# The Phases Formed by the Dehydration of Disodium Zirconium(IV) Bis(orthophosphate) Trihydrate and Their Ion-exchange Behavior

Yasushi Inoue* and Yoshimune Yamada
*Department of Nuclear Engineering, Faculty of Engineering, Tohoku University,*
*Aramaki-aza-Aoba, Sendai 980*

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The phase transformation of $Na_2Zr(PO_4)_2\cdot 3H_2O$ which had been obtained from zirconium(IV) bis(hydrogenphosphate) monohydrate(α-zirconium phosphate), prepared by the direct precipitation method, was studied by means of gravimetry, X-ray analysis, and acid-base titration. When the material was heated for 2 d, it was transformed to a monohydrate at 80 °C and then successively to three anhydrous phases, depending on the temperature. The monohydrate was also formed by letting the trihydrate stand over $P_2O_5$ at room temperature for longer than two weeks. The processes were confirmed to be irreversible by an examination of the rehydration behavior, from which the conditions of the storage of five modifications of disodium zirconium(IV) bis(orthophosphate) were established. It is of special interest that the second anhydrous phase reverted to the first one when it was allowed to stand at room temperature in air or in a desiccator. The rate of the reversion decreased with the temperature of heat-treatment and with a decrease in the relative humidity of the surroundings. The difference between the present results and Clearfield's[1,2] was clarified and attributed mainly to the difference in the crystallinity of the starting α-zirconium phosphate.

During our study of the isotopic exchange rate of $Na^+$ ions between crystalline disodium zirconium(IV) bis(orthophosphate) trihydrate ($Zr(Na_2PO)_2\cdot 3H_2O$) and aqueous solutions, it was difficult to obtain reproducible results. This irreproducibility is due to the difference in the crystal structure of the exchanger, which depends subtly on the conditions adopted in the preparation and in the storage of the material. The phases existing under various circumstances should, therefore, be clarified in order to obtain accurate rate data and to give a correct interpretation of the results.

There has been no literature referring to the subject except the studies of Clearfield *et al.*,[1,2] who first elucidated the structure and the dehydration behavior of $Na_2Zr(PO_4)_2\cdot 3H_2O$, which had been prepared by replacing the $H^+$ ions in $Zr(HPO_4)_2\cdot H_2O$ (zirconium(IV) bis(hydrogenphosphate) monohydrate, α-ZP) by $Na^+$ ions. They made it clear that one monohydrate and three anhydrous phases were irreversibly formed by thermal treatment. Their results will be helpful, but not directly applicable to our purpose, since the exchanger in sodium form prepared from α-ZP synthesized by the method recommended by the present authors will behave differently from that by Clearfield; in fact $H^+/Na^+$ titration and differential thermal analysis (DTA) studies have clearly shown the difference in crystallinity between these materials.[3]

The present report describes the studies made of the dehydration behavior of sodium-substituted α-ZP and the reversibility of the process by means of gravimetry, X-ray analysis, and pH titration; these studies were enabled us to find the most suitable conditions for the preparation and storage of various phases and to determine the phase changes brought about by immersing them in aqueous solutions.

## Experimental

α-Zirconium phosphate was prepared by a procedure recommended previously.[3] Five and a half grams of $ZrOCl_2\cdot 8H_2O$ were dissolved in distilled water in a polyethylene beaker. The desired amounts of hydrofluoric acid and of phosphoric acid were then vigorously stirred in successively to make the concentrations 0.715 mol $dm^{-3}$ and 9 mol $dm^{-3}$ respectively and to make total volume 130 $cm^3$. The solution was then kept at 60 °C in a thermostatted water bath for about 100 h. A white, flaky product was separated by filtration, washed with distilled water until the pH of the filtrate became 5, and stored over $P_2O_5$ for two weeks. The α-ZP thus prepared was then equilibrated with a mixture of 0.1 mol $dm^{-3}$ NaCl and NaOH solutions at pH 12. After filtration, the exchanger was washed with distilled water until the effluent became free of chloride ions; it was then dried in a desiccator over a saturated NaCl solution (relative humidity, 75%) for two weeks. The material thus prepared was confirmed to be $Na_2Zr(PO_4)_2\cdot 3H_2O$ (hereafter this material will be refereed to as Phase I).

The monohydrate and three anhydrous phases were obtained by the methods established in the present study, as will be described later; the monohydrate phase (Phase II) was obtained by drying Phase I over $P_2O_5$ for longer than three weeks, while the anhydrous phases (Phases III, IV, and V) were formed by heating Phase I at the desired temperatures (250 °C for Phase III, 700 °C for Phase IV and 820 °C for Phase V) for 2 d. These phases were then stored over $P_2O_5$.

The other experimental procedures were the same as had been described previously,[3] except for the analysis of sodium ions in the exchanger, which was carried out with a Jarrell-Ash atomic-absorption spectrophotometer, Model AA-782.

## Results and Discussion

The material obtained by replacing $H^+$ by $Na^+$ in α-ZP in the aqueous solution with a pH of 12 was identified by means of chemical, X-ray, and thermal analyses. The composition was: Found: $ZrO_2$, 32.63; $P_2O_5$, 37.23; $Na_2O$, 16.20; $H_2O$, 14.57%, which corresponded to the formula of $Na_2Zr(PO_4)_2\cdot 3H_2O$ (Phase I) and which was in good agreement with the data published by other authors.[2,4,5] The X-ray pattern indicated that this phase had an interlayer distance of 0.983 nm, which agreed well with the Phase D reported by Clearfield *et al.*[1,2] The thermogravimetric-analysis (TGA) and DTA curves of Phase I are shown in Fig. 1. The TGA curve reveals that this phase lost water in two steps; that is, it lost two molecules of water up to 100 °C, and then the last molecule of water before 250 °C. In the DTA curve, one large and one small endothermic peak appeared at 110 °C and 150 °C; they apparently corresponded to the release of two molecules of water and one molecule of water respectively, while no exothermic peak appeared.

The static method was then applied to the dehydration studies; Phase I was heated at various temperatures for two days, except as otherwise specified, followed by cooling to room temperature. When Phase I was heated to a constant weight at 80 °C, it lost two molecules of water to form a monohydrate, Phase II, which had an interlayer distance of 0.843 nm. This phase could alternatively be obtained in a pure form by letting Phase I stand over $P_2O_5$ for longer than two weeks. This can be verified from Fig. 2, which shows the dehydration behavior of Phase I in the $P_2O_5$ desiccator, and from the agreement of the X-ray pattern of the product with that of the monohydrate mentioned above. This phase will correspond to the Phase E which was prepared by Clearfield *et al.*[2] by heating Phase D at a temperature between 50—100 °C. However they reported that Phase E could not be obtained in pure form by dehydrating Phase D in a desiccator containing $P_2O_5$.

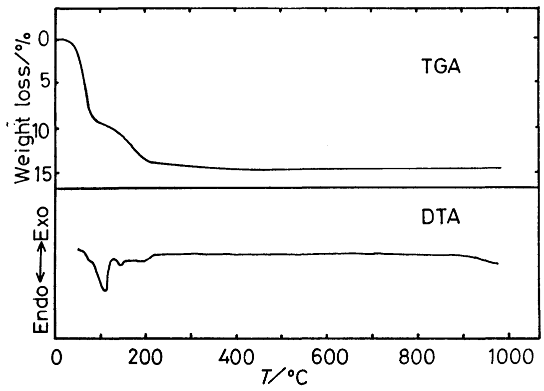

Fig. 1. TGA and DTA curves of Phase I. Heating rate: 5 °C/min.

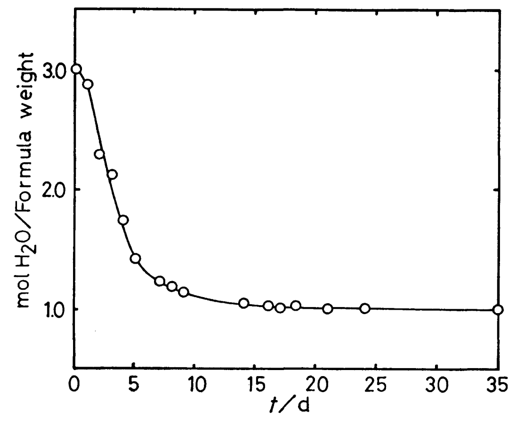

Fig. 2. Water content of Phase I as a function of time of standing over $P_2O_5$.

Over the range of 80—150 °C, an anhydrous phase, Phase III, with an interlayer distance of 0.839 nm, appeared in addition to Phase II. When the mixture was heated above 150 °C, Phase II disappeared, being completely transformed to Phase III, which began transforming to the second anhydrous phase, Phase IV, on further heating (above 300 °C). At 500 °C, Phase III was transformed completely to Phase IV, which had an interlayer distance of 0.763 nm. However, when Phase III was heated for longer than 10 d, it was transformed completely to Phase IV at a far lower temperature (170 °C). Only Phase IV was formed over the range of 500—800 °C. When it was heat-treated at a temperature above 800 °C, the third anhydrous phase, Phase V, which had an X-ray pattern appreciably different from those of the other phases mentioned above, was formed. This phase could not be formed by heating Phase I below 800 °C, no matter how long the heating period was. Figure 3 schematically illustrates the thermal transformation of Phase I.

It must be noted that an interesting phenomenon was observed concerning Phase IV. When being allowed to stand after cooling, Phase IV were transformed to Phase III. To make clear the factors affecting this behavior, the rate of transformation during storage was measured on samples subjected to heat-treatment under different conditions, as is shown in Figs. 4 and 5. The ordinate of these figures shows $R$, which is defined as $(I_{III}/I_{III+IV}) \times 100$, where $I$ represents the intensity of the diffraction line from the (002) plane which gives the strongest peak in

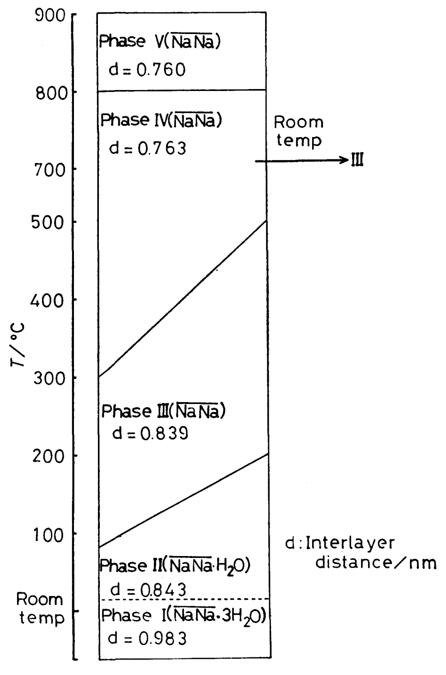

Fig. 3. Phase transformation of disodium substituted ZP.
d: Interlayer distance/nm.

the designated phase. $R$ is considered to be roughly equal to the abundance ratio of Phase III, since the density of the zirconium atom on the plane responsible for the reflection will not be appreciably changed by this phase transformation.

Figure 4 indicates that the rate of transformation was slower with the samples heat-treated at higher temperatures, but was independent of the length of heating. The relative humidity of the atmosphere strongly affected the rate of the transformation, as is shown in Fig. 5. A decrease in the humidity suppressed the transformation. From these facts, we can conclude that Phase IV can be stored in a desiccator over $P_2O_5$ without suffering from phase transition for at least two weeks. Phases III and IV respectively will correspond to Phases F and G reported by Clearfield *et al.*, but Phase G is more stable than Phase IV; Phase G, obtained by heating Phase F at a temperature higher than 200 °C, did not revert to Phase F at all.[2)]

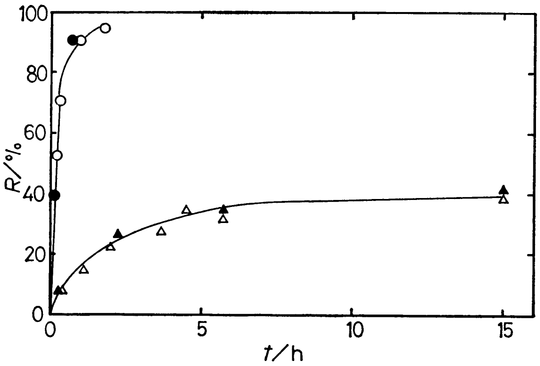

Fig. 4. $R$ as a function of the time of standing-I. Environment; air. Condition for heat-treatment; ○: 600 °C, 2 d, ●: 600 °C, 4 d, △: 700 °C, 2 d, ▲: 700 °C, 4 d.

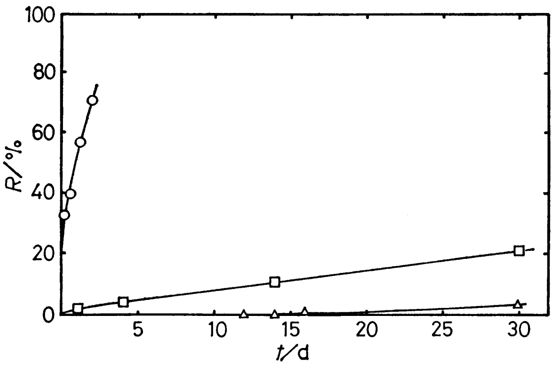

Fig. 5. $R$ as a function of the time of standing-II. Heat-treatment; 700 °C, 2 d. Condition of storage; ○: air, □: silica gel, △: $P_2O_5$.

In order to examine the reversibility of the dehydration process, the X-ray patterns and the weight recoveries were measured on samples obtained by heat-treatment when they were humidified to a constant weight in a desiccator containing a saturated NaCl solution. Their X-ray patterns were also measured after they had been immersed in 0.1 mol dm$^{-3}$ NaCl, 0.1 mol dm$^{-3}$ NaOH, and $H_2O$ for periods ranging from one day to two weeks. The results are summarized in the 4th through the 8th columns of Table 1. Phase II was gradually rehydrated and partially reverted to Phase I, the degree increasing with the lapse of time. Phase III, though it showed recovered water of 1.48 mole per unit of formula weight during humidifying, did not change its crystal form even when it was immersed in the aqueous solution. As to Phase IV, it completely reverted to Phase III in spite of the fact that it absorbed as much water as the same amount of Phase III. When Phase V was allowed to stand in the aqueous solutions for 10 d, it was transformed to a new phase, the crystal structure of which has not yet been identified.

The titration curves of these phases were constructed in order to ascertain the effect of heat-treatment on their ion-exchange properties, as is shown in Fig. 6. For the convenience of comparison, the abscissas of the figure are represented by percentages converted to hydrogen form. In addition, the samples were separated from the solutions at different stages of exchange, and their X-ray powder patterns were taken while they were wet. The curves for Phases I through IV were similar to each other; they all exhibited two plateaus, each of them corresponding to the replacement of each mole of the $Na^+$ ion with the $H^+$ ion. However, a comparison of the X-ray patterns of these four phases at various stages of ex-

TABLE 1. PREPARATION AND STORAGE OF THE VARIOUS PHASES OF DISODIUM ZIRCONIUM BIS(ORTHOPHOSPHATE)

| Phase | Formula | Heating temp for preparation °C | Recovery in weight[a)] % | Recovery in weight[a)] mol $H_2O$ / Formula weight | Phase transition[b)] in aqueous soln 1 d | Phase transition[b)] in aqueous soln One week[c)] | Condition of of storage[e)] |
|---|---|---|---|---|---|---|---|
| I | $Na_2Zr(PO_4)_2\cdot 3H_2O$ | Room temp | — | — | No change | No change | Saturated NaCl soln |
| II | $Na_2Zr(PO_4)_2\cdot H_2O$ | 80 | 1.50±0.02 | 1.29 | I, 54%<br>II, 46% | I, 72%<br>II, 28% | $P_2O_5$ |
| III | $Na_2Zr(PO_4)_2$ | 200—300 | 8.15±0.02 | 1.48 | No change | No change | $P_2O_5$ |
| IV | $Na_2Zr(PO_4)_2$ | 500—800 | 8.18±0.01 | 1.49 | III, 100% | III, 100% | $P_2O_5$ *in vacuo* |
| V | $Na_2Zr(PO_4)_2$ | 800 | 4.07±0.05 | 0.74 | No change | New phase, 100% ($d$=0.840)[d)] | $P_2O_5$ |

a) Each phase was allowed to stand for 30 d in a desiccator over a saturated NaCl soln. b) $H_2O$, 0.1 mol dm$^{-3}$ NaOH, 0.1 mol dm$^{-3}$ NaCl. c) For Phase V, 10 d. d) d: Interlayer distance/nm. e) Kind of desiccant.

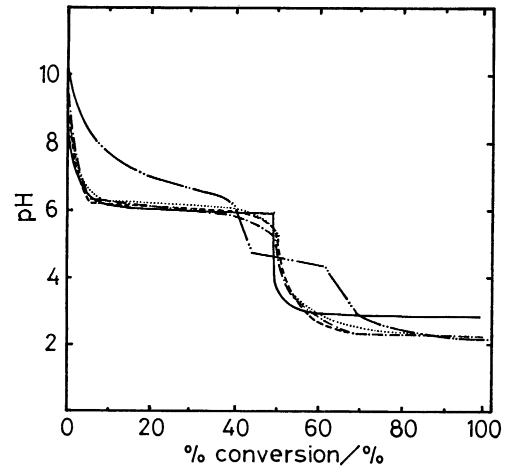

Fig. 6. $Na^+/H^+$ titration curves for various phases. ——: I, ……: II, ----: III, —·—: IV, —··—: V.

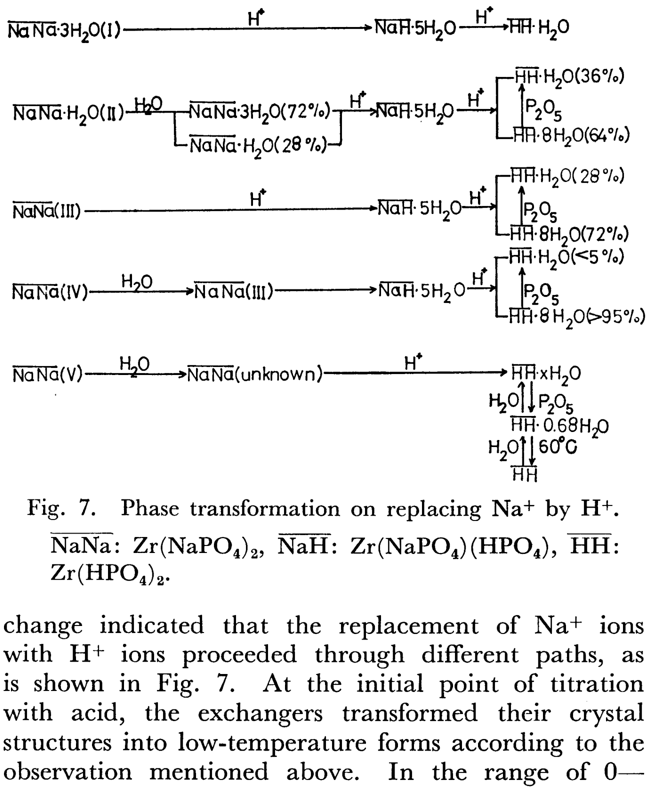

Fig. 7. Phase transformation on replacing $Na^+$ by $H^+$. $\overline{NaNa}$: $Zr(NaPO_4)_2$, $\overline{NaH}$: $Zr(NaPO_4)(HPO_4)$, $\overline{HH}$: $Zr(HPO_4)_2$.

change indicated that the replacement of $Na^+$ ions with $H^+$ ions proceeded through different paths, as is shown in Fig. 7. At the initial point of titration with acid, the exchangers transformed their crystal structures into low-temperature forms according to the observation mentioned above. In the range of 0—50% $H^+$ ion-uptake, however, the progressive exchange led to the formation of a monosodium phase of composition, $Zr(HPO_4)(NaPO_4) \cdot 5H_2O$, which was present exclusively at the half-exchange point of the titration, irrespective of the starting materials. Beyond this point, the exchangers in dihydrogen form, which resulted from the replacement of the second $Na^+$ ions with $H^+$ ions, consisted of a mixture of $Zr(HPO_4)_2 \cdot H_2O$ and $Zr(HPO_4)_2 \cdot 8H_2O$. The relative amount of the highly hydrated phase ($Zr(HPO_4)_2 \cdot 8H_2O$) differed with the difference in the phase of the starting materials; that is, at the end point of titration, the hydrogen form obtained from Phase II contained 64% $Zr(HPO_4)_2 \cdot 8H_2O$, while the hydrogen form obtained from samples heat-treated at 250 °C (Phase III) and 700 °C (Phase IV) contained 72% and more than 95% of the octahydrate respectively. In contrast, the samples without heat-treatment yielded no highly hydrated phase; *i.e.*, they returned to the original α-ZP. This highly hydrated phase could be converted to $Zr(HPO_4)_2 \cdot H_2O$ by drying over $P_2O_5$, as had been reported by Clearfield *et al.*[1] The hysteresis (dependence of the curves on the direction of titration) observed in the titration curves of the Phases from II through IV is ascribable to the appearance of $Zr(HPO_4)_2 \cdot 8H_2O$ when these phases are converted to the dihydrogen form. In this connection, it is worthwhile to cite the study of Alberti *et al.*,[6–8] who have described the dependence of the titration curves on the method of synthesizing α-ZP. They made it clear that the degree of crystallinity affected the reversibility of ion exchange and the resolution between two ion-exchange steps in the curves; the reversibility and the resolution became better with an improvement in the degree of crystallinity. Based on this view, it is considered, from the above findings, that the α-ZP prepared by the method recommended by the present authors possesses a very high degree of crystallinity, while a rise in the temperature of the thermal treatment of the sodium-substituted phase reduces the degree of crystallinity of the exchanger.

On the other hand, the $Na^+/H^+$ titration curve for Phase V exhibited a three-stage ion-exchange, unlike the titrations for the other phases described above. The complete substitution of $Na^+$ ions for $H^+$ ions led to the formation of the dihydrogen phase, which has an interlayer distance of 1.047 nm. When this phase was dried in a $P_2O_5$ desiccator, it was converted to a phase having an interlayer distance of 0.763 nm and the formula of $Zr(HPO_4)_2 \cdot 0.68H_2O$. Furthermore, this phase showed DTA and TGA curves different from those of α-ZP in that the former showed a two-step dehydration up to 150 °C, while the latter showed a one-step dehydration, as is shown in Fig. 1. Therefore, this phase is considered to have a crystal structure different from α-ZP and to be similar to the ι-phase reported by Clearfield *et al.*[9] Figure 8 indicates that the $H^+/Na^+$ titration curve of this phase was different from that of ι-ZP; the former had three plateaus at pH 2.3, 4.5, and

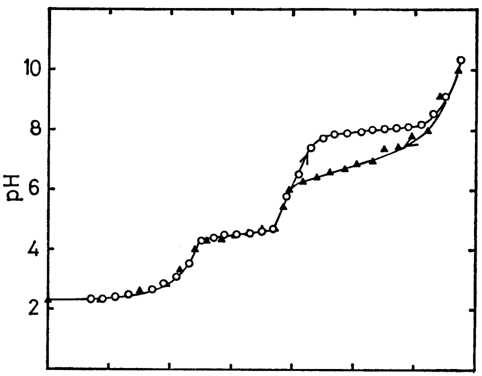

Fig. 8. Titration curves of ZP in $H^+$ form regenerated from Phase V.

○: Forward titration, 0.1 mol $dm^{-3}$ (NaCl+NaOH), ▲: backward titration, 0.1 mol $dm^{-3}$ (HCl+NaCl).

8.0, whereas the latter exhibited no plateau. Furthermore, the titration curve of $Zr(HPO_4)_2 \cdot 0.68H_2O$ showed hysteresis in the high-pH region. This irreversibility is due to the difference in phases participating in the titration.

There are many other disagreements between the present results and Clearfield's in addition to those explicitly described in this report. They are considered to be attributable mainly to the difference in the crystallinity of the starting $\alpha$-ZP, as was pointed out in the preceeding paper,3) although the difference in the details of the experimental conditions may be partly responsible.

In conclusion, the 3rd and the last columns of Table 1 summarize the recommended method for the preparation of, and the conditions for the storage of, five modifications of disodium substituted zirconium phosphate.

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