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SUBJECT: Crystal Structures of Some Compounds of
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TO: W. R. Grimes

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FROM: R. E. Thoma

Abstract

X-ray diffraction data and optical properties are reported for the compounds δ -2NaF·UF₄, δ -2NaF·ThF₄, δ -2RbF·UF₄, δ -2RbF·ThF₄, δ -NaF·KF·UF₄, and δ -NaF·RbF·UF₄. Additional properties are given for the compounds 7KF·6ThF₄ and 7RbF·6ThF₄.

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CRYSTAL STRUCTURES OF SOME COMPOUNDS
OF UF_4 AND ThF_4 WITH ALKALI FLUORIDES

I. A recent review of $\text{NaF}\cdot\text{KF}\cdot\text{UF}_4$ melts from thermal analysis experiments was made relative to phase studies being conducted with the system $\text{LiF}\cdot\text{NaF}\cdot\text{KF}\cdot\text{UF}_4$. Correlations of X-ray diffraction data for the compounds $2\text{NaF}\cdot\text{UF}_4$, $2\text{NaF}\cdot\text{ThF}_4$, $2\text{RbF}\cdot\text{UF}_4$, $2\text{RbF}\cdot\text{ThF}_4$, $\text{NaF}\cdot\text{KF}\cdot\text{UF}_4$ and $\text{NaF}\cdot\text{RbF}\cdot\text{UF}_4$ indicate that a polymorph of each of these materials is very probably a member of the same space group. This hexagonal crystal type was first assigned to the phase $\delta\text{-}2\text{NaF}\cdot\text{ThF}_4$.^{1,2} Agron, Borie, and Steele later designated the isostructural $2\text{NaF}\cdot\text{UF}_4$ phase as $\beta_3\text{-}2\text{NaF}\cdot\text{UF}_4$.³ Zachariasen reported no $\text{NaF}\cdot\text{UF}_4$ phase corresponding to $\delta\text{-}2\text{NaF}\cdot\text{ThF}_4$, although he observed this phase in $\text{NaF}\cdot\text{UF}_4$ melts after publication of $\text{NaF}\cdot\text{UF}_4$ data.^{1,4} Accordingly, a phase isostructural with $\delta\text{-}2\text{NaF}\cdot\text{ThF}_4$ will be designated hereafter as the delta form.

The compound $\text{NaF}\cdot\text{KF}\cdot\text{UF}_4$, previously believed to be $2\text{NaF}\cdot\text{KF}\cdot\text{UF}_4$ ^{5,6} is apparently isostructural with $\delta\text{-}2\text{NaF}\cdot\text{UF}_4$ as is also the compound $\text{NaF}\cdot\text{RbF}\cdot\text{UF}_4$.

Crystal structure studies in progress by L. A. Harris indicate that the delta polymorph occurs for the two compounds $2\text{RbF}\cdot\text{UF}_4$ and $2\text{RbF}\cdot\text{ThF}_4$.⁷

Table I shows the X-ray and optical properties of the compounds believed to comprise the known delta-type polymorphs of UF_4 and ThF_4 compounds with alkali fluorides.

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1. W. H. Zachariasen, "Double Fluorides of Potassium or Sodium with Uranium, Thorium, or Lanthanum," J. Am. Chem. Soc., 70 [6]2147-51 (1948).
 2. Metastable with respect to $\beta_2\text{-}2\text{NaF}\cdot\text{ThF}_4$.
 3. P. A. Agron, B. S. Borie, and R. M. Steele, Oak Ridge National Laboratory, unpublished work.
 4. Personal communication.
 5. R. E. Thoma, "X-ray Diffraction Results," Item T-1264, CF-55-12-94, December 13, 1955.
 6. H. Insley, et.al., "Optical Properties and X-ray Diffraction Data for Some Inorganic Fluoride and Chloride Compounds," ORNL-2192, October 23, 1956.
 7. Personal communication.

Table 1

X-ray and Optical Properties of Delta Forms of
UF₄ and ThF₄ Compounds with Alkali Fluorides

<u>Compound</u>	<u>X-ray Data</u>	<u>Optical Properties</u>
2NaF·ThF ₄	Hexagonal a ₁ = 6.14 ± 0.01 Å ^a a ₃ = 7.36 ± 0.02 Å ^a	Uniaxial -, low birefringence N _{av.} = 1.468
2NaF·UF ₄	Hexagonal ^{ob} a ₁ = 6.11 Å ^a a ₃ = 7.25 Å ^a	Uniaxial -, N _ω = 1.495, N _ε = 1.490
2RbF·UF ₄	Hexagonal ^c	Biaxial +, Optic angle 70° N _α = 1.473, N _γ = 1.487
2RbF·ThF ₄	Hexagonal ^c	Uniaxial +, N _ω = 1.468, N _ε = 1.494
NaF·KF·UF ₄		Uniaxial -, low birefringence N _{av.} = 1.47
NaF·RbF·UF ₄		Uniaxial +, N _ω = 1.484, N _ε = 1.486

^a W. H. Zachariasen, "Double Fluorides of Potassium or Sodium with Uranium, Thorium, or Lanthanum," J. Am. Chem. Soc., 70 [6] 2147-51 (1948).

^b P. A. Agron, B. S. Borie, and R. M. Steele, Oak Ridge National Laboratory, unpublished work.

^c L. A. Harris, personal communication.

II. ORNL studies have shown that the systems LiF-ThF_4 and NaF-ThF_4 contain the compounds $7\text{LiF}\cdot 6\text{ThF}_4$ and $7\text{NaF}\cdot 6\text{ThF}_4$.⁸ The occurrence of these 7:6 compounds in alkali fluoride-thorium tetrafluoride systems as well as in alkali fluoride-uranium tetrafluoride, -zirconium tetrafluoride, and -hafnium tetrafluoride systems has made possible predictions regarding the probability of occurrence of the 7:6 compound in a given system. One could expect each of the thorium tetrafluoride systems, KF-ThF_4 and RbF-ThF_4 , to contain a 7:6 compound. Published phase diagrams of these two systems^{9,10,11} show the occurrence of a 1:1 compound, $\text{KF}\cdot\text{ThF}_4$ and $\text{RbF}\cdot\text{ThF}_4$, but not a 7:6 compound. Thermal analysis melts were made at the Oak Ridge National Laboratory to examine the possibility that these 1:1 compounds had been misidentified. Slowly cooled melts of the compositions 53.8 KF -46.2 ThF_4 (mole %) and 53.8 RbF -46.2 ThF_4 (mole %) each produce a single thermal effect on cooling, and single phase material in the cooled melt. Results of thermal gradient quenching have shown that the compounds melt congruently at the compound compositions $7\text{KF}\cdot 6\text{ThF}_4$ and $7\text{RbF}\cdot 6\text{ThF}_4$. Table 2 shows the properties of several of the alkali fluoride-thorium tetrafluoride 7:6 compounds.

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8. R. E. Thoma, et.al., "Phase Equilibria in the Fused Salt Systems LiF-ThF_4 and NaF-ThF_4 ," Paper given at the 134th Annual Meeting of the American Chemical Society, Chicago, Illinois, September 7-12, 1958.
 9. W. J. Asker, E. R. Segnit, and A. W. Wylie, "The Potassium Thorium Fluorides," J. Chem. Soc., p. 4470-79, November 1952.
 10. V. S. Emelyanov and A. I. Evstyukhin, "An Investigation of Fused-Salt Systems Based on Thorium Tetrafluoride," J. Nuclear Energy, Vol. 5, pp. 108-114, Pergamon Press Ltd., London.
 11. E. P. Dergunov and A. G. Bergman, Doklady Akad. Nauk S.S.S.R. 60, 391-4 (1948).

Table 2

Properties of the Alkali Fluoride-Thorium Tetrafluoride 7:6 Compounds

<u>Compound</u>	<u>Melting Relations</u>	<u>Melting Temperature (°C)</u>	<u>Crystal Data</u>	<u>Optical Properties</u>
7LiF·6ThF ₄	Melts incongruently to LiF·2ThF ₄ and liquid	597 ± 3	Tetragonal ^a	Uniaxial +, N _ω = 1.502 ± 0.002, N _ε = 1.508 ± 0.002
7NaF·6ThF ₄	Metastable	—	Rhombohedral ^b	Uniaxial -, N _ω = 1.475 ± 0.002, N _ε = 1.468 ± 0.002
7KF·6ThF ₄	Melts congruently	899 ± 2 ^c	Rhombohedral ^b	Uniaxial -, N _ω = 1.474 ± 0.002, N _ε = 1.470 ± 0.002
7RbF·6ThF ₄	Melts congruently	828 ± 4 ^d	Rhombohedral ^b	Uniaxial -, N _ω = 1.486 ± 0.002, N _ε = 1.482 ± 0.002

^a L. A. Harris, unpublished work.

^b By comparison of the X-ray diffraction data for this compound with the spacings for 7NaF·6UF₄, 7KF·6UF₄, etc.

^c Asker, Segnit and Wylie report the congruent melting point for KF·ThF₄ to be 905°C. Emelyanov and Evstyukhin report the congruent melting point for KF·ThF₄ to be 893°C.

^d Dergunov and Bergman report the congruent melting point for RbF·6ThF₄ to be 828 ± 4°C.

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