CCA-464 548.73:546.31:546.8'181
Note

Preparation and Crystallographic Data of Phosphates with Common Formula $M^{I}M^{IV}_{2}(PO_4)_3$ (M^{I} = Li, Na, K, Rb, Cs; M^{IV} = Zr, Hf)*

M. Šljukić

Department of Analytical Chemistry, Faculty of Science, the University, Sarajevo, Bosnia and Herzegovina, Yugoslavia
and

B. Matković, B. Prodić and S. Šćavničar

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

Received May 19, 1967

The investigation of alkali metal salts of zirconium and hafnium phosphates began in connection with the study of similar thorium and tetravalent uranium phosphates. The common formula of these compounds is $M^{I}M^{IV}_{2}(PO_4)_3$ with M^{I} = Li, Na, K, Rb, Cs and M^{IV} = Th, U, Zr, Hf. The crystal growth and crystallographic data of $NaTh_2(PO_4)_3$, $NaU_2(PO_4)_3$ and $KTh_2(PO_4)_3$ have already been published[1,2]. They are monoclinic, space groups *C2/c* or *Cc* with four formula weights per unit cell, and have very close lattice parameters. The question is whether a similar compound with tetravalent metal other than thorium or uranium(IV) can be prepared in a similar way and whether it has similar crystallographic properties.

Preparation of the crystals

Starting materials for the preparation of all compounds were »analytical reagent« grade. Homogeneous mixtures of alkali metal phosphate and tetravalent metal oxide were placed in a platinum crucible and B_2O_3 was added as a flux. Its quantity was about 6 times that of the tetravalent metal oxide. The furnace was heated slowly for 6 hours before raising to the final temperature of 1200° C; then was kept at this temperature for 18 hours. The rate of cooling was also slow (about 10 hours). The same compounds were obtained by using stoichiometric quantities of tetravalent metal oxide and any of the alkali metal phosphate ($M^{I}_2HPO_4$, $M^{I}H_2PO_4$ or $M^{I}_3PO_4$; M^{I} = Li, Na, K, Rb, Cs) or by using an excess of alkali metal phosphate. Crystals were separated from the solid mass by dissolving the soluble substances in boiling water and then washing with HCl (1 : 1). The crystals obtained were insoluble in all acids except HF. The chemical compositions of zirconium compounds with lithium, sodium and potassium were determined by analysis. The results are given in table I, and correspond to the formulas $LiZr_2(PO_4)_3$, $NaZr_2(PO_4)_3$ and $KZr_2(PO_4)_3$. A conclusion as to the analogous chemical composition of the hafnium members of this series was made on the basis of the crystal isomorphism between the corresponding hafnium and zirconium compounds.

Crystallographic and X-ray data

Crystals of zirconium and hafnium compounds are similar. They grow as colourless and transparent polyhedra bounded only by the faces of a $\{10\bar{1}2\}$ rhombohe-

* Part of the paper was presented at the 2nd Yugoslav Conference of Pure and Applied Chemistry, Belgrade, June 1966.

TABLE I

Compound	% M^I_2O		% ZrO_2		% P_2O_5	
	Found	Theoretical	Found	Theoretical	Found	Theoretical
$LiZr_2(PO_4)_3$	3.21	3.150	51.88	51.958	44.56	44.892
$NaZr_2(PO_4)_3$	6.33	6.320	50.54	50.257	43.34	43.423
$KZr_2(PO_4)_3$	9.32	9.300	48.93	48.659	41.77	42.041

M^I = *Li, Na, K*

dron. The faces are usually unequal because of a marked flattening of the rhombohedron on the $(10\bar{1}2)$ face, see Fig. 1. The morphology and lattice constants are listed in table II. It contains: a list of the prepared substances with their identity periods along the $[\bar{2}\bar{4}\cdot 1]$ direction — the edges between the $(10\bar{1}2)$ and $(\bar{1}102)$ faces, polar distan-

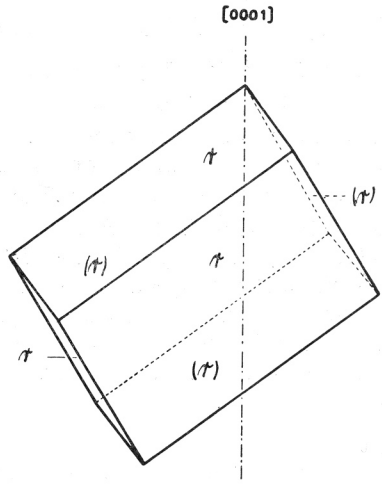

Fig. 1. $\{10\bar{1}2\}$ rhombohedron of $KZr_2(PO_4)_3$ flattened on its $(10\bar{1}2)$ face.

ces of $\{10\bar{1}2\}$ form, rhombohedral and hexagonal unit cell parameters, axial ratios, hexagonal unit cell volumes and densities. The polar distances ϱ were measured on an optical goniometer; the lattice constants were obtained from oscillation and Weissenberg X-ray diffraction photographs with nickel filtered CuKα radiation. The densities (D_m), determined by a pycnometer with decalin as liquid, agree with the calculated values (D_x) for six formula weights per hexagonal unit cell. There is good agreement between the values based on morphology and those derived from the lattice constants.

The observations on potassium dizirconium trisphosphate, $KZr_2(PO_4)_3$, are in agreement with a previous report[3], where the crystals were described as trigonal, $D_m = 3.18$ g. cm^{-3}. The absent spectra indicate space groups *R3c* or $R\bar{3}c$.

The crystals of sodium dizirconium trisphosphate, $NaZr_2(PO_4)_3$, have been described before[2] as combinations of tetragonal prisms and pinacoids, $D_m = 3.12 - 3.14$ g. cm^{-3}.

Similar values of lattice constants and the same space group extinctions between corresponding zirconium and hafnium compounds suggest either isomorphism or close structural relationships.

Acknowledgement. The authors wish to thank Professor Lj. Barić (Mineralogical and Petrological Museum, Zagreb) for his instructive help.

TABLE II

Compound	{10$\bar{1}$2} rhombohedron — the form of crystal growth			Rhombohedral unit cell		Hexagonal unit cell					Density in g. cm^{-3}	
	[24 · 1] Å	ϱ_m	ϱ_x	a_R(Å)	α	a(Å)	c(Å)	$(c:a)_m$	$(c:a)_x$	V(Å^3)	D_m	D_x
$LiZr_2(PO_4)_3$	12.63	56°13′ (±30′)	56°23′	9.10	57°18′	8.72	22.72	2.589	2.606	1496.13	3.14	3.16
$LiHf_2(PO_4)_3$	12.56	55°14′ (±03′)	55°16′	8.94	59°08′	8.82	22.03	2.495	2.498	1484.16	4.34	4.36
$NaZr_2(PO_4)_3$	12.71	56°10′ (±04′)	56°12′	9.11	57°36′	8.78	22.71	2.584	2.586	1516.12	3.21	3.22
$NaHf_2(PO_4)_3$	12.62	56°11′ (±05′)	56°13′	9.09	57°36′	8.76	22.68	2.587	2.589	1507.23	4.42	4.40
$KZr_2(PO_4)_3$	12.82	57°44′ (±02′)	57°44′	9.41	55°08′	8.71	23.89	2.743	2.743	1569.57	3.23	3.22
$KHf_2(PO_4)_3$	12.75	57°42′ (±15′)	57°37′	9.36	55°14′	8.68	23.71	2.739	2.732	1547.03	4.40	4.39
$RbZr_2(PO_4)_3$	12.89	58°26′ (±05′)	58°24′	9.53	54°02′	8.66	24.38	2.818	2.815	1583.43	3.51	3.48
$RbHf_2(PO_4)_3$	12.87	58°25′ (±05′)	58°26′	9.52	53°54′	8.63	24.34	2.817	2.820	1569.89	4.59	4.62
$CsZr_2(PO_4)_3$	12.94	59°05′ (±13′)	59°01′	9.66	52°58′	8.62	24.86	2.893	2.884	1597.79	3.72	3.75
$CsHf_2(PO_4)_3$	12.89	59°12′ (±03′)	59°12′	9.63	52°40′	8.54	24.81	2.905	2.905	1567.01	4.87	4.93
ali:	±0.01			±0.01		±0.01	±0.02					

m denotes measured values
x denotes calculated values from unit cell parameters

REFERENCES

1. B. Matković and M. Šljukić, *Croat. Chem. Acta* **37** (1965) 115.
2. B. Matković, M. Šljukić, and B. Prodić, *Croat. Chem. Acta* **38** (1966) 69.
3. J. M. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VII, Longmans, Green & Co., London, 1953, p. 164.

IZVOD

Priređivanje i kristalografski podaci o fosfatima sa zajedničkom formulom $M^{I}M_2^{IV}(PO_4)_3$ (M^{I} = Li, Na, K, Rb, Cs; M^{IV} = Zr, Hf)

M. Šljukić, B. Matković, B. Prodić i S. Šćavničar

Priređeni su monokristali deset spojeva čija je zajednička formula $M^{I}M_2^{IV}(PO_4)_3$, M^{I} = Li, Na, K, Rb, Cs; M^{IV} = Zr, Hf. Njihovi morfološki podaci i dimenzije elementarnih ćelija izneseni su u tabeli II. Svi spojevi su romboedrijski i imaju šest molekula u heksagonskim elementarnim ćelijama. Na temelju sistematskog pogašenja *hkl* refleksa ustanovljeno je da spadaju u *R3c* ili *R$\bar{3}$c* prostornu grupu.

PRIRODNO-MATEMATIČKI FAKULTET
SARAJEVO
i
INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB

Primljeno 19. svibnja 1967.

Redakcija zaključena 19. svibnja 1967.

CROATICA CHEMICA ACTA izlazi godišnje u četiri broja. Pretplata godišnje 100 N. din. (ili 9 $), a za članove 10 N. din. (ili 2 $). Za izdavača odgovara odgovorni urednik. Glavni i odgovorni urednik Prof. Dr Božo Težak, Zagreb, II. Cvjetno naselje 24. Uprava Zagreb, Marulićev trg 19/II (Pošt. pret. 131). Žiro račun: Hrvatsko Kemijsko društvo, Zagreb, broj 301-8-2068.

Tisak »VJESNIK«, Zagreb