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Preparation and properties of $HZr_2P_3O_{12}$ and related compounds

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$HZr_2P_3O_{12}$ (H-form) was prepared in air at 650° C by de-ammoniation of $NH_4Zr_2P_3O_{12}$ (NH_4-form) in order to study properties of proton in the $NaZr_2P_3O_{12}$-type structure. Hydration of H-form took place at 70° C, 0.15 GPa, and the final product is $(H_3O)Zr_2P_3O_{12} \cdot 0 \cdot 17H_2O$ (H_3O-form). H- and H_3O-forms reacted with alkali chloride solutions at 25° C. Rates of the exchange reactions were studied as a function of water content of H- and H_3O-bearing compounds. The H-form showed an excellent selectivity for univalent cations in the order: ammonium $<$ potassium $<$ rubidium $\ll$ sodium, lithium.

1. Introduction

$NaZr_2P_3O_{12}$ is an end component of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12} (0.4 < x < 2.8)$ which is the fast sodium ion conductor [1]. This structure consists of a skeleton made up of PO_4 tetrahedra sharing corners with ZrO_6 octahedra [2]. The sodium atom occupies the three-dimensionally linked interstitial space with four available positions (one M1 and three M2 sites) per formula unit. Sodium mobility may be intimately related to the nature of the interstitial space. A clue to elucidate the nature of this space may be given by examining behaviours of atoms and molecules in the $NaZr_2P_3O_{12}$-type structure. For this purpose we have prepared H-form by de-ammoniation of NH_4-form, and exchange reactions between H and univalent cations were investigated. Presence and properties of H_2O in H-form and related compounds were examined. In this paper, M-form is an abbreviation of $MZr_2P_3O_{12} \cdot nH_2O$, where M is H, H_3O, NH_4 or alkali metal atoms, and M-form, similar in X-ray powder diffraction pattern to Na-form, was regarded as having rhombohedral symmetry.

2. Experimental

$NH_4H_2PO_4$, KH_2PO_4, NaH_2PO_4, KOH, NaOH, NH_4OH, $ZrOCl_2 \cdot 8H_2O$ and distilled water were used for the synthesis. All materials used were analytical grade. Starting materials for M-forms (M: sodium, potassium or ammonium) were prepared by mixing 200 cm^3 of 0.15 mol dm^{-3} MH_2PO_4 solution with 200 cm^3 of 0.1 mol dm^{-3} zirconium chloride solution. The pH values of the mixed solutions adjusted by adding alkali solutions were 5.05, 2.6 and 3.8 to 4.8 for Na-, K- and NH_4-forms, respectively. The precipitate obtained was filtered and dried at 45° C. The product was ground in an agate mortar. The starting material of about 0.05 to 0.5 g was sealed in a gold capsule together with a small amount of water, less than 20% by weight. Synthesis was carried out using cold-seal high pressure vessels for 24 to 48 h at 350 to 400° C, 0.1 to 0.15 GPa. The product obtained was washed with distilled water, and then examined by X-ray powder diffraction. Lattice constants were determined at room temperature using KCl as an internal standard with a precision of ± 0.003 nm.

Differential thermal (DTA) and thermogravimetric (TG) analyses of NH_4-form were performed with DTA–TG instruments (Rigaku microbalance and ULVAC TA-1500 model HM-20E) using samples of 10 to 30 mg at the heating rate of 10° C min^{-1}. X-ray diffraction patterns and infrared spectra were measured for specimens heated at various temperatures in order to elucidate the significance of the TG curves. The infrared (IR) absorption spectra were obtained in KBr media using an Hitachi grating infrared spectrophotometer, model EP1-G3.

Ion exchange reaction between H-form and

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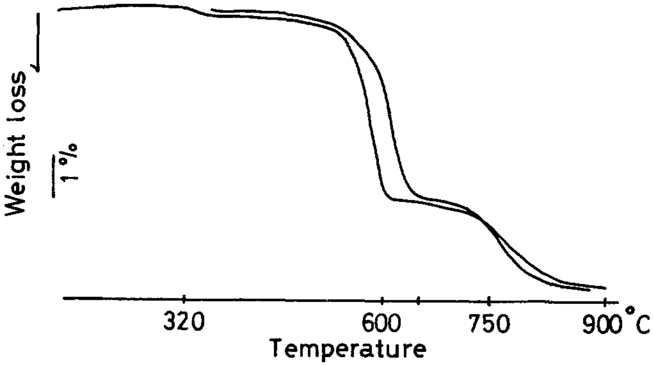

Figure 1 Thermogravimetric curves of NH_4-form. Weight losses occur in three stages at about 300° C, 520 to 650° C and 700 to 850° C.

0.1 mol dm^{-3} solution of alkali chloride was investigated at 25° C using a digital pH meter (TOA-pH meter model HM-20E). H-form of 20 mg and 10 cm^3 solution of MCl, where M is caesium, ammonium, rubidium, potassium, sodium or lithium, was used. The exchange reaction at low pH (0.00 to 0.01) was also carried out by adding a small amount of HCl to chloride solutions. The products were characterized by X-ray diffraction, IR spectra and DTA–TG measurements.

3. Results and discussion

3.1. Stability of NH_4-form

NH_4-form obtained here is similar in X-ray powder pattern to K-form. An IR absorption spectrum showed one strong band at 1435 cm^{-1}, which is attributed to the NH_4^+ antisymmetric bending frequency. Thermogravimetric curves of NH_4-form showed various patterns, depending on the ratio of water to sample in the Au capsule and the nature of the gel. Two representative TG curves are illustrated in Fig. 1. Weight losses occurred in three stages at about 300, 520 to 650 and 720 to 850° C. IR spectra and X-ray data indicate that water loss took place below 520° C, and subsequent weight loss was due to de-ammoniation of NH_4-form. H- and NH_4-forms coexist in the temperature range from 520 to 650° C. There is no change in the lattice constants of both phases in the two phase field.

Dehydration of H-form mainly occurs above 700° C accompanied by gradual change in the X-ray powder pattern at room temperature. Material heated above 750° C showed an X-ray powder pattern of rhombohedral symmetry (Fig. 3). Proton in the product heated at 900° C was not detected with an IR absorption spectrum. This is consistent with the weight loss data. In conclusion, thermogravimetric curves could be explained by dehydration and de-ammoniation of $NH_4Zr_2P_3O_{12} \cdot nH_2O$ ($n = 0.05$ to 0.2) below 650° C, and subsequent dehydration of H-form up to 900° C.

According to observations by scanning electron microscope (SEM) and electron diffraction microscope, a single grain of NH_4-form of about 5 to 20 μm changes to an aggregate of small crystals of H-form of about 100 to 300 nm in

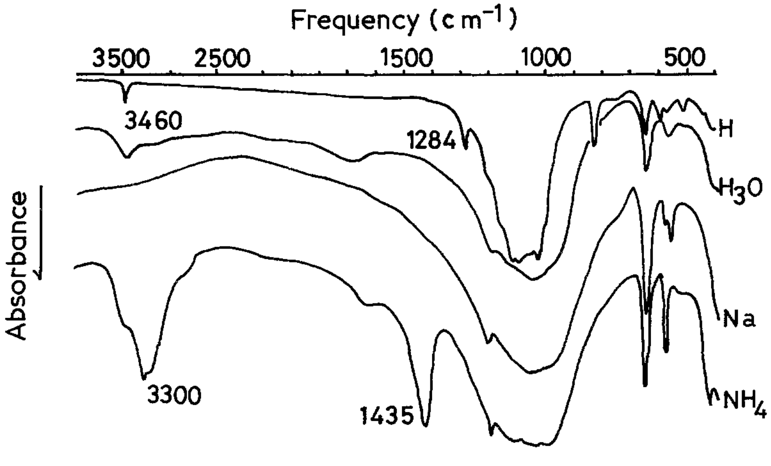

Figure 2 Infrared absorption spectra of H-form and related compounds. H: H-form prepared at 650° C, Na: anhydrous Na-form, H_3O: H_3O-form.

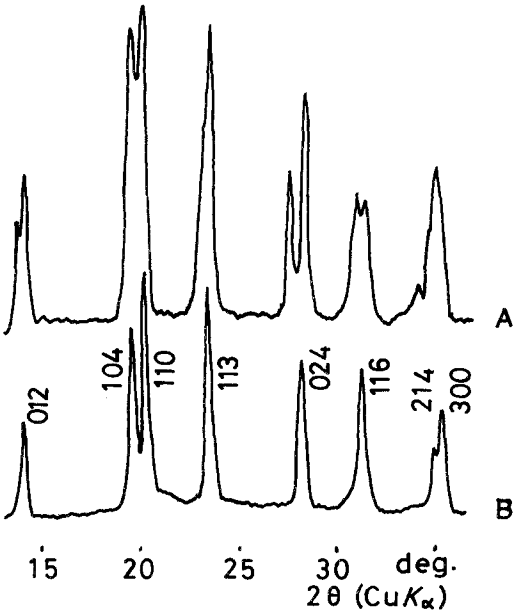

Figure 3 X-ray powder patterns of H-form and dehydrated H-form. A: H-form produced at 650° C. B: dehydrated H-form prepared at 900° C.

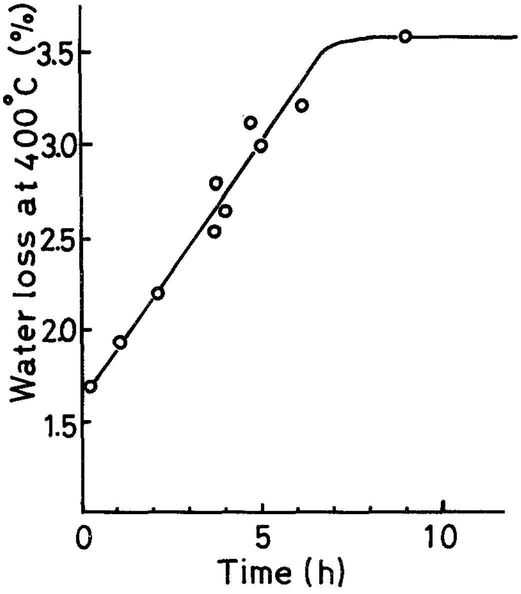

Figure 4 Rate of hydration of H-form at 100° C, 0.1 MPa water pressure. Degree of the hydration of H-form at a given run duration is represented by the water loss (% by weight) at 400° C determined by using a thermogravimetric instrument.

size which gave a single electron diffraction pattern.

3.2. Properties of H-form

IR spectra and X-ray patterns of H-form and related compounds are shown in Figs. 2 and 3, respectively. An OH stretching vibration band at 3560 cm^{-1} is evidence for presence of proton. An absorption band at 1284 cm^{-1}, which may by Zr–O–H vibration, is also characteristic of H-form. Structure of H-form is distorted from rhombohedral symmetry at room temperature. However, it has rhombohedral symmetry above 220° C, as was observed by high temperature X-ray powder diffraction.

The DTA–TG curves indicate hydration of H-form at 25 to 150° C with subsequent dehydration at 150 to 215° C and phase transition at about 220° C on heating. Reverse phase transformation and rehydration were observed on cooling. The amount of water in the final product is about 0.8 to 1.5% by weight.

3.3. Preparation of H_3O-form

H_3O-form was prepared at 70 to 400° C, 0.1 GPa by heat treatment of H-form under hydrothermal conditions. H_3O-form is similar in X-ray diffraction pattern to K-form, suggesting the presence of H_3O in the M1 site. IR absorption bands near 3560 and 1284 cm^{-1} characteristic of H-form are absent for H_3O-form. Water loss data of H_3O-form indicate that the chemical formula of H_3O-form could be represented by $(H_3O)Zr_2P_3O_{12} \cdot 0.17H_2O$.

H-form was sealed in an Au tube together with water, and the hydration rate was studied at 100° C, 0.1 MPa as a function of time. The result is shown in Fig. 4. Water content of the product was estimated by weight loss at 400° C. Crystals of more than 2 wt% in water content showed a rhombohedral X-ray powder pattern and the IR absorption bands characteristic of both H- and H_3O-forms. They are solid solutions composed of H- and H_3O-forms. Fig. 4 shows that the rate of hydration is constant and independent of the H_2O content of the solid solution. Heat-treatment for more than 7 h is necessary to produce H_3O-form. The rate determining process may be diffusion of H_2O through bottlenecks [3, 4] that lie near the faces of the MO_6-octahedra (M: H, H_3O).

3.4. Lattice constants

The univalent cations in the $NaZr_2P_3O_{12}$-type structure occupy the octahedral M1 site which shares faces with two adjacent ZrO_6 octahedra. Because there is an arrangement of

TABLE I Lattice constants of synthetic crystals and related compounds

Sample	a (nm)	c (nm)	Reference
Cu-form	0.8866	2.2191	[6]
Li-form	0.88429	2.2286	[7]
Na-form(w)	0.8812	2.2810	‡
Na-form(w)	0.88189	2.2810	[8]
Na-form	0.8043	2.27585	[2]
K-form	0.871	2.394	‡
K-form	0.8710	2.3841	[1]
H_3O-form	0.874	2.379	‡
NH_4-form	0.868	2.424	‡
NH_4-form(w)	0.868	2.415	‡
800*	0.883	2.298	‡
775(Rb)†	0.880	2.320	‡

(w): Hydrous crystalline material.

*: H-form, dehydrated at 800° C.

†: H-form, reacted with RbCl solution and partially dehydrated at 775° C.

‡: Present study.

TABLE II Water content and phase transformation temperature of H-form reacted with 0.1 mol dm^{-3} solution of alkali chloride or NH_4Cl

Sample	Salt used	Water loss (wt %)	*	Dehydration temp. (° C)
H-form	–	0.8–1.5	220	150–215
	CsCl	0.8	220	170–210
	NH_4Cl	0.6	220	160–215
	KCl	0.4	211	170–215
	RbCl	0.8	204	170–215
	NaCl	1.7	–	180–215
	LiCl	0.8	–	150–215
H_3O-form		4.3		160–600
Na-form		2.0		200–400
K-form		0.6		300–450
NH_4-form		0.2–0.7		300–

*: Transformation temperature (° C).

Water contents of several compounds prepared hydrothermally are listed in the lower column for comparison.

$O_3ZrO_3MO_3ZrO_3$ (M: alkali metal atom) along the c-axis, the c lattice constant increases with increase in size of alkali metal ion [5]. Lattice constants of Na-form and related compounds reported previously are listed in Table I together with our data [1, 2, 6–8]. Water contents of Na- and K-forms prepared at 370° C, 0.15 GPa are given in Table II. As shown in Fig. 5, the a lattice constant slightly decreases and the c lattice constant considerably increases with increases in size of the univalent cation occupying the M1 site.

If water is present in the M1 site, the c lattice constant may depend on water content. However, hydrous Na- and NH_4-forms showed similar lattice constants to those of anhydrous Na- and NH_4-forms, respectively, suggesting the presence of water in the M2 site. On the other hand, H_3O is present in the M1 site, as was described before.

3.5. Ion exchange reactions

H-form rapidly reacted with NaCl and LiCl solutions, and an abrupt change in pH values took place within 5 min. The products after the exchange reactions were hydrous Na- and Li-forms on the basis of X-ray and TG measurements. Li-form showed no IR band characteristic of H-form, but Na-form gave a very weak band near 1284 cm^{-1}, suggesting the presence of a small amount of proton. Na-form could also be prepared by the ion exchange reaction between H-form and an NaCl solution with a low pH value, 0.01.

The exchange reaction between H-form and MCl solution, where M is rubidium, potassium,

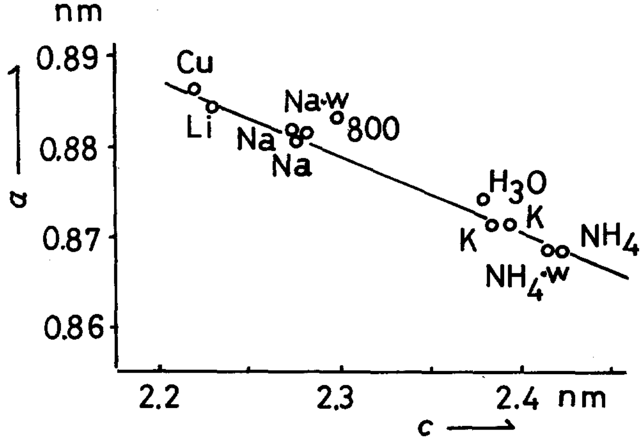

Figure 5 Relationship between the a and c lattice constants of materials with $NaZr_2P_3O_{12}$-type structure. Na·w and NH_4·w: Na- and NH_4-forms containing zeolitic water. Cu: Cu-form, 800: see Table I.

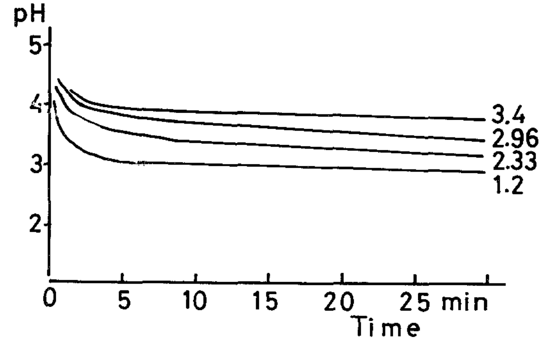

Figure 6 Time dependence of the pH value of the NaCl solution reacting with crystals in the system H- and H_3O-forms at 25° C. Crystals of 20 mg and 10 cm^3 of 0.1 mol dm^{-3} NaCl solution were used. Arabic numerals are amount of water loss at 400° C (% by weight) for the starting material.

ammonium or caesium, occurred slowly. For example, pH values of NH_4Cl solution were 4.42 and 4.13 after 1 h and 60 days, respectively. Univalent cations replacing protons are about 2 to 5 mol%, estimated by decrease in the pH values. Significant decrease in transformation temperature of H-form occurred due to the presence of small amount of cation replacing protons (Table II).

The results of exchange reaction between NaCl solution and H_3O-form or related compounds are illustrated in Fig. 6. The arabic numerals in Fig. 6 are the amount of water loss at 400° C for the material used. The pH values after 72 h were 2.71, 2.82, 2.97 and 3.08 for the samples in the order of increasing water content. Time necessary for attaining a given pH value is longer for samples containing larger amounts of H_2O. It is clear that sodium and H_3O mobilities decrease with increasing amount of H_3O ion in the M1 site. The ion exchange reaction may proceed from the surface of the crystal to the internal part. Therefore, H_3O-form reacting with NaCl solution may be coated with an Na-rich zone where H_3O diffusion is very slow because of smaller sizes of the M1 and M2 sites. This is a reason why the ion exchange reaction of H_3O-form is slow as compared with that of H-form. In this context, SEM observations indicate that the initial morphology of H-form remained unchanged after the ion exchange and hydration reactions. Another reason is low reactivity of H_3O with Na ion.

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References

1. H. Y-P. HONG, *Mater. Res. Bull.* **11** (1976) 173.
2. L. HAGMAN and P. KIERKEGAARD, *Acta Chem. Scand.* **22** (1968) 1822.
3. D. TRANQUI, J. J. CAPPONI, J. C. JOUBERT and R. D. SHANNON, *J. Solid State Chem.* **39** (1981) 219.
4. H. KOHLER, H. SCHULZ and O. MELINIKOV, *Mater. Res. Bull.* **18** (1983) 1143.
5. C. DELMAS, J-C. VIALA, R. OLAZCUAGA, G. LE FLEM, P. HAGENMULLER, F. CHERAOUI and R. BROCHU, *Solid State Ionics* **3/4** (1981) 209.
6. P. C. YAO and D. J. FRAY, *ibid.* **8** (1983) 35.
7. B. E. TAYLOR, A. D. ENGLISH and T. BERZINS, *Mater. Res. Bull.* **12** (1977) 171.
8. A. CLEARFIELD, P. JIRUSTITHIPONG, R. N. COTMAN and S. P. PACK, *ibid.* **15** (1980) 1603.

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