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Preparation of $Cs_2ZrY(PO_4)_3$ and Related New Compounds

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Synopsis. New compounds have been prepared with the chemical formula $A_2ZrM(PO_4)_3$ with A=K, Rb or Cs and M=Y or In. X-Ray diffraction data can be indexed based on a cubic cell with a langbeinite-type structure. $CsTi_2(PO_4)_3$ could not be obtained but $CsTi_3P_5O_{19}$ was synthesized between 1100—1275 °C. It crystallized with a space group C2/c or Cc with $Z=4$.

Nasicon-type compounds have been studied in relation to sodium ion conductor.[1,2] However, recent studies regarding these substances have revealed the existence of a new structural family of low thermal-expansion materials.[3,4] These studies have been carried out mainly on sodium- or calcium-bearing Nasicon-type compounds; therfore, we have investigated potassium-, rubidium-, and caesium-bearing compounds. During this study, we obtained novel compounds, such as $K_2ZrY(PO_4)_3$, $K_2ZrIn(PO_4)_3$, $Rb_2ZrIn(PO_4)_3$, $Rb_2ZrY(PO_4)_3$, $Cs_2ZrY(PO_4)_3$, $Cs_2ZrIn(PO_4)_3$ and $CsTi_3P_5O_{19}$. This article reports on the preparation and properties of these compounds.

Experimental

Cs_2CO_3, Rb_2CO_3, TiO_2, ZrO_2, In_2O_3, Y_2O_3, KH_2PO_4, and $NH_4H_2PO_4$ were mixed in stoichiometric ratios in an agate mortar with ethyl alcohol and then dried in air. The mixtures were fired at 250 °C for 15 h and calcined at 600 °C for 2 h. The calcines were heated at 1100 °C for 5 min before sealing in a platinum tube of 6 mm in diameter. The sample in platinum capsules were heated at 950—1315 °C for 1—72 h, and then quenched in water.

The products were identified by optical microscopy and X-ray powder diffraction. Lattice constants were determined at room temperature with a Toshiba diffractometer, ADG-301, at a scanning rate of 0.25° 2θ per min. Powdered quartz or KCl was added as an internal standard.

Weissenberg and Precession photographs for a single crystal of $CsTi_3P_5O_{19}$ were obtained using Ni-filtered or unfiltered Cu $K\alpha$ radiation. The unit-cell dimensions of a single crystal were determined using an automatic four-circle X-ray diffractometer, Rigaku Denki Co., Ltd. with Mo $K\alpha$ radiation filtered with a graphite monochromator.

The chemical composition of $CsTi_3P_5O_{19}$ was analyzed using an electron-probe microanalyzer, JXA 5 A. A single crystal of TiP_2O_7 was used as the standard for Ti and P.

Results and Discussion

$K_2ZrY(PO_4)_3$ and $K_2ZrIn(PO_4)_3$. These compounds were prepared below 1315 °C as isotropic granular aggregates. As shown in Table 1, X-ray patterns are similar to that of cubic $KTi_2(PO_4)_3$ with a langbeinite-type structure.[5] The lattice constant of $K_2ZrY(PO_4)_3$ is 1.0336 nm, and 1.0180 nm for $K_2ZrIn(PO_4)_3$. Solid solutions between rhombohedral $KZr_2(PO_4)_3$ and cubic $K_2ZrY(PO_4)_3$ or $K_2ZrIn(PO_4)_3$ were not produced judging from the lattice constants of the synthetic materials.

$Cs_2ZrY(PO_4)_3$ and $Cs_2ZrIn(PO_4)_3$. Single phases of isotropic crystals were prepared below 1315 °C

Table 1. X-Ray diffraction data

$K_2ZrY(PO_4)_3$			$CsTi_3P_5O_{19}$ a)		$CsTi_3P_5O_{19}$ b)		
hkl	*d*/nm	*I*	*d*/nm	*I*	*hkl*	*d*/nm	*I*
111	0.5972	13	0.753	14	020	0.830	9
210	0.4614	30	0.705	70	021	0.598	9
211	0.4226	20	0.608	12	130	0.493	15
300	0.3447	15	0.461	53	220	0.4541	15
310	0.3270	100	0.448	40	$11\bar{2}$	0.4146	50
311	0.3117	30	0.4287	47	131		
320	0.2866	13	0.4167	100	022	0.3830	9
321	0.2762	70	0.3931	15	041	0.3744	86
410	0.2507	8	0.3782	80	310	0.3531	66
411	0.2417	5	0.3656	65	$22\bar{2}$	0.3393	60
331	0.2373	5	0.3612	75	150	0.3195	9
421	0.2253	5	0.3525	14	$24\bar{1}$	0.3180	12
422	0.2109	20	0.3249	60	202	0.3114	14
430	0.2064	7	0.3217	50	311	0.3085	100
510	0.2029	20	0.3017	100	$15\bar{1}$	0.3030	28
511	0.1992	7	0.2960	40	$33\bar{1}$	0.2999	12
520	0.1921	19	0.2915	65	060	0.2769	25
521	0.1886	4	0.2769	50	331	0.2721	12
			0.2688	55	113	0.2618	11
			0.2615	20	313	0.2445	35
			0.2523	15	062	0.2320	14
			0.2458	10	263	0.1940	8

a) 1055°C, b) 1115°C.

from stoichiometric starting materials. The X-ray peaks could be indexed on the basis of a primitive isometric space lattice. The X-ray pattern was similar to that of K-bearing analogous compounds, but reflection peaks 111, 210, and 300 were very weak. The lattice constant of $Cs_2ZrY(PO_4)_3$ is 1.0471 nm and that of $Cs_2ZrIn(PO_4)_3$ is 1.0340 nm.

$Rb_2ZrY(PO_4)_3$ and $Rb_2ZrIn(PO_4)_3$. These compounds were prepared at 1115 °C for 24 h and these showed similar X-ray powder patterns. When these X-ray patterns were compared with those of K- and Cs-bearing analogous compounds, systematic changes were clearly observed. For example, the intensities of the 220 peaks increased with increasing sizes of the alkali metal atoms. On the other hand, the reverse was observed for the intensities of the 210 peaks. The lattice constant of $Rb_2ZrY(PO_4)_3$ is 1.0402 nm, and that of $Rb_2ZrIn(PO_4)_3$ is 1.0237 nm.

$CsTi_3P_5O_{19}$. Columnar crystal and glass were prepared by heating a stoichiometric mixture of $CsTi_2(PO_4)_3$ between 1100 and 1275 °C. The crystalline phase was formulated as $CsTi_3P_5O_{19}$ on the basis of a chemical analysis using an electron-probe microanalyzer. The single phase of $CsTi_3P_5O_{19}$ was obtained between 1100—1275 °C from a stoichiometric starting material. The X-ray powder pattern given in Table 1 was indexed on the basis of a monoclinic unit cell with $a=1.0966$ nm, $b=1.6572$ nm, $c=0.8754$ nm, $\beta=100.11°$. The density, measured by the method of Archimedes, was found to be 3.10 g cm^{-3}. This is in good agreement with the calculated value for four chemical formula units per cell.

The space-group of $CsTi_3P_5O_{19}$ was determined from the systematically missing reflections in the Weissenberg photographs. The single crystals were crystallized in a monoclinic symmetry with the following missing reflections: $h+k+l$: $h+k=2n$ (n: integer), $0kl$: $k=2n$, $h0l$: $l=2n$, $hk0$: $h+k=2n$, $h00$: $h=2n$ and $0k0$: $k=2n$. These extinctions indicate a space group of C2/c or Cc. Diffused streaks parallel to the a*-axis are present in an $h0l$ Precession photograph.

$CsTi_3P_5O_{19}$ melts incongruently at 1280 °C. TiP_2O_7 and glass are present in a product quenched from 1280 °C.

Crystalline materials prepared at 1055—1090 °C for 194 h showed the X-ray diffraction pattern given in Table 1. A single-crystal X-ray study of the low-temperature polymorph was impossible because of the small grain sizes. A chemical analysis using an electron-probe microanalyzer suggests that the Cs_2O contents of the crystals prepared from the starting materials with a $CsTi_3P_5O_{19}$ composition are consistent with that of $CsTi_3P_5O_{19}$; however, the Cs_2O contents of those prepared from starting materilas with a $CsTi_2(PO_4)_3$ composition were slightly higher than that of $CsTi_3P_5O_{19}$. We could not obtain $CsTi_2(PO_4)_3$ at any temperature, although analogous compounds such as $MTi_2(PO_4)_3$, M:Li, Na, K, Rb, or Tl, were crystallized in rhombohedral forms.[6]

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