January, 1985] © 1985 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jan., 58, 381—382 (1985) 381

Phase Relations in the System $NH_4Ti_2P_3O_{12}$-$NH_4Zr_2P_3O_{12}$

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(Received June 13, 1984)

Synopsis. Crystalline phases in the system $NH_4Ti_2P_3O_{12}$–$NH_4Zr_2P_3O_{12}$ were prepared in a high pressure vessel, and were investigated by X-ray method. New compounds, $(NH_4)_{1+x}Ti^{3+}{}_x(Ti^{4+},Zr)_{2-x}P_3O_{12}$ ($1 \geqq x$), with the langbeinite-type structure were produced under reducing conditions.

In recent years a number of compounds with the Nasicon-type structure have been studied in relation to the superionic conductor, Nasicon ($Na_3Zr_2Si_2PO_{12}$).[1—4] A characteristic framework of these compounds is that all the oxygen atoms are shared between MO_6 and TO_4 where M is Ti or Zr and T is Si,Al or P. Each octahedron is surrounded by six tetrahedra, and each tetrahedron by four octahedra. This framework with the formula $M_2(TO_4)_3$ can exist in three modifications: Nasicon-type, langbeinite-type and garnet-type structures.[5,6]

These structures may be conveniently described as a body-centered cubic rod packing or hexagonal packing of parallel cylinders.[7] For example, in the case of $KTi_2P_3O_{12}$ with cubic langbeinite-type structure,[8] the rods consist of a repeating sequence K, (K),O_3TiO_3,O_3TiO_3, where (K) is vacancy. The rods extend along four nonintersecting directions, parallel to the body diagonals of a cube. The P atoms in tetrahedral coordination hold the rods together. On the other hand, rods consist of a repeating sequence of K,O_3TiO_3,O_3TiO_3 in the rhombohedral $KTi_2P_3O_{12}$. The rods are oriented along the real axis $\bar{3}$.

Rhombohedral $NH_4Ti_2P_3O_{12}$ and $NH_4Zr_2P_3O_{12}$ were prepared,[9—11] but no cubic phase was obtained. However, solid solutions with cubic structure were produced during an investigation of the system $NH_4Ti_2P_3O_{12}$–$NH_4Zr_2P_3O_{12}$. The purpose of this work is to ellucidate phase relations in this and related systems.

Experimental

Reagents used for synthesis were $NH_4H_2PO_4$, TiO_2, and ZrO_2. All of them have a purity higher than 99%. These materials were weighed according to the prescribed proportion and mixed in an alcohol medium, and then dried at 323 K for 10 h. The ratio of P to (Ti+Zr) is 1.5 for all the starting materials except for two experimental runs where small amount of $NH_4H_2PO_4$ was added as a flux component to promote chemical reaction.

Three kinds of experiments were carried out. First, starting material was sealed in a gold capsule of 6 mm in diameter and 35 mm long with no water added. Second, double capsules were used. Starting material was sealed in an inner platinum capsule, and then hematite and water were put in between the inner and outer capsules in order to maintain low hydrogen fugacity. Third, a small amount of acetone was added to the starting material in a gold capsule in order to produce high hydrogen fugacity. The ratio $Ti^{4+}/(Ti^{4+}+Ti^{3+})$ in crystalline materials may be controlled by the hydrogen fugacity of fluid phase.

Synthesis was carried out in a cold seal high pressure vessel. Temperature was measured by an internal thermocouple, and pressure by a calibrated Heise Bourdon tube gauge.

X-ray powder patterns were recorded with a Toshiba diffractometer using Cu $K\alpha$ radiation. For unit cell determinations, the pattern was obtained at room temperature by the scanning speed of 0.25 degree 2θ per min. KCl or quartz powder was used as an internal standard.

Chemical analyses of the synthetic crystals were carried out with an electron probe microanalyzer (JXA 5A). $NH_4Ti_2P_3O_{12}$ prepared and analyzed before[10] was used as a standard. Apparent concentration was corrected by the procedure proposed by Bence and Albee.[12]

Results and Discussion

Experimental results are listed in Table 1 together with experimental conditions. X-ray studies on the products of the first kind of experiments (1—9 in Table 1) indicate that most of X-ray reflections could be indexed as a rhombohedral form. However, extra weak reflections were observed in four experimental products. These reflections could be indexed as a cubic form with the langbeinite-type structure. Cubic phases were not prepared by the second kind of experiments (10—13 in Table 1), suggesting that cubic phase is unstable under low hydrogen fugacity. On the other hand, cubic phases with blue colour were main products when acetone was added to the starting materials(14—19 in Table 1). These results suggest the presence of Ti^{3+} in the cubic phases. Further evidence for the existence of Ti^{3+} will be described afterward.

Formula unit volumes are presented on Fig. 1 as a function of the ratio Zr/(Zr+Ti) in the starting material. As is seen from Fig. 1, formula unit volumes slightly deviate from the Vegard's law. Two rhombohedral phases with different unit cell volume were present in the product obtained by the experiment 7 in Table 1. Chemical compositions of the coexisting phases were determined by using the relationship between composition and formula unit volume shown in Fig. 1, and plotted as circles A and B. The compositions of A and B are 0.56 ± 0.03 and 0.09 ± 0.01 in the Zr/(Zr+Ti) ratio, respectively.

The first and second kinds of experiments were unsuccessful in yielding a pure cubic phase. However, cubic phase with or without graphite was obtained by the third kind of experiments. Formula unit volume of the cubic phase is shown by the cross in Fig. 1. Two cubic phases with different unit cell volume were crystallized in two products (15 and 18), suggesting presence of an immiscibility field in the cubic solid solution system. One of the cubic phases in the product of experiment 15 showed weak X-ray peaks partially superimposed on nearby higher peaks.

Weight loss for the cubic phases(15 in Table 1) was 9.4 wt% at 1273 K, which was larger than the weight loss for $NH_4Ti_2P_3O_{12}$ (6.4%). Excess ammonium

Table 1. Experimental results

Run number	Starting material 100Zr/(Zr+Ti)	Temp K	Press GPa	Time h	Product[b)]	Lattice constant/10^{-1} nm Rhombohedral a	Rhombohedral c	Cubic c
1	0	823	0.15	40	R	8.318	23.44	
2	8.6	823	0.15	40	R	8.328	23.51	
3	63	823	0.16	25	R, (C)	8.533	23.97	10.07
4	82	823	0.15	30	R, (C)	8.597	24.14	10.14
5	89	823	0.15	48	R, (C)	8.627	24.20	10.17
6	100	823	0.15	48	R	8.680	24.24	
7[a)]	30	853	0.17	40	R	8.331 8.479	23.53 23.91	
8	20	878	0.19	48	R	8.33 8.450	23.53 23.87	
9	43	853	0.17	40	R, (C)	8.462	23.88	10.07
10	59	873	0.15	16	R	8.504	23.93	
11	63	828	0.15	40	R	8.511	23.90	
12	77	828	0.15	24	R	8.563	24.06	
13	89	828	0.15	40	R	8.621	24.17	
14	0	823	0.15	48	R, C, gr			9.922
15	22	823	0.15	40	C			9.970
16	42	828	0.15	6	C, gr			10.055
17	0	798	0.15	16	C, gr			9.925
18[a)]	30	798	0.15	16	C, gr			10.09, 9.962
19	63	703	0.15	60	C			10.140

R: rhombohedral phase, C: cubic phase, gr: graphite, (—): minor product.

a) Small amount of $NH_4H_2PO_4$ was added. b) Fluid phase is present in all products.

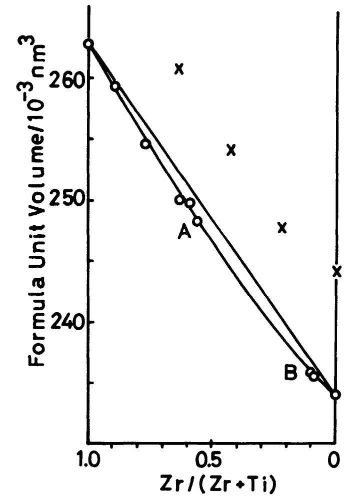

Fig. 1. Formula unit volume versus composition of starting materials. circle: rhombohedral phase not associated with cubic phase, cross: cubic phase prepared under reducing conditions, A—B; immiscibility field at 853 K, 0.17 GPa.

content may be explained by the presence of Ti^{3+} in the octahedral site. Chemical formula derived from the weight loss datum and the ratio of Zr to (Zr+Ti) in the cubic phase (0.22) is as follow: $(NH_4)_{1.55}Ti^{3+}_{0.55}$-$Ti^{4+}_{1.01}Zr_{0.44}P_3O_{12}$.

Zirconium-free crystals were of sufficient sizes for analysis using an electron probe microanalyzer. Composition of the cubic phase is: TiO_2=37.68; P_2O_5=50.52 (wt%). Because discrimination of TiO_2 and Ti_2O_3 contents is impossible for our analytical method, value of TiO_2 is total titanium calculated as TiO_2. The analytical data is consistent with the theoretical value for $(NH_4)_2Ti^{3+}Ti^{4+}P_3O_{12}$: TiO_2=37.74; P_2O_5=50.29 (wt%). On the other hand, rhombohedral phase coexisiting with graphite and cubic phase gave the same composition as the standard $NH_4Ti_2P_3O_{12}$.

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