In recent years, rare-earth phosphate crystals have attracted much attention, thanks to their possible use in miniature laser materials, color lumiphors, optic fiber communication, etc. In fact, the structures of monovalent and rare-earth metals condensed phosphates of the general formula \( \text{M}^{\text{III}}\text{M}^{\text{II}}(\text{PO}_3)_4 \) (where \( \text{M}^{\text{II}} = \text{alkali metal, M}^{\text{III}} = \text{rare earth} \)) are well-known. At room temperature, the corresponding representatives mainly exhibit two different structure types for the cyclotetraphosphates, \( \text{P}_4\text{O}_{12}^{4-} \), in the space groups \( \text{C}2/c \) and \( \text{I}43d \), and for the polyphosphates, \( (\text{PO}_3)_4^{4-} \).

The literature dealing with these compounds had been rather confusing for a long time, yet nowadays it is well-established that the \( \text{M}^{\text{II}}\text{M}^{\text{III}}(\text{PO}_3)_4 \) compounds can be classified into seven different structural types. Such compounds, many of which are isotopic and some are polymorphic, are currently denoted by roman numerals \( \text{I} \) to \( \text{VII} \) due to Palkina et al.\(^7\). The main crystallographic data for some trivalent-monovalent polyphosphates,\(^4\) gathered in Table 1, can explain the difference between these seven structure types. It is within this context that the present study lies to give birth to a new form of polyphosphate \( \text{LiLa}(\text{PO}_3)_4 \), whose chemical preparation and crystal structure were determined.

Crystals of \( \text{LiLa}(\text{PO}_3)_4 \) were prepared at room temperature by the slow evaporation of an aqueous solution of a mixture of \( \text{Li}_2\text{CO}_3 \) (Aldrich 99.9%) and \( \text{La}_2\text{O}_3 \) was slowly added to 20 ml of phosphoric acid \( \text{H}_3\text{PO}_4 \) (85%). The stoichiometric ratio \( 1:1:8 \). Schematically, the reactions are:

\[
\text{Li}_2\text{CO}_3 + \text{La}_2\text{O}_3 + 8\text{H}_3\text{PO}_4 \rightarrow 2\text{LiLaP}_4\text{O}_{12} + \text{CO}_2 + 12\text{H}_2\text{O},
\]

in which a new lanthanum lithium polyphosphate can be reported.

Diffraction data were collected at room temperature on an Enraf Nonius CAD4 four-circle diffractometer with graphite-monochromatized Mo \( \text{K}_\alpha \) (0.071073 nm) radiation. 2102 X-ray independent reflections with final \( R = 0.0377 \) and \( R_w = 0.0347 \) refined with 83 parameters. With regard to the atomic arrangement, it can be described as a long-chain polyphosphate organization. Besides, two infinite \( (\text{PO}_3)^{\mu} \) chains with a period of eight tetrahedral run along the [110] direction. As for the structure of \( \text{LiLaP}_4\text{O}_{12} \), it consists of \( \text{LaO}_8 \) polyhedral sharing oxygen atoms with a phosphoric group, \( \text{PO}_4 \). Each \( \text{Li}^+ \) ion is bonded to six oxygen atoms.

Table 1 | Main crystallographic data for some trivalent-monovalent polyphosphates

<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure type</th>
<th>( a(\text{Å}) )</th>
<th>( b(\text{Å}) )</th>
<th>( c(\text{Å}) )</th>
<th>( \beta(^\circ) )</th>
<th>S.G</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{LiNd}(\text{PO}_3)_4 ) [3]</td>
<td>I</td>
<td>( 16.408(3) )</td>
<td>( 7.035(4) )</td>
<td>( 9.729(5) )</td>
<td>( 126.38(5) )</td>
<td>( \text{C}2/c )</td>
<td>4</td>
</tr>
<tr>
<td>( \text{NaNd}(\text{PO}_3)_4 ) [5]</td>
<td>III</td>
<td>( 9.907(4) )</td>
<td>( 13.100(1) )</td>
<td>( 7.280(1) )</td>
<td>( 91.97(1) )</td>
<td>( \text{P}2_1/n )</td>
<td>2</td>
</tr>
<tr>
<td>( \text{KNd}(\text{PO}_3)_4 ) [4]</td>
<td>IV</td>
<td>8.008(1)</td>
<td>8.438(1)</td>
<td>7.280(1)</td>
<td>91.97(1)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>( \text{TNd}(\text{PO}_3)_4 ) [6]</td>
<td>V</td>
<td>10.440(3)</td>
<td>8.950(2)</td>
<td>11.007(1)</td>
<td>105.86(2)</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>( \text{KYb}(\text{PO}_3)_4 ) [6]</td>
<td>VI</td>
<td>7.766(1)</td>
<td>8.853(1)</td>
<td>14.831(2)</td>
<td>96.36(1)</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>( \text{CsPr}(\text{PO}_3)_4 ) [7]</td>
<td>VII</td>
<td>7.159(2)</td>
<td>9.190(3)</td>
<td>8.809(2)</td>
<td>99.66(2)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>( \text{KeEr}(\text{PO}_3)_4 ) [8]</td>
<td></td>
<td>11.750(1)</td>
<td>10.325(2)</td>
<td>17.310(1)</td>
<td>99.66(2)</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

\( ^\dagger \) To whom correspondence should be addressed.
E-mail: taharmhiri@yahoo.fr, m_boujelbene2010@yahoo.fr
reflections were measured for 1873 independent reflections and 83 parameters. The resolution structure was conducted with the crystallographic SHELX program. The chemical crystal data, the parameters used for the X-ray diffraction data collection as well as the strategy used for the crystal structure determination and their results, are listed in Table 2. Moreover, the final positions and equivalent isotropic thermal parameters are given in Table 3S.

The projection on the ab plane is depicted in Fig. 1. The basic structure units of LiLa(PO₃)₄ are two meandering chains formed by corner-sharing PO₄ tetrahedral with the PO₃⁻ formula. These chains are joined to one another by La and Li polyhedral forming a three-dimensional framework. The basic structure units of Na(Ag)La(PO₃)₄ are two meandering chains formed by corner-sharing PO₄ tetrahedral with the PO₃⁻ formula. The chains (PO₄)₄ run along a direction.

Furthermore, the Lanthanum atom occupies one coordination polyhedron that can be described as a distorted Archimedian anti-prism (Fig. 2). Eight oxygen atoms are involved in the coordination of the Lanthanum atom, with the La-O distances ranging from 2.3444(19) to 2.5476(19) Å. The eightfold coordinated La atoms present regular La-O bond distances of between 2.445 and 2.558 Å with a mean value of 2.51 Å for NaLa(PO₃)₄ and between 2.445 and 2.568 with a mean value for 2.52 Å for AgLa(PO₃)₄. Comparable values are encountered in other Lanthanum oxide structure.⁵,¹⁰ Each La polyhedron is connected by means of common corners and by common faces with Na or Ag polyhedral. The LaO₁₂ dodecahedron shares all of its oxygen atoms with the corners of the neighboring PO₄ tetrahedral, and with the faces of the neighboring Li polyhedral. The lithium cations are surrounded by six oxygen atoms (Fig. 2), which is a considerably-irregular environment just like another lithium polytetraphosphate.³ In fact, the Li-O distances vary from 1.970(5) to 1.986(2) Å with an average of 1.976 Å. For the sake of comparison with the coordination number around Ag⁺ in the structure AgLa(PO₃)₄, Na⁺ in the structure of NaLa(PO₃)₄ is surrounded by seven oxygen atoms. As for their polyhedron, it is relatively irregular with five distances ranging from 2.399 to 2.583 Å (Na) and from 2.483 to 2.670 Å (Ag), one long distance, 2.749 (Na) and 2.820 Å (Ag) and one very long at 3.050 (Na) and 3.041 Å (Ag). This result can be explained on the basis of the radii of the monovalent cations as r(Ag⁺) and r(Na⁺) ≥ r(Li⁺).

In addition, the asymmetric unit contains four crystallographically independent PO₄ groups. All phosphate groups consist of a phosphorus atom coordinated to four oxygen atoms in a tetrahedron, each of which is connected to another P tetrahedron by two common corners in the cis position, giving rise to a twisted chain of the general formula (PO₄)ₓ⁻. The main geometrical features in this entity are reported in Table 4S. In fact, the P-O distances may be divided into the linking or bridging P-Oi distances, which range from 1.481(2) to 1.591(2). Besides, the O-P-O angles are between 101.41(12) and 118.66(13), which are in good agreement with those usually met in polyphosphate anions. As for the atomic arrangement, it can be described as being a long-chain polyphosphate organization. Finally, the bond distances of P-O vary from 1.477 to 1.494 Å for NaLa(PO₃)₄ and from 1.466 to 1.487 for AgLa(PO₃)₄.

References