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The Crystal Structure of Lanthanum Metaphosphate LaP_3O_9

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The crystal structure of LaP_3O_9 has been determined by conventional single-crystal X-ray diffraction techniques. The compound is isostructural with NdP_3O_9. Crystals are orthorhombic, space group $C222_1$ with $a = 11.303(4)$, $b = 8.648(5)$, $c = 7.397(3)$ Å, $Z = 4$, $D_x = 3.45$ Mg · m^{-3}, $T = 298(2)$ K. The structure was refined based on 1000 diffractometer collected reflections with $I > 1.96\sigma(I)$. Final agreement factors were: $R = 0.027$ and $R_w = 0.033$. The structure is represented by "infinite" chains of corner-sharing PO_4 tetrahedra and edge-sharing LaO_8 dodecahedra. Lanthanum–oxygen coordination bond lengths vary from 2.415(4) to 2.749(4) Å. The closest La–La distance is 4.315(1) Å. No evidence was found for ninefold coordination around La atoms. © 1988 Academic Press, Inc.

Introduction

During recent years the interest in the structure of rare-earth phosphates has increased rather rapidly. This is due to several reasons. Of those the possibility of "modelling" the coordination sphere of the rare-earth central atom which could lead to the intentional variation of the metal–metal distance seems to hold exciting prospects in the field of new effective luminophors, mini-lasers, etc. (*1*, *2*). In general two main groups of interest may be specified when considering the structure of rare-earth phosphates. One is concerned with the correlation between ionic radius of a given rare-earth element and the structure of its corresponding phosphate (*3*, *4*). The second is involved with trying to determine the new structural types of coordinated phosphate ligands themselves (*5*). In the first group of problems only the orthophosphates were carefully examined (reexamined) and ninefold coordination was recently found in the case of cerium and lanthanum orthophosphates (*6*, *7*). When looking at the problem of other phosphates, at present there are no reports on the crystal structures of the rare-earth phosphates other than ultra-, meta-, and orthophosphates. Instead, a great number of polytypes and polymorphs of those three basic varieties has been examined (*6–19*). In our study of the series of lanthanum phosphates (*20*, *21*) we found that direct structural information on LaP_3O_9 would be valuable for further consideration of phase relationships. Consequently we decided to perform the structure solution of LaP_3O_9

(i) to check whether the relatively large ionic radius of La^{3+} (*22*), when compared with other third group elements, mediates

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against formation of polymorphs as is the case of "intermediate" rare-earth elements such as Tb, Dy (*10, 12*), and Sc (*13*);

(ii) to achieve reliable crystal data contributing to information on the system La_2O_3–P_2O_5;

(iii) to determine the actual coordination around La^{3+} ions and La–La distance-dependent interactions.

Experimental

Crystalline H_3PO_4 prepared from commercially available 85% H_3PO_4 (POCh), P_4O_{10} (Merck), and La_2O_3 (99.99%, Sojuzchimexport) was used for the preparation of LaP_3O_9. A nonstoichiometric excess of the phosphorus components was mixed with La_2O_3 and melted together in a platinum crucible. Crystallization occurred at moderate temperature (673 K). Colorless crystals grew in the form of well-developed polyhedra elongated in the (010) direction. Some other details of the preparative procedure are given in (*21*).

A crystal with no dimension exceeding 0.1 mm was carefully examined on a Weissenberg goniometer and it was found to be orthorhombic, space group $C222_1$. The results suggested that the compound was isomorphous with NdP_3O_9 (*8*). A Syntex $P2_1$ four-circle diffractometer was used for measuring lattice parameters and intensity data collection. Independent reflections (1032) were recorded below $2\theta = 70°$ using graphite monochromated Mo$K\alpha$ radiation ($\bar{\lambda} = 0.71069$ Å). The applied technique was 2θ-ω scan of variable speed. After each group of 50 reflections two control reflections were monitored and no significant fluctuation (ca 5%) in intensity was observed. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. Reflections (1000) with $I > 1.96\sigma(I)$ were used for structure determination and refinement. The (002) reflection was excluded from the calculations as it appeared to suffer from strong extinction. Relevant experimental and crystal data are listed in Table I. Most of the calculations were performed on a NOVA 1200 minicomputer with programs supplied by Syntex (*23*).

The atomic positions taken from (*8*) were initially applied for the starting model. Those were refined during several cycles of full matrix least-squares procedure first with isotropic and then with anisotropic temperature factors. Neutral-atom scattering factors were those listed in "International Tables for X-ray Crystallography" (*24*). Both real and imaginary contributions for anomalous dispersion were applied for lanthanum. The final atom positions and their equivalent thermal factors are listed in Table II.

The highest peak in final difference map corresponded to $1.3\ e \cdot Å^{-3}$. The refinement of the inverted structure gave higher discrepancies ($R = 0.031$ and $R_w = 0.038$).

Discussion

The structure of crystalline LaP_3O_9 may be described as built of helical chains of corner-sharing PO_4 tetrahedra that proceed down the c direction as imposed by screw-axis symmetry. Those oxygen atoms that do not link phosphate groups are involved in the coordination to lanthanum atoms. Thus the helices are held together and an extensive netting is extended in the a and b directions. The additional tightness in the c direction is achieved by sharing the edges of LaO_8 polyhedra. This is why the proposed formula for the lanthanum metaphosphate would be $[La(PO_3)_3]_n$, analogous to that suggested by Palkina and Jost (*25*) for $[Bi(PO_3)_3]_n$. Nevertheless we use the formula LaP_3O_9 throughout the text to keep the formula identical with that of the neodymium isomorph (*8*). The LaO_8 dodecahedra are irregular and La–O bond lengths range from 2.415(4) to 2.749(4) Å. The closest La–La distance is 4.315(1) Å. In each of two crystallographically different

TABLE I

EXPERIMENTAL AND CRYSTAL DATA

Diffractometer	Syntex $P2_1$
Radiation	Graphite monochromated $\lambda(MoK\alpha) = 0.71069$ Å
Scan mode	2θ-ω
Scan speed	2.0–29.3° min^{-1} (depending on intensity)
2θ max	<70°
Number of independent reflections	1032
Number of reflections used in calculations	1000
Criterion	$I > 1.96\sigma(I)$
Number of reflections used for l.s. lattice parameters and orientation matrix calculations	15
Control reflections	(0 0 4) and (3 3 3)
Formula	LaP_3O_9
M_r	375.8
System/space group	orthorhombic/$C222_1$
Cell parameters	$a = 11.303(4)$, $b = 8.648(4)$, $c = 7.397(3)$ Å
Volume of the unit cell	723.0 $Å^3$
Z	4
$F(000)$	696
Number of variables	61
Calculated density	3.45 $Mg \cdot m^{-3}$
μ ($MoK\bar{\alpha}$)	66.9 cm^{-1}
Final R and R_w	0.027 and 0.033
Weight	$w = 1\sigma^2(\lvert F_o \rvert)$
Temperature	RT

PO_4 tetrahedra there are two shorter (mean length, 1.486(5) Å) and two longer (mean length, 1.581(5) Å) P–O bonds. The shorter bonds are those between P atoms and the O atoms that coordinate to La atoms. The pairs of longer bonds are formed in the P–O–P bridges. The overall crystal structure of LaP_3O_9 is depicted in Fig. 1, which represents a perspective view (*26*) of the unit cell packing. Figure 2 shows the schematic view of the isolated skeletal structure of $(PO_3)_n$ helices while the flow of the LaO_8 dodecahedra chains in the unit cell is visualized in Fig. 3. The principal bond lengths and bond angles are reported in Tables III and IV, respectively. The atom numbering scheme used in this work corresponds to that in Hong's article (*8*) in order to simplify the direct comparison between the two compounds.

TABLE II

FINAL POSITIONAL PARAMETERS AND THERMAL FACTORS WITH e.s.d.'s IN PARENTHESES

$$B_{eq} = \tfrac{1}{3}\sum_{i=1}^{3} B_{ii}$$

	x	y	z	B_{eq}
La	0	0.12848(4)	$\frac{1}{4}$	0.41(2)
P(1)	0	0.7480(2)	$\frac{1}{4}$	0.57(8)
P(2)	0.3252(1)	0.9940(2)	0.2016(2)	0.71(8)
O(1)	0.3738(6)	0	0	1.9(5)
O(2)	0.4815(4)	0.3451(4)	0.0840(5)	0.7(3)
O(3)	0.1970(4)	0.0255(5)	0.2112(6)	1.4(3)
O(4)	0.1279(4)	0.3528(5)	0.2129(8)	2.0(4)
O(5)	0.3917(4)	0.1395(5)	0.2876(6)	1.4(3)

Concluding Remarks

The most important facts that have been established in our study are outlined briefly:

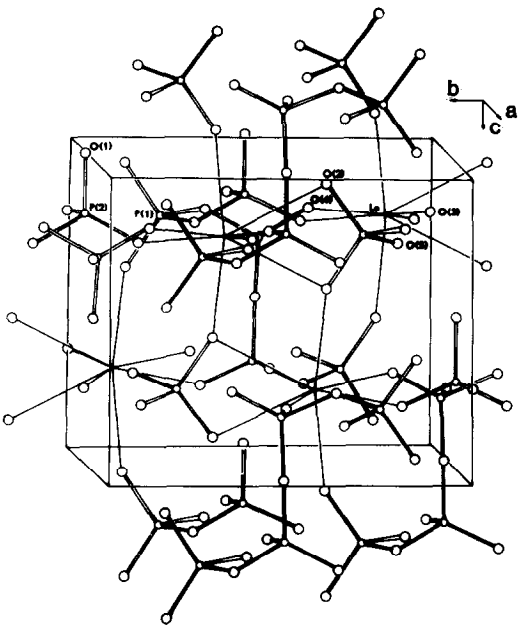

FIG. 1. Perspective view of the unit cell of LaP_3O_9.

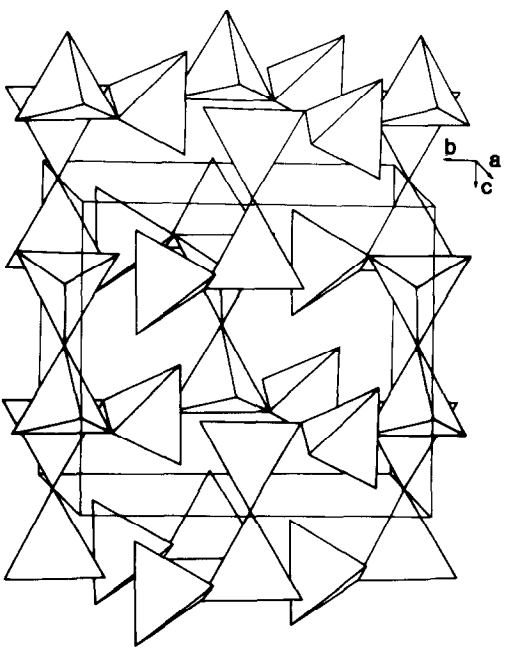

FIG. 2. Schematic view of the PO_4 tetrahedra arrangement with respect to the unit cell edges.

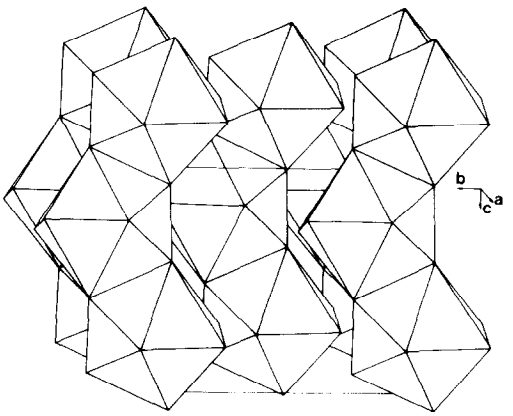

FIG. 3. Schematic view of the LaO_8 dodecahedra arrangement with respect to the unit cell edges.

(i) No evidence has been found for ninefold coordination of the lanthanum atom which appears to be the exclusive case for lanthanum in the orthophosphate. This may be due to the large La^{3+} ionic radius (*22*) and the reduced repulsive interactions between isolated PO_4 tetrahedra (and not bulky polyphosphate chains as in LaP_3O_9) in which case the chance is given to one of the oxygen atoms to be situated near the lanthanum at a distance which can be regarded as a ninth coordination bond (*6*).

TABLE III

INTERATOMIC DISTANCES (IN Å) IN LaP_3O_9

P(1)–O(2)^{i}	1.502(4)	P(2)–O(4)^{ii}	1.474(5)
P(1)–O(2)^{ii}	1.502(4)	P(2)–O(3)^{iii}	1.477(4)
P(1)–O(5)^{i}	1.568(5)	P(2)–O(1)^{iii}	1.590(3)
P(1)–O(5)^{ii}	1.568(5)	P(2)–O(5)^{iii}	1.596(5)
	La–O(3)	2.415(4)	
	La–O(3)^{iv}	2.415(4)	
	La–O(4)	2.435(5)	
	La–O(4)^{iv}	2.435(5)	
	La–O(2)^{v}	2.490(4)	
	La–O(2)^{vi}	2.490(4)	
	La–O(2)^{vii}	2.749(4)	
	La–O(2)^{viii}	2.749(4)	

Note. The symmetry code is: (i) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, 1 + y, z$; (iv) $-x, y, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $-\frac{1}{2} + x, \frac{1}{2} - y, -z$; (vii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (viii) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$.

TABLE IV

BOND ANGLES (IN DEGREES) IN LaP_3O_9

$O(2)^{i}$–P(1)–$O(2)^{ii}$	112.0(2)	$O(1)^{iii}$–P(2)–$O(3)^{iii}$	112.2(2)
$O(2)^{i}$–P(1)–$O(5)^{i}$	111.8(2)	$O(1)^{iii}$–P(2)–$O(4)^{ii}$	107.8(3)
$O(2)^{ii}$–P(1)–$O(5)^{ii}$	107.4(2)	$O(1)^{iii}$–P(2)–$O(5)^{iii}$	100.7(2)
$O(2)^{ii}$–P(1)–$O(5)^{i}$	107.4(2)	$O(3)^{iii}$–P(2)–$O(4)^{ii}$	119.0(3)
$O(2)^{ii}$–P(1)–$O(5)^{ii}$	111.8(2)	$O(3)^{iii}$–P(2)–$O(5)^{iii}$	107.3(3)
$O(5)^{i}$–P(1)–$O(5)^{ii}$	106.3(2)	$O(4)^{ii}$–P(2)–$O(5)^{iii}$	108.2(3)
$O(2)^{vi}$– La–$O(2)^{viii}$	68.4(1)	$O(3)^{iv}$– La–O(3)	136.7(2)
$O(2)^{vii}$– La–$O(2)^{viii}$	53.9(1)	O(4)– La–$O(2)^{viii}$	134.8(1)
$O(2)^{vii}$– La–$O(2)^{vi}$	122.1(1)	O(4)– La–$O(2)^{vi}$	82.2(2)
$O(2)^{v}$– La–$O(2)^{vi}$	169.5(1)	O(4)– La–$O(2)^{vii}$	135.7(1)
O(3)– La–$O(2)^{viii}$	71.8(1)	O(4)– La–$O(2)^{v}$	89.4(2)
O(3)– La–$O(2)^{vi}$	89.6(1)	O(4)– La–O(3)	74.5(2)
O(3)– La–$O(2)^{vii}$	69.8(1)	O(4)– La–$O(3)^{iv}$	148.7(2)
O(3)– La–$O(2)^{v}$	94.3(1)	$O(4)^{iv}$– La–O(4)	74.4(2)

Note. The symmetry code is that used in Table III.

(ii) In order to improve our structural knowledge on the system La_2O_3–P_2O_5 we performed some supplementary experiments based on the information reported in (*27*). Having obtained preparations of exactly the same X-ray powder diffraction patterns of those published in (*27*) (which are claimed to be the new types of rare-earth phosphates) we compared them directly with the results generated by the program LAZY PULVERIX (*28*) using crystal data for LaP_3O_9,[1] $LaPO_4$ (*6*), and LaP_5O_{14}[2] as an input. The experimental diffractograms were identical with the simulated ones. In our opinion it is very probable that one obtains mixtures of LaP_3O_9, $LaPO_4$, and LaP_5O_{14} instead of new compounds in the above-mentioned experiments.

(iii) Although numerous preparations were attempted using various experimental conditions, only one variety of LaP_3O_9 has been isolated and identified crystallographically. Thermal data on the other hand indicate a phase transition above 1093 K. Further experiments based on these facts are in progress.

On the grounds of the obtained results one can state that the lanthanum metaphosphate seems to have a very definite and unique structure and therefore it should be able to serve as the more stable "orthorhombic structural warp" for syntheses of mixed rare-earth metaphosphates of desired spectroscopic properties than its isomorph NdP_3O_9 (*8*) or other orthorhombic lanthanide metaphosphates.

[1] This work.

[2] Results obtained in our laboratory.

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