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SUBJECT: A Preliminary Survey of Some Fluoride Compounds - II

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ABSTRACT

Two compounds $\text{Na}_5\text{U}_3\text{F}_{17}$ and $\text{Na}_3\text{Th}_2\text{F}_{11}$ were determined to be face centered cubic. From parameter dimensions and intensity values these two compounds appear to be isomorphous. In turn $\text{Na}_5\text{U}_3\text{F}_{17}$ has an identical cell size with $\alpha\text{-Na}_2\text{UF}_6$ reported by Zachariasen.

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A PRELIMINARY SURVEY OF SOME FLUORIDE COMPOUNDS II

Previous work on the crystal structures of compounds found in the systems NaF-UF_4 and NaF-ThF_4 was done by Zachariasen⁽¹⁾ who reported an α form for Na_2UF_6 which was face centered cubic with the cube edge $a_0 = 5.565 \pm 0.004 \text{ \AA}$ and contains $4/3$ molecules per unit cell. No similar α form was found for the compound Na_2ThF_6 by Zachariasen.

In the investigations of the two systems mentioned above which were carried out at this laboratory⁽²⁾ two compounds $\text{Na}_5\text{U}_3\text{F}_{17}$ and $\text{Na}_3\text{Th}_2\text{F}_{11}$ were observed and found to be optically isotropic.⁽³⁾ The x-ray powder spectrometer data obtained from these two compounds were found to best fit a face centered cubic unit cell whose cube edges were $a_0 = 5.567 \pm 0.020 \text{ \AA}$ and $a_0 = 5.66 \pm 0.020 \text{ \AA}$, respectively.

Table 1 graphically shows the relationship which exists between the parameters of $\alpha\text{-Na}_2\text{UF}_6$, $\text{Na}_5\text{U}_3\text{F}_{17}$ and $\text{Na}_3\text{Th}_2\text{F}_{11}$. It appears that $\alpha\text{-Na}_2\text{UF}_6$ may be isostructural to $\text{Na}_5\text{U}_3\text{F}_{17}$ and that $\text{Na}_3\text{Th}_2\text{F}_{11}$ is in turn isostructural to $\text{Na}_5\text{U}_3\text{F}_{17}$ (Table 2). Both these compounds ($\text{Na}_5\text{U}_3\text{F}_{17}$ and $\text{Na}_3\text{Th}_2\text{F}_{11}$) have a limited temperature and composition range of stability which makes it difficult to obtain sufficiently large samples for density determinations.

TABLE 1
THE CUBE EDGE VALUES FOR THE COMPOUNDS

$\alpha\text{Na}_2\text{UF}_6$, $\text{Na}_5\text{U}_3\text{F}_{17}$ AND $\text{Na}_3\text{Th}_2\text{F}_{11}$		
$\alpha\text{Na}_2\text{UF}_6$	$\text{Na}_5\text{U}_3\text{F}_{17}$	$\text{Na}_3\text{Th}_2\text{F}_{11}$
$a_0 = 5.565 \pm 0.004 \text{ \AA}$	$a_0 = 5.567 \pm 0.020 \text{ \AA}$	$a_0 = 5.66 \pm 0.02 \text{ \AA}$

- (1) W. H. Zachariasen, J. Am. Chem. Soc., 70, 2147 (1948).
- (2) R. E. Thoma, J. of The American Ceramic Society, 41 (2), pp 63-69 (1958).
- (3) H. Insley, Consultant, T. N. McVay, Consultant, G. D. White and L. A. Harris, Metallurgy Division, C. Weaver, Chemistry Division, ORNL Report 2192.

TABLE 2

X-RAY POWDER DIFFRACTION DATA (Cu-K α RADIATION)
 BY A GEIGER COUNTER DIFFRACTOMETER FOR
 CUBIC Na₅U₃F₁₇ ($a_0 = 5.567 \pm 0.020$ Å)
 AND Na₃Th₂F₁₁ ($a_0 = 5.66 \pm 0.020$ Å)

(hkl)	Na ₅ U ₃ F ₁₇		Na ₃ Th ₂ F ₁₁	
	I	$\sin^2 \theta$ Observed	I	$\sin^2 \theta$ Observed
111	VS	0.0582	VS	0.0561
200	M	0.0770	M	0.0745
220	S	0.1536	S	0.1489
311	S	0.2090	M	0.2047
222	W	0.2289	W	0.2233
400	W	0.3046	W	0.2974

From the calculated volumes of the unit cells, it is quite apparent that only some fraction of a molecule can be present in each unit cell assuming the cell parameters have the values obtained by the x-ray powder method. Obviously, single crystals would enhance the structure calculations but for the above mentioned reasons these are presently not available. It is suggested from the intensities of the diffraction lines that both these compounds may possibly have a fluorite type structure which is the type structure assigned to α -Na₂UF₆ by Zachariasen⁽¹⁾

If this assumption were true it would indicate vacancies of some metal sites in these crystals. Thus one metal site out of 17, and one out of 11 would be vacant for Na₅U₃F₁₇ and Na₃Th₂F₁₁, respectively.⁽⁴⁾ A future paper will be written giving the detailed structures for both these compounds.

(4) B. S. Borie, Jr., (Metallurgy Division) Personal communication.

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