The Structures of Three Lanthanide Orthophosphates

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$TbPO_4$, $DyPO_4$, and $HoPO_4$ crystallize in space group $I4_1/amd$ (No. 141), zircon structure, $Z = 4$. The crystal structures have been determined from automated three-dimensional single-crystal X-ray diffraction analyses. Least-squares full-matrix refinements yielded final weighted R-values equal to 0.035, 0.037, and 0.036, respectively. The lanthanide metal atom in each compound is eight-coordinated to oxygen atoms forming two orthogonal interpenetrating tetrahedra. Each tetrahedron has distinct bond distances. The resultant polyhedron is best described as a distorted dodecahedron (D_{2d}). Important crystal data, parameters, bond lengths, and angles are tabularized.

Introduction

High level nuclear waste forms that are placed in long-term or permanent storage in deep geological repositories may be exposed to hydrothermal leaching conditions. Recent studies pertaining to the stability of borosilicate glass nuclear waste forms when exposed to a hydrothermal environment [1] have raised a number of questions regarding the suitability of these materials as primary hosts for long-term radioactive waste disposal. The stability requirements placed on a primary waste form are, of course, quite severe since the long half lives of some of the hazardous, α-active actinide isotopes dictate that these substances must be immobilized for 10^4 to 10^5 years. The necessity for such long periods of stability for a primary waste form, coupled with the questionable performance of borosilicate glasses under hydrothermal conditions, has recently led to renewed interest in the development of alternative containment materials.

One of the more promising alternate waste forms is based on the lanthanide orthophosphates—*i.e.*, on a matrix material representing a synthetic analog of the uranium and thorium bearing orthophosphate mineral monazite. The established geological history of monazites indicates that these minerals have existed in a stable form in the earth's crust for over 2 billion years. Additionally, monazites are always found in a non-metamict (*i.e.*, crystalline) state in nature in spite of the fact that they have received relatively large heavy-particle radiation doses as a result of their actinide content. In contrast to this observation, however, it has been reported that monazites can be transformed to a metamict state by bombardment with 3 MeV Ar ions at a fluence of ~3 ions/nm^2 [2]. These somewhat conflicting observations have resulted in the initiation of a series of in-depth experimental and theoretical investigations of heavy-particle radiation damage effects in the lanthanide orthophosphates. Precise structural data are required for these investigations and the present work represents part of a continuing effort to obtain structural information from single crystals of the entire series of rare-earth and related orthophosphates. Such information has been obtained previously for monoclinic $CePO_4$ [3] and for the zircon-structure orthophosphates [4, 5]. Additional information regarding the local crystal structure at the lanthanide site has been provided by the results of recent EPR studies [5, 6].

Experimental

A flux technique [7] was employed in obtaining single crystals of $TbPO_4$, $DyPO_4$, and $HoPO_4$. Oxides of the corresponding lanthanides were placed in tightly covered platinum crucibles containing lead diorthophosphate ($PbHPO_4$) which, at high temperature, will decompose to form the flux matrix (lead pyrophosphate, $Pb_2P_2O_7$). After 16 h at 1360 °C the Pt-crucibles were cooled at a rate of 1 °C h^{-1} to 900 °C. At this point, the crucibles were allowed

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to cool directly to room temperature. In order to free the lanthanide orthophosphate crystals, the lead pyrophosphate flux was dissolved in boiling HNO_3. Complete details of the crystal production process have been published elsewhere [5].

After preliminary optical examinations, single crystals of Tb, Dy, and $HoPO_4$ were selected and mounted on goniometer heads. X-ray measurements were made on an Enraf-Nonius CAD-4 diffractometer (MoKα, $\lambda_{mean} = 0.71073$ Å at 292 K) which is equipped with a lithium–silicon solid-state detector system [8] and a dense graphite monochromator assumed to be ideally imperfect. The orientation matrix used for each data collection was obtained from twenty-five carefully centered reflections using a least-squares refinement which also yielded the cell constants listed in Table I. The Ω–2θ scan technique, with a variable scan rate of 0.4 to 3.4° min^{-1} determined by a fast prescan of 3.4° min^{-1}, was used for collecting each data set (see Table I). The intensities of two check reflections from each data set were monitored every 2 h of exposure time in order to check the reliability of the electronics, the X-ray intensity measurements, and the crystal stability. Only random variations from mean intensity values were observed in each of the three sets of data (ea. $< 2.4\%$). Intensities having $I > 3\sigma(I)$ were used in the structure refinement [9]. All resultant diffraction data were corrected for Lorentz and polarization effects. Standard deviations in the intensities, $\sigma(I)$, were estimated by assuming Poisson counting statistics to be valid. Absorption corrections were applied to each data set and the redundant data were averaged. The standard deviations of the averaged data were determined as

$$\sigma(F) = \Sigma[1.02(F_i)]/N$$

where N is the number of redundant measurements and $\sigma(F_i)$ is the standard deviation for each individual measurement. The 4/mmm Laue group was verified ($hk0 = kh0 = h\bar{k}0 = k\bar{h}0$. The presence of 001 where $l = 4n$ as well as hk0 where $h,(k) = 2n$ (hk0 absent when h and k are odd) and the absence of hhl when $2h + l = 4n + 1$ lead to the space group assignment, $I4_1/amd$ (No. 141).

Space group $I4_1/amd$ has two origins, $\bar{4}m2$ and at the center (2/m). The latter has two symmetrically equivalent sets of fourfold positions having $\bar{4}m2$ point symmetry which were used for the lanthanide (Ln) and phosphorous atom positions (4a and 4b, respectively). Since the number of molecules in the unit cell is four and the orientation of the oxygen atoms about the phosphorous atoms forms a distinct phosphate group in the structure, the only suitable sixteenfold site (of the three available 16-fold sites) was 16 h. Full-matrix least-squares refinements [10] of the entered model using anisotropic thermal parameters and secondary extinction corrections (g) produced the final residual index values and 'goodness of fit' values (Σ_2) listed in Table I. The average cut-off values $[\Delta\xi_i/\sigma(\xi_i)]$ where ξ_i values are varied parameters are also presented. Reliability factors and Σ_2 are defined elsewhere [4]. Final difference electron density maps were quite featureless except for very low maximum and minimum peaks near the lanthanide atom positions which is reasonable (see Table I). Elsewhere peaks ranged from 0.7 to −0.8 e Å^{-3} which can be attributed to random fluctuating background. Atomic scattering factors and the applied anomalous-dispersion corrections were taken from Ibers and Hamilton [11]. Table II lists the final refined atomic and thermal parameters with their estimated standard deviations.

TABLE I. Crystal Data and Statistical Summaries.

	$TbPO_4$	$DyPO_4$	$HoPO_4$
a (Å)	6.940(1)	6.907(2)	6.882(2)
c (Å)	6.068(1)	6.046(2)	6.025(2)
V (Å^3)	292.26	288.43	285.36
M.W.	253.90	257.47	259.90
D_c (Mg m^{-3})	5.768	5.929	6.049
μ(MoK$_\alpha$, mm^{-1})	248.36	265.14	284.23
Unique refl.	420	163	214
$\Delta\theta$	1.5–55	1.5–35	1.5–40
R_1	0.0350	0.0371	0.0359
R_2	0.0351	0.0372	0.0361
Σ_2	1.09	2.32	2.02
g(10^{-5} e^{-2})	0.56(2)	2.2(1)	2.5(1)
Avg. $[\Delta\xi_i/\sigma(\xi_i)](10^{-5})$	4.82	3.62	1.04
Residual density (e Å^{-3})			
Max.	3.1(5)	3.0(5)	2.4(5)
Min.	−2.8(5)	−2.0(5)	−2.1(5)

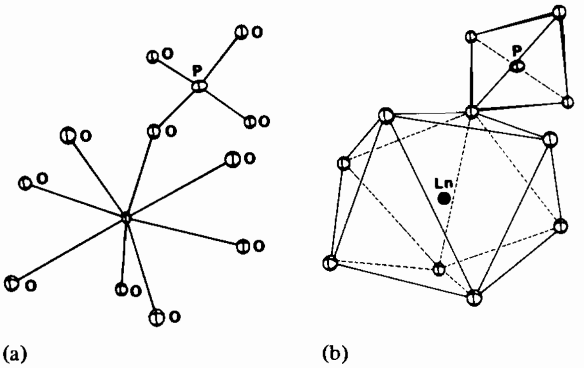
Discussion

Terbium, dysprosium, and holmium orthophosphates best fit the crystallographic model, $I4_1/amd$. Figure 1 presents this zircon-type structure. Eight oxygen atoms are coordinated to the central lanthanide metal atom forming two unique orthogonal interpenetrating tetrahedra, each having unique Ln–O bond distances, see Table III. The perpendicularly-viewed tetrahedron (Fig. 1a) of the bisphenoidal set associated with the PO_4 group has the shorter unique length. The structural polyhedron formed from the O–O contact distances (see Table III) is a distorted dodecahedron (D_{2d}) as seen in Fig. 1b. Demitras *et al.* [12] describe such a form as deriving from a distorted cube which can be visualized to designate its point group by considering the form as two perpendicular trapezoids. The bond distances determined in each data set (tabulated in Table III)

TABLE II. Atomic Positions ($\times 10^4$) and Thermal Parameters (Å^2 $\times$ 10^2)^a.

	Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$TbPO_4$	Tb	0	7500	1250	0.30(1)	–	0.76(2)	0	0	0
	P	0	2500	3750	0.25(5)	–	1.05(10)	0	0	0
	O	0	4238(6)	2218(8)	0.95(16)	0.57(12)	1.06(15)	0	0	0.1(1)
$DyPO_4$	Dy	0	7500	1250	0.52(6)	–	0.27(6)	0	0	0
	P	0	2500	3750	0.69(14)	–	0.35(23)	0	0	0
	O	0	4260(10)	2162(11)	0.36(31)	0.97(42)	0.82(32)	0	0	−0.1(3)
$HoPO_4$	Ho	0	7500	1250	0.63(4)	–	0.36(4)	0	0	0
	P	0	2500	3750	0.78(9)	–	0.58(10)	0	0	0
	O	0	4246(10)	2171(13)	0.89(24)	0.74(23)	1.32(29)	0	0	0.1(2)

^{a}The anisotropic temperature factors are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$ where U_{ij} values are the thermal parameters denoted in terms of mean-square amplitudes of vibration.



(a) (b)

Fig. 1. Tetragonal $LnPO_4$. (a) The two interpenetrating tetrahedral (bisphenoidal) sets, which are horizontal and perpendicular to the viewer, are quite distinguishable. (b) A distorted dodecahedron (bisbisphenoid) and a distorted tetrahedron.

TABLE III. Bond and Contact Distances (Å) and Bond Angles (°).

	$TbPO_4$	$DyPO_4$	$HoPO_4$
M–O	2.339(4) 2.425(5)	2.307(10) 2.403(9)	2.307(7) 2.386(8)
Avg.	2.382	2.355	2.347
P–O	1.523(4)	1.542(10)	1.533(7)
Phosphate group:			
O(1)–O(2) O(3)–O(4)	2.412(9)	2.431(20)	2.403(14)
O(1)–O(3),O(4) O(2)–O(3),O(4)	2.523(8)	2.562(17)	2.551(14)
O(1)–P–O(2) O(3)–P–O(4)	104.72(6)	104.05(14)	103.26(10)
O(1)–P–O(3),O(4) O(2)–P–O(3),O(4)	111.85(7)	112.35(14)	112.66(10)
Avg.	109.47	109.36	109.53

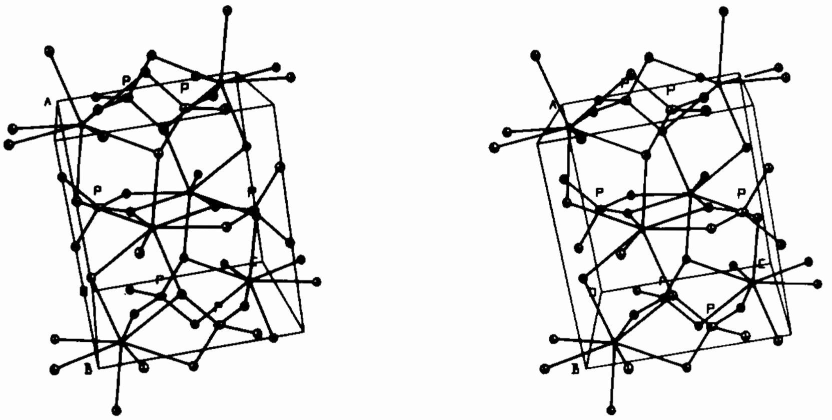


Fig. 2. A representative stereoview of the polyhedron in the tetragonal $LnPO_4$ system. Ln atoms are located at the center of the 8-coordinated polyhedron, P atoms are labeled, and all others are oxygen atoms.

were found to be in excellent agreement with previously reported bond lengths listed in the bibliography of the determination of inorganic crystal structures known as BIDICS [13] and are also internally consistent with the structural model. A representative stereoscopic view of the molecular packing in the unit cell for tetragonal Tb, Dy, and $HoPO_4$ is shown in Fig. 2, with 50% equiprobability ellipsoids represented.

The structural studies of terbium, dysprosium, and holmium orthophosphates detailed here are part of an extensive research program devoted to studies of the practicality of using the lanthanide orthophosphates as primary hosts for the isolation of nuclear wastes. The potential for accommodating chemically diverse cations such as thorium, uranium, α-active transuranic isotopes, and fission products such as strontium and cesium in the lattice of the predominantly trivalent $LnPO_4$ systems has been discussed elsewhere [3, 5].

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