Synthesis, Crystal Structure, and Ionic Conductivity of Tl₂Ta₂(PO₄)₂(HP₂O₁₆)

E. V. Murashova, N. N. Chudinova, A. B. Ilyukhin, V. A. Tarnopol’skii, and A. B. Yaroslavtsev

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninski pr. 31, Moscow, 119991 Russia

Received May 12, 2003; in final form, July 10, 2003

Abstract—Tl₂Ta₂(PO₄)₂(HP₂O₁₆) is synthesized at 400°C in molten polyphosphoric acids containing Tl, Ta, and P in the ratio 4 : 1 : 15, and its crystal structure is determined: monoclinic cell, \( a = 5.1469 \) Å, \( b = 18.4515 \) Å, \( c = 10.793 \) Å, \( \beta = 95.65^\circ \), \( Z = 2 \), sp. gr. \( P2_1/m \). The framework of the structure is made up of monophosphate and hydrogen pentaphosphate groups which share corners with TaO₆ octahedra. The Tl atoms reside in infinite channels. Neighboring pentaphosphate groups are hydrogen-bonded. In the range 60–350°C, the compound has a rather high ionic conductivity, which is tentatively attributed to proton transport. The activation energy of conduction is 48 ± 1 kJ/mol.

Acid salts of polyvalent metals are of interest as potential protonic conductors [1, 2]. In light of this, the synthesis of new compounds stable at high temperatures is of practical importance.

Earlier, Chudinova et al. [3] proposed a novel approach to the synthesis of mixed-cation phosphates: reactions in molten polyphosphoric acids containing Tl, Ta, and P in the ratio 4 : 1 : 15, and its crystal structure is determined: monoclinic cell, \( a = 5.1469 \) Å, \( b = 18.4515 \) Å, \( c = 10.793 \) Å, \( \beta = 95.65^\circ \), \( Z = 2 \), sp. gr. \( P2_1/m \). The framework of the structure is made up of monophosphate and hydrogen pentaphosphate groups which share corners with TaO₆ octahedra. The Tl atoms reside in infinite channels. Neighboring pentaphosphate groups are hydrogen-bonded. In the range 60–350°C, the compound has a rather high ionic conductivity, which is tentatively attributed to proton transport. The activation energy of conduction is 48 ± 1 kJ/mol.

Acid salts of polyvalent metals are of interest as potential protonic conductors [1, 2]. In light of this, the synthesis of new compounds stable at high temperatures is of practical importance.

The purpose of this work was to synthesize the compound Tl₂Ta₂(PO₄)₂(HP₂O₁₆) [4]. Hydrogen was located using a difference Fourier map. In the final least squares refinement (SHELXL-97 [6]), the temperature factors

<table>
<thead>
<tr>
<th>Table 1. Crystal data for Tl₂Ta₂(PO₄)₂(HP₂O₁₆), intensity data collection conditions, and refinement statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
</tr>
<tr>
<td>( a, ) Å</td>
</tr>
<tr>
<td>( b, ) Å</td>
</tr>
<tr>
<td>( c, ) Å</td>
</tr>
<tr>
<td>( \beta, ) deg</td>
</tr>
<tr>
<td>( Z )</td>
</tr>
<tr>
<td>( V, ) Å³</td>
</tr>
<tr>
<td>Diffractometer</td>
</tr>
<tr>
<td>Radiation</td>
</tr>
<tr>
<td>Crystal dimensions, mm</td>
</tr>
<tr>
<td>Sp. gr.</td>
</tr>
<tr>
<td>( d, ) g/cm³</td>
</tr>
<tr>
<td>( \mu, ) mm⁻¹</td>
</tr>
<tr>
<td>( \theta_{\text{max}} )</td>
</tr>
<tr>
<td>( N_c )</td>
</tr>
<tr>
<td>( N_i )</td>
</tr>
<tr>
<td>( N_o )</td>
</tr>
<tr>
<td>( N_p )</td>
</tr>
<tr>
<td>( R_{IwR_2} ) ( (I &gt; 2\sigma(I)) )</td>
</tr>
<tr>
<td>( R_{IwR_2} ) ( (\text{measured reflections}) )</td>
</tr>
<tr>
<td>Gof</td>
</tr>
</tbody>
</table>

Note: \( N_i \) is the number of measured reflections, \( N_o \) is the number of independent reflections, \( N_o \) is the number of observed reflections in terms of \( I > 2\sigma(I) \), and \( N_p \) is the number of variable parameters.
of Tl, Ta, and P were anisotropic, that of O was isotropic, and the hydrogen atom was fixed. The positional and thermal parameters are listed in Table 2.

\[ \text{Tl}_2\text{Ta}_2(\text{PO}_4)_2(\text{HP}_5\text{O}_{16}) \]

contains mono- and pentaphosphate anions which share corners with the TaO\(_6\) octahedra to form a three-dimensional framework. The Tl atoms reside in infinite channels running along [100] (Fig. 1). Neighboring Tl polyhedra are connected so as to form infinite chains. The nearest neighbor Tl–Tl distances in the chains are 3.758 and 3.798 Å. The rarely encountered pentaphosphate anion \([7, 8]\) has the shape of a horseshoe, with a proton attached to one of the terminal oxygens, O(9), of the middle tetrahedron P(3)O\(_4\). The structure can be regarded as consisting of layers made up of TaO\(_6\) octahedra and the surrounding monophosphate groups and pairs of PO\(_4\) tetrahedra of pentaphosphate groups. The layers are similar to those in the structures of AM\(_{s}^V(\text{PO}_4)_2\) compounds \([9]\), with the difference that the TaO\(_6\) octahedra in \(\text{Tl}_2\text{Ta}_2(\text{PO}_4)_2(\text{HP}_5\text{O}_{16})\) are brought apart by pairs of PO\(_4\) tetrahedra of the pentaphosphate anion (Fig. 2), and similar neighboring layers are separated not only by Tl atoms but also by the middle tetrahedron of the pentaphosphate group. The layers are well seen in Fig. 3. Thus, the Ta-containing layers alternate with the layers composed of Tl atoms and PO\(_4\) groups of pentaphosphate anions. The hydrogen attached to the middle PO\(_4\) tetrahedra of the pentaphosphate group is linked by a hydrogen bond to the O(8) atom of the neighboring pentaphosphate group (Fig. 4), leading to the formation of infinite [100] chains. The O(9)–H(1) distance is 0.92 Å, the H(1)···O(8) bond length is 1.93 Å, and the O(9)···O(8) bond length is 2.66 Å. The O(9)–H(1)–O(8) bond angle is 134°. The O(9) and O(8) atoms belong to the middle PO\(_4\) tetrahedra of pentaphosphate groups.

To evaluate the ionic conductivity of \(\text{Tl}_2\text{Ta}_2(\text{PO}_4)_2(\text{HP}_5\text{O}_{16})\) in the range 60–350°C, we measured its impedance spectrum at each temperature.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta(1)</td>
<td>0.19865(13)</td>
<td>0.47610(4)</td>
<td>0.80470(7)</td>
<td>0.01007(19)</td>
</tr>
<tr>
<td>Tl(1)</td>
<td>0.1945(2)</td>
<td>0.75</td>
<td>0.72548(11)</td>
<td>0.0281(3)</td>
</tr>
<tr>
<td>Tl(2)</td>
<td>-0.2466(2)</td>
<td>0.75</td>
<td>0.98301(11)</td>
<td>0.0304(4)</td>
</tr>
<tr>
<td>P(1)</td>
<td>0.1713(8)</td>
<td>0.3743(3)</td>
<td>0.5347(5)</td>
<td>0.0141(12)</td>
</tr>
<tr>
<td>P(2)</td>
<td>0.3301(8)</td>
<td>0.4148(3)</td>
<td>0.2996(4)</td>
<td>0.0136(12)</td>
</tr>
<tr>
<td>P(3)</td>
<td>0.3870(11)</td>
<td>0.2500</td>
<td>0.6684(6)</td>
<td>0.0147(17)</td>
</tr>
<tr>
<td>P(4)</td>
<td>0.7336(8)</td>
<td>0.4016(2)</td>
<td>0.9560(4)</td>
<td>0.0109(11)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.155(2)</td>
<td>0.4222(6)</td>
<td>0.6463(11)</td>
<td>0.025(3)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.3276(18)</td>
<td>0.4223(5)</td>
<td>0.4481(10)</td>
<td>0.007(2)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.390(2)</td>
<td>0.3177(7)</td>
<td>0.5741(12)</td>
<td>0.032(4)</td>
</tr>
<tr>
<td>O(4)</td>
<td>-0.064(2)</td>
<td>0.3409(6)</td>
<td>0.4783(11)</td>
<td>0.024(3)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.1075(18)</td>
<td>0.4663(6)</td>
<td>0.2477(10)</td>
<td>0.017(3)</td>
</tr>
<tr>
<td>O(6)</td>
<td>0.5849(19)</td>
<td>0.4527(6)</td>
<td>0.2752(11)</td>
<td>0.018(3)</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.302(2)</td>
<td>0.3429(7)</td>
<td>0.2548(11)</td>
<td>0.027(3)</td>
</tr>
<tr>
<td>O(8)</td>
<td>0.160(3)</td>
<td>0.25</td>
<td>0.7412(16)</td>
<td>0.018(4)</td>
</tr>
<tr>
<td>O(9)</td>
<td>0.6463(3)</td>
<td>0.25</td>
<td>0.7522(16)</td>
<td>0.025(5)</td>
</tr>
<tr>
<td>O(10)</td>
<td>0.4979(19)</td>
<td>0.4157(5)</td>
<td>0.8533(11)</td>
<td>0.011(3)</td>
</tr>
<tr>
<td>O(11)</td>
<td>0.712(2)</td>
<td>0.3362(6)</td>
<td>1.0232(11)</td>
<td>0.023(3)</td>
</tr>
<tr>
<td>O(12)</td>
<td>0.9737(19)</td>
<td>0.4073(5)</td>
<td>0.8794(10)</td>
<td>0.013(3)</td>
</tr>
<tr>
<td>O(13)</td>
<td>0.7545(18)</td>
<td>0.4692(6)</td>
<td>1.0453(10)</td>
<td>0.016(3)</td>
</tr>
<tr>
<td>H(1)</td>
<td>0.785</td>
<td>0.25</td>
<td>0.704</td>
<td>0.040</td>
</tr>
</tbody>
</table>