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Lower Valence Fluorides of Vanadium. 2. Characterization of the Tetragonal Phase K_xVF_3

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The tetragonal phase K_xVF_3 was found to range from $x = 0.450$ to 0.558. A new orthorhombic phase of approximate composition $K_{0.39}VF_3$, with lattice constants $a = 18.34 \pm 0.04$ Å, $b = 22.19 \pm 0.04$ Å, and $c = 7.742 \pm 0.016$ Å, was found which belongs to the unique space group $C222_1$. Single tetragonal crystals of composition $x = 0.558$ displayed a superlattice structure of dimensions, a(superlattice) = $2(2^{1/2})a$(sublattice), and c(superlattice) = $2c$(sublattice). With the exception of the hexagonal phase, the K_xVF_3 layer structures obey the empirical relationship, $c' = 0.628 \log x + 4.131$, where c' is the distance between layers. The tetragonal phase orders antiferromagnetically with $T_N \approx 45$ K, independent of x. The magnetic susceptibility indicates that the ordered state increases in ferrimagnetic behavior as x decreases.

Introduction

Crystal structures in which both divalent and trivalent first transition metal ions are found in fluoride octahedra include perovskite related compounds having the general formula $K_xM^{II}_xM^{III}_{1-x}F_3$, where x is between 0 and 1. These compounds, which are similar to the Magnéli potassium tungsten bronzes,[1] include a tetragonal phase with space group $P4/mbm$[2] in which x theoretically varies from 0.4 to 0.6. The tetragonal phase has been reported to exist in the KF–FeF_2–FeF_3[3] and KF–VF_2–VF_3[4,5] ternary phase systems. The phase has also been reported for heteroatomic mixed valence systems such as $KMnCrF_6$.[6]

We have characterized the tetragonal phase, $K_xV^{II}_xV^{III}_{1-x}F_3$ (K_xVF_3), to extend investigations of cooperative magnetic phenomena of lower valence vanadium fluorides. Magnetic properties of mixed valence fluorides of V(II) and V(III) have not been previously reported and the tetragonal phase offers the additional feature of varying the ratio V(II):V(III) within the same crystal lattice network. This not only presents interesting possibilities for studying magnetic properties which vary with composition but other structural anomalies as well.

Experimental Section

Samples consisted of stoichiometric mixtures of KF, VF_2, and VF_3 thoroughly mixed and vacuum encapsulated inside 0.64 cm diameter by 3.2 cm long Mo capsules by means of electron beam welding techniques. The VF_2 and VF_3 were prepared in this laboratory and optical grade KF was obtained commercially. All handling and transferring of reacting materials was carried out inside an inert atmosphere glove box. Multiphase samples were separated by Pasteur's method under a stereoscopic microscope. Products were analyzed by polarized microscopy and Debye–Scherrer x-ray powder techniques using Cu Kα radiation. Single-crystal specimens, when available, were studied by Weissenberg techniques and x-ray cylindrical camera rotation photographs to confirm or determine space groups, to correctly identify back reflection x-ray powder lines, and to check for superlattice structures. Magnetic susceptibilities of randomly oriented powder samples were measured from 4.2 to 300 K at 11 000 G using a PAR vibrating sample magnetometer equipped with a liquid helium dewar and gallium arsenide temperature controller and thermometer.

Results

The range of x for the tetragonal phase K_xVF_3 was determined to be 0.450 to 0.558. The composition having the maximum value of x existed in equilibrium with KVF_3 at 800 K. The tetragonal phase of this composition formed small single crystals with a preferred growth direction along their c axes. The composition having the minimum value of x was formed in the presence of two other phases. These were identified as: (1) a hexagonal phase of approximate composition $K_{0.25}VF_3$, related to the hexagonal Magnéli tungsten bronze Rb_xWO_3,[7] and (2) an orthorhombic phase of approximate composition $K_{0.39}VF_3$, consisting of elongated plates formed from the vapor phase. The lattice constants of the K_xVF_3 compounds are summarized in Table I.

Table I. Lattice Constants of K_xVF_3 Compounds

Compd	Crystal system	Lattice constants, Å
KVF_3	Cubic	$a = 4.131 \pm 0.004$
$K_{0.558}VF_3$	Tetragonal	$a = 12.705 \pm 0.013$
		$c = 3.973 \pm 0.004$
$K_{0.498}VF_3$	Tetragonal	$a = 12.651 \pm 0.013$
		$c = 3.942 \pm 0.004$
$K_{0.450}VF_3$	Tetragonal	$a = 12.595 \pm 0.013$
		$c = 3.912 \pm 0.004$
$K_{0.39}VF_3$	Orthorhombic	$a = 18.34 \pm 0.04$
		$b = 22.19 \pm 0.04$
		$c = 7.742 \pm 0.016$
$K_{0.25}VF_3$	Hexagonal	$a = 7.43 \pm 0.02$
		$c = 7.534 \pm 0.008$

Table II. Superlattice Reflections of Tetragonal $K_{0.558}VF_3$ Single Crystals from Cylindrical Camera Rotation Photographs

d obsd	I obsd	hkl	d calcd
		First–Layer Reflections	
3.04	W^{-5}	11,0,1	3.02
2.40	W^{-5}	14,3,1; 13,6,1	2.39
2.32	W^{-1}	14,5,1	2.31
2.26	W^{-4}	14,6,1	2.26
2.13	W^{-5}	16,3,1	2.13
2.03	W^{-4}	17,3,1	2.01
		Third–Layer Reflections	
2.48	W^{-1}	4,3,3; 5,0,3	2.48
2.46	W	5,2,3	2.46
2.33	W^{-2}	7,2,3	2.33
1.83	W^{-4}	14,2,3; 10,10,3	1.83

Long-exposure, x-ray, cylindrical-camera photographs of tetragonal $K_{0.558}VF_3$ single crystals rotated about their c axes revealed very weak reflections of intermediate layers. This was indicative of a superlattice in which the c dimension was doubled. Although tetragonal symmetry of the superlattice was confirmed from Weissenberg photographs, reflections of these films were too few and too weak to reliably determine their identities. Hence, they were identified by d values calculated from the rotation photographs using the relationship:

$$d = \frac{\lambda}{2 \sin \{1/2 \operatorname{arc\,cos} [r \cos (\Delta_i/2r)/(r^2 + s_i^2)^{1/2}]\}}$$

where λ = the wavelength of x radiation, r = the radius of the cylindrical camera, Δ_i = the distance measured across the center of the film to repeat reflections, and s_i = the distance from the zero layer to the ith layer. These d values, which are from the first and third layer reflections, and their relative intensities are given in Table II. Dimensions of the superlattice were established as: a(superlattice) = $2(2^{1/2})a$(sublattice), and c(superlattice) = $2c$(sublattice). The assigned Miller indicies and calculated d values are also given in Table II.

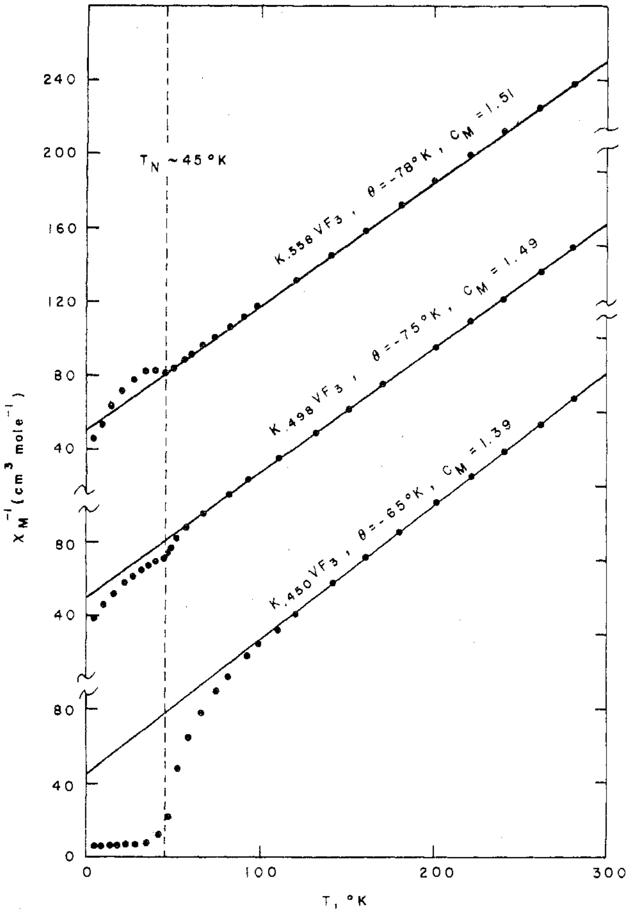

Figure 1. Inverse molar susceptibilities of tetragonal K_xVF_3 from 4.2 to 300 K for $x = 0.450$, 0.498, and 0.558.

X-ray cylindrical camera photographs of the orthorhombic phase single crystals rotated about their long axes revealed that it was also a layer structure similar to the hexagonal and tetragonal phases. The elongated direction was defined as the *c* axis because it was found to be perpendicular to the layers. Weissenberg photographs further revealed the structure to be base centered, belonging to the unique space group $C222_1$ (or being consistent with the assignment of lattice constants, $B22_12$). The values of d_{obsd} and I_{obsd} vs. d_{calcd} from powder x-ray data of the orthorhombic phase are shown in Table III.

The magnetic susceptibility of the tetragonal phase from 4.2 to 300 K was measured on samples of composition $x = 0.450$, 0.498, and 0.558. Plots of χ_M^{-1} vs. T are shown in Figure 1.

Discussion

The tetragonal phase, K_xVF_3, has many interesting features. The fact that the lattice constants of this phase are composition dependent offers a convenient method of quick identification. It is strange that the values of x in K_xVF_3 do not extend to the theoretical limits of 0.4 and 0.6. The limits of x previously reported by Cros et al.[5] to be 0.45 and 0.55 are in good agreement with our results. A further verification of these limits was obtained by comparing the unit cell volumes of tetragonal K_xVF_3 with those reported for tetragonal K_xFeF_3.[3] Although the volumes are not identical for the same value of x, the ionic radii of iron and vanadium are close, and changes in unit cell volumes per change of x are very nearly identical.

A linear relationship was found between the interlayer distance (c') and log x. This empirical rule holds for KVF_3 and the entire composition range of tetragonal K_xVF_3. It appears that it is also true for the orthorhombic phase, but the relationship does not hold true for the hexagonal phase.

Table III. X-Ray Powder Data of Orthorhombic $K_{0.39}VF_3$ ($a = 18.34 \pm 0.04$ Å, $b = 22.19 \pm 0.04$ Å, $c = 7.742 \pm 0.015$ Å)

hkl	d_{obsd}	d_{calcd}	I_{obsd}
020	11.04	11.09	10
200	9.21	9.17	15
220	7.06	7.07	10
230	5.77	5.76	15
410	4.488	4.490	15
430 002	3.877	3.897 3.871	70
440	3.536	3.534	15
260	3.428	3.430	70
232 450	3.205	3.213 3.189	70
600	3.056	3.057	15
610	3.044	3.028	15
270	2.994	2.996	6
412	2.937	2.932	20
460	2.875	2.879	10
432	2.742	2.747	15
062	2.673	2.674	10
442	2.609	2.610	15
262	2.567	2.567	10
303	2.377	2.378	15
191	2.338	2.330	15
810	2.282	2.280	15
490	2.165	2.171	15
840	2.121	2.119	15
004	1.935	1.936	55
870 0,12,0	1.859	1.858 1.849	30
682 2,12,0	1.814	1.814 1.813	6
6,10,0	1.797	1.796	4
4,10,2	1.777	1.775	15
2,11,2	1.756	1.756	6
254 10,4,0	1.741	1.742 1.741	10
4,12,0	1.714	1.715	6
264 872	1.678	1.686 1.675	15
10,1,2	1.653	1.653	15
614 274	1.626	1.631 1.626	15
464	1.605	1.606	4
10,4,2 0,14,0	1.587	1.588 1.585	15
4,12,2	1.567	1.568	6
12,2,0	1.514	1.514	10
874 0,12,4	1.340	1.340 1.337	15
6,10,4	1.318	1.316	15
10,4,4	1.295	1.295	15
14,0,2 14,1,2	1.241	1.241 1.239	4
0,14,4 14,3,2	1.225	1.226 1.224	6
12,2,4	1.195	1.193	4

This is shown in Figure 2 which is a plot of c' vs. (−)log x. The equation for the straight line is $c' = 0.628 \log x + 4.131$.

The superlattice structure of $K_{0.558}VF_3$ is probably a consequence of V(II)–V(III) ionic ordering, and its size is a function of x. No definite conclusions can be drawn, however, since single crystals of other compositions were not available.

The orthorhombic structure appears to be related to those of the hexagonal and tetragonal phases. The single-crystal x-ray data revealed that it is a layer structure which further suggests that it belongs to the K_xVF_3 series. Its composition could not be accurately determined by chemical analysis because of insufficient sample, but the c' vs. (−)log x plot predicts the value of x to be 0.385. An important difference between this structure and the other layer structures is that alternate layers are translated $^1/_2$ the vector distance along the a axis, making it base centered. This translation suggests that the structure may not have channels perpendicular to its

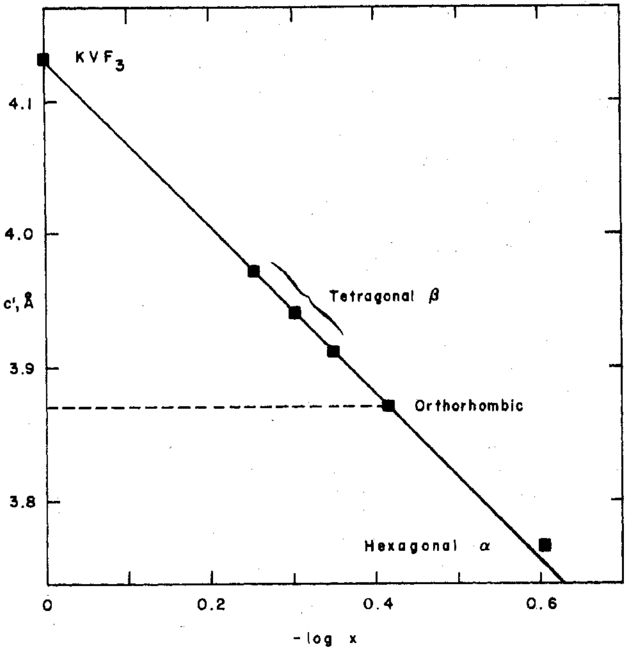

Figure 2. Linear plot of (−)log x vs. interlayer distance c' of K_xVF_3 compounds.

layers, as the hexagonal and tetragonal phases do, and that it is probably a compound of fixed composition.

The magnetic susceptibility measurements of the tetragonal phase indicate that antiferromagnetic ordering occurs at about 45 K. The values of Θ, C_M, and T_N are not very sensitive to composition. The shapes of the χ_M^{-1} vs. T plots, however, show that the nature of the ordering changes significantly with changes in x. From these plots, it appears that as x approaches the theoretical limit of 0.6, the ordering approaches classical antiferromagnetic behavior. In the tetragonal K_xWO_3 structure, space group $P4/mbm$,[2] there are two distinct lattice positions occupied by the smaller cations. These are the 2(c) and 8(j) sites. Buchanan[8] and Banks[6] independently established by Mössbauer that in tetragonal K_xFeF_3, the 2(c) sites are preferentially occupied by Fe(II), whereas, the 8(j) positions are occupied by both Fe(II) and Fe(III). If this condition prevails in K_xVF_3, the magnetic tendencies observed can qualitatively be explained. If the 2(c) sites are only occupied by V(II) ions, as x approaches 0.6, the ratio of V(III):V(II) on 8(j) sites approaches 1. This suggests that in the magnetically ordered state there is antiferromagnetic ordering of V(II) ions within 2(c) sites and of V(II) and V(III) ions within 8(j) sites such that no resultant ferromagnetic moment is observed. As x decreases, however, the tendency toward ferrimagnetic behavior is probably a consequence of the ratio of V(III):V(II) on 8(j) sites increasing toward the maximum possible value of 3 at the theoretical limit of x = 0.4. The fact that T_N does not change significantly with x is a fair indication that the overall ordering mechanism is also independent of x. The possible magnetic structures of these compounds are exciting and the observed effects are almost certain to be field dependent. Further studies are necessary to understand this system completely.

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Registry No. KVF_3, 27498-34-6.

References and Notes

(1) A. Magnéli and B. Blomberg, *Acta Chem. Scand.*, **5**, 372 (1951).
(2) A. Magnéli, *Ark. Kemi*, **1**, 213 (1949).
(3) R. de Pape, *Bull. Soc. Chim. Fr.*, 3489 (1965).
(4) B. J. Garrard, B. M. Wanklyn, and S. H. Smith, *J. Cryst. Growth*, **22**, 169 (1974).
(5) C. Cros, R. Feurer, M. Pouchard, and P. Hagenmuller, *Rev. Chim. Miner.*, **11**, 585 (1974).
(6) E. Banks, O. Berkooz, and J. A. DeLuca, *Mater. Res. Bull.*, **6**, 659 (1971).
(7) A. Magnéli, *Acta Chem. Scand.*, **7**, 315 (1953).
(8) D. N. E. Buchanan, M. Robbins, H. J. Guggenheim, G. K. Wertheim, and V. G. Lambrecht, Jr., *Solid State Commun.*, **9**, 583 (1971).

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Crystal Chemistry of Dealuminized Mordenites

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Unit cell dimensions have been determined for dealuminized NH_4 mordenites having SiO_2/Al_2O_3 ratios of 10–100. The lattice contractions which occur on aluminum removal are strongly anisotropic and nonlinear. An explanation for the differing dependence of the a, b, and c parameters on the SiO_2/Al_2O_3 ratio is proposed in terms of aluminum site distribution within the as-synthesized zeolite, there being three basic types of siting in the mordenite structure. Strong additional effects are observed where ammonium is replaced by sodium or by hydronium ion, effects attributed to the smaller size of these latter species.

Introduction

Mordenite is both a naturally occurring and a synthetic zeolite, with an idealized composition of $Na_8Al_8Si_{40}O_{96}\cdot24H_2O$. Its structure, solved by Meier,[1] is orthorhombic with cell parameters of a = 18.11, b = 20.53, and c = 7.528 Å in the sodium form.[2] The structure is derived from interconnected chains of SiO_4 and AlO_4 tetrahedra whose projection along the c axis is shown in Figure 1. It possesses large, 12-ring pores parallel to [001], linked by 8-ring tortuous channels about [010].

Both naturally occurring and synthetic mordenites vary only slightly in chemical composition. On the basis of x-ray diffraction and elemental analysis data on 35 natural samples, Passaglia reported a range in the $SiO_2/(Al_2O_3 + Fe_2O_3)$ ratio