to produce perfectly clear material but returns in less than 24 hours at room temperature. The spectrum shown at the bottom of Fig. 3. was obtained for LaPO_4 containing 10 wt% plutonium dioxide. These crystals have a deep brown color which can be identified as due to tetravalent plutonium. The brown color darkens slightly following an anneal at 1000°C. This color change cannot be explained at this time.

MÖSSBAUER INVESTIGATIONS

Mössbauer effect studies were performed using $\text{La}(\text{Am})\text{PO}_4$ as a source and NpO_2 as an absorber at 4.2 K. The observed Mössbauer spectrum (see Fig. 4.) shows that an absorption with a small splitting has occurred with an isomer shift in the neighborhood of +17 mm/sec and that a second absorption with a larger splitting has occurred with an isomer shift in the neighborhood of -35 mm/sec. The observed splitting is believed to result from a small electric field gradient (efg) for the absorption at 17 mm/sec (consistent with Np^{5+}) and a larger efg for the absorption at -35 mm/sec (consistent with Np^{3+}). The absorption at -35 mm/sec is probably a result of the recoiling ^{237}Np having found a normal NpPO_4 site prior to its recoilless γ de-excitation. The large 5+ Mössbauer absorption is somewhat surprising since the parent Am is trivalent. A permanent change in valence of this type following α -decay is very unusual and could have far-reaching implications concerning the leachability of the actinides.

ELECTRON PARAMAGNETIC RESONANCE STUDIES

The technique of electron paramagnetic resonance (EPR) was used to determine the local site symmetry of Gd^{3+} impurity ions in single crystals of the lanthanide orthophosphates, and these results were compared with the EPR spectra obtained from powders formed using the

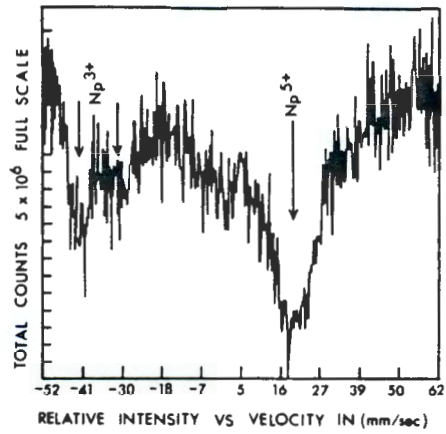


Fig. 4. Mössbauer Spectrum of the ^{237}Np Daughter of ^{241}Am in LaPO_4

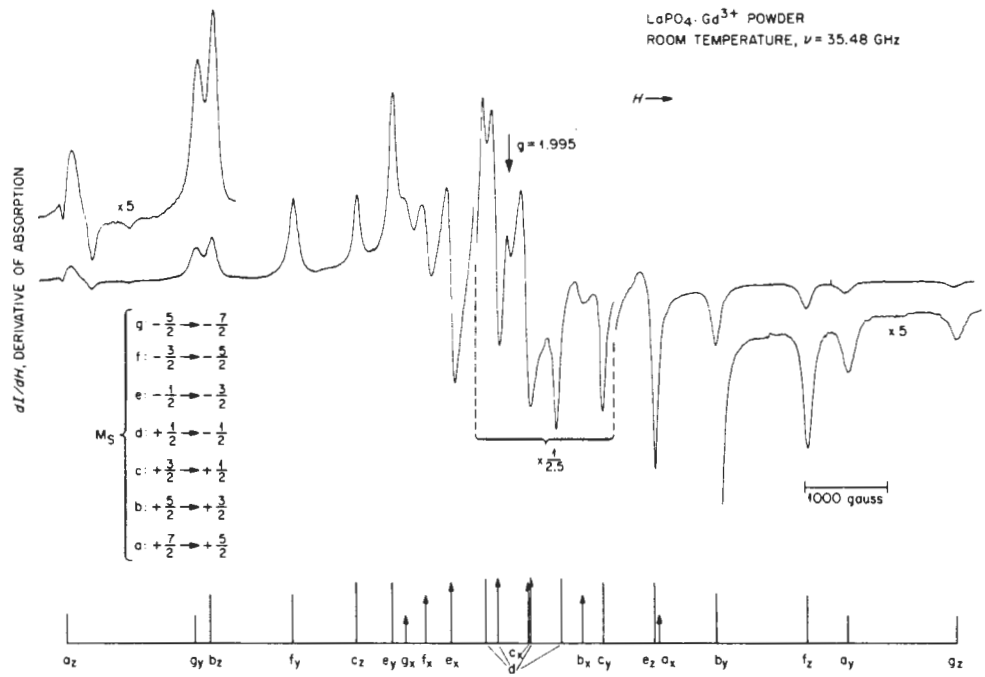


Fig. 5. EPR Powder Spectrum of Gd^{3+} Doped LaPO_4 . Positions of the shoulders and divergences (arrows) are indicated by the scale.

urea process (3). An example of a Gd^{3+} powder spectrum is shown in Fig. 5. By comparing powder spectra such as this with the spectra obtained from single crystals, it was possible to show that the Gd^{3+} impurities occupy identical substitutional sites in both the single crystal and urea-precipitated powder specimens. Since the crystal-line electric field splitting of the $Gd^{3+} 8S_{7/2}$ ground state can be used as a sensitive probe of the local environment, experiments are underway to exploit this sensitivity in investigations of α -particle damage in the lanthanide orthophosphates.

LEACHING STUDIES

The leachability of a waste form is one of the most important factors in determining its suitability for use in a nuclear waste repository. Leach tests of orthophosphate crystals resulted in IAEA leach indices that were smaller than those reported for grouts or borosilicate glasses by a factor of 16 for $CePO_4$ into 4 M NaCl at 200°C and 250 psi and a factor of 295 for $La(Am)PO_4$ into distilled water at 200°C and 250 psi (6). These results are even more striking since the leaching studies on the glasses and grouts were conducted at room temperature and atmospheric pressure.

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