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Structural Investigations of YPO_4, $ScPO_4$, and $LuPO_4$

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YPO_4, $ScPO_4$, and $LuPO_4$ crystallize in the tetragonal system conforming to space group model $I4_1/amd$ (D_{4h}^{19}, No. 141), $Z = 4$. The refined crystal structures have been determined from three-dimensional single-crystal X-ray diffraction data. Final least-squares full-matrix refinement yielded respective R-values of 0.024, 0.028, and 0.038. The metal atom in each compound is 8-coordinated to oxygen atoms. The resultant polyhedron is viewed as two interpenetrating tetrahedra forming a bis-bisphenoid (D_{2d}). The phosphate group in each compound is a distorted tetrahedron. Important bond and contact distances and bond angles as well as Ortep-II drawings are presented to foster a wider base for future investigations related to potential employment of lanthanide orthophosphates as hosts for radioactive nuclear waste.

Introduction

The borosilicate glasses and related amorphous materials have been proposed as primary hosts for the isolation of nuclear wastes. These substances have recently been challenged as appropriate containment materials, however, due to physical and chemical degradation brought about by the exposure of glasses to hydrothermal conditions. Accordingly, a number of crystalline materials including substances such as orthophosphates of the lanthanide series (*i.e*, analogs of the mineral monazite) are now being considered as alternate hosts for a resolution of the nuclear waste problem.

A number of naturally occurring minerals including monazite contain considerable amounts of thorium and uranium. In fact, monazite ores are commercial sources for both of these actinide elements. Geological studies indicate that monazite crystals have survived approximately two billion years of weathering [1] and have preserved their crystalline structure after extended exposure to alpha particles and the associated recoil nuclei. A structural study of cerium orthophosphate [2], a component synthetic analogue of monazite, has recently been carried out using modern X-ray crystallographic techniques. The structure of $CePO_4$ was found to consist of irregular 9-coordinated cerium atoms linked together by distorted tetrahedral phosphate groups. The system is monoclinic, $P2_1/n$.

The compounds YPO_4 and $ScPO_4$ represent orthophosphates that are structurally related to the lanthanide orthophosphate $LuPO_4$. Recent electron paramagnetic resonance (EPR) investigations of Gd^{3+} in single crystals and powders of the orthophosphates of yttrium, scandium, and lutetium were performed at Oak Ridge National Laboratory [3]. These EPR studies have shown that Gd^{3+} impurities in YPO_4, $ScPO_4$, and $LuPO_4$ occupy identical substitutional sites in both the powder and single-crystal samples. These experiments were undertaken to provide a basis for future studies related to effects of heavy-particle radiation damage in the lanthanide orthophosphates and an associated study to obtain precise structural information for these compounds is considered to be vital. The investigations reported here were initiated in order to obtain such data.

Experimental

Single crystals of the subject orthophosphates were grown using the flux method [4], in tightly

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covered platinum crucibles containing lead pyrophosphate as the flux matrix. After 16 h at 1360 °C, the crucibles were cooled at a rate of 1 °C/h to 900 °C and then, directly to room temperature. The $Pb_2P_2O_7$ flux was then dissolved in boiling HNO_3 in order to remove the crystals. Complete details of the crystal growth are given elesewhere [3]. The crystal sizes and calculated densities are listed in Table I.

Crystal X-ray Analysis

Single crystals of Y, Sc, and $LuPO_4$ were selected for three-dimensional data collection after preliminary optical examinations. All X-ray measurements were made on an Enraf-Nonius CAD-4 autodiffractometer which is equipped with a dense graphite monochrometer (Mo K_α, $\lambda = 0.71073$ Å) (take-off angle, 5.8°) and an Ortec Si(Li) energy-dispersive detector. A routine application of the solid-state detector was to obtain X-ray fluorescence data on the same single crystal from which X-ray diffraction data were collected [5]. Each of the heavy metal elements was quickly verified in the crystal under consideration. Twenty-five carefully centered reflections, using least-squares refinement, produced the orientation matrix for data collection (experimental temperature, 290 K) and the cell parameters for each crystal listed in Table I. Intensity data were collected by the $\Omega-2\theta$ scan technique in the range and scan speed limits found in Table I. During the prescan, all reflections having less than 75 counts above background were considered unobserved. For each crystal the intensities of two check reflections were monitored every 2 h of data collection. Examination of these intensities revealed only random variations (Y, < 1.4%; Sc, < 0.7%; $LuPO_4$, < 3.0%) which did not constitute any trend. The reliability of the diffractometer hardware and electronics and the stability of the crystals were thus ensured. The observed reflections in each data set obeyed the condition $I_{net} > 3\sigma(I)$ with $I_{net} = (P - 2B)$ and $\sigma(I) = (P + 2B + p^2 I_{net}^2)^{1/2}$, where P is the peak intensity, B is the sum of the time-scaled background counts on both sides of the peak and p is the ignorance factor (0.02). Lorentz and polarization corrections were made on the resultant intensities as well as analytical absorption corrections (see Table I for linear absorption coefficients and transmission factor ranges). It was observed that hk0 = kh0 and hkl = khl, thus the 4/mmm Laue group was established. After averaging equivalent reflections in each data set, 241, 287, and 153 unique reflections for Y, Sc, and $LuPO_4$ were obtained, respectively, for refinement. The respective residual averaging errors (2.4, 3.0, and 3.3%) were determined according to $R' = \Sigma\Delta|F|/\Sigma F_o$ where $\Delta|F| = |F_o - F_{avg}|$. The standard deviations of the averaged data were calculated according to Peterson and Levy [6], $\sigma(F) = N^{-1}\Sigma 1.02\sigma(F_i)$ where N is the number of equivalent data and $\sigma(F_i)$ = S.D. for each individual reflection. The presence of 00l where l = 4n and of 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, $I4_1/amd$ (D_{4h}^{19}, No. 141). Crystal data and experimental conditions are presented in Table I.

TABLE I. Experimental and Statistical Summaries.

		YPO_4	$ScPO_4$	$LuPO_4$
a. (Å)		6.8817(5)	6.574(1)	6.792(2)
c. (Å)		6.0177(6)	5.791(1)	5.954(2)
V (Å^3)		284.98	250.27	274.67
M. W.		183.88	139.93	269.94
D_c(mg m^{-3})		4.28	3.71	6.53
Crystal size (mm)		0.062 × 0.084 × 0.137	0.091 × 0.135 × 0.324	0.049 × 0.068 × 0.378
μ(MoK_α)(mm^{-1})		20.95	3.35	36.39
$\Delta\omega$(°)($\omega-2\theta$ scan)		1.25 + 0.35 tan θ	1.35 + 0.35 tan θ	1.30 + 0.35 tan θ
$\Delta\theta$(°)		1.5–55	1.5–55	1.5–27.5
Scan Limits (°)(min^{-1})		0.39–3.35	0.42–3.37	0.39–3.35
Transimission factor range		0.179–0.306	0.401–0.742	0.076–0.208
Unique refl.		241	287	153
Systematic absences		h + k + l = 2n + 1	h + k + l = 2n + 1	h + k + l = 2n + 1
R_1		0.0235	0.0280	0.0381
R_2		0.0237	0.0281	0.0363
Gnft (Σ_2)		0.90	1.05	1.90
g(e^{-2})(10^{-5})		0.22(2)	2.16(9)	2.1(1)
Avg. [$\Delta\xi_i/\sigma(\xi_i)$] (10^{-4})		0.028	2.4	0.19
Residual σ(e Å^3)	Max	1.4(2)	2.1(1)	2.3(5)
	Min	−1.3(2)	−1.0(1)	−1.9(5)

Structural Refinement

The tetragonal space group $I4_1/amd$ has two origins, $\bar{4}m2$ at the centre (2/m). The latter was chosen and has two symmetrically equivalent sets of fourfold positions into which the metal and phosphorus atoms were placed. The respective number positions with Wyckoff notation are 4a and 4b both having $\bar{4}2m$ point symmetry. There are 4 molecules in each unit cell (Z = 4). Since the oxygen atoms are oriented about the phosphorus atom to form a discrete phosphate group in the structure, only one of the three available sixteenfold sets yields suitable oxygen positions (16 h). This model was initially refined isotropically for each data set using a full-matrix least-squares refinement program [7]. The isotropic reliability factors of 0.051, 0.055, and 0.067 were obtained for the respective phsophates of Y, Sc, and Lu. Several more cycles varying anisotropic thermal parameters and applying secondary extinction corrections (g) yielded final residual index values (R_1 & R_2) and 'goodness of fit' values (Σ_2) presented in Table I. The reliability factors are defined as: $R_1 = \Sigma\Delta F/\Sigma|F_o|$ and $R_2 = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$ where $w = \sigma^{-2}(|F_o|)$ and $\Delta F = [|F_o| - |F_c|]$. The 'goodness of fit' value is explained as: Gnft $= \Sigma_2 = [\Sigma(w\Delta F^2)^2/N_G]^{1/2}$ where ΔF is defined above and $N_G = (N_o - N_v)$, N_o is the number of independent observations and N_v is the number of parameters varied in the refinement. The largest values of abscission $[\Delta\xi_i/\sigma(\xi_i)]$, where ξ_i values are varied parameters (12 in each data set) are: 1.3×10^{-5}, 1.8×10^{-3}, and 1.7×10^{-4} respectively for the title compounds (see Table I for average values). One of the subroutines in the full-matrix least-squares refinement program [7] contains a correlation coefficient matrix and for each data set, no unusual relationships were perceived. The quantity of minimization used in the least-squares refinement was $\Sigma w(||F_o| - |F_c||)^2$. A final difference Fourier map revealed some density in the region of the metal atom positions for each compound (see Table I) which is reasonable. Elsewhere, the map was virtually featureless revealing only a random fluctuating background. Atomic scattering factors and anomalous dispersion correction factors for all atoms were taken from the usual source, Ibers and Hamilton [8]. Final atomic positions and thermal parameters with their estimated standard deviations (e.s.d. s) are presented in Table II.

Discussion

Yttrium, scandium, and lutetium phosphates crystallize in the tetragonal zircon-type structure according to space group $I4_1/amd$. The metal atom is 8-coordinated to oxygen atoms with two unique metal–oxygen bond distances. Each of these discrete lengths are tetrahedrally oriented orthogonal to one another (see Fig. 1a) thus forming a dodecahedron (D_{2d}), (see Fig. 1b), which is derived from a distorted cube visualized to give its point group by considering it as two perpendicular trapezoids [9]. Further, a cube distorted so as to lessen repulsions between oxygen atoms while maintaining good metal–oxygen interaction can also be recognized as two interpenetrating tetrahedra. Tetraheda distorted in this manner are called bisphenoids (symmetry D_{2d}) and the resultant polyhedron of eight vertices made-up by the two interpenetrating bisphenoids is often called a bisbisphenoid (symmetry D_{2d}). The eight vertices of the dodecahedron are not equivalent but, are divided into two bisphenoidal sets, those within each set are equal [10]. This is the case in this study as illustrated in Fig. 1 ($LuPO_4$ was arbitrarily chosen for presentation). Table III lists the metal (M) to oxygen and phosphorus to oxygen bond lengths as well as perti-

TABLE II. Atomic Positions 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}
YPO_4	Y	0	3/4	1/8	0.42(2)	–	0.25(3)	0	0	0
	P	0	1/4	3/8	0.45(5)	–	0.33(8)	0	0	0
	O	0	0.4251(4)	0.2147(4)	0.81(11)	0.57(10)	0.51(10)	0	0	0.15(9)
$ScPO_4$	Sc	0	3/4	1/8	0.43(1)	–	0.34(2)	0	0	0
	P	0	1/4	3/8	0.39(2)	–	0.24(3)	0	0	0
	O	0	0.4305(2)	0.2071(2)	0.89(5)	0.52(4)	0.38(3)	0	0	0.07(3)
$LuPO_4$	Lu	0	3/4	1/8	0.54(6)	–	0.26(7)	0	0	0
	P	0	1/4	3/8	0.63(18)	–	1.07(33)	0	0	0
	O	0	0.4262(16)	0.2126(18)	0.79(41)	0.80(42)	0.62(37)0	0	0	0.08(35)

[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.

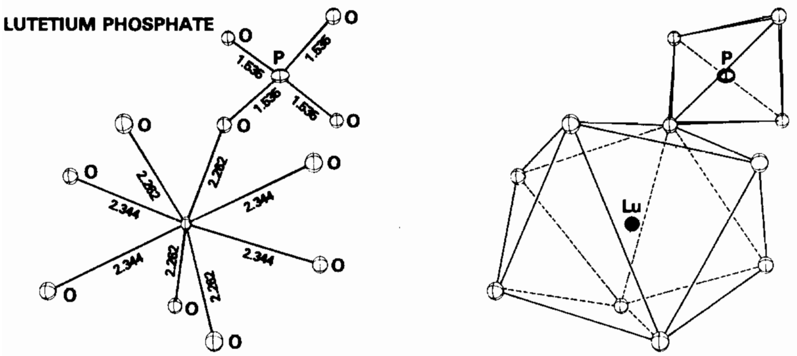

Fig. 1. Lutetium orthophosphate. (a) The two interpenetrating tetrahedral (bisphenoidal) sets are distinguishable by the bond lengths, Lu–O's = 2.262 and Lu–O's = 2.344. (b) The eight-coordinated oxygen atoms form a distorted dodecahedron (bibisphenoid) and the four-coordinated oxygen atoms associated with the phosphorus atoms form a distorted tetrahedron.

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

	YPO_4	$ScPO_4$	$LuPO_4$
M–O	2.300(3) 2.373(3)	2.153(1) 2.260(1)	2.262(10) 2.344(10)
Avg.	2.336	2.206	2.303
P–O	1.543(3)	1.534(1)	1.534(10)
Phosphate group			
O(1)–(O(2) O(3)–O(4)	2.409(6)	2.374(3)	2.394(21)
O(1)–O(3), O(4) O(2)–O(3), O(4)	2.574(5)	2.569(2)	2.561(19)
O(1)–P–O(2) O(3)–P–O(4)	102.64(2)	101.39(2)	102.58(17)
O(1)–P–O(3), O(4) O(2)–P–O(3), O(4)	113.04(2)	113.72(2)	113.18(17)
Avg. (O–P–O)	109.57	109.61	109.65

nent oxygen to oxygen contact distances and bond angles associated with the phosphate group. This group in each compound is a distorted tetrahedron as evidenced by the bond angles even though the average O–P–O angles for each are 109.6°.

Comparisons drawn between the experimental lattice constants determined in this work and those found in the literature [11–14] show that all these values are equivalent within experimental error. The main differences occur, however, when considering the oxygen atomic positions, bond and contact distances, and bond angles. All bond lengths listed in Table III are not only internally consistent with the model but are also in good agreement with experimental literature values found in BIDICS [15]. Furthermore, when considering the summation of the atomic radii of pertinent atoms, it is found that there is uniformity. The radii of Y, Sc, and Lu were corrected from a coordination number of six to eight according to Pauling's [16] treatment of the charge effect of ligancy in interionic distances (Born exponent values: Y, n = 10; Sc, n = 9; and Lu, n = 12 with respective correction factors of 1.032, 1.037, and 1.026). The 6-coordinated ionic radius values (Y = 0.900; Sc = 0.745; Lu = 0.861 Å) from the revised work of Shannon and Prewitt [17] were respectively corrected to 0.929, 0.773, and 0.883 Å. Shannon and Prewitt have presented the anion radii for different coordination numbers of O^{2-} (IV, 1.38; VI, 1.40; VIII, 1.42 Å). The calculated summation bond lengths of Y–O, Sc–O, and Lu–O are 2.349, 2.193, and 2.303 Å. Compared to the averaged values presented in Table III, the respective differences are 0.013, 0.013, and 0.000 Å (0.6, 0.6, and 0.0% variance). Similarly, the effective ionic radius of phosphorus is 0.17 Å when 4-coordinated, as in the phosphate group; and, the summation of the involved ions (P and O) is 1.55 Å as compared to the P–O bond distances of 1.543, 1.534, and 1.534 Å obtained experimentally (see Table III).

A stereoscopic view of $LuPO_4$, arbitrarily picked as representative of the three compounds, is exhibited in Fig. 2. A discussion of the possibility of these synthetics accommodating chemically diversed cations such as thorium and uranium in a predominant trivalent system is found elsewhere [2, 3]. The accuracy of the experimental values obtained in this work is expected to prove invaluable in future investigations of radiation damage in lanthanide (Ln) orthophosphates synthesized as hosts for radioactive nuclear waste. Studies related to structural analysis of the $LnPO_4$ series are being continued.

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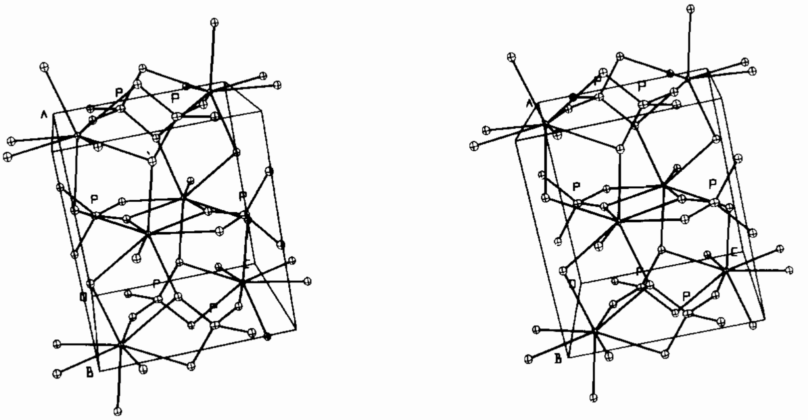

Fig. 2. $LuPO_4$, a representative stereoview of the molecular packing within the unit cell of the zircon-type structure. Lu atoms are located at center of 8-coordinated polyhedron, P atoms are labeled, and all other atoms are oxygen atoms.

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