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Crystal Structure of 1:1 Gadolinium/Ytterbium Orthophosphate

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Abstract

The crystal structure of 1:1 gadolinium/ytterbium orthophosphate has been determined by means of single crystal X-ray diffraction techniques. The compound is isostructural with the pure lanthanide orthophosphates having the zircon structure. The crystal system is tetragonal, space group $I4_1/amd$ ($D_{4h}{}^{19}$, No. 141), with $a = 6.865(2)$ and $c = 6.004(2)$ Å. A full-matrix least-squares refinement of the structure yielded an R-factor of 0.0554. The Gd and Yb atoms share the lanthanide-atom site, with a fifty-percent occupancy for each ion, and the lanthanide (Ln) atoms are eight-coordinated to oxygen atoms, with two unique Ln–O bond distances (2.279 and 2.381 Å). Each of these distinct lengths are tetrahedrally oriented orthogonal to each other, forming a resultant dodecahedral polyhedron ($D2h$).

Introduction

The lanthanide orthophosphates represent an interesting class of compounds both from the fundamental and practical point of view. They are of basic interest since it is possible to investigate the structural chemistry of the entire $4f^n$ transition series in the orthophosphate form. Additionally, as exemplified by the present work, perfect solid solution 'mixed crystals' for the lanthanide orthophosphates can be formed over a wide range of mixed rare-earth compositions. This implies that it is possible, within certain limits, to tailor the local crystal-field strength at the lanthanide site and thereby control the optical, magnetic, and other properties of rare-earth dopant ions in mixed hosts such as $Lu_{1-x}Y_xPO_4$, etc. From the practical point of view, these materials are of potential importance as hosts for nuclear waste disposal [1, 2], phosphors, and laser hosts. The present work investigates the structural properties of the mixed lanthanide host $Gd_{0.5}Yb_{0.5}PO_4$.

Experimental

Single crystals of 1:1 gadolinium/ytterbium orthophosphate were synthesized by previously described techniques [1, 2] using an equimolar mixture of gadolinium and ytterbium oxide. The composition of the subject compound was confirmed by a semi-quantitative X-ray fluorescence analysis, using a Novascan 30 scanning electron microscope equipped with a PGT microprobe (1:1, Gd/Yb).

The single crystal used in the X-ray diffraction experiment was selected on the basis of optical quality and was mounted on a goniometer head which, in turn, was placed on an Enraf-Nonius CAD-4F autodiffractometer. Cell dimensions were established, ($a = 6.865(2)$ and $c = 6.004(2)$ Å) based on 25 accurately centered reflections. Diffraction data were collected using the ω–2θ mode (Mo Kα radiation, $\bar{\lambda} = 0.71073$ Å), out to a maximum 2θ angle of 50°. A variable scan rate was employed, determined by a fast prescan (3.35° $\min^{-1}$). Two standard reflections were monitored every two hours of exposure time in order to detect any decomposition of the crystal or change in instrument stability. Examination of the intensities of the test reflections revealed only random variations (<1%). Lorentz, polarization, and analytical absorption corrections were applied. After equivalent reflections were averaged ($R_{int} = 0.056$), the 60 unique reflections having $I > 3\sigma(I)$ were used in the refinement.

The positions of the lanthanide, phosphorus, and oxygen atoms were taken from previous structural refinements of the pure lanthanide orthophosphates, space group $I4_1/amd$. The origin was chosen at the center ($2/m$). Gadolinium and ytterbium atoms were placed in the special position $4a$, with each lanthanide atom having a fifty-percent population. Phosphorus

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TABLE I. Experimental and Statistical Summary

Formula: $Gd_{0.5}$, $Yb_{0.5}$, PO_4
$a = 6.865(2)$ Å
$c = 6.004(2)$ Å
$V = 283.0(3)$ Å
Tetragonal
Space group: $I4_1/amd$
$M_r = 260.12$
$D_c = 6.103$ Mg m^{-3}
$Z = 4$
$F(000) = 456$ e
Crystal size: 0.29 × 0.40 × 0.50 mm
μ(Mo Kα) = 28.63 mm^{-1}
Transmission range: 0.0020–0.0453
$R_{int} = 0.056$
$\Delta\theta$: 1.5–25°
Unique reflections ($I > 3\sigma(I)$): 60
$R = 0.0554$, $R_w = 0.0530$
Maximum shift/error: 0.0003
$g = 4.8(6) \times 10^{-6}$ e^{-2}

TABLE II. Atomic Positional Parameters (×10^3) and Equivalent Isotropic Thermal Parameters (×10^4 for Yb and Gd, ×10^3 for P and O)

Atom	x	y	z	U_{eq}[a]
Yb[b]	0	750	125	24(7)
Gd[b]	0	750	125	28(8)
P	0	250	375	14(3)
O	0	428(3)	216(4)	8(5)

[a] Isotropic equivalent thermal parameter (U_{eq}) defined as one-third the trace of the orthogonalized U_{ij} tensor. [b] Fifty-percent occupancy.

and oxygen atoms were placed into atom positions 4*b* and 16*h*, respectively ($Z = 4$). This model was refined by the full-matrix least-squares technique using anisotropic thermal parameters for all atoms and secondary extinction corrections (g). The occupancies on the two lanthanide atoms were refined but did not deviate appreciably from the initially set values (0.5). The refinement was stopped when the R-factors stabilized and the maximum shift-to-error ratio was less than 0.001. The final reliability factors are $R = \Sigma\Delta F/\Sigma F_o = 0.0554$ and $R_w = \Sigma\sqrt{w}\Delta F/\Sigma\sqrt{w}F_o = 0.0530$, where $\Delta F = [|F_o| - |F_c|]$ and $w = \sigma^{-2}(F_o)$. A difference Fourier map showed a small amount of residual electron density in the vicinity of the lanthanoid atom site – a feature that is quite common to compounds of the heavy lanthanides. Atomic scattering factors and anomalous dispersion correction factors for all atoms were taken from the International Tables [6]. A summary of crystal data and experimental conditions are given in Table I. Final atomic positions, thermal parameters, and selected contact and bond distances and angles are presented in Tables II, III, and IV.

TABLE III. Anisotropic Thermal Parameters (×10^4 for Yb and Gd, ×10^3 for P and O)

Atom	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Yb[a]	7(12)	U(1,1)	58(20)	0	0	0
Gd[a]	10(14)	U(1,1)	63(22)	0	0	0
P	12(5)	U(1,1)	17(7)	0	0	0
O	8(10)	2(11)	15(9)	0	0	−3(10)

The form of the anisotropic thermal parameter is:
$\exp\{-2\pi^2[h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)]\}$.

[a] Fifty-percent occupancy.

TABLE IV. Selected Contact and Bond Distances (Å) and Angles (°) for 1:1 Gd/YbPO$_4$

Ln–O	2.279(11)	O–O^{ii}	2.439(21)
Ln–O^{i}	2.381(12)	O–O^{iii,iv}	2.576(21)
average	2.330		
P–O	1.550(11)	O–P–O^{ii}	103.8(9)
		O–P–O^{iii,iv}	112.4(4)
		average	109.5

Symmetry codes:
(i) $0, 1 - y, -z$ (ii) $0, \frac{1}{2} - y, z$
(iii) $\frac{1}{4} - y, \frac{1}{4}, \frac{3}{4} - z$ (iv) $y - \frac{1}{4}, \frac{1}{4}, \frac{3}{4} - z$

Discussion

The mixed lanthanide compound gadolinium/ytterbium orthophosphate is characterized by the space group model $I4_1/amd$ and has the tetragonal, zircon-type structure. The Ln atoms are eight-coordinated to oxygen atom, and there are two distinct Ln–O lengths (2.279 and 2.381 Å). Each of these unique distances forms a tetrahedron. The tetrahedra are oriented perpendicular to each other (see Fig. 1). The point group ($D2h$) of the resulting dodecahedral polyhedron may be visualized by considering it as two orthogonal trapezoids. Alternately, tetrahedra that are oriented in such a manner are also called bisphenoids, and the two intersecting bisphenoids form a bisbisphenoidal polyhedron (dodecahedron, see ref. 3). The bisphenoidal set with the shorter discrete bond distance (2.279 Å, see Table IV) is associated with the phosphate group contained in the asymmetric unit. The average Ln–O bond distance of 2.330 Å is well within the range of values for Gd–O and Yb–O compiled in BIDICS [7]. This is also true for all bond and contact distances and angles presented in Table IV. The phosphate group is a distorted tetrahedron, as evidenced by the bond angles. The oxygen atoms are three-coordinated, being bonded to the phosphorus atom and two

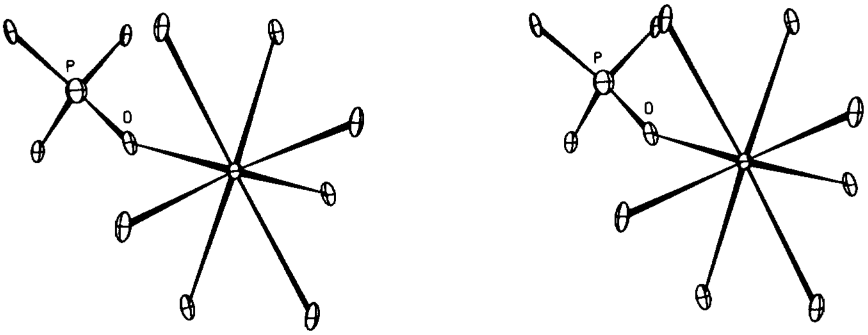

Fig. 1. Gd/YbPO$_4$. Tetrahedra arranged in this manner are called bisphenoids (symmetry *D2h*), and connecting the eight vertices forms a resultant bisbisphenoidal polyhedron (dodecahedron).

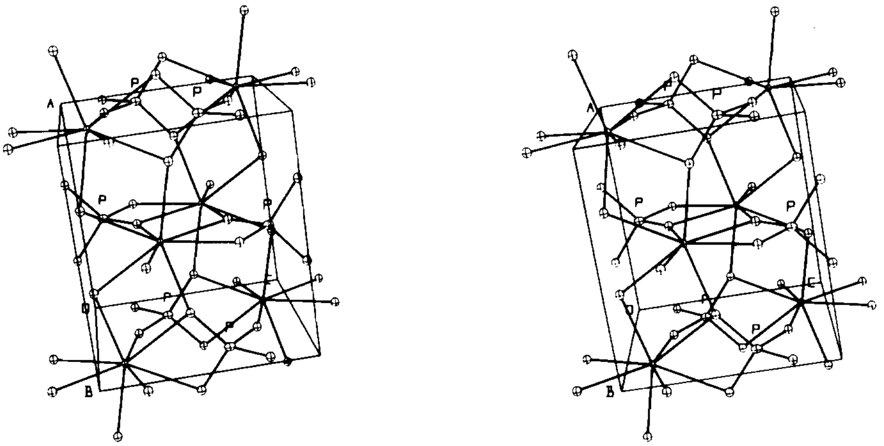

Fig. 2. A stereoscopic view of the molecular packing within the unit cell of the zircon-type structure. Gd/Yb atoms are located at the center of the 8-coordinated polyhedra, P atoms are labeled, and all other atoms are oxygen atoms.

lanthanide atoms. The molecular packing within the unit cell of Gd/YbPO$_4$ is stereoscopically presented in Fig. 2.

The experimentally determined cell parameters for the 1:1 mixed Gd–Yb orthophosphate are within the range of values for the pure lanthanoid compounds with the zircon-type structure [3–5, 8]. The Gd–Yb mixed crystal cell parameters correspond quite closely to the cell constants for erbium orthophosphate ($a = 6.860(1)$ Å and $c = 6.003(1)$ Å). The cell constants of this crystalline phase of the rare-earth orthophosphates have previously been shown to be dependent on the effective ionic radius of the central lanthanide atom [8]. This would indicate that the observed ionic radius for the 1:1 mixture of Gd and Yb approximates the value for Er (0.904 Å). This ionic radius value was obtained from the experimental work by Templeton and Dauben [9] after a correction from coordination number 6 to coordination number 8 according to the treatment proposed by Pauling [10]. A more realistic value of 1.004 Å for Er is found, however, in the revised work of Shannon [11]. His effective ionic radii are based on structural data, empirical bond strength–bond length relationships and plots of radii *versus* volume, coordination number, and oxidation state. Employing the same empirical approach as that found in ref. 8 and using Shannon's values [11] instead of those of Templeton and Dauben [9], a calculation of the ionic radius from the experimental cell constants of Gd/YbPO$_4$ yields an average value of 1.005 Å (compared to the literature value of 1.004 Å for Er, ref. 11). Note that the experimentally-determined effective ionic radius of 1.005 Å obtained for Gd/YbPO$_4$ is much smaller than the value of 1.019 Å obtained from a direct average of the ionic radii of Gd and Yb (1.053 and 0.985 Å, respectively). Packing within the crystal lattice appears to restrict the expansion of the lanthanide atomic site. This is a significant effect that also has practical implications, since the lanthanide orthophosphates are of interest as primary hosts for the isolation of nuclear wastes. Structural data for the mixed lanthanide orthophosphates containing two or more lanthanide elements with varying percentage compositions provide a basis for future studies related to the potential of these substances for accommodating diverse cations, including the α-active transuranic isotopes and fission products [12].

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