

Phase Equilibrium Relations in the Pseudo Binary System TIPO₃-Ce(PO₃)₃

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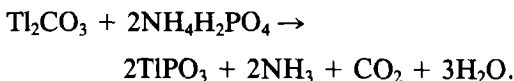
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The TIPO₃-Ce(PO₃)₃ system has been investigated by DTA, X-ray diffraction, and infrared spectroscopy. In this system the existence of two compounds, TlCe(PO₃)₄ and Tl₂Ce(PO₃)₅, was observed. Both compounds melt in a peritectic reaction: at 1078 K for the first and 843 K for the second one. TlCe(PO₃)₄ has a monoclinic unit cell with $a = 10.541(3) \text{ \AA}$, $b = 9.133(3) \text{ \AA}$, $c = 11.034(3) \text{ \AA}$, $\beta = 105.92(1)^\circ$, $Z = 4$, and space group $P2_1/n$. Tl₂Ce(PO₃)₅ is triclinic, $P1$, with the unit cell dimensions: $a = 7.218(3) \text{ \AA}$, $b = 13.286(4) \text{ \AA}$, $c = 7.243(3) \text{ \AA}$, $\alpha = 90.25(4)^\circ$, $\beta = 107.71(2)^\circ$, $\gamma = 90.29(3)^\circ$, and $Z = 2$. These compounds are long chain polyphosphates; the first is isotypic with RbNd(PO₃)₄ and the second corresponds to a new structure type determined with the ammonium salt.

Rare earth phosphates are attractive as promising materials for quantum electronics (1, 2). However, the literature does not give much information on condensed rare earth phosphates, particularly cerium phosphates. Continuing our systematic investigation of the formation of cerium alkali condensed phosphates (3, 4), the present paper deals with the study of the TIPO₃-Ce(PO₃)₃ system.

Experimental

Thallium polyphosphate was made from analytical reagent grade ammonium dihydrogen phosphate and thallium carbonate



The initial substances were thoroughly ground in an agate mortar and slowly

heated until all the water and gases had been removed and the material had melted.

Ce(PO₃)₃ was made by complete dehydration of CeP₃O₉ · 3H₂O prepared as described earlier (5).

Samples were mixed with the desired composition ratios, ground several times, and reacted in silica crucibles for several days at 573 K. For the Ce(PO₃)₃ rich compositions, the mixtures were further heated at 873 K.

The equilibrium diagram was established with differential thermal analysis (DTA) using a M5 Micro DTA Setaram apparatus by recording the heating curves of specimens up to the melting point in platinum crucibles. Pt/Pt-Rh thermocouples (calibrated against the melting point of NaCl) were used to detect thermal phenomena. The heating rate of the furnace was 10°/min and $\alpha\text{-Al}_2\text{O}_3$ was used as reference. The accu-

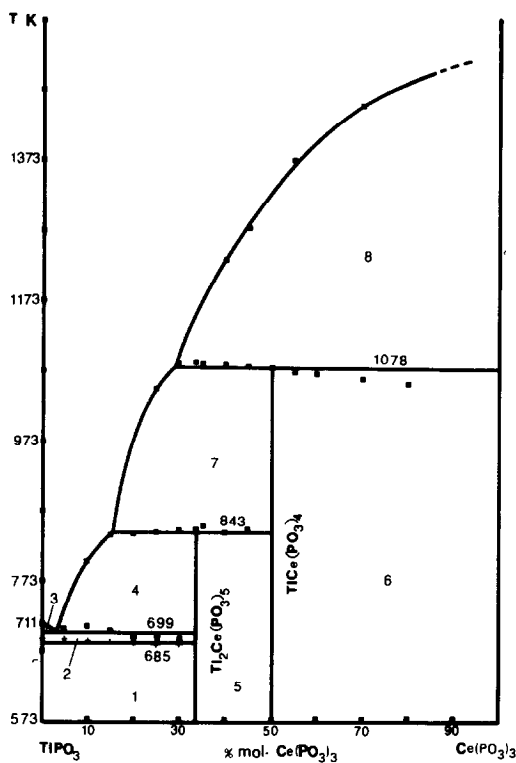


FIG. 1. Equilibrium diagram of the $\text{TiPO}_3\text{-Ce}(\text{PO}_3)_3$ system: (1) $\alpha\text{-TiPO}_3 + \text{Ti}_2\text{Ce}(\text{PO}_3)_5$; (2) $\beta\text{-TiPO}_3 + \text{Ti}_2\text{Ce}(\text{PO}_3)_5$; (3) $\beta\text{-TiPO}_3 + \text{liquid}$; (4) $\text{Ti}_2\text{Ce}(\text{PO}_3)_5 + \text{liquid}$; (5) $\text{Ti}_2\text{Ce}(\text{PO}_3)_5 + \text{TiCe}(\text{PO}_3)_4$; (6) $\text{TiCe}(\text{PO}_3)_4 + \text{Ce}(\text{PO}_3)_3$; (7) $\text{TiCe}(\text{PO}_3)_4 + \text{liquid}$; (8) $\text{Ce}(\text{PO}_3)_3 + \text{liquid}$.

racy of temperature measured from DTA was about $\pm 5^\circ$ below 1273 K and $\pm 10^\circ$ above this temperature.

The initial components and the new phases formed in the system were identified by X-ray diffraction on a Norelco-Philips diffractometer with nickel filtered copper radiation.

The ir absorption spectra were recorded on a IR-580 Perkin-Elmer spectrophotometer using pellets formed by mixing the specimens with KBr.

Results and Discussion

The results of the thermal analysis of the system $\text{TiPO}_3\text{-Ce}(\text{PO}_3)_3$ are given in Fig. 1.

The components of the system form two definite phases, $\text{TiCe}(\text{PO}_3)_4$ and $\text{Ti}_2\text{Ce}(\text{PO}_3)_5$, which decompose on heating in a peritectic reaction at 1078 and 843 K, respectively. The branches of the liquidus curve intersect at monovariant peritectic points at 16 and 28 mole% $\text{Ce}(\text{PO}_3)_3$. The eutectic invariant occurs at 699 K and the eutectic point is at 3% $\text{Ce}(\text{PO}_3)_3$. The invariant at 685 K corresponds to a polymorphic transformation of TiPO_3 .

The individuality of the various compounds was established by X-ray diffraction (Tables I, II). Indexing the X-ray diffraction patterns of both compounds by the Hess method (6) established that

(1) $\text{TiCe}(\text{PO}_3)_4$, isomorphous with $\text{RbNd}(\text{PO}_3)_4$ (7), has a monoclinic unit cell with

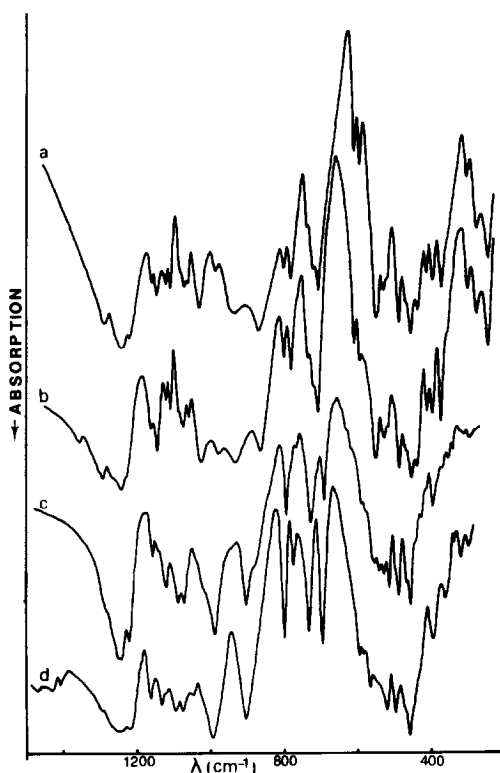


FIG. 2. Infrared absorption spectra of (a) $\text{TiCe}(\text{PO}_3)_4$; (b) $\text{RbNd}(\text{PO}_3)_4$; (c) $\text{Ti}_2\text{Ce}(\text{PO}_3)_5$; (d) $(\text{NH}_4)_2\text{Ce}(\text{PO}_3)_5$.

TABLE I
 X-RAY POWDER DATA FOR $\text{TlCe}(\text{PO}_3)_4$

| hkl | $d_{\text{cal.}}(\text{\AA})$ | $d_{\text{obs.}}(\text{\AA})$ | $I(\%)$ | hkl | $d_{\text{cal.}}(\text{\AA})$ | $d_{\text{obs.}}(\text{\AA})$ | $I(\%)$ |
|-------------|-------------------------------|-------------------------------|---------|-------------|-------------------------------|-------------------------------|---------|
| $\bar{1}01$ | 8.60 | 8.61 | 17 | 023 | 2.796 | 2.797 | 22 |
| 011 | 6.92 | 6.92 | 32 | $\bar{2}04$ | 2.670 | 2.671 | 33 |
| 002 | 5.30 | 5.30 | 43 | 032 | 2.640 | 2.641 | 15 |
| 111 | 5.29 | | | $\bar{2}30$ | 2.610 | 2.609 | 17 |
| $\bar{2}00$ | 5.07 | 5.07 | 11 | $\bar{2}14$ | 2.563 | 2.562 | 14 |
| 012 | 4.59 | 4.59 | 22 | $\bar{4}11$ | 2.530 | 2.530 | 18 |
| $\bar{2}11$ | 4.49 | 4.49 | 28 | $\bar{4}12$ | 2.481 | 2.482 | 13 |
| $\bar{2}02$ | 4.30 | 4.30 | 96 | $\bar{4}13$ | 2.316 | 2.316 | 32 |
| 120 | 4.16 | 4.16 | 24 | 033 | 2.307 | 2.307 | 21 |
| $\bar{1}21$ | 4.03 | 4.03 | 25 | 040 | 2.283 | 2.282 | 10 |
| 112 | 3.850 | 3.851 | 18 | $\bar{4}21$ | 2.281 | | |
| 211 | 3.779 | 3.778 | 35 | $\bar{2}33$ | 2.258 | 2.257 | 15 |
| 121 | 3.735 | 3.736 | 21 | $\bar{4}22$ | 2.245 | 2.244 | 33 |
| $\bar{1}03$ | 3.667 | 3.666 | 12 | 420 | 2.216 | 2.216 | 20 |
| $\bar{3}01$ | 3.510 | 3.507 | 42 | $\bar{2}32$ | 2.221 | 2.220 | 20 |
| $\bar{1}22$ | 3.471 | 3.472 | 79 | $\bar{1}05$ | 2.202 | 2.202 | 22 |
| 220 | 3.393 | 3.394 | 100 | $\bar{4}04$ | 2.151 | 2.151 | 24 |
| 013 | 3.298 | 3.297 | 23 | 331 | 2.133 | 2.132 | 15 |
| $\bar{3}11$ | 3.276 | 3.277 | 24 | 124 | 2.131 | | |
| 202 | 3.247 | 3.248 | 15 | $\bar{2}41$ | 2.088 | 2.087 | 21 |
| $\bar{2}13$ | 3.158 | 3.158 | 24 | $\bar{3}33$ | 2.087 | | |
| 122 | 3.109 | 3.111 | 52 | 240 | 2.082 | 2.082 | 19 |
| 103 | 3.086 | 3.086 | 54 | 421 | 2.072 | 2.072 | 20 |
| 301 | 2.991 | 2.991 | 17 | $\bar{3}05$ | 2.071 | | |
| 031 | 2.926 | 2.924 | 20 | $\bar{5}03$ | 2.013 | 2.011 | 24 |
| 113 | 2.924 | | | 142 | 2.011 | | |
| $\bar{1}31$ | 2.870 | 2.869 | 65 | $\bar{2}34$ | 2.008 | 2.001 | 24 |
| $\bar{3}03$ | 2.867 | | | 241 | 2.001 | | |
| $\bar{1}23$ | 2.859 | 2.860 | 59 | 034 | 2.000 | | |

parameters $a = 10.541(3) \text{ \AA}$, $b = 9.133(3) \text{ \AA}$, $c = 11.034(3) \text{ \AA}$, $\beta = 105.92(1)^\circ$, and $Z = 4$. The space group is $P2_1/n$. The structural motif consists of infinite chains of PO_4 tetrahedra joined by bridging oxygen atoms. The $(\text{PO}_3)_\infty$ chains are extended parallel to the $[101]$ direction, and the unit cell contains two chains.

(2) $\text{Tl}_2\text{Ce}(\text{PO}_3)_5$, isomorphous with $(\text{NH}_4)_2\text{Ce}(\text{PO}_3)_5$ (8), is triclinic, $P1$, with the unit cell dimensions: $a = 7.218(3) \text{ \AA}$, $b = 13.286(4) \text{ \AA}$, $c = 7.243(3) \text{ \AA}$, $\alpha = 90.25(4)^\circ$, $\beta = 107.71(2)^\circ$, $\gamma = 90.29(3)^\circ$, and $Z = 2$. This compound is a long chain polyphos-

phate. The most interesting crystallographic feature of this salt is the existence of two independent infinite (PO_3) chains in the unit cell, one running along the a axis, the other along the c axis. This is the first long chain polyphosphate to exhibit such a feature.

The comparison of the vibrational spectra of $\text{TlCe}(\text{PO}_3)_4$ with that of $\text{RbNd}(\text{PO}_3)_4$ ¹ and of $\text{Tl}_2\text{Ce}(\text{PO}_3)_5$ with that of $(\text{NH}_4)_2\text{Ce}(\text{PO}_3)_5$ ² in Fig. 2, confirms the isotopy,

¹ These compounds were prepared by comparing them with Tl-containing compounds.

² See footnote 1.

TABLE II
 X-RAY POWDER DATA FOR $\text{Ti}_2\text{Ce}(\text{PO}_3)_5$

| hkl | $d_{\text{cal.}}(\text{\AA})$ | $d_{\text{obs.}}(\text{\AA})$ | I (%) | hkl | $d_{\text{cal.}}(\text{\AA})$ | $d_{\text{obs.}}(\text{\AA})$ | I (%) |
|-------------|-------------------------------|-------------------------------|---------|-------------------|-------------------------------|-------------------------------|---------|
| $\bar{1}00$ | 6.88 | 6.88 | 14 | $\bar{1}\bar{4}1$ | 2.631 | 2.631 | 23 |
| 020 | 6.64 | 6.64 | 22 | $12\bar{3}$ | 2.271 | 2.271 | 13 |
| $0\bar{1}1$ | 6.14 | 6.14 | 13 | $0\bar{1}3$ | 2.269 | | |
| $\bar{1}11$ | 5.35 | 5.34 | 17 | $21\bar{3}$ | 2.223 | | |
| $11\bar{1}$ | 5.34 | | | $\bar{2}13$ | 2.222 | | |
| $0\bar{2}1$ | 4.80 | 4.80 | 12 | $\bar{3}12$ | 2.220 | 2.223 | 22 |
| $\bar{1}20$ | 4.79 | | | $\bar{1}33$ | 2.115 | | |
| 101 | 4.27 | 4.27 | 30 | 241 | 2.114 | 2.112 | 16 |
| $1\bar{1}1$ | 4.07 | 4.07 | 18 | $0\bar{6}1$ | 2.112 | | |
| $0\bar{3}1$ | 3.737 | 3.739 | 18 | $0\bar{5}2$ | 2.111 | | |
| $1\bar{2}1$ | 3.602 | 3.599 | 35 | $33\bar{1}$ | 2.109 | | |
| $\bar{2}01$ | 3.536 | 3.537 | 55 | $2\bar{1}2$ | 2.108 | | |
| 200 | 3.438 | 3.438 | 50 | $0\bar{3}3$ | 2.046 | 2.047 | 16 |
| 012 | 3.334 | 3.334 | 100 | $3\bar{3}0$ | 2.041 | 2.039 | 12 |
| $12\bar{2}$ | 3.132 | 3.132 | 27 | 033 | 2.036 | | |
| $0\bar{2}2$ | 3.069 | 3.069 | 23 | $\bar{1}62$ | 1.876 | 1.873 | 13 |
| $\bar{2}12$ | 2.852 | 2.851 | 18 | $26\bar{1}$ | 1.874 | | |
| $21\bar{2}$ | 2.851 | | | 062 | 1.869 | | |
| $13\bar{2}$ | 2.772 | $\bar{3}23$ | 1.868 | | | | |
| $\bar{2}31$ | 2.768 | 2.768 | 20 | 331 | 1.818 | 1.816 | 22 |
| 102 | 2.765 | | | $\bar{1}04$ | 1.808 | 1.809 | 22 |
| $\bar{1}32$ | 2.764 | | | 343 | 1.679 | 1.678 | 8 |
| 032 | 2.713 | $2\bar{1}3$ | 1.677 | | | | |
| $1\bar{1}2$ | 2.711 | $3\bar{2}2$ | 1.675 | | | | |
| 230 | 2.708 | | | 213 | 1.674 | | |

suggested by X-ray diffraction, of each pair of compounds. Interpreted according to the same principles as in previous investigations (9, 10), these spectra are characteristic of long chain polyphosphates. They differ from those of metaphosphates (11) by their distinctive absorption in the regions of stretching and deformation vibrations of the PO_2 and POP bonds. The group of absorption bands at $350\text{--}600\text{ cm}^{-1}$ and the multiplet at $700\text{--}800\text{ cm}^{-1}$ are typical of chain polyphosphates (11). Likewise the number of the other bands, their positions, and relative intensities in each quasi-characteristic region for the POP stretching vibrations are in good agreement with the chain structure of $[(\text{PO}_3)_4]_\infty$ and $[(\text{PO}_3)_5]_\infty$ polyphosphate anions. The differences in ir

spectra of these compounds result from symmetry differences of PO_4 tetrahedra and from the way they are stacked in each structure.

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