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Preliminary Note

Synthesis and Crystallographic Data of Sodium Thorium Triphosphate, $NaTh_2(PO_4)_3$, and Sodium Uranium(IV) Triphosphate, $NaU_2(PO_4)_3$

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Sodium thorium triphosphate was first prepared by K. A. Wallroth[1] and sodium uranium(IV) triphosphate by M. A. Colani[2]. Both compounds are very stable and practically insoluble in acids. Single crystals of these compounds were prepared by methods which slightly differ from the above mentioned.

To obtain the single crustals of $NaTh_2(PO_4)_3$, a mixture of 2.5 g. $Na_4P_2O_7 \cdot 10H_2O$, 1.3 g. ThO_2 and 2.5 g. NaCl was heated to 850°C for 24 hours in a platinum crucible. The insoluble residuum, left after boiling in water, was heated again with 2.5 g. $Na_4P_2O_7 \cdot 10H_2O$ and 3.0 g. B_2O_3 to 1200°C for 24 hours. This time the fused mixture was cooled very slowly and then washed with acidulated water. The crystals obtained were colourless, transparent monoclinic prisms which were insoluble in all acids; their chemical composition, determined by analysis (ThO_2 = 68.35%, P_2O_5 = 27.72%), corresponds to the formula $NaTh_2(PO_4)_3$.

To obtain single crystals of $NaU_2(PO_4)_3$ a mixture of 4.0 g. $NaPO_3$, 2.7 g. UO_2 and 3.0 g. B_2O_3 was kept in nitrogen atmosphere for 24 hours at 1200°C in a graphite crucible and then very slowly cooled. The crystals, separated from the solid mass by washing with acidulated water, were dark green monoclinic prisms; they are soluble in a mixture of aqua regia and hydrofluoric acid. The results of the complete chemical analysis ($Na_2O \equiv 4.15\%$, P_2O_5 = 27.53% and UO_2 = 67.25%) are in agreement with the formula $NaU_2(PO_4)_3$.

Crystallographic data

The crystallographic data of both compounds are as follows:

Compound	a(Å)	b(Å)	c(Å)	β	D_m	D_c	Z	Space group
$NaTh_2(PO_4)_3$	17.39	6.80	8.13	101° 8′	5.41 g. cm^{-3}	5.44 g. cm^{-3}	4	C_{1s}^4 (Cc)
$NaU_2(PO_4)_3$	17.23	6.70	8.03	101°22′	5.63 g. cm^{-3}	5.71 g. cm^{-3}	4	C_{1s}^4 (Cc)

The lattice constants were determined from oscillation and Weissenberg photographs using CuKα radiation. The a : b : c ratios and the angle β for $NaU_2(PO_4)_3$ found in this and in previous work are in close agreement:

a : b : c = 2.5605 : 1 : 1.1918, β = 101° 3′ (Colani [2])
a : b : c = 2.571 : 1 : 1.194, β = 101°22′ (this work).

The densities (D_m) were determined pycnometrically using decalin as liquid, and (D_c) were calculated for four formula units in the elementary cell. The

space group can be C_s^4 (Cc) or C_{2h}^6 (C2/c) because hkl reflections are absent with h + k odd and h0l reflections are absent with l odd. Because the piezoelectric effect was found on both compounds, the space group is C_s^4 (Cc). The test was made by the Bergman method as modified by Iitaka[3]. The complete crystal structure determination on the thorium compound is now in progress.

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REFERENCES

1. K. A. Wallroth, *Bull. Soc. Chim.* **39** (1883) 316.
2. M. A. Colani, *Ann. Chim. Phys.* **12** (1907) 107.
3. Y. Iitaka, *Acta Cryst.* **6** (1953) 663.

IZVOD

Preparacija i kristalografski podaci o natrijevom torijevom fosfatu i natrijevom uran(IV) fosfatu

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Opisane su metode za dobivanje monokristala natrijevog torijevog fosfata i natrijevog uran(IV) fosfata. Oba spoja kristaliziraju u monoklinskom sustavu. Metodom rendgenske difrakcije određeni su njihovi kristalografski podaci:

Spoj	a(Å)	b(Å)	c(Å)	β	Z	Prostorna grupa
$NaTh_2(PO_4)_3$	17.39	6.80	8.13	101° 8′	4	C_s^4 (Cc)
$NaU_2(PO_4)_3$	17.23	6.17	8.03	101°22′	4	C_s^4 (Cc)

Na kristalima oba spoja ustanovljen je piezoelektrični efekt.

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