The Formation of Metastable Potassium Trivanadate from Melts

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Potassium vanadates, which were prepared from melts by rapid quenching and slow cooling over the composition range of K_2O-contents of $C=(K)/(V)=0$—0.50, were examined by means of IR spectrometry and X-ray powder diffraction. In the composition range of $C\leq 0.17$, mixtures of V_2O_5, $K_2V_{18}O_{45}$, and $K_2V_8O_{21}$ were produced by the slow cooling. At the composition of $C=0.33$, however, an unknown compound and $K_2V_8O_{21}$ were the main products upon rapid quenching from melts, while at $C=0.50$ the main products were $K_3V_5O_{14}$ and an additional unknown compound. The unknown compound was confirmed to be metastable and was formed as a single compound only by a rapid quenching from melts of K_2O and V_2O_5 especially at $C=0.37$. The X-ray diffractions for the compound were characterized as $d=8.2$ (very strong), 4.05, and 3.27 Å, and the V=O stretching frequencies, as 995, 968, and 955 cm^{-1}. By comparing these characteristic data with those of lithium trivanadate and sodium trivanadate (γ-phase), it was suggested that the unknown compound was isomorphous with trivanadate ($M_{1+x}V_3O_8$).

In the previous paper, it was examined how alkali tri- and/or hexavanadates could be produced or not by the procedures of the rapid quenching and slow cooling of the melts which had been prepared from mixtures of M_2CO_3 and NH_4VO_3 or V_2O_5 as the starting materials with the composition of $C=(M)/(V)=0.33$.[1] Only in the case of K_2O-containing samples, however, was neither the trivanadate nor the hexavanadate formed by those procedures,while the mixtures of $K_2V_8O_{21}$, an unknown compound, and $K_3V_5O_{14}$ were formed. The reasons why the tri- or hexavanadate could not be formed only in the K_2O–V_2O_5 binary system, and also what the unknown compound was, have remained to be investigated. With a potassium oxide–vanadium oxide binary system, five stable compound have been reported by Holtzberg *et al.*,[2] corresponding to these five formulas: $K_2V_8O_{21}$, KVO_3, $K_{32}V_{18}O_{61}$, $K_4V_2O_7$, and K_3VO_4. Kelmers[3] also found $K_3V_5O_{14}$ as a high-temperature phase; he further suggested the existence of $K_2V_{12}O_{30}$ and metastable $K_2V_{18}O_{45}$. However, no such compounds, the composition of which is near 0.33 ($C=0.33$), have yet been reported to be formed from high-temperature melts.

On the other hand, potassium hexavanadate ($K_2V_6O_{16}$) has been prepared by Kelmers[4] from V_2O_5 solution with alkali dissolved in it. Evans and Block called the potassium vanadate prepared by this procedure potassium trivanadate(KV_3O_8) based on an exact X-ray analysis.[5] The potassium trivanadate is monoclinic; its X-ray powder data has also been shown on an ASTM-card.[6] However, any diffraction peaks are inconsistent with the unknown compound formed from high-temperature melts in a previous experiment.[1]

In the present experiment IR spectrometry and X-ray powder diffraction were used for analysing in detail the potassium vanadates formed by slow cooling and/or rapid quenching from the melts of K_2O and V_2O_5 over the composition range of $C=0$—0.50. Especially, in order to characterize the unknown compound, many samples formed in the region near $C=0.33$ were investigated.

Experimental

1) Materials and Preparations. Potassium vanadates in the composition range of $C=(K)/(V)=0$—0.17 (in atomic ratio) were prepared from K_2CO_3 (Wako Pure Chem. Co., Ltd.; guaranteed grade) and NH_4VO_3,which had been purified cautiously,[7] by the following procedures. The NH_4VO_3 was immersed into a K_2CO_3 aq soln, dried at 120 °C, and calcined in a quartz tube with opening to the air at 600 °C for 20 h. After the heating, they were cooled slowly in the furnace. The samples will be called K-1—6. Sample K-7, with the composition of $C=0.33$, was prepared by the same procedures except for the final cooling procedures; it was rapidly quenched in ice-water. For preparing Sample K-8, K_2CO_3 and V_2O_5 (both Kanto Chem. Co., Ltd.; guaranteed grade) were well mixed in the composition of $C=0.33$ in an agate mortar and then heated in a quartz tube (outer diameter, $d_o=10$ mm) with an opening to the air at 530 °C for 14 h.

TABLE 1. K-CONTENTS OF POTASSIUM VANADATES PREPARED BY MELTS AND THEIR V=O STRETCHING FREQUENCIES, AS ESTIMATED FROM Figs. 1 AND 2

Sample	C/[M]/[V]	V=O Stretching ν/cm^{-1}					
K-1	0.020(s)[a]	1022	—	—	960	—	940
K-2	0.040(s)	1022	—	—	970	—	942
K-3	0.063(s)	1020	1005	—	—	—	942
K-4	0.087(s)	1023	1000	—	972	—	941
K-5	0.119(s)	1020	1000	—	972	—	942
K-6	0.171(s)	1021	1001	—	972	—	942
K-7	0.33 (r)	—	995	985	967	955	940
K-8	0.33 (s)	—	995	—	970	955	937
K-9	0.33 (r)	—	995	985	967	955	938
K-10	0.50 (r)	—	995	980	—	955	935

a) The letters of s and r in parentheses denote the procedures of the slow cooling and the rapid quenching respectively.

Table 2. The K_2O-contents of samples V-1—7

Sample	C/(K)/(V)
V-1	0.261
V-2	0.285
V-3	0.310
V-4	0.334
V-5	0.350
V-6	0.374
V-7	0.399

After further heat-treatment at 590 °C for 8 h, it was cooled slowly in the furnace. For preparing Samples K-9 and 10, the compositions of which were $C=0.33$ and 0.50 respectively, given amounts of K_2CO_3 and NH_4VO_3 were well mixed in an agate mortar and then heated in a quartz tube ($d_o=10$ mm) with an opening to the air at 620 °C for 72 h. Finally they were quenched rapidly in ice-water. The compositions of the samples thus prepared are summarized in Table 1. In order to investigate the unknown compound in detail, K_2CO_3 and V_2O_5 were mixed well in the composition of $C=0.26$—0.40 and then heated in a quartz tube ($d_o=6$ mm) with an opening to the air at 750 °C for 22 h. After the heat-treatment they were quenched in ice-water. The compositions of the samples, V-1—7, are summarized in Table 2.

2) IR and X-Ray Measurements. The IR spectra of Samples K-1—10 were measured in the frequency range from 650 to 1200 cm^{-1} by using the normal KBr-disk method. The IR spectrometer used was JASCO, model DS-402 G. The IR spectrum for Sample V-6 was measured in the range of 400—1100 cm^{-1} by the use of a JASCO model A-202 spectrometer. The X-ray powder diffraction was carried out on all the samples in the range of $2\theta=4$—60 °. The X-ray diffractometer used was a Rigaku-Denki model; GF-Rad-γA; Cu $K\alpha$-radiation (at 40 kV, 120 mA) and a Ni-filter were used.

Results

The IR spectra of Samples K-1—7 are shown in Fig. 1, in which the spectrum of pure-V_2O_5 is also given for the sake of comparison. The 1022 cm^{-1} band appearing in pure-V_2O_5 has already been assigned to the V=O stretching vibration.[8,9] It may be seen that sharp bands appear at 1000, 972, and 942 cm^{-1} in Samples K-1—7 and that the intensities of those bands increase with an increase in the K_2O-content. In the IR spectra of Samples K-7—9, which differ in their starting materials and with the procedures used to prepare them but whose are the same in the K_2O-content ($C=0.33$), the band peaks were seen at 995, 985, 955, and 940—937 cm^{-1}, a little different from those of Samples K-1—6. In Sample K-10 ($C=0.50$), the characteristic broad and sharp bands appeared at about 980 and 935 cm^{-1} respectively, while a shoulder band seemed to appear at 995 cm^{-1}. In Samples K-8 and 10, a very weak band was seen in the region of 905—908 cm^{-1}. The frequencies for the V=O stretching bands of Samples K-1—10 are summarized in the third colum of Table 1. The 967 cm^{-1} band seems to be more intensive than the 995 cm^{-1} band in Sample K-9, while the two intensities are similar in extent in Sample K-7. The broad 980 cm^{-1} and the sharp 935 cm^{-1} bands became relatively intensive in Sample K-10. With respect to Samples K-1—6, the peak intensities for the sharp band in the region of 930—1000 cm^{-1} were estimated by drawing a base line smoothly under the bands of the spectra according to the previous papers;[1,10] their relative intensities are given in Table 3. As the band separations were not good enough for us to estimate the intensities of each peak in the K-7 —10 samples, these values were excluded from the table.

Table 3. The relative intensities of the V=O stretching bands for samples K-1—6

Sample	C/[M]/[V]	Band Intensities			
		1022	1000	972	942 cm^{-1}
K-1	0.020	0.92	0.047	0.017	0.018
K-2	0.040	0.87	0.077	0.037	0.019
K-3	0.063	0.784	0.134	0.041	0.041
K-4	0.087	0.76	0.160	0.040	0.037
K-5	0.119	0.61	0.246	0.065	0.079
K-6	0.171	0.48	0.30	0.13	0.09

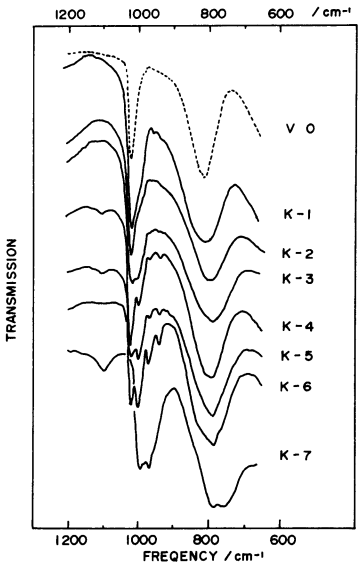

Fig. 1. IR-spectra of Samples K-1—7 recorded in the frequency range of 650—1200 cm^{-1}. The spectrum for V_2O_5 was added for comparison.

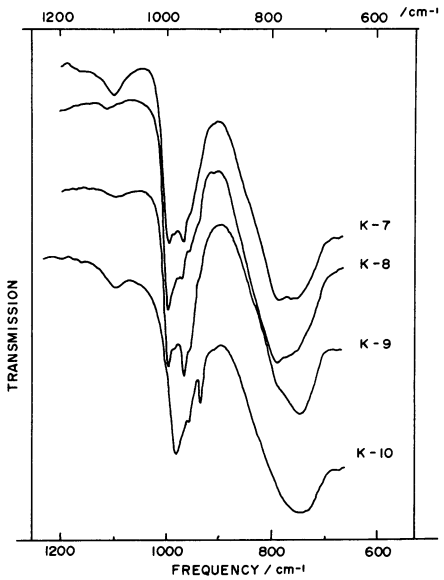

Fig. 2. IR-spectra of Samples K-7—10.

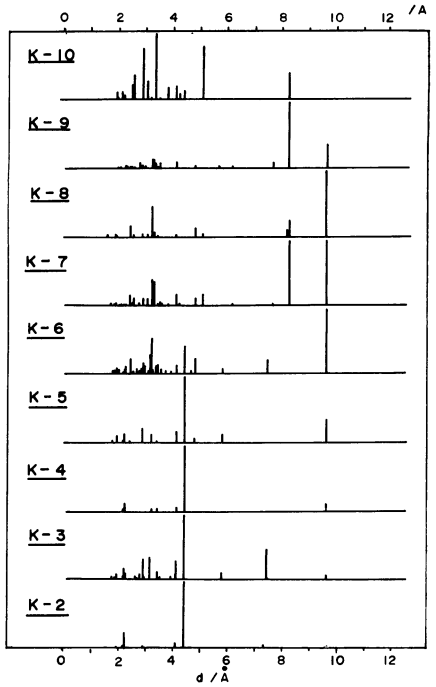

Fig. 3. The X-ray powder diffraction patterns for Samples K-2—10, recorded in the angles of 2θ =4—60° (d=22—1.54 Å).

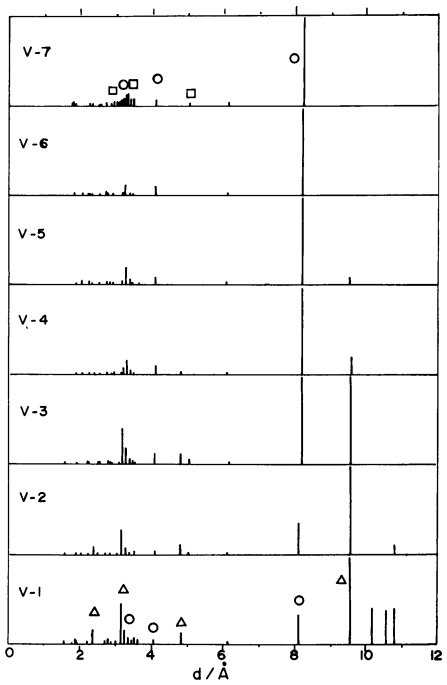

Fig. 4. The X-ray powder diffraction patterns for Samples V-1—7 recorded in the angles of 2θ=4—60° (d=22—1.54 Å). The signs, △, ○, and □, denote the lines for $K_2V_8O_{21}$,[12] the unknown compound, and $K_3V_5O_{14}$,[13] respectively. See also text.

The X-ray diffraction patterns of Samples K-2—10 are shown in Fig. 3. The diffraction peak corresponding to the interplanar spacing of d=4.38 Å, which has been characterized as V_2O_5,[11] was the highest in Samples K-2—5 (C=0.040— 0.12), but it completely disappeared in Samples K-7—10 (C=0.33—0.50). On the other hand, the peak for d= 9.60 A, characteristic of $K_2V_8O_{21}$,[12] appeared at first in the K-2 sample (C= 0.04), became intensive with an increase in the K_2O-content, and reached its highest point in the K-6—8 samples (C=0.17—0.33). In the K-10 sample (C= 0.50), the peak at d=3.28 Å, characteristic of the $K_3V_5O_{14}$ phase[13] became the highest.

At a rather low content, especially in the K-3 sample, the intensive diffraction peak appeared at d=7.4 Å, which was characteristic of the $K_2V_{18}O_{45}$ phase.[12] With respect to the highest peak at d=8.2 Å in the K-9 sample, the corresponding compound was not found out in any ASTM-cards for potassium vanadates; thus, it has been called an unknown compound. From the comparisons of the diffraction intensities at d=9.6, 8.2, and 3.28 Å, which are the highest of the compounds of $K_2V_8O_{21}$, the unknown compound, and $K_3V_5O_{14}$, respectively, $K_2V_8O_{21}$ seems to be a major component in the K-8 sample and the unknown compound seems to be the major in the K-9 sample. Similarly $K_3V_5O_{14}$ seems to be a major component in the K-10 sample.

The X-ray diffraction patterns of Samples V-1—7 are shown in Fig. 4. In the V-1 sample the most intensive peak is seen at 9.5 Å, and the second most intensive at 3.16 Å: they are characteristic of $K_2V_8O_{21}$.[12] With an increase in the potassium content (C=0.26→0.37), it may be seen in the figure that the peak at 8.2 Å, becomes intensive, while, on the contrary, that at 9.5 Å, decreases. Similarly, the intensities of the peaks at 4.05 and 3.27 Å, (marked with ○) increase relative to the peaks at 4.85, 3.15, and 2.12 Å (marked with △). Finally in the V-6 sample (C=0.374), those peaks assigned to $K_2V_8O_{21}$ disappear completely, while the very strong peak at d=8.2 Å and weak peaks at 4.05 and 3.27 Å which have been ascribed to the unknown compound remain. In Sample V-7 (C=0.399), the other peaks assigned to $K_3V_5O_{14}$[13] appear at d=5.01, 3.29, and 3.02 Å (marked with □). Therefore, it is clearly suggested that the unknown compound is formed as a single compound only by the rapid quenching from the melt at C=0.37. Furthermore, the characteristic X-ray peaks of the unknown compound may be regarded as corresponding to the interplanar distances of 8.2 (very strong), 4.05 and 3.27 Å. The IR spectrum of the

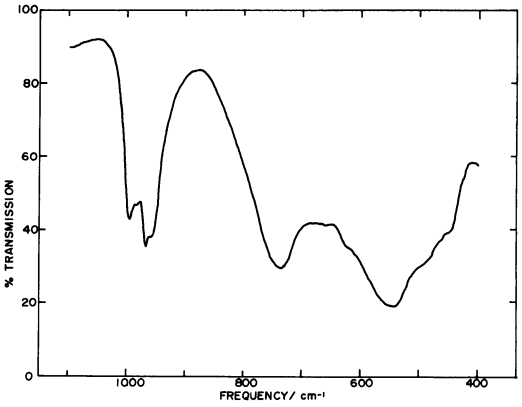

Fig. 5. IR-spectrum of Sample V-6, in which the unknown compound was regarded to be purely contained, recorded in the frequency range of 400—1100 cm^{-1}. See also text.

V-6 sample is shown in Fig. 5. The V=O stretching frequencies characteristic of this compound were determined exactly to be 995, 968, and 955 cm^{-1}.

Discussion

1) The V=O Stretching Frequencies of the Potassium Vanadates Formed from the Melts of K_2O-V_2O_5 in the Range of C=0—0.50. V_2O_5, $K_2V_{18}O_{45}$, and $K_2V_8O_{21}$ were the main components in the samples of $C=0.04$—0.17, as has been pointed out above. Furthermore, the content of the $K_2V_8O_{21}$ phase has been seen to increase with C, and simulteneously the 1000, 972, and 942 cm^{-1} bands have been seem to become intensive, while the 1022 cm^{-1} band weakens, as is shown in Fig. 1 and Table 3. The band intensities are plotted against C in Fig. 6, in which the plot for the 1022 cm^{-1} band can be linearly extrapolated toward the point at $C=0.33$ on the abscissa. As has already been noted above,the V_2O_5 phase is not contained in the samples of $C\geq0.33$. In fact, the X-ray diffraction peak for d=4.38 Å ascribed to V_2O_5 was not detected completely in Samples K-7—10. The intensities of the 1000, 972, and 942 cm^{-1} bands increase linearly with C, keeping approximntely a constant relation with one another, although the content ratio of $K_2V_8O_{21}$ and $K_2V_{18}O_{45}$ differs considerably among Samples K-2—6. Therefore, it can be suggested that the V=O stretching frequencies in $K_2V_8O_{21}$ are nearly the same as those in $K_2V_{18}O_{45}$.

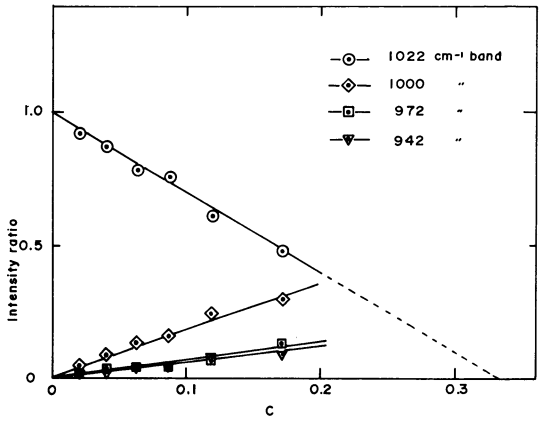

Fig. 6. Changes in the relative intensities of the V=O stretching bands (Intensity ratio) with increasing the K_2O-contents (C) for Samples K-1—6. The 1022 cm^{-1} band is ascribed to pure-V_2O_5 and the 1000, 972, and 942 cm^{-1} for $K_2V_8O_{21}$ (or $K_2V_{18}O_{45}$).

From comparisons of the IR spectra and X-ray diffraction lines between the K-8 and 9 samples, the 967 cm^{-1} band could be assigned to the unknown compound because the band in Sample K-9 was more intensive than that in Sample K-8, while, simultaneously, the existing ratio of the unknown compound to $K_2V_8O_{21}$ in K-9 was higher than that in K-8. It has been reported by Zurkova *et al.*[13] that the characteristic bands of $K_3V_5O_{14}$ were found at 985 and 940 cm^{-1}. The broad band at 980 cm^{-1} and the sharp band at 935 cm^{-1} in the K-10 sample seemed to correspond to these bands, although the frequencies deviated a little bit because of the overlapped spectrum with those of the unknown compound. Therefore, the bands at 995 and 955 cm^{-1} remaining in the spectrum of the K-10 sample could be regarded as having been caused by the unknown compound. Thus, the V=O stretching bands of the unknown compound were established as appearing at 995, 967, and 955 cm^{-1}. These values are in good agreement with those determined from the spectrum for the V-6 sample, $C=0.37$ (995, 968, and 955 cm^{-1} respectively).

2) Chemical Formula and Structural Features of the Unknown Compound. With the increase in C, the diffraction peaks at d=8.2, 4.05, and 3.27 Å, became intensive relative to those at d=9.5, 4.85, 3.15, and 2.12 Å, which are ascribed to the diffraction of $K_2V_8O_{21}$ ($C=0.25$)[12] until finally, at $C=0.37$, only those lines remained, as is shown in Fig. 4. Therefore, those at d= 8.2, 4.05, and 3.27 Å should be ascribed to the unknown compound. Thus, the unknown compound might be expressed by this formula: $K_{1+x}V_3O_8$ ($x=0.11$). If this $K_{1+x}V_3O_8$ is assumed to be isomorphous with lithium and sodium trivanadates ($K_{1+x}V_3O_8$, γ-phase), both the X-ray diffraction lines and the V=O stretching bands should correspond to one another. Furthermore, those values should be expected to vary more or less among themselves depending upon the alkali-metal-ion size. The strongest peak at d= 8.2 Å for the $K_{1+x}V_3O_8$ compound seems to correspond to that at 6.4 Å, which has been assigned to the interplanar spacing of the (100) plane with $Li_{1+x}V_3O_{7.9}$ ($x=0.12$)[14] and that at d=7.0 Å with NaV_3O_8,[15] although it has not been assigned.

In order to compare the d-values of not only 8.2 Å but also 4.05 and 3.27 Å for $K_{1+x}V_3O_8$ with the the

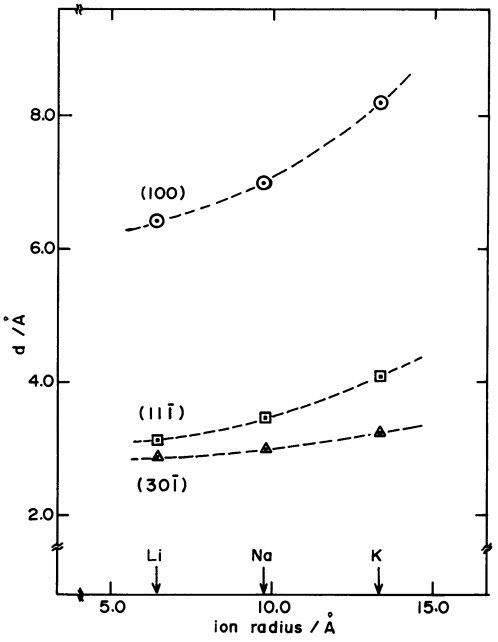

Fig. 7. Comparisons of the X-ray diffraction lines characterized to the compound $K_{1+x}V_3O_8$ (just assigned) with those referred to Li and Na-trivanadates (γ-phase) by use of the alkali metal ion radii as an parameter. The d-values for $Li_{1+x}V_8O_{7.9}$($x\leq0.12$)[14] 6.36, 3.15, and 2.216 Å has been assigned to the (100), (11$\bar{1}$), and (30$\bar{1}$), as were shown in the figure.

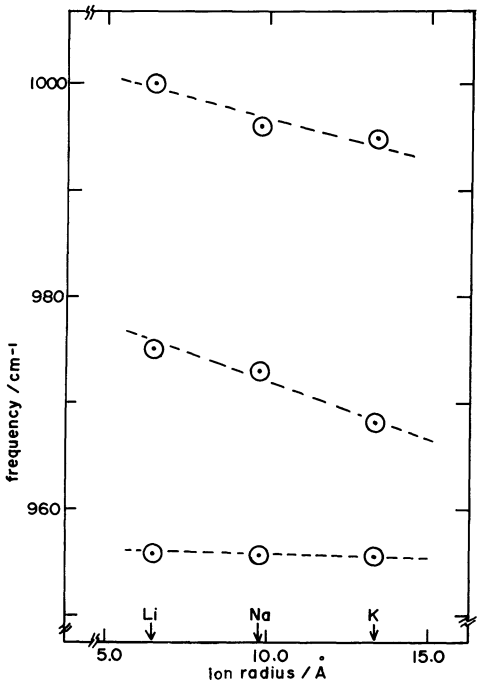

Fig. 8. Comparisons of the V=O stretching frequencies characterized to the compound $K_{1+x}V_3O_8$ (just assigned) with those reported previously for Li and Na-trivanadates[1] by use of the alkali metal ion radii as an parameter.

corresponding *d*-values for $Li_{1+x}V_3O_{7.9}$ and NaV_3O_8 respectively, the *d*- values were plotted against alkali ion radii;[16] they are shown in Fig. 7. Those values are known to correlate well with the alkali-metal-ion radii in the figure. Especially, such a large change in the *d*-value with the (100) can be understood reasonably because alkali-metal-ions are placed into the interplanar spacing along the a-axes in the monoclinic lattice. Thus, from the good coorelations, these three compounds might be concluded to be isomrphous with each other.

Such correlation is consistent with those found in the hexavanadates of potassium, ammonium, rubidium, and cesium, being isomorphous with each other, reported by Kelmers.[4] The V=O stretching bands, 995, 968, and 955 cm^{-1} for the $K_{1+x}V_3O_8$, seem to correspond to those of 1000, 975, and 957 cm^{-1} for LiV_3O_8 and those of 996 , 973, and 957 cm^{-1} for NaV_3O_8, respectively.[1] In fact, the V=O stretching frequencies also gave a good correlation to the alkali-metal-ion radii, as is shown in Fig. 8.

Therefore, throughout any discussions it should be emphasized that the metastable potassium trivanadate (KV_3O_8), being isomorphous with lithium and sodium trivanadates (γ-phase), was favorably formed, especially upon rapid quenching from high-temperature melts (≃750 °C). Furthermore, it should be noted that the present potassium trivanadate differs completely in its X-ray diffraction patterns from the potassium hexavanadate($K_2V_6O_{16}$) reported by Kelmers[4] and from the potassium trivanadates (KV_3O_8) reported by Evans and Block,[5] prepared from aq soln and regarded as isomorphous with $(NH_4)_2V_2O_{16}$, $Rb_2V_2O_{16}$ and $Cs_2V_2O_{16}$.

3) The V=O Bond Lengths of The Potassium Vanadates, $K_2V_8O_{21}$, $K_{1+x}V_3O_8$, and $K_3V_5O_{14}$. From the 1000, 972, and 942 cm^{-1} bands ascribed to the V=O stretching bands for $K_2V_8O_{21}$, the corresponding bond lengths were evaluated as 1.599, 1.618, and 1.630 Å respectively, according to the same procedure as was used in previous papers.[1,10] Similarly, the V=O bond lengths corresponding to the 995, 968, and 955 cm^{-1} bands of $K_{1+x}V_3O_8$ were evaluated as 1.603, 1.622, and 1.630 Å respectively, and those corresponding to the 980 and 935 cm^{-1} bands of $K_3V_5O_{14}$ as 1.613 and 1.645 Å respectively.

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