Synthesis and Crystal Structure of Potassium and Sodium Vanadium Phosphates

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The isomorphic crystal structures of K_2VPO_6 and Na_2VPO_6 were determined from single-crystal X-ray diffraction data. The two compounds crystallize in the monoclinic space group $P2_1/n$ with four formula units per unit cell. For K_2VPO_6, a = 6.863 (2) Å, b = 13.479 (5) Å, c = 7.505 (1) Å, β = 111.02 (1)°, V = 648.0 (3) Å^3, R = 0.046, and R_w = 0.071. For Na_2VPO_6, a = 6.1805 (7) Å, b = 12.436 (1) Å, c = 7.386 (1) Å, β = 107.00 (1)°, V = 542.9 Å^3, R = 0.030, and R_w = 0.046. The compounds may be described as infinite helical chains of vanadium, phosphorous, and oxygen running perpendicular to the 101 plane. Between these chains, there are two crystallographically distinct sites for the alkali cations, but both sites may be described as highly irregular 6-fold coordination. The potassium compound melts at 480 °C, and the sodium compound melts at 466 °C.

Introduction

Previous investigations of the K(I)/V(V)/P(V)/O system[1-5] have suggested compounds of the formulas KV_2PO_8, $K_4V_2P_4O_{17}$, $K_{11}V_3P_4O_{23}$, $K_3V_2PO_9$, K_2VPO_6, $K_6V_2P_2O_{13}$, $K_3V_8PO_{24}$, $K_3V_4P_2O_{14}$, $K_3V_2PO_9$, and $K_{24}V_2P_8O_{37}$. These should not all be regarded as firmly established discrete compounds. For example, the formulas given as $K_6V_2P_2O_{13}$ and $K_{11}V_3P_4O_{23}$ might really be the same phase. A greater tendency for glass formation was observed for the Na(I)/V(V)/P(V)/O system, and only one compound, $Na_{12}V_3P_3O_{21}$, was reported.[2] Structures were not reported for any of these compounds. We have prepared single crystals of K_2VPO_6 and solved its structure. Isostructural Na_2VPO_6 was prepared for the first time.

Experimental Section

Yellow crystals of K_2VPO_6 were prepared by mixing NH_4VO_3 (Matthey Electronics, 99%), $(NH_4)_2HPO_4$ (EM Science, reagent), and KNO_3 (EM Science, reagent) in the molar ratios 1:1:2, respectively. After grinding in an agate mortar, the mixture was placed in a Pt crucible and heated at 50 °C/h to 350 °C and held there for 2 h. The temperature was then raised to 440 °C; after being held, for 1 h, it was allowed to cool to room temperature at a rate of 10 °C/h. The same procedure was used for the sodium compound using $NaNO_3$ (Spectrum Chemical, reagent) in place of the KNO_3. This procedure resulted in a mass of crystals, some of which were well separated from one another. Both compounds readily dissolve in water, but they are stable in air for at least several weeks.

Differential thermal analysis was carried out using a Netzsch STA 409 system. On heating K_2VPO_6 at 5 °C/min, melting commenced at about 480 °C. On cooling K_2VPO_6 at 5 °C/min, crystallization occurred at 352 °C. Melting of Na_2VPO_6 occurred at 466 °C, and recrystallization did not occur when cooling at a rate of 5 °C/min. Both compounds appear to melt congruently. Infrared spectra of the compounds in KBr pellets were obtained on a Nicolet 5PC FTIR spectrometer.

Crystals of dimensions 0.222 × 0.185 × 0.777 mm for K_2VPO_6 and 0.185 × 0.296 × 0.296 mm for Na_2VPO_6 were mounted on glass fibers for collection of single-crystal X-ray diffraction data. Details of the data collection, reduction and refinement are summarized in Tables I and II. The cell dimensions were refined by least-squares refinement of 20 reflections that had been centered on a Rigaku AFC6R diffractometer. The intensities of three standard reflections measured every 300 reflections throughout the data collection exhibited no significant excursions. The structure was solved and refined with programs from the TEXSAN crystallographic software package.[6] The vanadium atoms were located by direct methods using SHELXS.[7] The phosphorous, oxygen, and alkali atoms were found in subsequent analysis of difference electron density maps. The final atomic position and isotropic thermal parameters are given in Tables III and IV. Anisotropic thermal parameters are given in Tables V and VI, and selected interatomic distances and angles are given in Table VII and VIII.

Discussion

The structures of K_2VPO_6 and Na_2VPO_6 are shown in Figures 1 and 2. The structures contain the same helical chains, but the chain nature is not obvious in Figures 1 and 2 because there is such a small chain fragment in the unit cell. However, the chain nature can be appreciated from Figure 3 when considering that every O1, O2, and O3 atom is actually bonded to one phosphorous and one vanadium atom. Thus, an extended chain is formed. The square pyramidal vanadium polyhedra share one edge (O1 and O2) and one corner (O3) with a phosphate tetrahedron leaving two terminal oxygens (O4 and O6) on vanadium and one (O5) on the phosphorous. The bonds to all terminal oxygens are shorter as would be expected. The

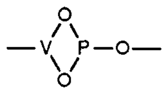

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Table I. Crystal Data and Intensity Collection for K_2VPO_6

empirical formula	K_2VPO_6
formula wt (g/mol)	256.11
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	6.863 (2)
b (Å)	13.479 (5)
c (Å)	7.505 (1)
β (deg)	111.02 (10
V (Å^3)	648.0 (3)
Z	4
diffractometer	Rigaku AFC6R
radiation	Mo Kα (λ = 0.710 69 Å) graphite monochromated
temp (°C)	23
maximum 2θ	70
data collected	$-11 < h < 11, 0 < k < 21, 0 < l < 13$
scan speed (deg/min)	16.0 in ω and 32.0 in 2θ
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2496
data/parameter ratio	27.43
R	0.047
R_w	0.072

Table II. Crystal Data and Intensity Collection for Na_2VPO_6

empirical formula	Na_2VPO_6
formula wt (g/mol)	223.89
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	6.1805 (7)
b (Å)	12.436 (1)
c (Å)	7.386 (1)
β (deg)	107.00 (1)
V (Å^3)	542.9 (1)
Z	4
diffractometer	Rigaku AFC6R
radiation	Mo Kα (λ = 0.710 69 Å) graphite monochromated
temp (°C)	23
max 2θ (deg)	120
data collected	$-9 < h < 9, 0 < k < 20, -11 < l < 11$
scan speed (deg/min)	16.0 in ω and 32.0 in 2θ
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	1447
data/parameter ratio	16.07
R	0.030
R_w	0.045

Table III. Atomic and Isotropic Thermal Parameters for K_2VPO_6

atom[a]	x	y	z	B_{eq} (Å^2)[b]
V	0.29598 (7)	0.20049 (3)	0.90012 (7)	1.25 (1)
P	0.9247 (1)	0.12171 (5)	0.6971 (1)	1.19 (2)
K1	0.3617 (1)	0.13192 (5)	0.4469 (1)	2.15 (2)
K2	0.8050 (1)	0.08066 (5)	0.0893 (1)	2.30 (2)
O1	0.9862 (3)	0.1958 (1)	0.8661 (3)	1.49 (6)
O2	0.1469 (3)	0.1044 (2)	0.6907 (3)	1.54 (6)
O3	0.2801 (4)	0.3283 (2)	0.0117 (3)	1.88 (7)
O4	0.4593 (4)	0.2349 (2)	0.7969 (4)	2.7 (1)
O5	0.8250 (4)	0.0291 (2)	0.7339 (3)	1.90 (7)
O6	0.4230 (4)	0.1281 (2)	0.0763 (3)	2.16 (8)

[a] All atoms occupy site 4e in space group $P2_1/n$. [b] $B_{eq} = (8\pi^2/3)S_iS_jU_{ij}a^*_ia^*_ja_ia_j$.

O–P–O and O–V–O angles involved in the edge sharing of the polyhedra are also small due to the repulsion between the vanadium and the phosphorous atoms (Tables VII and VIII).

Table IV. Atomic and Isotropic Thermal Parameters for Na_2VPO_6

atom[a]	x	y	z	B_{eq} (Å^2)[b]
V	0.28512 (5)	0.21674 (3)	0.8780	0.65 (1)
P	0.90775 (8)	0.11170 (4)	0.69579 (7)	0.63 (2)
Na1	0.3213 (2)	0.13985 (8)	0.4245 (1)	1.5 (3)
Na2	0.8054 (2)	0.07118 (8)	0.0713 (1)	1.72 (3)
O1	0.9514 (3)	0.1977 (1)	0.8554 (2)	0.81 (4)
O2	0.1530 (3)	0.1057 (1)	0.6782 (2)	1.11 (5)
O3	0.2398 (3)	0.3467 (1)	0.0120 (2)	0.96 (5)
O4	0.4428 (3)	0.2732 (1)	0.7609 (3)	1.43 (6)
O5	0.8037 (3)	0.0075 (1)	0.7579 (2)	1.21 (5)
O6	0.4476 (3)	0.1424 (1)	0.0432 (2)	1.48 (6)

[a] All atoms occupy site 4e in space group $P2_1/n$. [b] $B_{eq} = (8\pi^2/3)S_iS_jU_{ij}a^*_ia^*_ja_ia_j$.

Table V. Anisotropic Thermal Parameters ($\times 10^{-4}$ Å) for K_2VPO_6

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	177 (2)	149 (2)	184 (2)	−5 (2)	107 (2)	−8 (2)
P	181 (3)	98 (3)	204 (3)	−7 (2)	104 (3)	1 (2)
K (1)	390 (4)	201 (3)	311 (4)	−122 (3)	231 (3)	−64 (2)
K(2)	322 (4)	239 (3)	396 (4)	70 (3)	228 (3)	60 (3)
O(1)	191 (9)	144 (8)	270 (10)	−8 (7)	134 (8)	−46 (7)
O(2)	195 (9)	193 (9)	233 (9)	−2 (7)	122 (7)	−60 (8)
O(3)	230 (10)	162 (9)	300 (10)	10 (8)	71 (8)	−56 (8)
O(4)	370 (10)	400 (10)	370 (10)	−170 (10)	290 (10)	−120 (10)
O(5)	330 (10)	133 (8)	310 (10)	−66 (8)	170 (10)	−5 (8)
O(6)	300 (10)	280 (10)	260 (10)	100 (10)	120 (10)	36 (9)

Table VI. Anisotropic Thermal Parameters ($\times 10^{-4}$ Å) for Na_2VPO_6

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	65 (2)	85 (2)	96 (2)	−1 (1)	19 (2)	−4 (1)
P	85 (2)	56 (2)	92 (2)	−1 (2)	14 (2)	−1 (2)
Na1	185 (5)	123 (5)	270 (5)	−47 (3)	83 (4)	−9 (4)
Na2	197 (5)	237 (5)	223 (5)	−91 (4)	65 (4)	−12 (4)
O1	88 (6)	103 (6)	119 (7)	0 (5)	34 (5)	38 (5)
O2	199 (6)	172 (8)	149 (7)	−5 (6)	33 (6)	75 (6)
O3	114 (7)	93 (7)	130 (7)	−3 (5)	−7 (5)	28 (5)
O4	156 (7)	216 (8)	203 (8)	39 (7)	100 (6)	7 (7)
O5	204 (7)	84 (7)	155 (7)	39 (6)	28 (6)	−27 (6)
O6	159 (8)	185 (8)	189 (8)	−68 (6)	8 (6)	−47 (6)

The I chains are all parallel to one another, and an array of these chains is shown in Figure 4. As might be expected of an array of parallel chains, the chains tend to be hexagonally close packed. However, several factors necessarily destroy the true hexagonal symmetry. The chain axis itself does not possess symmetry approaching a 6-fold axis. Furthermore, rotation of the chains by 180° perpendicular to the chain axis is not an identity operation. Thus, we may arbitrarily consider that half of the chains are in an up orientation and half are in a down orientation. Figure 4 shows horizontal rows of up-chains alternating with horizontal rows of down-chains. The up-chains are all twisted 180° about their axes relative to the down-chains. The chains are further apart in K_2VPO_6 than in Na_2VPO_6 due to larger size of potassium. The center-to-center distances for chains of the same orientation (i.e., up-up or down-down) are 6.557 and 7.099 Å for Na_2VPO_6 and K_2VPO_6, respectively. The center-to-center distances for chains of opposite orientation are 5.465 and 5.924 Å for Na_2VPO_6 and K_2VPO_6, respectively. Thus, chains of opposite orientation are closer to each other, but all chains are slightly more than eight percent further apart in the potassium compound. The chains are also elongated in K_2VPO_6 relative to Na_2VPO_6. Taking the cation–cation distances along the chain as the indicator of this elongation, one concludes that the elongation is about 3%. Bond distances have not changed significantly, but several of the bond angles have changed significantly. Most of the elongation or compression of the chains can be attributed to a change in the angle centered on the oxygen atom which forms a single bridge between vanadium and phosphorous. This bond angle (V–O3–P) can readily change to compress or expand the chain length. This angle increases by about

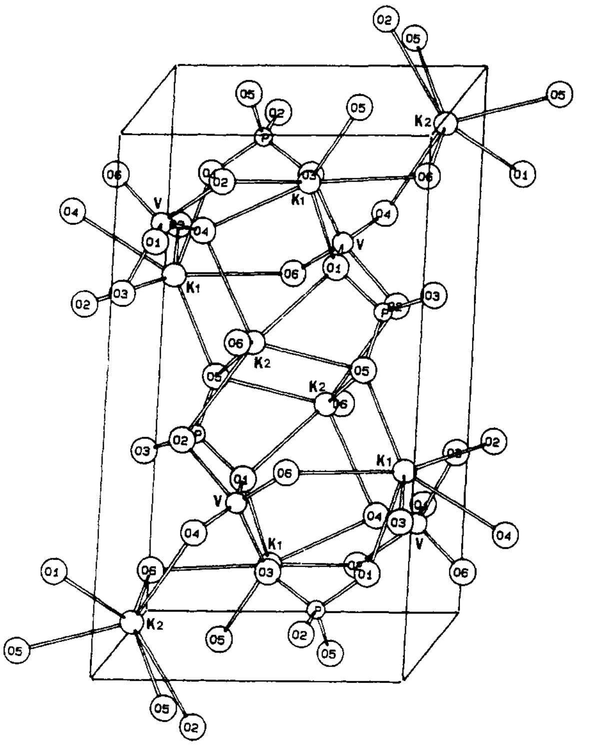

Figure 1. Unit cell of K_2VPO_6 showing complete polyhedra of cations.

Table VII. Bond Distances (Å) and Angles (deg) for K_2VPO_6

V	O6	1.623 (2)	P	O5	1.497 (2)
	O4	1.642 (2)		O3	1.545 (2)
	O3	1.935 (2)		O1	1.549 (2)
	O2	2.010 (2)		O2	1.561 (2)
	O1	2.050 (2)			
K1	O1	2.620 (2)	K2	O6	2.667 (3)
	O5	2.635 (2)		O5	2.806 (3)
	O2	2.756 (2)		O5*	2.825 (3)
	O3	2.788 (3)		O1	2.873 (2)
	O4	2.831 (3)		O4	2.923 (3)
	O6	2.959 (3)		O2	2.944 (2)
	O4*	3.144 (3)			

O3–V–O2	145.1 (1)	O6–V–O2	102.9 (1)
O4–V–O1	143.5 (1)	O3–V–O4	96.1 (1)
O6–V–O1	108.2 (1)	O4–V–O2	93.2 (1)
O6–V–O4	107.2 (2)	O3–V–O1	82.22 (9)
O6–V–O3	106.2 (1)	O1–V–O2	70.62 (9)
O5–P–O2	113.4 (1)	O1–O–O3	110.8 (1)
O5–P–O1	113.3 (1)	O5–P–O3	110.0 (1)
O2–P–O3	110.9 (1)	O2–P–O1	98.0 (1)
O6–K1–O2	155.80 (7)	O4–K1–O3	81.81 (8)
O6–K1–O4	144.54 (8)	O4–K1–O1	77.97 (8)
O4–K1–O5	142.32 (7)	O6–K1–O5	73.04 (7)
O5–K1–O1	138.53 (7)	O6–K1–O3	71.46 (7)
O3–K1–O2	132.32 (8)	O6–K1–O1	68.26 (7)
O2–K1–O1	124.72 (7)	O3–K1–O1	57.89 (7)
O3–K1–O5	121.90 (8)	O4–K1–O2	56.97 (7)
O2–K1–O5	87.37 (7)		
O5*–K2–O6	148.13 (7)	O4–K2–O5*	95.85 (8)
O2–K2–O1	143.11 (6)	O1–K2–O5*	93.01 (7)
O4–K2–O5	125.84 (7)	O4–K2–O6	88.80 (8)
O2–K2–O4	118.38 (7)	O5*–K2–O5	88.55 (8)
O1–K2–O6	118.34 (7)	O4–K2–O1	72.64 (7)
O5–K2–O6	114.03 (8)	O1–K2–O5	53.21 (6)
O2–K2–O5	106.80 (7)	O2–K2–O5*	52.55 (6)
O2–K2–O6	97.72 (7)		

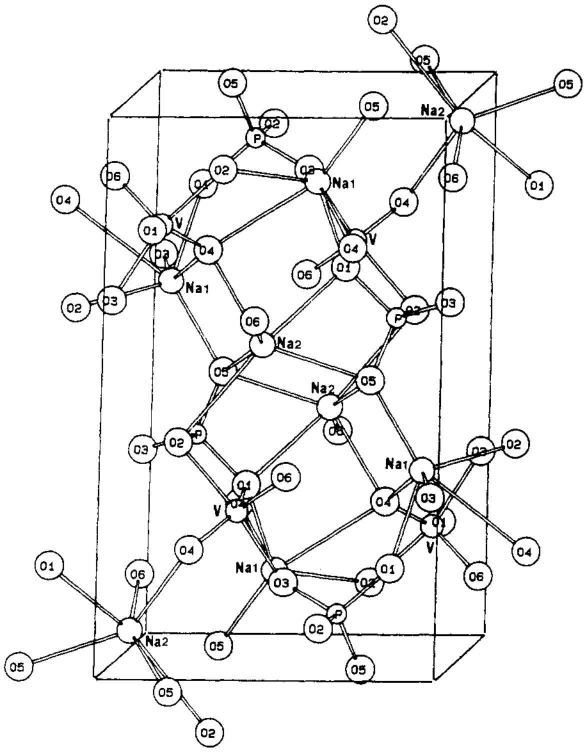

Figure 2. Unit cell of Na_2VPO_6 showing complete polyhedra of cations.

Table VIII. Bond Distances (Å) and Angles (deg) for Na_2VPO_6

V	O6	1.624 (2)	P	O5	1.498 (2)
	O4	1.638 (2)		O3	1.538 (2)
	O3	1.957 (2)		O1	1.556 (2)
	O2	2.011 (2)		O2	1.561 (2)
	O1	2.034 (2)			
Na1	O1	2.287 (2)	Na2	O6	2.3348 (2)
	O5	2.305 (2)		O4	2.394 (2)
	O2	2.432 (2)		O5	2.438 (2)
	O3	2.482 (2)		O5*	2.494 (2)
	O4	2.539 (2)		O1	2.583 (2)
	O4*	2.897 (2)		O2	2.838 (2)
	O6	3.135 (2)			

O2–V–O3	148.23 (6)	O2–V–O6	100.94 (8)
O4–V–O1	138.78 (8)	O4–V–O3	96.23 (7)
O1–V–O6	112.63 (7)	O4–V–O2	94.78 (7)
O4–V–O6	107.95 (9)	O1–V–O3	81.14 (6)
O3–V–O6	103.80 (7)	O1–V–O2	71.06 (6)
O2–P–O5	112.8 (1)	O1–P–O5	111.27 (9)
O3–P–O5	111.65 (9)	O1–P–O3	111.13 (8)
O2–P–O3	111.33 (9)	O1–P–O2	97.95 (8)
O4*–Na1–O5	156.22 (6)	O4–Na1–O2	84.20 (6)
O4–Na1–O3	147.15 (7)	O4–Na1–O5	84.20 (6)
O1–Na1–O5	132.97 (7)	O4–Na1–O1	81.53 (6)
O1–Na1–O2	125.71 (7)	O4*–Na1–O3	75.46 (6)
O2–Na1–O3	117.34 (7)	O4*–Na1–O1	70.48 (6)
O3–Na1–O5	114.94 (7)	O1–Na1–O3	65.84 (6)
O4*–Na1–O5	97.82 (5)	O4*–Na1–O2	60.07 (5)
O2–Na1–O5	96.81 (7)		
O5–Na2–O6	154.73 (7)	O1–Na2–O5	97.38 (6)
O1–Na2–O2	153.32 (6)	O5*–Na2–O6	93.11 (6)
O4–Na2–O5*	133.78 (7)	O4–Na2–O6	84.83 (7)
O5*–Na2–O6	110.66 (7)	O4–Na2–O5	84.62 (7)
O2–Na2–O5*	109.92 (6)	O4–Na2–O1	74.97 (6)
O4–Na2–O2	107.24 (7)	O1–Na2–O5*	59.51 (5)
O2–Na2–O6	104.74 (6)	O2–Na2–O5	57.15 (5)
O1–Na2–O6	101.95 (7)		

seven degrees (124.4° to 131.3°) on going from Na_2VPO_6 to K_2VPO_6.

All the alkali cations in Na_2VPO_6 and K_2VPO_6 might be described as six-coordinated to oxygen. However, the coordination in all cases is highly irregular. Thus, designating a specific coordination number is somewhat arbitrary. It is interesting to note that the six oxygens

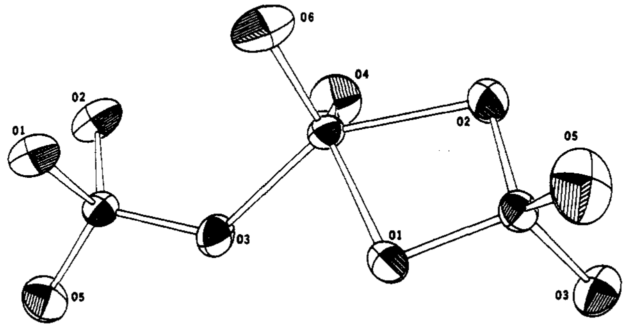

Figure 3. Chain fragment for both K_2VPO_6 and Na_2VPO_6.

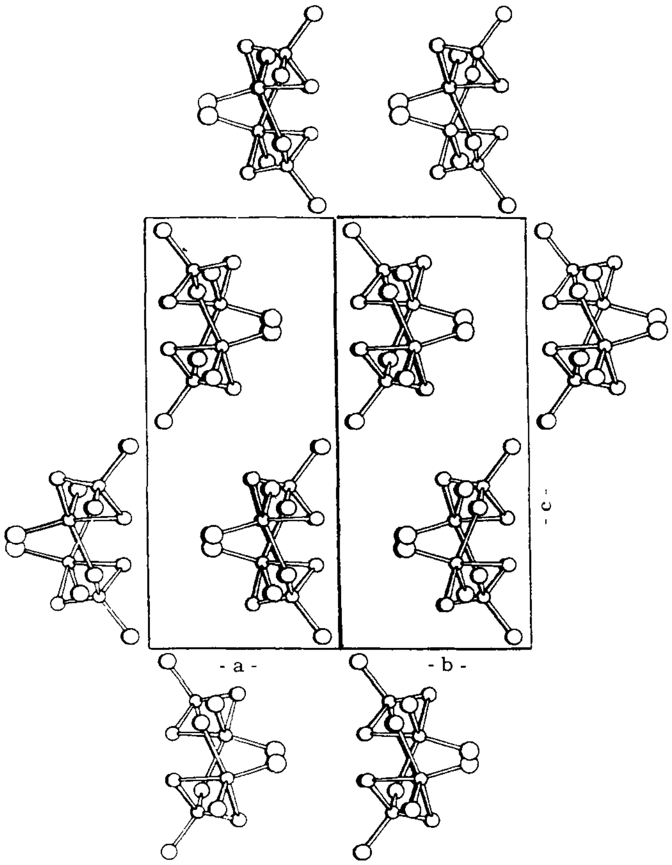

Figure 4. View down the 101 plane of K_2VPO_6 perpendicular to the $-VO_2PO-$ chains. Large circles represent oxygen atoms. Each chain in this projection shows two vanadium atoms near the center of the chain and two phosphorous atoms further out.

closest to Na1 are not the same as the six oxygens closest to K1 (Tables VII and VIII and Figures 1 and 2).

The infrared spectra for Na_2VPO_6, K_2VPO_6, and Li_2VPO_6[8] are shown in Figure 5 with suggested band assignments in Table IX.[9-11] As expected, the spectra for Na_2VPO_6 and K_2VPO_6 are essentially the same because they contain essentially identical I chains. In contrast, the Li_2VPO_6 structure has sheets with octahedrally coordinated vanadium and a substantially different infrared spectrum. Also shown in Figure 5 are the infrared spectra of glasses of the composition Na_2VPO_6 and K_2VPO_6. These spectra are essentially broadened spectra of their crystalline analogs. We can assume that these glasses contain segments of the same chains found in crystalline Na_2VPO_6 and K_2VPO_6.

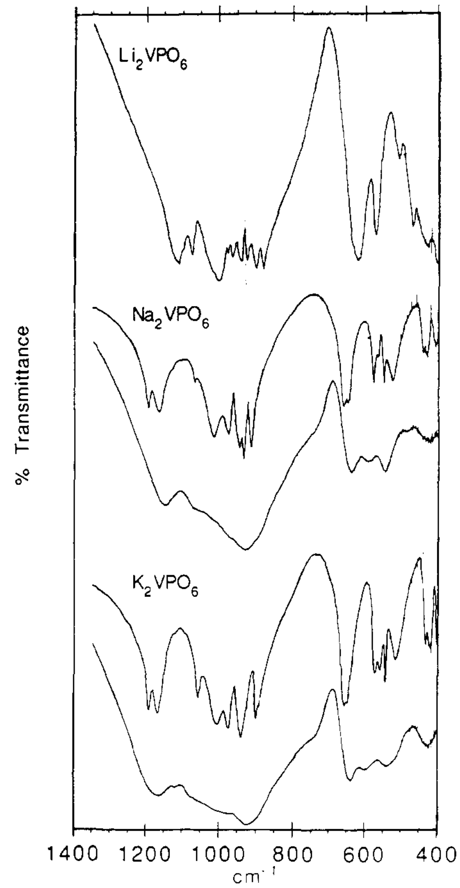

Figure 5. IR spectra of Li_2VPO_6, K_2VPO_6 and Na_2VPO_6. Below the spectra of the crystalline Na and K compounds are the spectra of the glass analogs of the same composition.

Table IX. IR Peak Wavenumbers (cm^{-1}) and Empirical Assignments

K_2VPO_6	Na_2VPO_6	Li_2VPO_6	assignment
1191	1195		ν_{as} P–O
1167	1166	1112	
1057	1067	1075	
1005	1014	1019	
		1002	V=O Stretch
974	975	977	
939	947	967	ν_s P–O Stretch
	934	941	
899	916	926	
892		902	
		882	
655	660	623	δ_{as} O–P–O
648	647	616	
575	578	572	δPO + δVO
560			
546	549		
518	524	507	
436	439	470	δ_s O–P–O
420	427	427	
400	404		

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Supplementary Material Available: Structure factor tables for Na_2VPO_6 and K_2VPO_6 (28 pages). Ordering information is given on any current masthead page.

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