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(27) Abbreviations: HMP = hematoporphyrin, $TPPS_4$ = tetraphenylporphyrinsulfonate, TPP = tetraphenylporphyrin, TPyP = tetrapyridylporphyrin.

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Lower Valence Fluorides of Vanadium. 3. Structures of the Pseudohexagonal A_xVF_3 Phases (Where A = K, Rb, Tl, or Cs)

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Hexagonal tungsten bronze like A_xVF_3 compounds (A = K, Rb, Tl, or Cs) were prepared and their structures studied by using polarized microscopy and X-ray diffraction techniques. Superlattice reflections were observed on Debye–Scherrer films which made the *a* dimensions of A_xVF_3 twice those of A_xWO_3. Relative intensities of these reflections suggest ordering of A^+ ions in partially filled sites. Weissenberg and Guinier–Hägg photographs revealed that K_xVF_3, Rb_xVF_3, and Tl_xVF_3 are distorted slightly from hexagonal and are orthorhombic. The distortion ratio $|a|/3^{1/2}|b|$ demonstrates the magnitude and direction of the distortion, and for lower values of x, it is approximately 1.005. For samples of composition $Rb_{0.32}VF_3$ and $Tl_{0.30}VF_3$ (x is near its maximum theoretical value $^1/_3$), the direction of the distortion is reversed, and the distortion ratios found were 0.996 and 0.991, respectively. Typical lattice constants: for $K_{0.25}VF_3$ a = 12.895, b = 7.398, and c = 7.533 Å; for $Rb_{0.25}VF_3$ a = 12.904, b = 7.411, and c 7.550 Å; for $Tl_{0.25}VF_3$ a = 12.928, b = 7.427, and c = 7.563 Å; for $Rb_{0.32}VF_3$ a = 12.874, b = 7.464, and c = 7.567 Å; for $Tl_{0.30}VF_3$ a = 12.841, b = 7.479, and c = 7.572 Å. These orthorhombic compounds form domains which are oriented 120° with respect to each other giving a macroscopic effect of hexagonal symmetry. X-ray photographs of Cs_xVF_3 compounds display weak superlattice reflections; however, no distortion from hexagonal symmetry was observed. The lattice constants of this phase increase slightly with x.

Introduction

Hexagonal structures, similar to the Magnêli tungsten bronzes (A_xWO_3),[1] have been reported for first-row transition-metal fluorides of the general formula $A_xM^{II}{}_xM^{III}{}_{1-x}F_3$ (A_xMF_3), where x has the maximum theoretical value of $^1/_3$, A = K, Rb, Cs, or Tl, and M = Fe,[2] Cr,[3] or V.[4] The bronze structure ($P6_3/mcm$) may be described as a rigid lattice of WO_3 units having parallel tunnels of hexagonal cross section. These tunnels provide sites for the monovalent ion whose size and relative number affect crystallographic dimensions.

In the bronze structures, there is not only the atomic ordering of the parent WO_3 lattice but also the possibility of ordering within tunnels. The latter offers an explanation for the superlattices observed in tetragonal bronze structures by early investigators.[5] More recently, ordering within tunnels has been substantiated by lattice-imaging electron microscopy in both hexagonal and tetragonal tungsten bronzes. Hexagonal K_xWO_3,[6] studied by this technique, revealed clusters of empty tunnels which appeared randomized with no apparent long-range ordering. This qualifies the system as being truly nonstoichiometric. Atomic ordering in the tetragonal bronze-like region of the Nb_2O_5–WO_3[7-9] system consists of empty or filled pentagonal tunnels which exhibit two-dimensional ordering in a variety of patterns. Resultant phases of different stoichiometry possess characteristic superlattices and in some instances give rise to domain structures.

Neither superstructures nor domains have been previously reported for materials having hexagonal tungsten bronze like structures. Both have been found in the A_xVF_3 systems. This paper reports these structures from X-ray diffraction results aided by polarized microscopy.

Experimental Section

Sample preparation consisted of vacuum encapsulating appropriate quantities of thoroughly mixed alkali fluoride, VF_2, and VF_3 inside 0.64-cm diameter by 3.2-cm long Mo capsules by using electron-beam welding techniques. VF_2 and VF_3 were prepared from 99.9% V metal, as previously described by Stout and Boo.[10] Optical grade KF, RbF, and CsF were obtained commercially along with 99.9% TlF. All handling and transferring of starting materials were carried out inside an inert-atmosphere glovebox. The sealed capsules were fired in a vacuum furnace at 800 °C. Formation of the hexagonal-like phases was found to be complete in 30 h, but to ensure equilibrium, all samples were heated for 30 days. Weight checks were made on capsules following each step of the procedure.

Products were examined by stereoscopic and polarized microscopy. Limiting values of x in the A_xVF_3 phases were determined from two-phase samples (except in the case of $K_{0.27}VF_3$ where a trace of a third phase was present and in $Tl_{0.30}VF_3$ where considerable oxidation–reduction occurred between Tl^+ and V^{2+}). When possible, these phases were separated by Pasteur's method and their compositions determined by chemical analyses. When phases could not be satisfactorily separated, compositions were estimated from relative amounts of phases present as observed by optical microscopy or measured by X-ray powder methods. Pseudohexagonal symmetry of $K_{0.25}VF_3$ was determined from Weissenberg photographs by using Cu Kα and Fe Kα radiation in conjunction with Guinier–Hägg results. Guinier–Hägg data were taken with Cu Kα_1 and Cr Kα_1 radiation and refined by least squares. Elemental analyses of products were obtained commercially.

Results

Hexagonal-like A_xVF_3 phases were studied in which x had minimum, intermediate, and maximum values. Sample compositions prepared and products formed are given in Table I. Tiny needle-shaped crystals were obtained from $K_{0.25}VF_3$.

Polarized Microscopy. The hexagonal-like A_xVF_3 phases were formed in every sample and were easily identified by polarized microscopy. They are optically dense and their transmitted color is brownish red. When viewed between crossed nicols, they appear weakly birefringent. By contrast, both tetragonal and orthorhombic phases of the KF–VF_2–VF_3 system (previously described in this series[11]) are less optically dense, brighter red, and moderately birefringent. Transmitted colors of the modified pyrochlores $Rb_{0.50}VF_3$ and $Cs_{0.50}VF_3$ are also brighter red but are optically dense and weakly birefringent.

X-ray Diffraction. K_xVF_3. Laue symmetry $6mm$ was exhibited by low-angle reflections on ($hkin$) Weissenberg photographs of $K_{0.25}VF_3$ single crystals. Low-angle reflections on even-layer films (n = 0, 2, or 4) resembled those of hexagonal tungsten bronzes;[1] however, weak reflections found on odd-layer films (n = 1 or 3) doubled the a dimension.

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Table I. A_xVF_3 Samples

sample designation	rel moles of reactants			products
	KF	VF_2	VF_3	
A-K167VF3	0.167	0.167	0.833	VF_3 and pseudohexagonal $K_{0.19}VF_3$
A-K250VF3	0.250	0.250	0.750	pseudohexagonal $K_{0.25}VF_3$
A-K333VF3	0.333	0.333	0.667	pseudohexagonal $K_{0.27}VF_3$, tetragonal $K_{0.45}VF_3$, and a trace of orthorhombic $K_{0.39}VF_3$
	RbF	VF_2	VF_3	
A-RB167VF3	0.167	0.167	0.833	VF_3 and pseudohexagonal $Rb_{0.19}VF_3$
A-RB250VF3	0.250	0.250	0.750	pseudohexagonal $Rb_{0.25}VF_3$
A-RB333VF3	0.333	0.333	0.667	pseudohexagonal $Rb_{0.32}VF_3$, and orthorhombic $Rb_{0.5}VF_3$
	CsF	VF_2	VF_3	
A-CS167VF3	0.167	0.167	0.833	VF_3 and hexagonal $Cs_{0.19}VF_3$
A-CS250VF3	0.250	0.250	0.750	hexagonal $Cs_{0.25}VF_3$
A-CS333VF3	0.333	0.333	0.667	hexagonal $Cs_{0.31}VF_3$, and tetragonal $Cs_{0.5}VF_3$
	TlF	VF_2	VF_3	
A-TL167VF3	0.166	0.166	0.833	VF_3 and pseudohexagonal $Tl_{0.20}VF_3$
A-TL250VF3	0.250	0.250	0.750	pseudohexagonal $Tl_{0.25}VF_3$
A-TL333VF3	0.333	0.333	0.667	pseudohexagonal $Tl_{0.30}VF_3$, Tl metal, and a trace of another phase

Furthermore, high-angle reflections on these films were peculiarly split. Many reflections which appeared as four equally spaced spots with Cu $K\alpha$ radiation were in fact seen to be a composite of six overlapping reflections (three sets of $K\alpha_1$–$K\alpha_2$) when Fe $K\alpha$ radiation was used. Other reflections were seen as doublets (two sets of $K\alpha_1$–$K\alpha_2$ reflections) and some as singlets. On even-layer films, except for a few very weak low-angle spots, only reflections having h and k even were observed. On these films doublets were observed for $(h\bar{h}0l)$ and $(hh\bar{2}hl)$, but other high-angle reflections appeared as triplets. On odd-layer films (i.e., $l = 1$ or 3) we observed similar doublets or triplets if h and k were both even but singlets if h, k, or both were odd. On $(nkil)$ Weissenberg photographs, $(000l)$ reflections showed no multiple splittings. The reflecting condition, $000l$ where $l = 2n$, was also noted. Tiny crystals, which displayed no twinning when viewed with polarized light, showed the same splitting of reflections on Weissenberg photographs.

All low-angle reflections from Debye–Scherrer photographs of $K_{0.19}VF_3$, $K_{0.25}VF_3$, and $K_{0.27}VF_3$ were indexed as hexagonal. The existence of one apparent superlattice reflection $(21\bar{3}3)$, which became weaker in intensity as x increased, showed the a dimension to be twice that of hexagonal potassium tungsten bronze.

Guinier–Hägg photographs of K_xVF_3 samples showed many doublet reflections with relative intensities in the ratio 2:1 or 1:2. Specifically, reflections indexed as hexagonal $(h\bar{h}0l)$ were doublets of relative intensity 1:2, and reflections indexed as hexagonal $(hh\bar{2}hl)$ were split into doublets of relative intensity 2:1. Other reflections were singlets or unresolvable triplets. These results indicate quite clearly that the hexagonal unit cell is distorted (or has collapsed) to orthorhombic symmetry. A measure of this distortion and its direction is easily seen from the ratio $|a|/3^{1/2}|b|$. The distortion ratios for $K_{0.19}VF_3$, $K_{0.25}VF_3$, and $K_{0.27}VF_3$ are 1.007, 1.006, and 1.006, respectively.

Rb_xVF_3 and Tl_xVF_3. Low-angle Debye–Scherrer X-ray powder data of $Rb_{0.19}VF_3$, $Rb_{0.25}VF_3$, $Rb_{0.32}VF_3$, $Tl_{0.20}VF_3$, $Tl_{0.25}VF_3$, and $Tl_{0.30}VF_3$ were indexed as hexagonal with approximately the same dimensions as K_xVF_3. Superlattice reflections observed on films of $Rb_{0.19}VF_3$ were $(21\bar{3}3)$, $(11\bar{2}1)$, $(21\bar{3}1)$, $(32\bar{5}1)$, $(30\bar{3}3)$, and $(52\bar{7}1)$. These same reflections were present on photographs of $Rb_{0.25}VF_3$ but with weaker relative intensities and were not observed at all on those of $Rb_{0.32}VF_3$. Debye–Scherrer photographs of $Tl_{0.20}VF_3$ displayed all of the superlattice reflections observed for $Rb_{0.19}VF_3$ and $Rb_{0.25}VF_3$ plus $(51\bar{6}1)$, $(61\bar{7}1)$, and $(61\bar{7}3)$. Most of these lines were manifested on films of $Tl_{0.25}VF_3$, but relative intensities were weaker and, again, none occurred for $Tl_{0.30}VF_3$.

Guinier–Hägg photographs of Rb_xVF_3 and Tl_xVF_3 were similar to those of K_xVF_3, indicating they also have pseudohexagonal structures which have been distorted slightly to orthorhombic. The distortion ratios of $Rb_{0.19}VF_3$, $Rb_{0.25}VF_3$, $Tl_{0.20}VF_3$, and $Tl_{0.25}VF_3$ are 1.005, 1.005, 1.006, and 1.005, respectively. The distortion ratios for $Rb_{0.32}VF_3$ and $Tl_{0.30}VF_3$, however, are 0.996 and 0.991, respectively.

Guinier–Hägg photographs taken with Cr $K\alpha_1$ radiation displayed additional lines not seen on Debye–Scherrer films which would be interpreted as superlattice reflections when indexed as hexagonal. When indexed as orthorhombic, these are the (101), (011), (211), (301), (411), (031), (213), (303), and (431) reflections. Most of these reflections were seen on films of $K_{0.19}VF_3$, $K_{0.25}VF_3$, $K_{0.27}VF_3$, $Rb_{0.19}VF_3$, $Rb_{0.25}VF_3$, $Tl_{0.20}VF_3$, and $Tl_{0.25}VF_3$, but on photographs of $Rb_{0.32}VF_3$ and $Tl_{0.30}VF_3$ only a few of them were observed and were an order of magnitude weaker in intensity.

Cs_xVF_3. All lines on Debye–Scherrer X-ray films of hexagonal Cs_xVF_3 samples were easily identified as no multiple reflections were present. Unique reflections were observed for $Cs_{0.19}VF_3$ which could be fitted to a hexagonal or orthorhombic unit cell of the same approximate dimensions as those of K_xVF_3, Rb_xVF_3, and Tl_xVF_3. These superlattice reflections, although much weaker in intensity, are the same series of lines seen in the other three systems. Although none of these reflections were seen on Debye–Scherrer photographs of $Cs_{0.25}VF_3$ or $Cs_{0.31}VF_3$, Guinier–Hägg Cr $K\alpha_1$ films confirmed their presence as extremely weak lines. Table II summarizes the structures and lattice constants of the A_xVF_3 compounds.

Discussion

Phases of K_xVF_3, Rb_xVF_3, and Cs_xVF_3 ($x \approx 0.25$) were previously reported by Cros et al.[4] as hexagonal. The ranges of x found in this laboratory are consistent with their findings except for K_xVF_3. The Tl_xVF_3 phase was not previously reported.

Magnéli[1] found the space group for the hexagonal A_xWO_3 compounds to be $P6_3/mcm$-D_{6h}^3, the only general requirement for which is $h\bar{h}0l$ where $l = 2n$. Although the A_xVF_3 compounds appeared similar to the bronzes, their structures are actually quite different. The potassium, rubidium, and thallium fluorides were found to be pseudohexagonal, and all

Table II. Lattice Constants of A_xVF_3 Compounds[a]

compd	a	b	c	$a/3^{1/2}\|b\|$
$K_{0.19}VF_3$	12.881	7.387	7.528	1.007
$K_{0.25}VF_3$	12.895	7.398	7.533	1.006
$K_{0.27}VF_3$	12.891	7.396	7.527	1.006
$Rb_{0.19}VF_3$	12.913	7.415	7.558	1.005
$Rb_{0.25}VF_3$	12.904	7.411	7.550	1.005
$Rb_{0.32}VF_3$	12.874	7.464	7.567	0.996
$Tl_{0.20}VF_3$	12.924	7.420	7.565	1.006
$Tl_{0.25}VF_3$	12.928	7.427	7.563	1.005
$Tl_{0.30}VF_3$	12.841	7.479	7.572	0.991
$Cs_{0.19}VF_3$	14.956		7.624	
$Cs_{0.25}VF_3$	14.994		7.646	
$Cs_{0.31}VF_3$	15.020		7.680	

[a] All parameters are ±0.005 Å.

of the A_xVF_3 compounds exhibit the $(2\bar{2}03)$ and other $(h\bar{h}0l)$ reflections when indexed as hexagonal. This eliminates the Magnéli space group as being correct for these systems.

Weissenberg photographs of single crystals of $K_{0.25}VF_3$ display hexagonal symmetry; however, the relative intensities, shapes, and modes of overlap of the diffraction spots for high Bragg angles, combined with the knowledge that the unit cell is orthorhombic, indicate that trilling exists at the microscopic level. This is better described as a domain structure in which orthorhombic domains are oriented at 120° to each other giving the macroscopic effect of hexagonal symmetry. It is likely that at the temperatures which they were formed (800 °C), the A_xVF_3 compounds are truly hexagonal, but at lower temperatures, either atomic ordering or a collapse of the VF_3 network, or both, occurs causing a lowering of crystal symmetry. The fact that at least two kinds of distortion exist (and these depend on composition) is significant. The data suggest rather strongly that atomic ordering of A^+ ions occurs in those compounds having a distortion ratio greater than unity. In $K_{0.19}VF_3$, $K_{0.25}VF_3$, $K_{0.27}VF_3$, $Rb_{0.19}VF_3$, $Rb_{0.25}VF_3$, $Tl_{0.20}VF_3$, and $Tl_{0.25}VF_3$, x is considerably smaller than the maximum value 0.33, making possible the ordering of partially filled A^+ sites. Superlattice reflections increase in number and intensity as A increases in atomic number. Furthermore, as x decreases within a series, the intensities of superlattice reflections increase while the distortion ratio remains approximately constant. These effects are not satisfactorily explained as simply a collapse of the VF_3 parent lattice or by anion displacement. They are consistent, however, with what would be expected for ordering of partially filled A^+ sites.

In the case of Cs_xVF_3 compounds, one would expect atomic ordering of partially filled Cs^+ sites to be restricted by the size of the Cs^+ ion. The distortion or collapse of the VF_3 network would also be withstood by the Cs^+ ions because of their larger size. Superlattice reflections were observed in $Cs_{0.19}VF_3$, suggesting some ordering of partially filled Cs^+ sites. These weak X-ray reflections did not fit a Cs_xWO_3-size unit cell but could be indexed as hexagonal by doubling a or as orthorhombic by letting $|a|(\text{ortho}) = 3^{1/2}|b|(\text{ortho}) = 3^{1/2}|a|(\text{hex})$. The evidence of Cs_xVF_3 being orthorhombic is not conclusive as the parent lattice appears to retain hexagonal symmetry over the entire composition range.

Structural properties of the hexagonal bronze-like materials, A_xVF_3, are probably representative of a large number of mixed-valence compounds. It is expected that physical properties of these compounds will reflect structural phenomena. Additional studies of these materials are in progress which include neutron diffraction, magnetic susceptibilities, high-resolution electron microscopy, and low-temperature thermal measurements.

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Registry No. Potassium vanadium fluoride, 55957-20-5; rubidium vanadium fluoride, 63774-72-1; thallium vanadium fluoride, 66792-15-2; cesium vanadium fluoride, 63774-59-4.

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