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# Preparation and Properties of the New High Pressure Phase $\beta$-Zr(OH)PO$_4$

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**Synopsis.** A new phase with chemical formula Zr(OH)PO$_4$ was prepared above 1.5 GPa using a high pressure apparatus. Stability field of the compound was investigated, and X-ray study for a single crystal revealed that it is orthorhombic with space group Cmca or C2ca. The X-ray data are similar to those of $Zr_2O(PO_4)_2$.

Phosphate compounds in the system $ZrO_2$–$P_2O_5$–$H_2O$ have been studied in relation to the inorganic ion exchanger, $Zr(HPO_4)_2\cdot H_2O$[1] and the ceramic material with low thermal expansion, $Zr_2O(PO_4)_2$.[2,3] Other crystalline phases in this system are $Zr_{0.25}Zr_2(PO_4)_3$,[4] $ZrP_2O_7$ and Zr(OH)PO$_4$.[5] We have prepared a new high pressure compound isochemical with Zr(OH)PO$_4$ reported by Chernorukov *et al.*[9] Hereafter, the low and high pressure phases will be called $\alpha$-Zr(OH)PO$_4$ and $\beta$-Zr(OH)PO$_4$, respectively. Preparation and properties of the new phase will be described below.

## Experimental

*Starting Materials.* Reagents used for synthesis were $NH_4H_2PO_4$, $ZrO_2$, and $ZrOCl_2\cdot 8H_2O$ of a high purity. Three kinds of starting materials were used. First one was prepared from a mixture of $ZrO_2$ and $NH_4H_2PO_4$ with the Zr/P ratio equal to 1/2. The mixture was dried at 473 K for 24 h and then heated at 873 K for 5 h, and crystalline $ZrP_2O_7$ was obtained. A mixture of $ZrP_2O_7$ and water was used as a starting material for obtaining single crystals large enough for X-ray studies. Second starting material was an equimolar mixture of $ZrP_2O_7$ and $ZrO_2$, which was used for most of the experiments carried out above 1 GPa. Third starting material was a gel prepared by mixing equimolar solutions of $ZrOCl_2\cdot 8\,H_2O$ and $H_3PO_4$. The gel dried at 323 K was used as a starting material for experiments below 0.2 GPa.

*High Pressure Experiments.* A piston cylinder type high pressure apparatus was used for experiments above 1 GPa. A pressure cell consists of a concentric assemblage of NaCl with 10% $MoS_2$, a carbon heater and pure NaCl. A platinum capsule containing the starting material and water (10—50 wt%) was put in the center of the pressure cell. Sizes of the cell are 12.7 mm in diameter and 400 mm in length. Temperature was measured by an alumel–chromel thermocouple in contact with the Pt capsule. Pressure was gradually raised up to a desired value at a given temperature. Pressure is a nominal value not corrected for friction. Run durations are 48 to 72 h.

Experiments below 0.2 GPa were performed using a cold seal high pressure vessel in order to establish the stability range of $\alpha$-Zr(OH)PO$_4$. Temperature was measured by an internal thermocouple, and pressure by a calibrated Heise Bourdon tube pressure gauge. Pressure medium is pure water. The third starting material was sealed in a gold capsule together with water.

*Characterization of the Products.* After washing with distilled water, experimental products were examined using an optical microscope, an X-ray diffractometer, a Weissenberg camera, an infrared spectrometer and a differential thermal analyzer. X-Ray powder patterns taken with a Toshiba ADG 301 diffractometer were obtained at room temperature in the range $2\theta=7$ to 60° using Cu $K\alpha$ radiation. Weissenberg photographs for a single crystal of $\beta$-Zr(OH)PO$_4$ were obtained using Ni-filtered Cu $K\alpha$ radiation. Infrared (IR) spectra recorded on a Hitachi model EPI-G3 IR spectrometer were measured in the frequency range 400 to 4000 cm$^{-1}$ by using the normal KBr disk method. Thermal analyses were performed in air with an ULVAC TA-1500 at a heating rate of 10 K min$^{-1}$.

Synthetic crystals were analyzed using an electron probe microanalyzer, JXA 5A. Single crystals of $ZrO_2$, $ZrP_2O_7$, and $Zr_2O(PO_4)_2$ were used as standards. Apparent concentration was corrected after the Bence-Albee method.[6]

## Results and Discussion

*1) $\beta$-Zr(OH)PO$_4$.* This phase was obtained above 1.5 GPa as shown by open circle in Fig. 1. Single crystals up to 100 μm were prepared together with $Zr(HPO_4)_2\cdot H_2O$ when $ZrP_2O_7$ and water were used as the starting material. From Weissenberg photographs it was seen that $\beta$-Zr(OH)PO$_4$ crystallized in the orthorhombic system, the following reflexions being systematically absent, $hkl$: $h+k=2n$ ($n$: integer), $0kl$: $k=2n$, $h0l$: $l=2n$, $hk0$: $h=2n$, $00l$: $l=2n$. These extinctions indicate the space group to be Cmca or C2ca. Lattice constants are: $a=0.6607$, $b=0.8657$, $c=1.1718$ (nm). These are similar to those of $Zr_2O(PO_4)_2$: $a=0.6624$, $b=0.8637$, $c=1.1872$ (nm).[7]

Weight loss for $\beta$-Zr(OH)PO$_4$ took place in the temperature range 683 to 943 K. Amount of the water loss is 4.2 wt%, which is consistent with the theoretical value of 4.4%. The X-ray diffraction pattern of the final product is the same as that of $Zr_2O(PO_4)_2$. The X-ray data for $\beta$-Zr(OH)PO$_4$ and $Zr_2O(PO_4)_2$ obtained here are listed in Table 1.

An IR spectrum of $\beta$-Zr(OH)PO$_4$ illustrated in Fig. 2 A exhibits an absorption band at 3560 cm$^{-1}$ which may be attributed to the OH stretching vibration and is absent for $Zr_2O(PO_4)_2$. Analytical result of $\beta$-Zr(OH)PO$_4$ using an electron probe microanalyzer is; Found: $ZrO_2$, 60.32; $P_2O_5$, 35.26; Total, 95.58; $H_2O$, 4.42

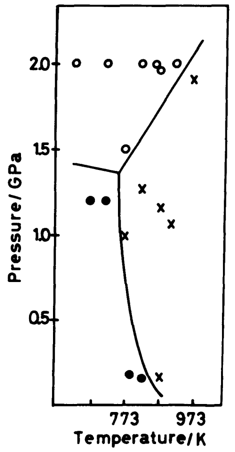

Fig. 1. Stability field of $\beta$-Zr(OH)PO$_4$.
○: $\beta$-Zr(OH)PO$_4$, ●: $\alpha$-Zr(OH)PO$_4$, ×: $Zr_2O(PO_4)_2$.

Table 1. X-Ray powder diffraction data

|  | $\beta$-Zr(OH)$PO_4$ |  |  |  | $Zr_2O(PO_4)_2$ |  | $\alpha$-Zr(OH)$PO_4$ |  |
|---|---|---|---|---|---|---|---|---|
| *h k l* | $d$ / $10^{-1}$ nm | $d_{cal}$ / $10^{-1}$ nm | $I_{obsd}$ | *h k l* | $d$ / $10^{-1}$ nm | $I_{obsd}$ | $d$ / $10^{-1}$ nm | $I_{obsd}$ |
| 0 0 2 | 5.86 | 5.859 | 55 | 0 0 2 | 5.94 | 50 | 5.88 | 44 |
| 0 2 0 | 4.33 | 4.328 | 40 | 0 2 0 | 4.33 | 60 | 5.48 | 23 |
| 0 2 1 | 4.06 | 4.060 | 66 | 0 2 1 | 4.06 | 74 | 5.08 | 23 |
| 1 1 2 | 3.91 | 3.910 | 38 | 1 1 2 | 3.94 | 50 | 4.83 | 23 |
| 0 2 2 | 3.49 | 3.481 | 33 | 0 2 2 | 3.49 | 43 | 4.53 | 100 |
| 2 0 0 | 3.30 | 3.303 | 100 | 2 0 0 | 3.31 | 100 | 4.37 | 92 |
| 1 1 3 | 3.14 | 3.134 | 36 | 1 1 3 | 3.16 | 52 | 4.27 | 77 |
| 0 0 4 | 2.95 | 2.929 | 17 | 0 0 4 | 2.96 | 13 | 4.08 | 23 |
| 0 2 3 | 2.90 | 2.899 | 36 | 0 2 3 | 2.92 | 32 | 3.94 | 77 |
| 2 2 0 | 2.62 | 2.626 | 7 | 2 2 0 | 2.63 | 15 | 3.69 | 34 |
| 1 3 1 | 2.58 | 2.579 | 39 | 1 3 1 | 2.58 | 88 | 3.66 | 74 |
| 1 1 4 | 2.56 | 2.558 | 55 | 1 1 4 |  |  | 3.62 | 23 |
| 1 3 2 | 2.41 | 2.410 | 28 | 1 3 2 | 2.41 | 33 | 3.31 | 53 |
| 2 0 4 | 2.19 | 2.192 | 9 | 2 0 4 |  |  | 3.17 | 84 |
| 0 4 0 | 2.167 | 2.164 | 5 | 0 4 0 |  |  | 3.12 | 61 |
| 0 4 1 | 2.130 | 2.128 | 14 | 0 4 1 | 2.125 | 16 | 3.10 | 30 |
| 3 1 1 | 2.100 | 2.099 | 7 | 3 1 1 |  |  | 2.91 | 16 |
| 0 2 5 | 2.060 | 2.061 | 15 | 0 2 5 | 2.03 | 15 | 2.85 | 54 |
| 3 1 2 | 2.004 | 2.005 | 20 | 3 1 2 | 2.01 | 38 | 2.78 | 43 |
| 3 2 0 | 1.960 | 1.962 | 11 | 3 2 0 | 1.97 | 22 | 2.74 | 30 |
| 0 0 6 | 1.956 | 1.953 | 17 | 0 0 6 |  |  | 2.69 | 17 |
| 0 4 3 | 1.896 | 1.893 | 24 | 0 4 3 | 1.897 | 31 | 2.65 | 33 |
| 3 1 3 | 1.874 | 1.873 | 8 | 3 1 3 | 1.886 | 9 | 2.59 | 23 |
| 1 1 6 | 1.833 | 1.830 | 14 | 1 1 6 | 1.853 | 28 | 2.56 | 38 |
| 0 2 6 | 1.782 | 1.780 | 6 | 0 2 6 | 1.801 | 18 |  |  |
| 3 3 1<br>3 1 4 | 1.728 | 1.725<br>1.731 | 38 | 3 3 1<br>3 1 4 | 1.735 | 66 |  |  |
| 3 3 2 | 1.679 | 1.677 | 8 | 3 3 2 | 1.682 | 16 |  |  |
| 1 5 1 | 1.657 | 1.658 | 29 | 1 5 1 | 1.657 | 50 |  |  |
| 0 4 5 | 1.589 | 1.590 | 22 |  |  |  |  |  |

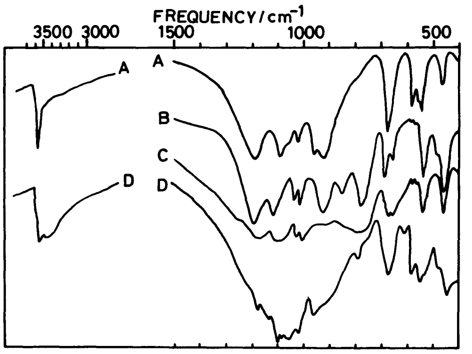

Fig. 2. IR spectra.
A: $\beta$-Zr(OH)$PO_4$, B: $Zr_2O(PO_4)_2$ prepared by heating $\beta$-Zr (OH)$PO_4$ at 973 K, C: $Zr_2O(PO_4)_2$ prepared at 1.15 GPa, D: $\alpha$-Zr(OH)$PO_4$ obtained at 1.2 GPa.

[100-Total]. Calcd for Zr(OH)$PO_4$: $ZrO_2$,60.64; $P_2O_5$,34.93 (wt%).

*2) α-Zr(OH)PO*$_4$. This phase was prepared below 1.2 GPa and represented by solid circle in Fig. 1. The X-ray powder pattern of $\alpha$-Zr(OH)$PO_4$ obtained at 1.2 GPa is similar to that given in the literature.5) Figure 2 D shows an IR spectrum for this material. An absorption band near 3560 cm$^{-1}$ is attributed to the OH stretching vibration.

*3) Zr*$_2$O($PO_4$)$_2$. An IR spectrum of this material prepared at 873 K, 1.15 GPa is illustrated in Fig. 2C. The X-ray powder pattern of this phase is the same as that listed in Table 1.

The structure of dizirconium diorthophosphate7) consists of chains composed of edge sharing $ZrO_7$ polyhedra which are connected by the P atoms in tetrahedral coordination. The chains are, however, partly bonded directly with each other by sharing an oxygen atom. If hydration of $Zr_2O(PO_4)_2$ takes place at the site of this oxygen atom, $Zr_1$–O–$Zr_2$ may change to $Zr_1$–OH+$Zr_2$–OH where $Zr_1$ and $Zr_2$ represent different chains. We propose that the structure of $\beta$-Zr(OH)$PO_4$ is similar to that of $Zr_2O(PO_4)_2$, but each chain is not joined directly. A structure similar to the proposed one is known for Hf$(OH)_2SO_4$.8) Hf$(OH)_2SO_4$ contains chains of $[Hf(OH)_2]_n^{2+}$ which are joined by sulfate groups. The chains do not share any oxygen atom with each other.

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