September, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 2761—2765 (1986) 2761

Preparation of Cubic $HZr_2(PO_4)_3$ and Related Compounds

Akira Ono* and Yoshiyuki Yajima
National Institute for Research in Inorganic Materials, Namiki, Ibaraki 305

(Received January 11, 1986)

A single phase of cubic $NH_4Zr_2(PO_4)_3$ with a langbeinite-type structure was prepared at 235 °C by a hydrothermal method. A series of analogous compounds containing various monovalent cations or vacancies were made by starting with cubic $NH_4Zr_2(PO_4)_3$. They are polymorphs with respect to Nasicon-type compounds and have rigid skeleton structures with interstitial spaces partially occupied by monovalent ions and water molecules. Maximum water contents of the cubic compounds decrease with increasing sizes of the monovalent ions. Proton-bearing cubic compound exhibited ion exchange reactions with NaCl and LiCl solutions at 20 °C. This suggests the existence of bottlenecks large enough for permitting diffusion of Na^+ and Li^+ ions. Low thermal expansion of cubic $NaZr_2(PO_4)_3$ was studied by high-temperature X-ray diffraction.

Phosphate compounds with the formula $AM_2(PO_4)_3$ where A is an alkali metal atom, H_3O, H, or NH_4 and M is Zr or Ti have three dimensional skeleton structures. Most of the compounds have rhombohedral Nasicon-type structures, but cubic langbeinite-type compounds are also known.[1,2] Here, Nasicon is a solid solution series of the formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($3>x>0$), and langbeinite is a mineral formulated as $K_2Mg_2(SO_4)_3$. Recently, we have prepared cubic $AZr_2(PO_4)_3$ (abbreviated as AZP) and $Zr_4P_6O_{23}$ (abbreviated as VZP, V stands for a vacancy) by a series of heat treatments of cubic NH_4ZP under dry and hydrothermal conditions and ion-exchange reactions between HZP and alkali chloride solutions.[3] The novel cubic compounds, however, were not investigated in detail because of the presence of a considerable amount of monoclinic ZrO_2. This paper describes the preparation and properties of a single phase of cubic NH_4ZP and its related compounds. The cubic phases obtained were characterized by X-ray powder diffraction, high temperature X-ray diffraction, thermal gravimetric analysis(TG), differential thermal analysis(DTA), infrared(IR) spectroscopy and scanning electron microscopy(SEM). An analysis of complex impedance data on cubic HZP[4] will be reported in the near future.

Both cubic and rhombohedral skeleton structures consist of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra with interstitial spaces partially occupied by monovalent cations. Their structures have been explained by a cubic or hexagonal packing of rods[5] consisting of a repeating sequence A,(A),O_3ZrO_3, O_3ZrO_3 or A,O_3ZrO_3,O_3ZrO_3, respectively, where (A) is a vacancy. Rhombohedral AZP has one M_1 octahedral site occupied by an A^+ ion and three vacant M_2 sites per formula unit. The M_1 and M_2 sites constitute a three-dimensional network. Any M_1 site is surrounded by six M_2 sites. The spaces linking the M_1 and M_2 sites are considered to be ion-pathways.[6,7]

Cubic AZP has two kinds of cation sites occupied by A^+ ions, and half of the sites are vacant in a statistical sense. Figure 1 illustrates the schematic view parallel to [111] showing the two cation sites in a large ellipsoidal cage which is bounded by a network of six 6-membered and three 4-membered rings consisting of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra. The monovalent ion is surrounded by nine oxygen atoms.[2] Judging from the rapid ion-exchange reaction between cubic HZP and a LiCl or NaCl solution,[3] diffusion of Na and Li ions took place rapidly through the windows of the 6-membered rings.

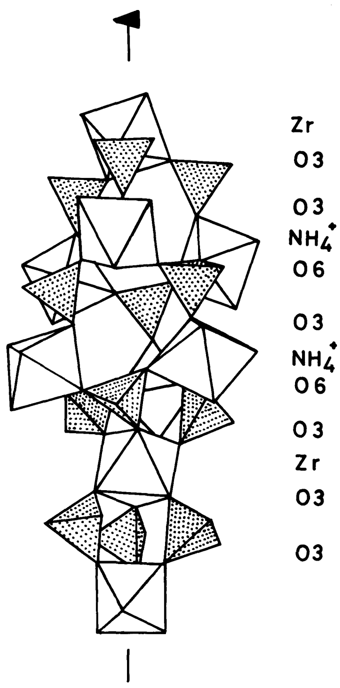

Fig. 1. The schematic view showing the framework of an ellipsoidal cage occupied by a monovalent ion. Two kinds of sites are available for an NH_4^+ ion.

Experimental

Hydrothermal syntheses were carried out in a Teflon-lined bomb of 20 cm³ capacity. The bomb was heated in an oven at a prescribed temperature. The pressure was believed to be about 0.1 to 0.2 GPa calculated from the per cent fill of the container. Two kinds of starting materials were used for the preparation of cubic NH_4ZP. The first one was obtained as follows: $ZrOCl_2\cdot 8H_2O$, $(NH_4)_2HPO_4$, and $NH_4H_2PO_4$ were mixed in a Teflon container, and then water was added. NH_4F and NH_4NO_3 solutions of 1.5 mol dm^{-3} were also used in some experiments to promote crystallization reactions. The precipitate obtained was well homogenized by stirring with a rod made of bamboo. The Zr/P ratio of the precipitate was 2/3 judging from the mixing ratio of the starting materials. The pH values of the solutions were adjusted by changing the mixing ratio of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, but in a few cases a dilute solution of HCl or aqueous ammonia was added to the starting materials. Experimental conditions are given in Table 1.

The other starting material was a gel obtained by mixing solutions of $NH_4H_2PO_4$ and $ZrOCl_2\cdot 8H_2O$ under controlled pH values.[8] The gel was crystallized in a dilute HCl solution. A small amount of NH_4F or LiCl was added as a mineralizer in a few runs. Experimental conditions are summarized in Table 2.

The yields were filtered and washed with distilled water after the determination of the pH values of the solutions. The products were examined by X-ray methods, IR spectra, TG, DTA, and SEM. All the measurements were carried out on the same laboratory equipment and by the methods described previously.[3,8] Various cubic compounds were prepared from cubic NH_4ZP by the same procedure used before.[3] Chemical compositions of these cubic phases were determined by the combined data of lattice constants, IR spectra, and TG, assuming that the Zr/P ratio of all the cubic phases studied here was 2:3. To confirm the validity of this method, sodium in cubic NaZP was analyzed by the atomic absorption method. The sample was brought into solution in the mixed acid of HF and H_2SO_4.

The interplanar spacing d_{311} of cubic NaZP was measured up to 520 °C for the determination of the coefficient of linear thermal expansion. X-Ray diffraction patterns were recorded with a high-temperature X-ray powder diffractometer, JEOL, DX-COH-V2, using Ni-filtered Cu $K\alpha$ radiation with a scanning speed of 0.25° 2θ min^{-1}. The temperature was measured with a Pt-Pt13%Rh thermocouple in contact with a platinum sample holder which was also heater. Quartz was used as an internal standard. The spacing d_{310} of quartz at 520 °C was calculated by using the lattice constants given in the literature.[9] During the slow heating up to 520 °C, seven lattice constants were measured under constant temperatures, and two lattice constants during the cooling process.

Results and Discussion

Preparation of Cubic AZP. Table 1 shows the results of experiments which were carried out at 235 °C using the precipitates made in a Teflon-container. Cubic NH_4ZP was obtained as a main product under high pH values, but a minor rhombohedral phase was present when no mineralizer was used. A single phase of cubic NH_4ZP was prepared by the addition of a small amount of NH_4F. At low pH values both rhombohedral and cubic NH_4ZP were pepared, but a considerable amount of amorphous materials were obtained together with cubic and rhombohedral phases in a pH range 7—8.3.

Cubic NH_4ZP obtained in NH_4F solutions exhibited euhedral crystal forms with 0.5—1.2 μm in sizes under the SEM. At 925 °C for 25 min this compound loses NH_3 and H_2O to yield cubic VZP which has crystal forms retaining the morphology of the original cubic compound. We could not find any effects of degassing of volatile components on the crystal surfaces of VZP. This may be due to a small volume difference between NH_4ZP and VZP.

For the hydration of VZP at 340 °C and 0.1 GPa,[3] the duration was 5 h previously, but it was 9 h in the

Table 1. Hydrothermal Crystallization at 235 °C

Sample	Time / h	Zr$^+$ / g	pH	V / cm^3	Product : Remarks
8-45	96	5.22	8.68	9	R+C(0.06)
7-38	95	3.22		7	R+C(0.05)
7-44	72	3.22	8.82	12	R+C(0.16) : NH_4OH added
8-28	96	3.22	8.66	12	R+C+amp(0.12)
7-43	72	3.22	8.55	12	R+C(0.08)
8-27	73	3.22	8.09	12	R+C+amp(0.18)
7-45	27	3.22	7.95	12	R+C+amp(0.67)
8-39	115	3.22	7.05	13	R+C+amp(0.83)
7-42	72	3.22	1.75	12	R+C(0.9)
7-41	72	3.22	1.01	10	R+C(1.8)
7-69	72	3.22	0.35	12	R+C(0.86) : HCl added
9-05	86	3.22	8.58	12	C : 1.5 mol dm^{-3} NH_4F
9-09	87	3.22	8.70	12	C : 0.75 mol dm^{-3} NH_4F
9-12	78	3.22	8.32	12	C+amp : 0.5 mol dm^{-3} NH_4NO_3

R: rhombohedral phase, C: cubic phase, amp: amorphous phase, ( ): X-ray intensity ratio of rhombohedral 012 to cubic 111, Zr$^+$: weight of $ZrOCl_2\cdot 8H_2O$, V: volume of solution added.

present study that was long enough for the formation of cubic H_3OZP. The weight loss of cubic H_3OZP took place in the two temperature ranges as shown in Fig. 2A. Cubic HZP was formed after the first water loss of 3.9 wt%, and cubic VZP after the second water loss of 1.85 wt%. The TG curve of cubic HZP showed a weight gain due to absorption of moisture in the temperature range 25 to 220 °C as shown in Fig. 2B. Actually, rehydration of cubic HZP, i.e. formation of H_3OZP, occurred rapidly at 25 °C by addition of a small amount of water. Hydrated VZP ($Zr_4P_6O_{23}\cdot 4H_2O$) was obtained by the hydration of cubic VZP at 100 °C for 24 h under one atmosphere.

Preparation of cubic H_3OZP was undertaken by the hydration of VZP at 245 °C for 48 h in the Teflon-lined bomb. The material obtained showed a water loss of 1.0 wt% in the temperature range 500—900 °C, which indicated that H_3O^+ ions occupy 60% of the available cation sites. The hydrated phase obtained was heated at 400 °C in air to prepare a proton-bearing compound which might exhibit an ion-exchange reaction with a NaCl solution at room temperature. The ion-exchange reaction, monitored by a pH meter, mainly took place within 0.5 min after the mixing of the solid and the liquid phases and was completed after 48 h. The final product did not show a weight loss above 500 °C, suggesting the complete exchange of protons by sodium ions. The sodium content of the final product is 2.7 wt% determined by the atomic absorption method. It is, therefore, concluded that sodium ions occupy 56% of the available cation sites that is in good agreement with the value obtained by the water loss datum.

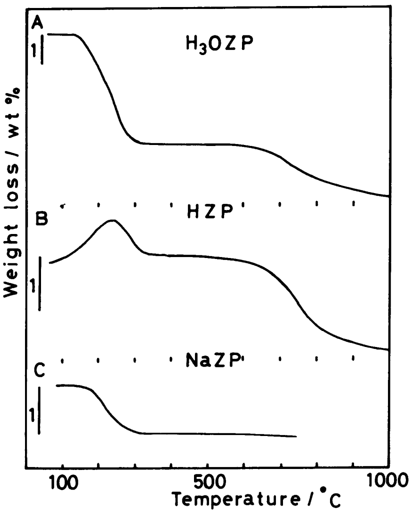

Fig. 2. TG curves of three cubic AZP.
A, C: Materials prepared hydrothermally, B: HZP heated at 500 °C and quenched to room temperature. Scale bar: 1 wt%. Heating rate: 10 °C min^{-1}.

Cubic LiZP was prepared at room temperature by the ion-exchange reaction between cubic HZP and a LiCl solution. In a dilute HCl solution cubic LiZP was changed to cubic H_3OZP after 80 h at 25 °C.

The results of experiments performed by using gels are summarized in Table 2. Cubic NH_4ZP was prepared together with the rhombohedral phase in most of the products. The amount of the cubic phase varied depending upon the different starting gels, and it did not show any systematic relationships to the pH values of the solutions. With respect to this problem, no rhombohedral phase was present when 1.5 mol dm^{-3} solution of NH_4F was added to the dilute HCl solution of 4 cm^3, although the pH value was below 2.0 (Table 2, 9—39). The fluorine ions in the solvent are the strong influencing factor for the formation of the cubic phase. On the other hand, the aging of a gel promoted the formation of the rhombohedral phase over the cubic phase. The result is presented in Table 2, 9—51 for the xerogel aged for 90 d at room temperature before heating.

Stability of Cubic AZP. The thermodynamical stabilities of cubic and rhombohedral AZP are

Table 2. Hydrothermal Crystallization at about 0.15 GPa

Sample	Gel g	Vol cm^3	Temp °C	Time h	Yield g	pH	Additives	Products$^{a)}$
9-32	4	12	255	67	3.1	0.79		R+amp
9-33	4	10.7	235	41				amp
9-36	4	9	245	92	1.35	0.45		R+C(6.6)
9-39	4	8	245	68	2.15	1.76	NH_4F	C
9-42	4	7	245	86	2.7	0.25		R+C(1.7)
9-43	2.4	7.8	245	72	1.7	0.34	LiCl	R+C(1.5)
9-44	3	7.9	255	67	1.9	0.61		R+C(0.8)
9-46	3.7	7	243	72	2.4	0.25		R+C(0.18)
9-48	3.2	7	243	72	2.4	0.25		R+C(1.0)
9-50	3.2	7.2	243	72	2.7	0.58		R+C(1.3)
9-51	2.0	6.7	240	64	1.4	0.50		R+C(9.6)

vol: volume of solution, a): see Table 1.

Table 3. X-Ray Data for Cubic AZP[a)]

	$NaZr_2(PO_4)_3\cdot 0.3H_2O$		$Zr_4P_6O_{23}$	
hkl	$\frac{d}{Å}$	I_{obsd}	$\frac{d}{Å}$	I_{obsd}
111	5.89	70	5.86	51
210	4.564	100	4.537	100
211	4.166	47	4.142	35
221	3.401	34	3.382	30
310	3.227	80	3.208	56
311	3.077	37	3.059	27
320	2.830	28	2.814	10
321	2.727	92	2.711	67
400	2.551	9	2.536	4
410	2.475	14	2.461	9
331			2.327	5
422	2.083	12	2.071	9
430	2.041	11	2.029	7
510	2.001	11	1.990	8
511	1.964	15	1.952	11
520	1.895	37	1.884	26
521	1.863	17	1.852	11

a) Data obtained with Ni-filtered Cu $K\alpha$ radiation. Quartz used as an internal standard. Space group; $P2_13$.

Table 4. Lattice Constants of Cubic AZP

Crystalline material	Lattice constant / Å
$NH_4Zr_2(PO_4)_3$	10.192
$H_3OZr_2(PO_4)_3\cdot 0.1H_2O$	10.190
$Na\ Zr_2(PO_4)_3\cdot 0.3H_2O$	10.205
$Li\ Zr_2(PO_4)_3\cdot 0.7H_2O$	10.200
$Zr_4P_6O_{23}\cdot 4H_2O$	10.218
$Na\ Zr_2(PO_4)_3$	10.173
$Li\ Zr_2(PO_4)_3$	10.168
$H\ Zr_2(PO_4)_3$	10.165
$Zr_4P_6O_{23}$	10.146

problematic because formation of the phases depend on the nature of the starting materials, the pH value and the anion species in the solution equilibrated with the solid phase. According to the previous study,[3)] however, cubic NH_4ZP crystallized at 340 °C and 0.1 GPa at the initial stage of the reaction, and was then gradually changed to the rhombohedral phase by further heating. This result indicates the instability of cubic NH_4ZP above 340 °C under 0.1 GPa.

Here, we have carried out experiments to evaluate the stability of cubic H_3OZP under hydrothermal conditions. Cubic VZP sealed in a gold capsule together with water was heated in a cold sealed pressure vessel for various times. At 350 °C and 0.1 GPa cubic H_3OZP was formed after 9 h, but it was transformed completely to the rhombohedral phase after the subsequent hydrothermal heating for 6 h. It is evident that cubic H_3OZP is a metastable transient phase at 350 °C. At 410 °C and 0.1 GPa, rhombohedral H_3OZP crystallized together with the cubic phase after 1 h. However, on further heating both phases decomposed partially to give unknown oxide compounds. Thus, both cubic and rhombohedral H_3OZP are unstable at 410 °C under 0.1 GPa. The stability ranges of cubic NH_4ZP and H_3OZP, if present, are below 350 °C under 0.1 GPa according to the available data.

Properties of Cubic AZP. X-Ray powder data of cubic VZP and NaZP are listed in Table 3. Here, the intensity (I_{obsd}) was measured as the peak height above the background. The other compounds obtained here showed similar X-ray powder patterns to those listed in Table 3 or Table 1 of the literature.[3)] Chemical formulas and lattice constants of cubic AZP prepared in hydrous conditions are listed in Table 4 together with those of anhydrous cubic compounds which were obtained by heating the hydrous compounds at 500 °C in air. The amount of zeolitic water in the hydrous AZP was estimated by the weight loss taking place mainly in the temperature range 110—300 °C. An example of TG curves is given in Fig. 2 C.

Lattice constants of hydrous AZP are similar and do not show any relationships to the size of the monovalent ions. The hydrous cubic phases appear to have similar dimensions and configurations of the rigid framework structures. The lattice constant of hydrous cubic AZP is larger than that of the anhydrous one, and hydrous VZP has the largest lattice constant as listed in Table 4. These facts suggest that the lattice constant of cubic AZP may increase by the incorporation of water molecules into the vacant sites located in the large ellipsoidal cages shown in Fig. 1. If the vacant sites were completely occupied by water molecules, the lattice constant of hydrous AZP would be larger than the value given in Table 4. Since such a hypothetical highly hydrous phase could not be prepared, hydrous cubic AZP must become unstable when its lattice constant exceeded a certain value by the increasing number of water molecules in the structure. This value may be in the narrow range 10.190 to 10.205 Å for various cubic AZP. If this is true, the amount of zeolitic water is highly dependent on the size of the monovalent ion, because effects of a water molecule on the expansion of the ellipsoidal cage may be more effective when a water molecule is incorporated into the sites located nearby the larger monovalent ions. Actually, the amount of the zeolitic water in the cubic phases decrease systematically with increasing sizes of the monovalent ions as shown in Table 4.

The lattice constants of the anhydrous cubic phases increase slightly with the increasing sizes of the monovalent ions. The difference in the molar

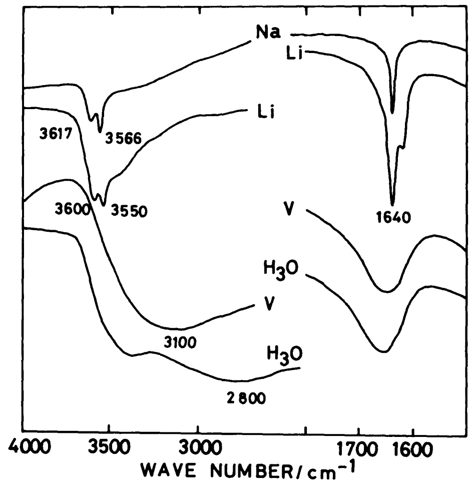

Fig. 3. IR spectra of hydrated cubic phases. Na, Li, V and H_3O are cations located in the interstitial sites of the framework. Here, V stands for a vacancy.

volumes of NH_4ZP and LiZP is 1.1 cm^3 for the cubic phases and 7.2 cm^3 for the rhombohedral phases.[8] The small difference in the cubic phases may be due to the presence of rigid and large ellipsoidal cages which various monovalent ions occupy without considerable changes in the configuration.

Hydrous LiZP and NaZP showed narrow absorption bands in the frequency range 1500 to 4000 cm^{-1} as illustrated in Fig. 3. The wave number of the sharp bands depends on the nature of the monovalent cation. These narrow bands are attributed to OH absorption bands of water molecules whose oxygen atoms interact with adjacent Li or Na ions (ion-dipole interaction). Similar narrow absorption bands of water are common for zeolites.[10]

Cubic H_3OZP showed a broad absorption band near 2800 cm^{-1} which was absent for hydrated VZP. The latter phase exhibited a broad band near 3100 cm^{-1} which could be attributed to a hydrogen-bonded OH stretching vibration.

The d_{310} values of cubic NaZP were approximately constant up to 520 °C. The lattice constant at 520 °C is 10.186 Å which is similar to the value (10.173 Å) at room temperature. The coefficient of linear thermal expansion is 1.6×10^{-6} K^{-1}.

The existence of large vacant sites in a skeleton structure is a necessary condition for the materials of low thermal expansion. Nasicon-type compounds fulfil this requirement and $Ca_{0.5}Zr_2(PO_4)_3$, $ZrNb(PO_4)_3$, and $KTi_2(PO_4)_3$ were demonstrated to be of low thermal expansion.[11–14] Structural analysis of a single crystal of Nasicon has revealed that configurations of polyhedra exhibited little temperature dependence.[6] Therefore, the thermal expansion of Nasicon was mainly caused by changes of bond angles between the adjacent polyhedra.

Cubic AZP has also a three dimensional skeleton structure. Moreover, half of the interstitial cation sites are vacant. These structural features satisfy the requirement for low thermal expansion. Therefore, cubic AZP may have low thermal expansion.

Lattice constants of cubic AZP do not increase considerably when the monovalent cations were completely replaced by the other larger ions as mentioned earlier. This suggests that an increase in size of a monovalent ion caused by a rise in temperature has little effect on the lattice constant of cubic AZP. In fact, cubic NaZP was proved to be of low thermal expansion by high temperature X-ray diffraction.

References

1) L. Hagman and P. Kierkegaard, *Acta Chem. Scand.*, **22**, 1822 (1968).
2) R. Masse, A. Durif, J-C. Guitel, and I. Tordjman, *Bull. Soc. Fr. Mineral. Cryistallogr.*, **95**, 47 (1972).
3) A. Ono, *J. Mater. Sci. Lett.*, **4**, 936 (1985).
4) M. Ohta, F. P. Okamura, and A. Ono, *Abst. Solid State Ionics (Jpn)*, **12**, 65 (1985).
5) M. O'Keefe and S. Andersson, *Acta Crystallogr., Sect. A*, **33**, 914 (1977).
6) D. Tranqui, J. J. Capponi, J. C. Jourbert, and R. D. Shannon, *J. Solid State Chem.*, **39**, 219 (1981).
7) H. Kohler, H. Schulz, and O. Melinikov, *Mater. Res. Bull.*, **18**, 1143 (1983).
8) A. Ono, *J. Mater. Sci.*, **19**, 2691 (1984).
9) D. Taylor, *Mineral. Mag.*, **38**, 593 (1972).
10) L. Bertsch and H. W. Habgood, *J. Phys. Chem.*, **67**, 1621 (1963).
11) R. Roy, D. K. Agrawal, J. Alamo, and R. A. Roy, *Mater. Res. Bull.*, **19**, 471 (1984).
12) D. K. Agrawal and V. S. Stubican, *Mater. Res. Bull.*, **20**, 99 (1985).
13) G. E. Lenain, H. A. McKinstry, S. Y. Limaye, and A. Woodward, *Mater. Res. Bull.*, **19**, 1451 (1984).
14) T. Oota and I. Yamai, *Ann. Rep. Ceram. Engin. Res. Lab. Nagoya Inst. Tech.*, **10**, 9 (1983).