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Ninefold Coordination in $LaPO_4$: Pentagonal Interpenetrating Tetrahedral Polyhedron

D. F. MULLICA, W. O. MILLIGAN, DAVID A. GROSSIE

Departments of Chemistry and Physics, Baylor University, Waco, Tex. 76798, U.S.A.

G. W. BEALL

Weston Co., Rockville, Md., 20850, U.S.A.

and L. A. BOATNER

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830, U.S.A.

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The crystal structure of $LaPO_4$ has been determined from three-dimensional single-crystal X-ray diffraction data. The respective residual indices R_1 and R_2 have been refined to 0.020 and 0.021, based on 625 unique reflections. Crystallization occurs in the monoclinic space group $P2_1/n$ (No. 14) with $a = 6.825(4)$, $b = 7.057(2)$, $c = 6.482(2)$ Å, and $\beta = 103.21(4)°$. $Z = 4$. The lanthanum metal atom is nine-coordinated to oxygen atoms forming a polyhedron best described as a pentagonal interpenetrating tetrahedron. The nine-coordinated La atoms are linked together by distorted tetrahedral phosphate groups. Important interatomic distances and angles are presented.

Introduction

A recent structural study of cerium phosphate [1], which is a synthetic analog of the naturally occurring mineral monazite, classified the refined structure as being made up of irregular nine-coordinated cerium atoms linked together by distorted tetrahedral phosphate groups. The polyhedron around the cerium atom was delineated as resembling a very distorted monocapped square anti-prism arrangement. In previous structural determinations of $CePO_4$ [2–4], the cerium polyhedron was depicted as being eight coordinated. The La atom in lanthanum orthophosphate has also been described by Wyckoff [5] and Jaulmes [6] as having a coordination number of eight. The conclusions of the latter investigator were based on a single crystal analysis. $LaVO_4$ crystallizes in the monazite structure (MXO_4) and is isomorphous with monoclinic $LaPO_4$ and $CePO_4$ [5]. The XO_4 component units are approximately tetrahedral. Work of Rice and Robinson [7] by means of single crystal analysis has shown that the La atom in lanthanum orthovanadate is nine-coordinate and not eight-coordinate. Further, these workers [7] state that the coordination polyhedron about the La atom is not regular, *i.e.*, the polyhedron is an irregular pentagon with two oxygens atoms above and two oxygen atoms below the plane of the pentagon.

In light of the recent work related to $CePO_4$ [1], as well as the work dealing with $LaVO_4$ [7] and discrepancies in the literature, it was considered necessary to re-examine structurally the compound $LaPO_4$. Naturally occurring minerals such as monazite, a crystalline mixed lanthanide (Ln) orthophosphate [(Ce, La, Nd, Th, Ca, Pb, V)PO_4] of varying composition, have recently been proposed as primary hosts for the isolation of nuclear wastes. The established geological history of monazites indicates that they have existed in the earth's crust as stable materials for over 2 billion years. Precise structural data are required for future investigations of heavy-particle radiation damage effects in the $LnPO_4$ series. Accordingly, the present crystallographic structural study of $LaPO_4$ is relevant to the two topics of lanthanide coordination chemistry and the characteristics of nuclear waste materials.

Experimental

The process for the growth of single crystals of lanthanum orthophosphate has been described elsewhere [8, 9]. An optical examination of a number of $LaPO_4$ specimens assured the selection of a non-twinned crystal which was subsequently placed in a Nonius crystal grinder. A spherically ground crystal of $LaPO_4$ (270 μ diameter) was then mounted on a goniometer head. X-ray measurements were made on an Enraf-Nonius CAD-4 diffractometer. The diffractometer is equipped with a dense graphite

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TABLE I. Crystal Data and Statistical Summary for $LaPO_4$.

$LaPO_4$; MW = 233.88
$a = 6.825(4)$, $b = 7.057(2)$, $c = 6.482(2)$ Å, $\beta = 103.21(4)°$
Volume: 303.9(3) Å^3/unit cell
Calculated density: 5.12 g cm^{-3}
Monoclinic; $P2_1/n$ (No. 14); $Z = 4$
$\mu = 144.7$ cm^{-1}; $\mu R = 3.91$; $g = 1.69(4) \times 10^{-5}$ e^{-2}
Radiation: MoK_α, $\lambda = 0.71073$ Å; $T = 18$ °C
Max 2θ: 54; unique reflections: 625
$R_1 = 0.020$, $R_2 = 0.021$
Max and avg $\Delta\zeta_i/\sigma(\zeta_i)$: 0.012; 0.0035
No. of variables (ζ_i): 56; $\Sigma_2 = 1.38$

monochromator and a Si(Li) solid-state detector which permitted routine X-ray fluorescence analysis on the same single crystal from which single-crystal X-ray diffraction data were collected [10]. The lanthanum metal constituent was qualitatively identified and likewise, the absence of any possible heavy metal contaminant was assured. All X-ray measurements were made at 291 K using MoK_α radiation (λ mean = 0.71073 Å). A least squares set of 25 accurately centered reflections was used to obtain a workable orientation matrix and reliable unit cell dimensions, see Table 1. A conventional method (Ω–2θ scan) was used for measuring intensities while varying rates (0.46–3.35° min^{-1}) over a range of $3 < 2\theta < 54°$ using a fixed aperture width of 2.0°. All reflections having less than 75 counts above background during the fast prescan (3.35° min^{-1}) were viewed as unobserved. During data collection, two standard reflections were examined every 2 hr. Monitoring revealed only random fluctuations from the mean. Thus, crystal stability and reliability of electronic and hardware components were confirmed. A total of 625 reflections were unique, after obeying $I_{(\mathrm{net})} > 3\sigma(I)$ and averaging. $I_{(\mathrm{net})} = (P - 2B)$ and $\sigma(I) = (P + 2B + p^2 I_{\mathrm{net}}^2)^{1/2}$), where P is the peak intensity, B is the sum of time-scale background counts on both sides of the peak and p is an ignorance factor (0.02). All resulting diffraction data were corrected for Lorentz and polarization effects. A spherical absorption correction was applied according to Bond [11] for $\mu R = 3.91$ where $\mu = 144.7$ cm^{-1}. The residual averaging error was 1.2% according to $R' = \Sigma\Delta|F|/\Sigma F_o$ where $\Delta|F| = |F_o - F_{\mathrm{avg}}|$. A statistical summary is presented in Table 1.

After verifying the monoclinic space group $P2_1/n$ (No. 14), atomic positions obtained from the literature [1] were used to initiate the structural refinement. These atomic parameters were refined using a full-matrix least-squares program [12]. Several cycles varying the anisotropic thermal parameters and applying secondary extinction corrections (g) produced final reliability factors. $R_1 = \Sigma\Delta F/\Sigma|F_o| = 0.020$ and $R_2 = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2} = 0.021$ where $\Delta F = (|F_o| - |F_c|)$ and $w = \sigma^{-2}(F_o)$. The quantity minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$. The 'goodness of fit' value (Σ_2) was 1.38 and the largest value of abscission $[\Delta\zeta_i/\sigma(\zeta_i)]$ where ζ_i values are varied parameters, was 0.012 (see Table I for the average value). A final difference Fourier map revealed only random fluctuating background density. Scattering factors with appropriate anomalous dispersion corrections applied to each atom were obtained from the usual source, Ibers and Hamilton [13]. Final atomic positions and thermal parameters with their estimated standard deviations (e.s.d.) are tabulated (See Table II).

Discussion

The experimental lattice parameters for monoclinic $LaPO_4$ (space group $P2_1/n$, No. 14) are a = 6.825(4), b = 7.057(2), c = 6.482(2) Å, and β = 103.21(4)°. These values are in fair agreement with a number of references cited in the X-ray diffraction powder work of Pepin and Vance [14].

A comparison between the present investigation of $LaPO_4$ and the work of Jaulmes [6] is informative, since the two crystallographic analyses present the lanthanum atom as being 9- and 8-coordinated, respectively. Our results demonstrate that the La atoms are nine-coordinated and are linked by tetrahedral phosphate groups. Table III presents the bond distances and angles experimentally obtained from this work and that of Jaulmes [6]. The phosphate group in both structures is a distorted tetrahedron as evidenced by the bond distances and angles. The averaged P–O distances and O–P–O angles derived from both studies are in very good agreement [1.534(10) and 1.54(4) Å, 109.5 and 109.5°, respectively]. Disagreement between the two structural investigations is obvious when examining the geometry of the polyhedron surrounding the lanthanum atom. The work of Jaulmes [6] identifies an 8-coordinated polyhedron with a very skewed arrangement which could have been symmetrically presented if a ninth oxygen atom were considered to be part of the polyhedron. The ninth oxygen to lanthanum bond distance was considered to be too long (2.81 Å) [6]. A nine-coordinated geometry for $CePO_4$, the analogue to $LaPO_4$, was first considered by Krstanovic [15] who used the Weissenberg photographic method for a single-crystal analysis. Another recent study of $CePO_4$ [1] has offered fairly conclusive evidence that this lanthanide orthophosphate system is 9-coordinated. Additionally, the crystallographic investigation of $LaVO_4$, an analogue of

TABLE II. Atomic Coordinates ($\times 10^5$ for La, $\times 10^4$ for P, O) and Equivalent Thermal Parameters ($\times 10^4$) for Lanthanum Orthophosphate.

	x	y	z	U_{eq}*
La	28160(5)	16030(4)	10070(5)	68(3)
P	3044(2)	1636(2)	6120(2)	66(7)
O(1)	2494(6)	0077(6)	4458(7)	104(19)
O(2)	3803(6)	3306(6)	4970(7)	113(21)
O(3)	4760(6)	1081(6)	8023(7)	112(20)
O(4)	1289(7)	2150(7)	7104(7)	132(21)

*$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$

Anisotropic Thermal Parameters[a] ($\times 10^4$) for Lanthanum Orthophosphate

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La	61(3)	49(3)	106(3)	2(1)	22(1)	5(1)
P	56(7)	47(7)	108(7)	5(5)	29(5)	−4(5)
O(1)	109(19)	75(20)	138(19)	32(16)	20(16)	20(17)
O(2)	80(20)	104(22)	175(21)	−37(15)	42(17)	4(16)
O(3)	100(20)	129(20)	109(19)	7(16)	−1(16)	−5(17)
O(4)	118(21)	137(22)	141(20)	−2(17)	59(17)	3(17)

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

TABLE III. Comparative Bond Distances (Å) and Angles (°) with E.s.d.s for $LaPO_4$.

	This work	Jaulmes [6]		This work	Jaulmes [6]
La–O(1)	2.537(4)	2.58(3)	P–O(1)	1.525(5)	1.58(3)
	2.473(4)	2.40(4)	P–O(2)	1.546(4)	1.48(3)
			P–O(3)	1.543(4)	1.56(3)
			P–O(4)	1.523(5)	1.54(2)
La–O(2)	2.665(4)	2.62(3)			
	2.591(4)	2.48(4)	Avg.	1.534(10)	1.54(4)
	2.775(4)	2.81(4)			
			O(1)–P–O(2)	105.4(2)	112(1)
La–O(3)	2.498(4)	2.55(3)			
	2.609(4)	2.68(3)	O(1)–P–O(3)	113.6(2)	–
La–O(4)	2.535(4)	2.59(3)	O(1)–P–O(4)	112.2(2)	107(1)
	2.473(5)	2.48(3)			
			O(2)–P–O(3)	107.6(3)	109(1)
O(1)–O(2)	2.443(6)	–			
O(1)–O(3)	2.567(6)	–	O(2)–P–O(4)	113.7(2)	–
O(1)–O(4)	2.530(6)	–			
O(2)–O(3)	2.493(6)	–	O(3)–P–O(4)	104.5(2)	110(1)
O(2)–O(4)	2.570(6)	–			
O(3)–O(4)	2.424(6)	–	Avg.	109.5	109.5

both $LaPO_4$ and $CePO_4$, by Rice and Robinson [7] reports ninefold coordination about the La atom. A consideration of all factors shows that there is little doubt that the stereochemistry associated with the structure of the chemical moiety of $LaPO_4$, is 9-coordinate. The structural study of $LaPO_4$ detailed here has yielded accurate bond distances and angles which should be valuable in future investigations regarding the practicality of employing orthophosphates of the lanthanide series as primary hosts for the isolation of nuclear waste. The possibility of incorporating diverse cations such as thorium, uranium, α-active transuranic isotopes, and fission products in the lattice of analogs of polycrystalline

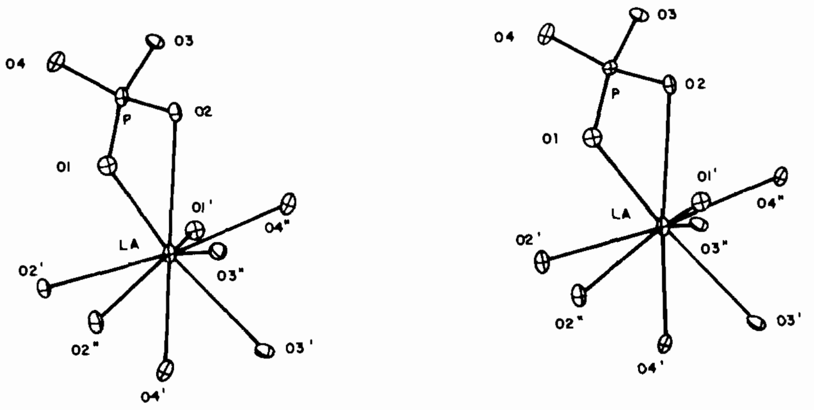

Fig. 1. Monoclinic $LaPO_4$. Stereoscopic view with proper labeling and numbering scheme.

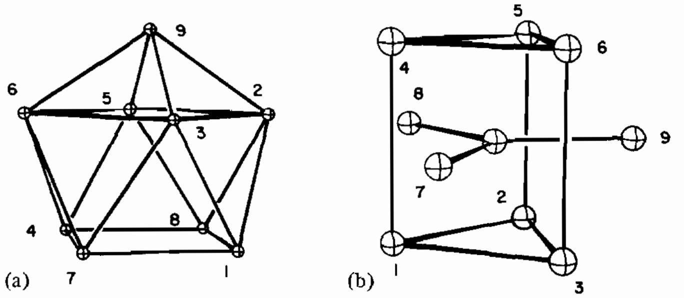

Fig. 2. The ideal forms of monocapped square anti-prism (MSAP) and tricapped trigonal prism (TTP).

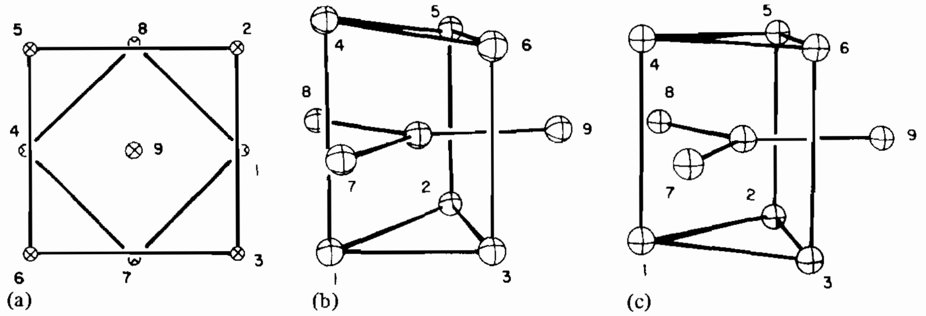

Fig. 3. (a) A shift in view of MSAP showing top cap perpendicular to page, (b) rotation of MSAP to a distorted view which can be related to TTP, and (c) the ideal TTP form for comparative purposes.

synthetic monazite has been discussed elsewhere [1].

The polyhedron surrounding the cerium atom in $CePO_4$ has been described as an irregular 9-coordinated system, *i.e.*, a very distorted monocapped square anti-prism [1]. After a careful re-examination of the stereochemistry of the 9-coordinated $CePO_4$ system using a scale model constructed with a Supper Model Builder and after investigating the geometric form of $LaPO_4$ determined structurally in this paper, a pentagonal interpenetrating tetrahedral polyhedron is considered to be the proper structural description (see Fig. 1). A nine-coordination polyhedron described as an intermediate between a monocapped square anti-prism (MSAP) and a tricapped trigonal prism (TTP) has been delineated in the literature [16, 17]. The close relationship between the idealized forms of MSAP and TTP is discussed by Guggenberger and Muetterties [18] and Robertson [19]. Figure 2 presents ideal MSAP and TTP polyhedra. The MSAP (C_{4v}) can be generated from the TTP (D_{3h}) by stretching the 1–4 contact distance causing distortions of the parallel apical trigonal planes (AT planes), see Fig. 3(a) and 3(b). These AT planes of the now MSAP are not parallel as in the TTP polyhedron, see Fig. 3c. The dihedral angle between these AT planes is 15.7°. This then can be considered as one of the principal criteria distinguishing the MSAP from the TTP. Otherwise, the MSAP is merely a distorted TTP and not a valid geometry. Likewise,

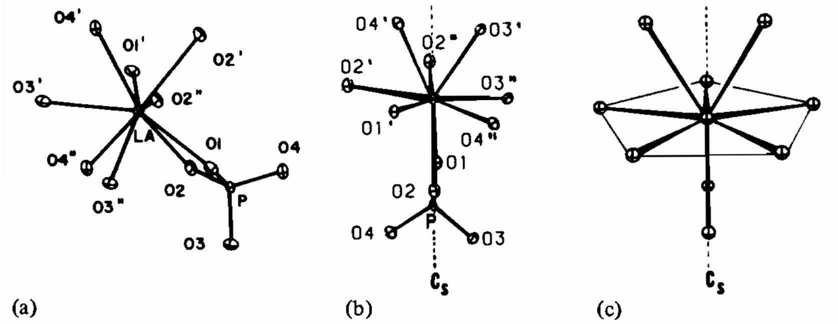

Fig. 4. (a) LaPO$_4$, structurally oriented for discussion purposes, (b) LaPO$_4$, pentagonal interpenetrating tetrahedral polyhedron (PITP), (c) idealized PITP demonstrating the plane of symmetry, C_s.

in order to corroborate the uniqueness of the MSAP, the square anti-prism planes of the polyhedron should also be parallel or at least reasonably parallel, see planes 2, 3, 6, 5 and 1, 8, 4, 7 in Fig. 2(a). The proposed nonacoordinated geometry for the monazite structure (MXO$_4$) where M atoms are lanthanide metals (La and Ce, at this time) and X atoms can be P, V, or As for example, is a pentagonal interpenetrating tetrahedral polyhedron (PITP). The point group symbol is C_s, a plane of symmetry (see Fig. 4(c)). If this structural arrangement is called a distorted monocapped square anti-prism (see Fig. 4(a)), the criterion of uniqueness related to MSAP would be disobeyed. The least-squares plane defined by atoms O(1), O(2), O(3″), O(4″) reasonably indicates planarity [O(1) 0.097, O(2) –0.097, O(3″) –0.084, O(4″) 0.095], but the least-squares fit to the plane O(1′), O(2′), O(2″), O(3′) shows no resemblance to a plane, [O(1′) –0.314, O(2′) 0.413, O(2″) –0.389, O(3′) 0.294], see Table IV. Further, in no way can these two planes be considered to be parallel as evidenced by the dihedral angle between the planes (18.9°) (see Table IV). The dihedral angle is even greater than the dihedral angle of 15.7° which distinguishes the MSAP from the TTP. The least-squares planes program used in the structural analysis is an adaptation of the method developed by Schomaker *et al.* [20]. The pentagonal interpenetrating tetrahedral polyhedron illustrated in Fig. 4(b) does not resemble a hybrid or intermediate between MSAP and TTP. While it is true that an irregular nine-coordinate polyhedron may be characterized by comparing it to either MSAP or TTP, the question arises: When does the term distorted or irregular cease to have meaning? *i.e.*, how much can a unique idealized geometry be distorted? Dropping of the term 'distorted' should seriously be considered when another unique or new stereochemical geometry is observed. The structural rigidity maintained by LaPO$_4$, CePO$_4$, and LaVO$_4$ as well as other related lanthanide monazite type compounds, is undoubtedly related to the bidentate bonding of the tetrahedral groups. The La atoms are apically linked by distorted tetrahedral groups forming chains. Each of the equatorial oxygen atoms forming the pentagonal plane are interconnected to five surrounding strands. This bridging serves as a locking device which supports and secures the pentagonal plane. The locking effect causes negligible torsion in the pentagonal plane. Investigations are in progress that are expected to substantiate and broaden the base of the present study.

TABLE IV. Least-Squares Planes for Lanthanum Orthophosphate. The equation of the plane is of the form: $A^*x + B^*y + C^*z - D = 0$ where x, y and z are orthogonalized coordinates.

Plane No.	Atom	x	y	z	Distance
1	O1	1.0384	0.0542	2.8125	0.097
	O2	1.8551	2.3335	3.1352	–0.097
	O3″	3.2796	–0.7632	1.2474	–0.084
	O4″	3.9761	2.0115	1.3273	0.095
				mean	0.093
2	O1′	1.6284	3.5832	0.3418	–0.314
	O2′	–0.8117	1.1955	–0.0190	0.413
	O2″	0.8117	–1.1955	0.0190	–0.389
	O3′	3.5394	0.7632	–1.2474	0.294
				mean	0.353
3	La	1.7707	1.1314	0.6353	–0.001
	O1′	1.6284	3.5832	0.3418	0.214
	O2′	–0.8117	1.1955	–0.0190	–0.185
	O2″	0.8117	–1.1955	0.0190	0.303
	O3″	3.2796	–0.7632	1.2474	–0.098
	O4″	3.9761	2.0115	1.3273	–0.022
				mean	0.137

Dihedral Angles Between Planes:

Plane No.	Plane No.	Dihedral Angle
1	2	18.9

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