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Preparation and Crystallographic Characterization of the Polyphosphate $TlPO_3$

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Chemical preparation and crystallographic data are specified for thallium polyphosphate. $TlPO_3$ crystallizes in the monoclinic system, space group $P2_1/n$, with the following unit-cell parameters: $a = 12.270(7)$ Å; $b = 4.263(2)$ Å; $c = 6.328(4)$ Å; $\beta = 96°.72(3)$; $Z = 4$. This compound is isotypic with two previously described polyphosphates, namely $RbPO_3$ and $CsPO_3$.

Introduction

Crystallographic studies have been carried out for two thallium condensed phosphates: the cyclotetraphosphate $Tl_4P_4O_{12}$ (*1*) and the cyclotriphosphate $Tl_3P_3O_9$ (*2*). These two compounds are transformed, by heating, to a long-chain polyphosphate, $TlPO_3$ (*3*). The transformations are not reversible and proceed according to the process:

$$Tl_4P_4O_{12} \xrightarrow{T=631\ K} 4\ TlPO_3.$$

$TlPO_3$ has not been studied up to now.

Chemical Preparation

During experiments made to prepare a thallium–lithium phosphate, $TlPO_3$ single crystals were obtained accidentally in a flux containing 0.546 g of Li_2CO_3, 14 g of Tl_2CO_3, and 4.5 cm^3 of H_3PO_4 heated at 473 K for 3 days. Crystals of $TlPO_3$ grow as needles.

Powder samples were prepared from a stoichiometric mixture of Tl_2CO_3 and $(NH_4)_2HPO_4$. The initial heating temperature was 523 K and produced an amorphous material which crystallized after calcination at 573 K for 4 days.

Crystallographic Study

Single crystal study by the Weissenberg technique shows this compound to be isotypic with the two polyphosphates $CsPO_3$ (*4*) and $RbPO_3$ (*5*).

The powdered sample was studied by X-ray diffraction, Data were recorded with a Philips Norelco diffractometer using copper $K\alpha_1\alpha_2$ radiation and operating at a low scan speed [$1/8°(\theta)$ min^{-1}]. An indexed powder diagram is provided in Table I. Intensities reported in this table are peak heights above the background. Unit-cell dimensions have been obtained from a least squares refinement using the angular data of the powder diffractogram. Table II compares the crystallographic constants of $TlPO_3$ with those of $CsPO_3$ and $RbPO_3$. It reveals that these three condensed phosphates are isotypic.

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TABLE I

INDEXED POWDER DIAGRAM FOR $TlPO_3$

hkl	$d_{cal.}$	$d_{obs.}$	$I_{obs.}$	hkl	$d_{cal.}$	$d_{obs.}$	$I_{obs.}$
$\bar{2}00$	6.09	6.09	14	$\bar{3}11$	2.581	2.580	4
$\bar{1}01$	5.87	5.88	12	$\bar{1}12$	2.524	2.524	9
101	5.34	5.33	26	$\bar{4}10$	2.479	2.480	23
$\bar{1}10$	4.02	4.02	15	$\bar{2}12$	2.418	2.417	21
$\bar{3}01$	3.609	3.610	57	$\bar{4}11$	2.385	2.385	6
$\bar{2}10$	3.493	3.494	37	$\bar{5}01$	2.368	2.370	7
$\bar{1}11$	3.450	3.450	38	$\bar{4}02$	2.328	2.327	6
111	3.331	3.330	18	212	2.262	2.262	15
301	3.243	3.244	13	510	2.116	2.116	10
$\bar{2}11$	3.144	3.143	100	$\bar{1}20$	2.100	2.098	6
400	3.046	3.045	24	$\bar{5}11$	2.070	2.072	16
211	2.970	2.969	20	600	2.031	2.030	19
$\bar{2}02$	2.936	2.936	25				

TABLE II

MAIN CRYSTALLOGRAPHIC FEATURES FOR $TlPO_3$, $CsPO_3$, AND $RbPO_3$

Polyphosphate	Space group	a(Å)	b(Å)	c(Å)	β(°)	Z	Ref.
$TlPO_3$	$P2_1/n$	12.270(7)	4.263(2)	6.328(4)	96.72(3)	4	This study
$CsPO_3$	$P2_1/n$	12.71	4.32	6.83	97	4	(*4*)
$RbPO_3$	$P2_1/n$	12.123(2)	4.228(2)	6.479(2)	96.3(3)	4	(*5*)

References

1. J. K. FAWCETT, V. KOCMAN, AND S. C. NYBURG *Acta Crystallogr. Sect. B* **30,** 1979 (1974).
2. N. BOUDJADA Thèse de doctorat d'Etat, Grenoble (1985).
3. C. CAVARO GHERSI, Thèse 3ème cycle, Grenoble (1975).
4. D. E. C. CORBRIDGE, *Acta Crystallogr.* **8,** 520 (1955).
5. D. E. C. CORBRIDGE, *Acta Crystallogr.* **9,** 308 (1956).