

Single-Crystal Analysis of Mixed (*Ln*/TbPO₄) Orthophosphates*

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Structural investigations of the mixed lanthanide orthophosphates have been carried out by means of three-dimensional single-crystal X-ray diffractometry. Each mixed orthophosphate compound crystallized in the tetragonal space group $I4_1/amd$ (D_{4h}^{19} , No. 141) ($Z = 4$) with lattice constants of $a = 6.9449(9)$, $6.9647(7)$, $6.8003(8)$ and $c = 6.0680(18)$, $6.0900(6)$, $5.9638(6)$ for 1:1 (Gd/Tb)PO₄, 3:1 (Gd/Tb)PO₄, and 9:1 (Lu/Tb)PO₄, respectively. The final least-squares full-matrix refinements, based on 313, 310, and 283 unique reflections, yielded R -values equal to 0.023, 0.017, and 0.030, respectively. The lanthanide ions are eight-coordinated to oxygen atoms, and the resulting polyhedra are best described as two orthogonal interpenetrating tetrahedra, bis-bisphenoidal (D_{2d}) geometry. Important bond distances and angles, crystal data and parameters, as well as optical and X-ray fluorescence analyses are presented. © 1992 Academic Press, Inc.

Introduction

In the present work, we report structural data for several mixed lanthanide orthophosphates with varying relative rare-earth compositions. These results provide a basis for future solid-state chemical investigations dealing with the process of the structural integration and association of diverse

cations, α -active transuranic isotopes, and fission productions into the lattices of mixed $Ln/LnPO_4$ systems (1-4). Additionally, from the practical point of view, unresolved problems related to radioactive waste disposal (e.g., selecting a long-term actinide encapsulation material (5) that is both chemically and physically stable) are impacted by the results of solid-state structural studies of the type presented here. Such results, in fact, directly address the question of the practicality of using monazite-type and/or zircon-type structural analogues (6, 7) as primary host lattices for actinide waste disposal (8, 9).

Investigations of mixed lanthanide orthophosphates are possible because solid solutions of these compounds can be synthe-

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sized over a wide range of mixed rare-earth composition, $(Ln_{1-x}^{(A)}/Ln_x^{(B)})PO_4$. This capability suggests that, within certain limitations, it should be possible to adjust the local crystal-field strength at the Ln -site. This type of structural regulation could allow control of the magnetic, optical, and other properties of dopant ions in mixed systems to be controlled. The ability to determine whether or not certain impurities will occupy a particular crystallographic site following a multistep chemical or physical process, and that incorporated impurities have not transferred to other (e.g., interstitial) sites within the structure is also a motivating factor for crystallographically studying mixed lanthanide orthophosphate systems.

Experimental

Clear colorless crystals of 1:1 (Gd/Tb)PO₄, 3:1 (Gd/Tb)PO₄, and 9:1 (Lu/Tb)PO₄ were synthesized using the proper molar ratios of high purity ~99.99% constituents by a high-temperature flux method described elsewhere (10, 11). The compositional ratios of the metal constituents in each mixed lanthanide orthophosphate were confirmed by X-ray fluorescence analyses using a Novascan 30 scanning electron microscope (SEM) equipped with a Princeton Gamma-Tech (PGT) microprobe. An optically pure single crystal of each mixed lanthanide orthophosphate compound was mounted on a glass fiber and transferred to an automated X-ray diffractometer (Enraf-Nonius, CAD4-F). Graphite monochromatized MoK α ($\lambda_{\text{mean}} = 0.71073 \text{ \AA}$) radiation was used (5.8° take-off angle). The orientation matrices used for data collections (experimental temperature, 293 K) resulted from least-squares refinements of 25 accurately centered reflections in each data set. Final unit-cell dimensions (see Table I) were obtained at high θ angles, 20°–40°. Measured intensities on each set of data were collected by the ω -2 θ scan technique

at a scan rate of 0.35°–3.35° min⁻¹, determined by a fast prescan of 3.35° min⁻¹. Data for each compound were collected in the range of 3° < 2 θ < 90° at a varied scan width of 1.25 + 0.35 tan θ . No significant variations were observed in the intensities of the monitored standards (every 2 hr exposure time: $\bar{2} \bar{2} \bar{3}$, $\bar{4} \bar{1} 1$, dev. < 0.2%; 2 0, 0 2 $\bar{4}$, dev. < 1.2%; 0 4 0, 2 1 3, dev. < 0.2%, respectively). Thus, the reliability of the electronic hardware and crystal stability were verified. Lorentz and polarization corrections were applied to each collected data set as well as absorption corrections based on crystal shapes and dimensions (see Table I). The numerical absorption corrections (12) are based on Gaussian integration techniques described by Coppens *et al.* (13). For the three subjects 1:1 (Gd/Tb)PO₄, 3:1 (Gd/Tb)PO₄, and 9:1 (Lu/Tb)PO₄, 1796, 1117 and 1337 reflections were collected, respectively (h : 0 → 13, k : 0 → 13, l : 0 → 12; h : → 14, k : 0 → 14, l : 0 → 13; h : 0 → 13, k : → 13, l : 0 → 11). After averaging ($R_{\text{int}} = 0.035, 0.017, \text{ and } 0.026$, respectively), and using programs *Reject* and *Perfact* (12) with a $3\sigma(I)$ cutoff, 313, 310, and 283 unique reflections, respectively, were retained and used in the full-matrix least-squares refinements (12). The standard deviations of the averaged data were determined as $\sigma(F_i) = \sum\{1.02(F_i)\}/N$, where N is the number of redundant measurements and $\sigma(F_i)$ is the standard deviation for each individual measurement (14). The presence of 00 l , where $l = 4n$, and of $hk0$, where $h, (k) = 2$ ($hk0$ absent when h and k are odd), and the absence of hhl when $2h + l = 4n + 1$ lead to the space group assignment, $I4_1/am$ (D_{4h}^{19} , No. 141). The crystal data, experimental conditions, and statistical data are presented in Table I.

Space group $I4_1/amd$ has two origins $\bar{4}m2$ and $2/m$ (at the center). The latter origin (choice 2) which has two, 4-fold positions was chosen. The lanthanide (Ln) and phosphorous atoms were placed in the

TABLE I
 CRYSTAL, EXPERIMENTAL, AND STATISTICAL DATA SUMMARIES

	1 : 1 (Gd/Tb)PO ₄	3 : 1 (Gd/Tb)PO ₄	9 : 1 (Lu/Tb)PO ₄
Lattice type	Tetragonal	Tetragonal	Tetragonal
Space group	<i>I4₁/amd</i>	<i>I4₁/amd</i>	<i>I4₁/amd</i>
<i>a</i> (Å)	6.9449(9)	6.9647(7)	6.8003(8)
<i>c</i> (Å)	6.0680(18)	6.0900(6)	5.9638(6)
<i>M_r</i>	253.06	252.64	268.33
<i>Z</i>	4	4	4
<i>D_x</i> (Mg m ⁻³)	5.742	5.680	6.462
Crystal size (mm)	0.06 × 0.10 × 0.42	0.08 × 0.05 × 0.18	0.05 × 0.16 × 0.21
<i>F</i> (000) (e ⁻)	446	445	470
<i>μ</i> (MoKα)(mm ⁻¹)	23.97	23.31	35.24
<i>g</i> (e ⁻²)(10 ⁻⁶)	6.2(2)	3.6(2)	5.5(2)
<i>Δθ</i> (°)	1.5–45.0	1.5–45.0	1.5–45.0
Unique Refl.	313	310	283
<i>R_{int}</i>	0.035	0.017	0.026
<i>R</i> (<i>R_w</i>)	0.023 (0.026)	0.017 (0.018)	0.030 (0.028)
Gnft (<i>Σ</i> ₂)	1.67	1.38	1.50
Transmission range			
Maximum	0.2645	0.1793	0.1034
Minimum	0.0877	0.0393	0.0088
Average	0.2070	0.1151	0.0422
Shift/error			
Max. (10 ⁻⁵)	3.1	2.6	2.7
Avg. (10 ⁻⁶)	12.0	9.0	9.0
Residual Density (eÅ ⁻³)			
Maximum	1.13(6)	1.3(2)	3.2(4)
Minimum	0.78(6)	-1.2(2)	-2.4(4)

equivalent sets which have $4m2$ point symmetry ($4a$ and $4b$, respectively, $Z = 4$). Only one of the three 16-fold sets yields suitable oxygen positions, $16h$. Several cycles varying the anisotropic thermal parameters and applying secondary extinction corrections (g) yielded final reliability factors and "goodness of fit" values ($Gnft$, Σ_2), see Table I. The residual index factors are defined as $R = \frac{\sum \Delta F}{\sum F_o}$ and $R_w = \frac{\sum \sqrt{w} \Delta F}{\sum \sqrt{w} F_o}$, where ΔF equals $||F_o|| - |F_c|$ and the weighting factor w is specified as $\sigma^{-2}(F_o)$. Σ_2 is expressed as $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_{vp})]^{1/2}$, where N_o is the number of independent observations and N_{vp} is the number of varied parameters in the full-matrix least-squares refinement. The maximum (and average) absolute values of con-

vergence and final residual densities related to each structure are also found in Table I.

It should be mentioned that the multiplicities of the lanthanide (Ln) metal atom positions were refined. Each of the refined occupancies did not deviate appreciably from the set values which were established by semi-quantitative X-ray fluorescence analyses, mentioned earlier. Atomic scattering factors and anomalous dispersion corrections applied to the scattering factors were obtained from the usual source (15). Atomic positions with equivalent isotropic thermal parameters and anisotropic thermal parameters are presented in Table II. [Tables of observed and calculated structure factors are available from the authors (DFM).]

TABLE II

FRACTIONAL ATOMIC COORDINATES ($\times 10^3$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\times 10^4$)

Atom	Occupancy	x	y	z	$U_{eq}(\text{\AA}^2)^a$
Gd	0.50(1)	0	750	125	47.2(7)
Tb	0.50(1)	0	750	125	37.4(6)
P	1.00	0	250	375	52(2)
O	1.00	0	424.9(3)	218.0(3)	65(3)
Gd	0.75(1)	0	750	125	43.1(3)
Tb	0.25(1)	0	750	125	54(1)
P	1.00	0	250	375	56(2)
O	1.00	0	424.0(3)	218.7(4)	77(3)
Lu	0.90(1)	0	750	125	50.5(4)
Tb	0.10(1)	0	750	125	22(3)
P	1.00	0	250	375	70(3)
O	1.00	0	426.5(4)	213.5(6)	70(3)

^a Isotropic equivalent thermal parameter (U_{eq}) is defined as one-third the trace of the orthogonalized U_{ij} tensor.

Discussion

The structural characterization of the subject orthophosphate compounds has shown that these mixed (Ln/Tb) PO_4 solid solutions are isomorphous with other zircon-type lanthanide orthophosphates (6, 7, 16), characterized by the tetragonal space group model $I4_1/amd$. The representative drawing presented in Fig. 1a shows the eight-coordina-

tion about the central lanthanide atoms that is best described as two interpenetrating tetrahedral sets. Each of the orthogonal tetrahedrons has unique bond lengths (see Table III) and the resultant polyhedron formed from $O\cdots O$ contact distances is a distorted dodecahedron (D_{2d}) (see Fig. 1b). Cotton and Wilkinson (17) have thoroughly discussed this type of eight-coordination geometry, i.e., the distorted triangulated dodecahedron is derived by first recognizing that a cube is a composite of two equivalent interpenetrating tetrahedra and that distortion occurs so as to lessen repulsion between the oxygen atoms while good metal-oxygen interaction is maintained. Thus, the formation of two bisphenoidal sets, with each set having unique (equivalent) metal-oxygen bond lengths, is encountered and this is the case in the present crystallographic and structural investigation.

It should be noted in Table III that $Ln-O$ bond lengths are well within the range of values found in BIDICS (18), and when considering the summation of the radii of the involved lanthanide (in proper ratios) and oxygen ions found in the work of Shannon (19), the mean experimental and calculated bond distances are within standard devia-

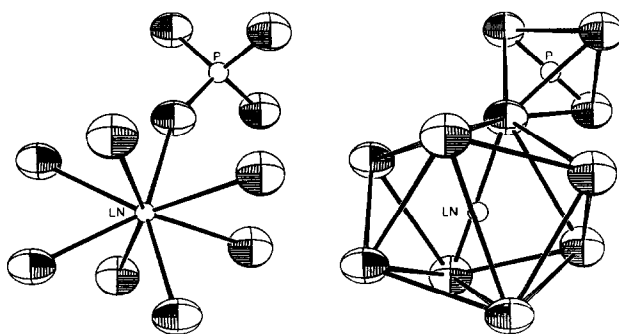


FIG. 1. A projected view of the eight-coordinated mixed (Ln/Tb) PO_4 system. (a) The two interpenetrating tetrahedral (bisphenoidal) sets, which are horizontal and perpendicular to the viewer, are quite distinctive. (b) A distorted triangulated dodecahedron (bis-bisphenoid, D_{2d}) is formed by connecting the oxygen vertices. The four-coordinated phosphate group displays a distorted tetrahedral geometry.

TABLE III
SELECTED INTERATOMIC BOND AND CONTACT DISTANCES (Å) AND ANGLES (°)

	1 : 1 (Gd/Tb)PO ₄	3 : 1 (Gd/Tb)PO ₄	9 : 1 (Lu/Tb)PO ₄
Ln-O	2.327(2)	2.341(2)	2.261(2)
Ln-O ⁱ	2.410(2)	2.419(2)	2.346(3)
Avg.	2.368	2.380	2.304
P-O	1.544(2)	1.541(2)	1.537(3)
Phosphate group			
O-O ⁱⁱ	2.430(5)	2.423(5)	2.399(6)
O-O ^{iii,iv}	2.565(4)	2.561(5)	2.564(6)
O-P-O ⁱⁱ	103.8(1)	103.7(1)	102.6(2)
O-P-O ^{iii,iv}	112.34(6)	112.43(7)	113.0(1)
Avg.	109.5	109.5	109.5
Symmetry codes			
(i)	0, 1 - y, z	(iii)	$\frac{1}{4} - y, \frac{1}{4}, \frac{3}{4} - z$
(ii)	$0, \frac{1}{2} - y, z$	(iv)	$y - \frac{1}{4}, \frac{1}{4}, \frac{3}{4} - z$

tions. This holds also true for the mean phosphorous-oxygen bond distances. Bond angles in each of the studied crystal systems investigated are internally consistent with the structural model. The distorted tetrahedra associated with the phosphorous groups are evidenced by the oxygen-phosphorous-oxygen angles listed in Table III, however, the averaged O-P-O angle in each compound is 109.5°.

The experimental cell parameters for 1 : 1

(Gd/Tb)PO₄, 3 : 1 (Gd/Tb)PO₄, and 9 : 1 (Lu/Tb)PO₄ are well within the standard deviation range of values when comparing them to pure *Ln*PO₄ compounds (20) with the zircon-type structure after accounting for the proper ratios. Furthermore, the rounded-off lattice constants of 1 : 1 (Gd/Tb)PO₄ are $a = 6.945(1)$ and $c = 6.068(2)$ Å, which are in good agreement with the experimental values of $a = 6.947(2)$ and $c = 6.065(2)$ Å obtained from an X-ray powder

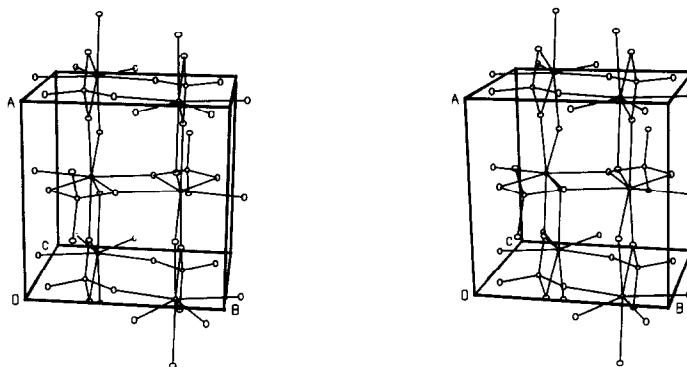


FIG. 2. A representative stereoscopic view (50% equiprobability) of the molecular packing within the unit cell of the mixed (*Ln*/Tb)PO₄ systems. The bridging effect between the molecules is evident.

diffraction study for 1:1 (Gd/RE)PO₄ compounds, where the RE = Y, Tb, Er, and Yb (21). It has been found that in an isotopic series such as the mixed rare-earth orthophosphates with a fixed anion, least-squares linear equations of a_0 , c_0 , and $V^{1/3}$ versus ionic radii can predict unit cell dimensions of other zircon-type 1:1 (Gd/RE)PO₄ compounds in the series (21). The predicted values for 1:1 (Gd/Tb)PO₄ are $a = 6.947(2)$ and $c = 6.063(3)$ Å. These predicted lattice constants are within the summation of the standard deviations of the experimental values obtained in this paper. Figure 2 is a representative stereoscopic view of the contents of the unit cell.

The possibility of these mixed solid solutions and other synthetic analogues to zircon-type and monazite-type compounds being used to accommodate chemically diverse cations in their lattices are discussed elsewhere (1, 6–9, 11). The experimental structural results here can provide new information for future studies dealing with radiation damage and defect effects in mixed lanthanide orthophosphates. Additional related structural investigations are in progress for other mixed (Ln^(A)_{1-x}/Ln^(B))PO₄ systems.

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References

1. G. W. BEALL, L. A. BOATNER, D. F. MULLICA, AND W. O. MILLIGAN, *J. Inorg. Nucl. Chem.* **43**, 101 (1981).
2. D. F. MULLICA, DAVID A. GROSSIE, AND L. A. BOATNER, *Inorg. Chim. Acta.* **118**, 173 (1986).
3. D. F. MULLICA, E. L. SAPPENFIELD, G. A. WILSON, AND L. A. BOATNER, *Lanthanide Actinide Res.* **3**, 51 (1989).
4. D. F. MULLICA, E. L. SAPPENFIELD, AND L. A. BOATNER, *Inorg. Chim. Acta.* **174**, 155 (1990).
5. M. PETEK, M. M. ABRAHAM, AND L. A. BOATNER, in "Scientific Basis for Nuclear Waste Management" (S. V. Topp, ed.), Vol. 4, p. 181, Elsevier-North Holland, The Netherlands (1982).
6. F. WESGEL, V. SCHERER, AND H. HENSCHL, *J. Am. Ceram. Soc.* **48**, 383 (1965).
7. W. O. MILLIGAN, D. F. MULLICA, G. W. BEALL, AND L. A. BOATNER, *Inorg. Chim. Acta.* **70**, 133 (1983).
8. G. J. MCCARTHY, W. B. WHITE, AND D. E. PFOERTSCH, *Mater. Res. Bull.* **13**, 1239 (1978).
9. L. A. BOATNER, G. W. BEALL, M. M. ABRAHAM, C. B. FINCH, P. G. HURAY, AND M. RAPPAZ, in "Scientific Basis for Nuclear Waste Management" (C. J. Northrup, Ed., Vol. 2, p. 289, Plenum, New York (1980).
10. L. A. BOATNER, G. W. BEALL, M. M. ABRAHAM, C. B. FINCH, R. J. FLORAN, P. G. HURAY, AND M. RAPPAZ, "Management of Alpha-Contaminated Wastes," p. 411, IAEA-SM-245/73, International Atomic Energy Agency, Vienna (1981).
11. M. RAPPAZ, L. A. BOATNER, AND M. M. ABRAHAM, *J. Chem. Phys.* **73**, 1095 (1980).
12. Enraf-Nonius, "Enraf-Nonius VAX Structure Determination Package," Delft, The Netherlands (1982).
13. P. COPPENS, L. LESEROWITZ, AND D. RABINOVICH, *Acta Crystallogr.* **18**, 1035 (1965).
14. S. W. PETERSON AND H. A. LEVEY, *Acta Crystallogr.* **10**, 70 (1957).
15. J. A. IBERS AND W. C. HAMILTON, "International Tables for X-ray Crystallography," Vol. 4, Kynoch, Birmingham (1974).
16. W. O. MILLIGAN, D. F. MULLICA, G. W. BEALL, AND L. A. BOATNER, *Acta Crystallogr. Sect. C* **39**, 23 (1983).
17. F. A. COTTON AND G. WILKINSON, "Advanced Inorganic Chemistry," p. 53, Wiley, New York (1980).
18. "Bond Index of the Determination of Inorganic Crystal Structures," BIDICS, Institute for Material Research, Hamilton, Canada (1969–1981).
19. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
20. W. O. MILLIGAN, D. F. MULLICA, H. O. PERKINS, G. W. BEALL, AND L. A. BOATNER, *Inorg. Chim. Acta* **77**, L23 (1983).
21. D. F. MULLICA AND M. R. MEDLEY, *Lanthanide Actinide Res.*, in press (1991).