Synthesis and Structural Investigation of a New Potassium Vanadium Oxide Bronze: ρ-K$_{0.50}$V$_2$O$_5$

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ρ-K$_{0.50}$V$_2$O$_5$, synthesized at 350°C by interaction of K$_2$C$_2$O$_4$ on V$_2$O$_5$, crystallizes in the orthorhombic system, space group *Cmcm*, with the cell parameters $a = 3.674(1)$ Å, $b = 11.607(3)$ Å, $c = 18.670(8)$ Å, $V = 756.20(4)$ Å^3, and $Z = 8$. Despite the poor quality of the single crystal obtained, structural determination gave an R factor of 0.067 for 498 reflections. The original layer structure of ρ-K$_{0.50}$V$_2$O$_5$ exhibits [V$_2$O$_5$]$_n$ sheets built up by four VO$_6$ octahedra sharing edges and making quadruple endless strings associated by edges along [100]. These sheets, depicted as double layers D4, and their mirror image D4M alternate along [001]. The intercalated potassium atoms hold together the [V$_2$O$_5$]$_n$ layers. They partially occupy two sites, 80% in K1 at the center of an oxygenated rectangular prism (CN8) and 20% in K2 surrounded by six oxygen atoms forming a trigonal prism (CN6). K1O$_8$ and K2O$_6$ polyhedra share a rectangular face, with the short distance between the potassium sites preventing simultaneous occupancy. The K2 site occupancy is related to an electronic localization within the [V$_2$O$_5$]$_n$ layers. Finally, a comparison is made with other prototype structures containing D4 layers like δ- and ν-K$_x$V$_2$O$_5$ phases. © 1992 Academic Press, Inc.

Introduction

The vanadium–oxygen–potassium system has been extensively investigated and the presence of numerous phases with original structures has been found (*1–6*). In this paper a new phase found while studying the intercalation chemistry of V$_2$O$_5$ by transition metal complexes (*7*) is presented.

Experimental

Black lamellar crystals of ρ-K$_{0.50}$V$_2$O$_5$ were obtained using the oxalate method of synthesis (*8*). A mixture of V$_2$O$_5$ and K$_2$C$_2$O$_4$, in molecular yield 4/1, was heated to 350°C under vacuum. The formula of the resulting compound was determined by chemical analysis: $\%$K/$\%$V$_{exp} = 0.1919$, $\%$K/$\%$V$_{calc} = 0.1918$. A differential chemical analysis of the vanadium atoms in oxidation state IV and V shows 71% of the vanadium atoms to be in oxidation state V. This is consistent with a quantity of one potassium atom per four vanadium atoms (75% V^v). The low temperature of the synthesis is not conducive to a good compound crystallization. Synthesis attempts at a higher temperature lead to a mixture of potassium VOB phases: that is, mainly β phases with a few δ and ν phases, indicating an imbalance system.

A selected crystal of 0.14, 0.15, and 0.016 mm was mounted on an Enraf–Nonius CAD4 diffractometer for full data collection using a Mo$K\alpha$ wavelength. Lattice parame-

TABLE I

PHYSICAL PROPERTIES AND PARAMETERS PERTINENT TO DATA COLLECTION AND
REFINEMENT OF ρ-$K_{0.50}V_2O_5$

Physical properties	
Formula	$K_{0.50}V_2O_5$
Mol wt (g)	201.428
Crystal system	Orthorhombic
Space group	*Cmcm*
a (Å)	3.674(1)
b (Å)	11.607(3)
c (Å)	18.670(8)
V (Å^3)	796.16(4)
Z	8
d_{calc}(g/cm^3)	3.36
$F(000)$	764
Crystal shape	Lamellar
Faces	$\{0\ 0\ 1\}$, $\{1\ 0\ 0\}$, $\{0\ 1\ -4\}$
Distances to center (cm)	0.0008, 0.007, 0.0075
Parameters of data collection and refinement	
Measurements	
Temperature (°C)	20
λ(Å)	0.7107
Take off (°)	6.0
Detector width (mm)	4×4
Scan type	$\omega/2\theta$
Scan width (°)	$1.00 + 0.35 \tan \theta$
hkl range	$h\ 0 \rightarrow 18,\ k\ 0 \rightarrow 6,\ l\ -30 \rightarrow 30$
θ range (°)	$0.0 \rightarrow 35.0$
No. of measured reflections (with $h + k = 2n$)	1646
Standards (period)	
Intensity (1 hr)	$\{0\ 0\ 8\}$, $\{0\ -6\ 0\}$, $\{2\ 0\ -6\}$
Orientation (100 reflections)	$\{0\ 0\ -8\}$, $\{0\ 6\ 0\}$, $\{-4,\ 0\ 0\}$
Absorption correction	
μ (Mo$K\alpha$) (cm^{-1})	49.7
Gaussian grid	20, 26, 2
Transmission factor	0.71–0.96
Averaging	
$R_{av} = \Sigma(I - I_{av})/(\Sigma I)$	0.054
Refinements	
No. of variables (NV)	51
No. of unique reflections with $I > 3\sigma$ (NO)	498
Weighting scheme	$w = 4.83/\{\sigma^2(I) + (0.07 * I)^2\}^{1/2}$
Maximum shift/e.s.d.	0.018
Agreement factors	
$R = (\Sigma \| |F_{obs}| - |F_{calc}| \|)/(\Sigma|F_{obs}|)$	0.067
$R_w = [\Sigma(|F_{obs}| - |F_{calc}|)^2/(\Sigma|F_{obs}|)^2]^{1/2}$	0.085
$s = [\Sigma(|F_{obs}| - |F_{calc}|)^2/(NO - NV)]^{1/2}$	0.994

ters were determined from the setting angles of 25 reflections chosen in the angle range $20° < 2\theta < 34°$. The extinction rules determined during fast data collection led to the space groups $Cmc2_1$, $C2cm$, or $Cmcm$. The details of the parameters used for data collection are reported in Table I. No significant variation in the intensity of the standard

TABLE II

FINAL LEAST-SQUARES ATOMIC PARAMETERS WITH
ESTIMATED STANDARD DEVIATIONS FOR ρ-K$_{0.50}$V$_2$O$_5$

Atom	x	y	z	B_{eq}(Å^2)
K1	0	0.5775(5)	$\frac{1}{4}$	1.3(1)
K2	0	0.395(2)	$\frac{1}{4}$	1.4(5)
V1	0	−0.0655(2)	0.0788(1)	0.71(7)
V2	0	0.2314(2)	0.0806(1)	0.79(7)
O1	0	0.0796(7)	0.0480(5)	1.2(3)
O2	0	0.2425(8)	−0.0592(6)	1.4(3)
O3	0	0.2106(9)	0.1653(6)	2.2(3)
O4	0	0.4008(7)	0.0646(4)	0.7(2)
O5	0	−0.0498(9)	0.1651(6)	1.9(3)

Note. $B_{eq} = 8\pi^2/3$ trace u (u, diagonalized U matrix).

reflections has been observed. The data were rectified for absorption according to Coppens *et al.* (9). A statistical study of the data leads to the selection of the *Cmcm* space group. The structure was determined from the Patterson function and refined with full matrix program SHELX76 (*10*). Atomic and anomalous f' and f'' scattering factors are taken from the "International Tables for X-ray Crystallography" (*11*). From the difference Fourier synthesis, potassium atom K1 was first found at site $4i$ and refined. Then potassium K2 was obtained at another site $4i$. The optimization of the multiplicity of both atoms yields an occupation factor of 80 and 20%, respectively, for K1 and K2. The resulting total number of potassium atoms per one V$_2$O$_5$ unit is 0.50, which is consistent with the chemical analysis. The parameters of relevance for data processing are also listed in Table I. The poor quality of the crystal leads to a relatively high R factor, 0.068, corresponding to a high average agreement factor, 0.054, of the intensity of the equivalent reflections hkl and hk-l.

The final atomic parameters are presented in Table II. A selected list of interatomic distances and bond angles is given in Table III. Anisotropic thermal parameters and a set of interatomic distances and bond angles

together with a list of structure factors are deposited as supplementary material.

Description of the Structure

A ball-and-stick drawing of the structure projected onto the plane (100) is given in Fig. 1. Vanadium atoms, V1 and V2, are octahedrally surrounded by oxygen atoms. V1O$_6$ and V2O$_6$ octahedra are distorted; the vanadium atoms establish a short bond, typical of the vanadyl group, i.e., V1–O5 = 1.62 Å and V2–O3 = 1.60 Å. Two octahedra, V1O$_6$ and V2O$_6$, connected by corner O1 and repeated by the twofold axis make a block of four octahedra sharing edges. These blocks develop as an endless string along [100] by corner sharing (Fig. 2). These strings, held together via edge sharing after alternate slips of $a/2$, build up a so-called D4 double layer [V$_2$O$_5$]$_n$. The formation of such D4 double layers together with their mirror image D4M (as well as another type, DZ) from simple S layers, whose prototype exists in V$_2$O$_5$, has been detailed elsewhere
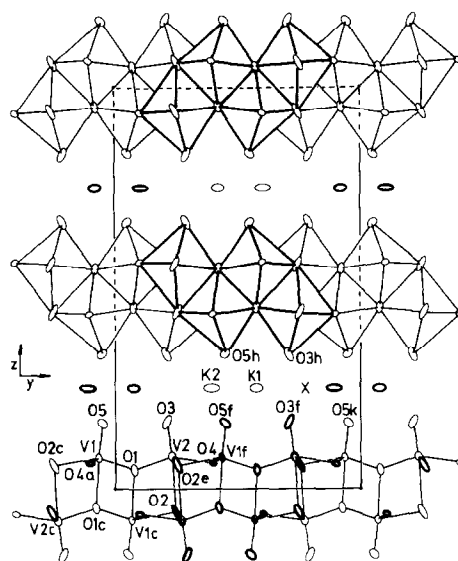

FIG. 1. Projection onto the (100) plane of the structure of ρ-K$_{0.50}$V$_2$O$_5$.

TABLE III

Selected Interatomic Distances (Å) for ρ-$K_{0.50}V_2O_5$

Octahedral CN6: VIO_6

V1–O5	1.62(1)	V1–O1	1.779(8)
V1–O4a	1.897(3)	V1–O4b	1.897(3)
V1–O2c	2.085(9)	V1–O1c	2.373(9)
O1–O1c	2.58(1)	O1–O5	2.65(1)
O1–O4a	2.789(9)	O1–O4b	2.789(9)
O2c–O4a	2.480(8)	O2c–O4b	2.480(8)
O1c–O2c	2.75(1)	O2c–O5	2.98(1)
O1c–O4a	2.803(9)	O1c–O4b	2.803(9)
O4a–O5	2.69(1)	O4b–O5	2.69(1)

Octahedral CN6: $V2O_6$

V2–O3	1.60(1)	V2–O1	1.863(8)
V2–O2d	1.905(3)	V2–O2e	1.905(3)
V2–O4	1.988(8)	V2–O2	2.61(1)
O1...O2	2.75(1)	O1...O2d	2.772(9)
O1...O2e	2.772(9)	O1...O3	2.67(1)
O2...O2d	2.88(1)	O2...O2e	2.88(1)
O2...O4	2.95(1)	O2d...O3	2.76(1)
O2d...O4	2.480(8)	O2e...O3	2.76(1)
O2e...O4	2.480(8)	O3...O4	2.90(1)

Rectangular prism CN8: KIO_8

K1–O5f = K1–O5g = K1–O5H = K1–O5i = 2.842(9)
K1–O3f = K1–O3g = K1–O3h = K1–O3i = 2.874(9)
O5f...O5g = O5h...O5i = O3f...O3g = O3h...O3i = 3.675(3)
O5f...O5h = O5g...O5i = 3.17(2)
O3f...O3h = O3g...O3i = 3.16(2)
O5f...O3f = O5g...O3g = O5h...O3h = O5i...O3i = 3.02(1)

Trigonal prism CN6: $K2O_6$

K2–O5f = K2–O5g = K2–O5h = K2–O5i = 2.510(9)
K2–O3 = K2–O3j = 2.66(2)
O5f...O5g = O5h...O5i = 3.675(3)
O5f...O5h = O5g...O5i = 3.17(2)
O3...O3j = 3.16(2)
O3...O5f = O3...O5g = O3j...O5h = O3j...O5i = 3.33(1)

Intermetallic distances

V2...V1f = V2...V1g = 2.988(2)
V1...V1c = 3.311(4)   V1...V2 = 3.446(2)   V1...V2c = 2.543(3)
K1...K2 = 2.11(2)
K1...X = 2.12(1)   K2...Xf = K2...Xg = 2.41(1)
K1...V1f = K1...V1g = K1...V1h = K1...V1i = 4.045(3)
K1...V2f = K1...V2g = K1...V2h = K1...V2i = 4.071(3)
K2...V1f = K2...V1g = K2...V1h = K2...V1i = 3.716(3)
K2   V2 = K2...V2j = 3.692(3)

Note. X, expected position of metal included in the O3f,g,h,i and O5k, O5l trigonal prism (coordinates: 0.0, 0.7606, 0.25). Symmetry operators: a, $\frac{1}{2} + x$, $-\frac{1}{2} + y$, z; b, $-\frac{1}{2} + x$, $-\frac{1}{2} + y$, z; c, x, $-y$, $-z$; d, $\frac{1}{2} + x$, $\frac{1}{2} - y$, $- z$; e, $-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$; f, $\frac{1}{2} + x$, $\frac{1}{2} + y$, z; g, $-\frac{1}{2} + x$, $\frac{1}{2} + y$, z; h, $\frac{1}{2} + x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; i, $-\frac{1}{2} + x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; j, x, y, $\frac{1}{2} - z$; k, x, $1 + y$, z; l, x, $1 + y$, $\frac{1}{2} - z$.
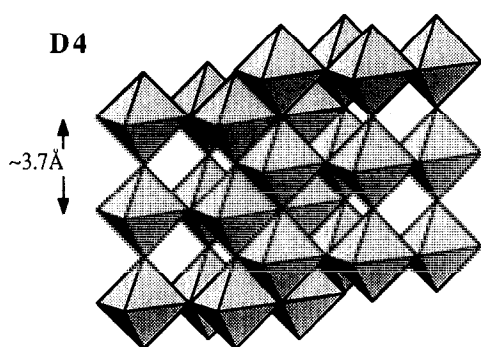
FIG. 2. Association of the quadruple endless strings in the double layers of ρ-K$_{0.50}$V$_2$O$_5$.

(12). The size of the intercalated cation, K$^+$, is directly responsible for their existence prior to the network organization. As seen in Fig. 1, D4 and D4M sheets alternate along the [001] direction, yielding an original layered structure. Between the layers the intercalated potassium atoms occupy two distinct crystallographic sites.

The former K1 is surrounded by eight oxygen atoms forming a rectangular prism of 3.67, 3.02, and 3.17 Å. The two sets of K–O distances are nearly identical, K1–O3f,g,h,i = 2.874(9) Å and K1–O5f,g,h,i = 2.842(9) Å. These O5fO5hO3hO3fO3gO5g O5iO3i prisms share a (100) face, making an infinite tunnel along [100] with a rectangular section. The second type of cavity, in which potassium K2 is inserted, is built up by oxygen atoms O5f, O5g, O5h, O5i, O3, and O3j situated at the apex of a distorted trigonal prism, the threefold axis being parallel to [001]; two types of distances are observed: K2–O3 = K2–O3$_j$ = 2.66(2) Å and K2–O5f,g,h,i = 2.510(9) Å. These trigonal prisms K2O$_6$ share the face O5f,g,h,i with the rectangular prism K1O$_8$ and are also edge shared (O5$_f$–O5$_h$) along [100]. Opposite K2O$_6$, the K1O$_8$ rectangular prism face is shared with an empty trigonal prism. The slab formed by the association of oxygenated trigonal and rectangular prisms around potassium atoms, is depicted in Fig. 3.

Worthy of note is the 2.11(2) Å distance between the crystallographic sites K1 and K2. These sites cannot be occupied simultaneously. In this case, 80% of potassium is located at site K1 and the remainder at the other site. The analysis of these structural details shows that the ρ-K$_{0.50}$V$_2$O$_5$ structure represents the upper limit of this potassium VOB phase.

Discussion

As previously noted, the short vanadyl V=O bonds border the [V$_2$O$_5$]$_n$ double layer. Also, as usually occurs, vanadium atoms are pulled out of the equatorial plane of the octahedra toward the apices O5 and O3 (0.466 and 0.471 Å, respectively). Then the longest V–O bonds are intralayer ones, V1–O1c = 2.373(9) Å and V2–O2 = 2.61(1) Å. The volume of the V1O$_6$ octahedra (9.15 Å^3) is smaller than that of the V2O$_6$ one (9.64 Å^3). According to the formal formulation of this VOB, i.e., K$_{0.50}$V$_{1.50}^{5+}$ V$_{0.50}^{4+}$O$_5$, it seems reasonable to assume that V^{4+} preferentially occupies the V2 site. This is clearly demonstrated using Pauling's concept of the strength of electrostatic bond (13). The empirical formula proposed by Bachmann et al. (14), Brown et al. (15), and Waltersson (16) leads to a valency of 4.76(8) for atom V1 and 4.66(8) for atom V2, indicating that the V2 site contains slightly more V^{4+} than the V1 site.

Thus, the corresponding O5 and O3 oxygen atoms, which belong to the V1=O5 and V2=O3 vanadyl groups, must carry charges proportional to the vanadium ones. The consequences of these different charges can be observed in the potassium surrounding. At site K1, the distances K1–O5 (2.842(9) Å) are smaller than the K1–O3 distances (2.874(9) Å), leading to an offset of the potassium atom from the center of the cavity toward the O5f,g,h,i face of 0.033(9) Å. At site K2, the same thing can be observed: K2–O5 = 2.510(9) Å and
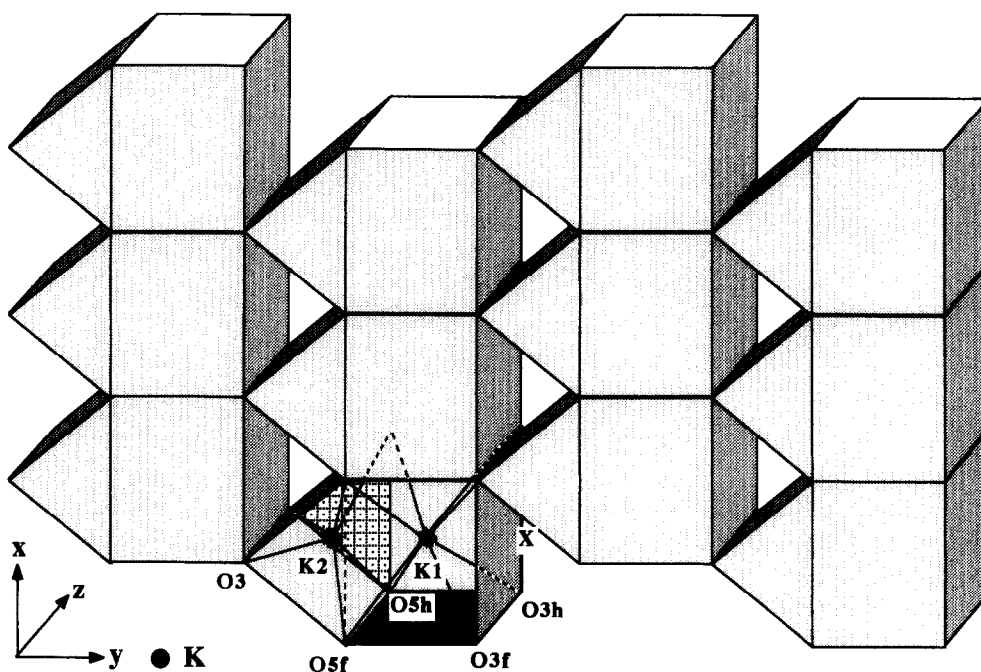
FIG. 3. Potassium–oxygen polyhedra packing between the D4 and D4M layers.

K2–O3 = 2.66(2) Å with an offset of 0.29(1) Å toward the same O5f,g,h,i face. Assuming pure electrostatic interactions, these offsets can be considered a displacement of the equilibrium point of the electrostatic forces due to the difference between the charges q_{O3} of atoms O3 and q_{O5} of atom O5. A rate of q_{O5}/q_{O3} of 1.2(2), which is similar to that of the valency of atoms V1 and V2 (1.02), can be calculated.

In the meantime, it has been noted that potassium atoms partially occupy two crystallographic sites, K1 and K2, which are mutually exclusive, and that a trigonal prism, opposite the $K2O_6$ with respect to the $K1O_8$ rectangular prism, remains empty (referenced as X in the text and figures). A tentative explanation based on pure electrostatic interactions can be made. Assuming that a potassium atom can be put at site X, using the same method as that employed previously and the results for sites K1 and

K2, an 0.23(9) Å offset toward the O3f,g,h,i face can be calculated. Then this value allows the electrostatic energy of a potassium atom at this site to be calculated and compared with the corresponding atom at sites K1 and K2. These energies, derived from an unknown charge factor, are proportional to 1.0 for site K1, 0.85 for K2, and 0.6 for X. Taking into account the experimental rates of occupancy of sites K1 and K2, 0.8 and 0.2 respectively, the resolution of the Boltzmann equation leads to a rate of 0.02 potassium atom at site X. This is in good agreement with the fact that no potassium atom was found at site X at the precision obtained.

Although the ionic formula infers one V^{4+} per four vanadium atoms and then a statistical distribution of this V^{4+} between both vanadium sites, an electronic localization is found. Moreover, a strong correlation occurs between this electronic localization

TABLE IV

CRYSTALLOGRAPHIC DATA FOR THE VOB'S STRUCTURE TYPES δ(Ag) AND ν(Ca), THEIR ISOSTRUCTURAL POTASSIUM RELATIVE (δ AND ν) PHASES, AND THE ORIGINAL p-$K_xV_2O_5$ PHASE

Compound	x	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	Z	V/Z (Å^3)	Space group	Ref.
δ-$Ag_xV_2O_5$	0.68	11.742(8)	3.667(3)	8.738(5)	90.5(1)	376.2	4	94.1	$C2/m$	17
δ-$K_xV_2O_5$	0.50	11.68(1)	3.662(3)	9.48(1)	92.1(1)	405.0	4	101.2	$C2/m$	20
ν-$Ca_xV_2O_5$	0.60	11.805(2)	3.709(1)	9.270(2)	101.9(1)	396.2	4	99.0	$C2/m$	18
ν-$K_xV_2O_5$	0.62	11.63(1)	3.668(8)	9.55(1)	101.5(1)	399.2	4	99.8	$C2/m$	20
p-$K_xV_2O_5$	0.50	11.607(3)	3.674(1)	18.670(8)	90.0	796.2	8	99.5	$Ccmm$	This study
β-$K_xV_2O_5$	0.28	10.039(3)	3.605(3)	15.335(3)	109.20(5)	524.1	6	87.3	$A2/m$	21

within the $[V_2O_5]_n$ layers and the occupancy of the potassium sites between the layers. Furthermore, the presence of some potassium atoms in the trigonal prisms strengthens the network by diversifying the anchoring points between the layers.

Comparison with Other Potassium Double Layer Structures

The first prototype involving double layers D4 was provided by S. Andersson, who synthesized and determined the structure of the silver VOB δ-$Ag_xV_2O_5$ ($x = 0.68$) (17). The VOB $Ca_xV_2O_5$ ($x = 0.60$) investigated by A. Kutogolu (19) is directly related to the silver one; the double layers D4 are correlatively shifted, increasing the β angle of the unit cell. The relationships between these structures have been established elsewhere (19). The prototype structure $Ca_xV_2O_5$ was denoted ν based on a single crystal study. The unit cell parameters of phases ν- and ν'-$K_xV_2O_5$ prepared by Pouchard (20) are obviously related to the δ-$Ag_xV_2O_5$ and ν-$Ca_xV_2O_5$ prototypes. Thus, these phases have been renamed, the former ν ($x \sim 0.48$) becoming δ, and the latter ν' ($0.61 \leq x \leq 0.65$) becoming ν. The unit cells of these phases are given in Table IV. Given the structural features of the δ, ν, and p phases, the chemical feature and homogeneity range can be accounted for. The mechanism per-

mitting the formation of the D4 and D4M layers from the single layer of square pyramids which forms the network of the vanadium pentoxide V_2O_5 has already been described elsewhere (12). Galy points out that the intercalation of cations which are wider than lithium causes the D4 or D4M layer to slip by steps, with the δ and ν structures directly resulting from each other. During examination of the δ-$K_xV_2O_5$ structure, the oxygenated trigonal prisms encapsulating the potassium crystallographic sites sharing a common rectangular face cannot reasonably provide more than 50% of the potassium atoms, the upper limit being $K_{0.50}V_2O_5$ (see Fig. 4). This is in good agreement with the homogeneity range observed ($0.48 \leq x \leq 0.51$) between 550 and 650°C for the δ phase. When the amount of potassium inserted between the layers is increased, these atoms induce a slip of the D4 layers, the angle of the monoclinic cell increases from ~90° up to ~100°, and the ν-$K_xV_2O_5$ is formed (Fig. 4). In the meantime, two possible distinct sites appear for potassium: one as a rectangular prism (CN8 : KO_8) and the other as a trigonal prism (CN6 : KO_6). If the sites that are fully occupied by six potassium atoms could be introduced, an upper limit formula of $K_{1.50}V_2O_5$ could be obtained. In fact, because of some steric impossibilities, only half these sites can be filled. Then the
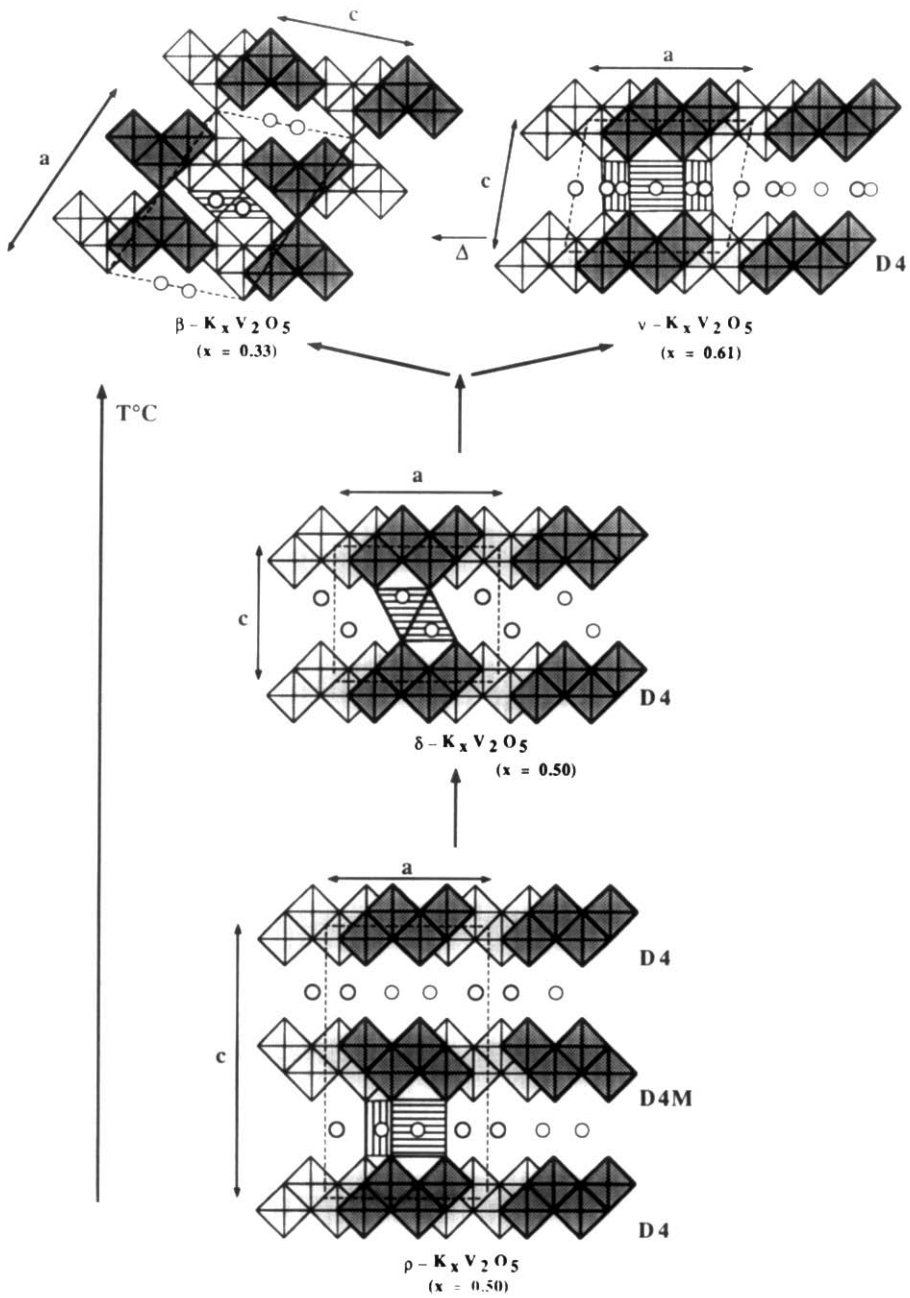
FIG. 4. Idealized representation of the potassium double layer VOB, $K_xV_2O_5$. Evolution of the structures versus temperature: $\rho \rightarrow \delta \rightarrow \nu$ and β.

ν-K$_x$V$_2$O$_5$ upper limit is reached for x = 0.75. This is also in good agreement with the homogeneity range observed at 550°C for this phase, i.e., $0.61 \leq x \leq 0.65$.

The ρ phase prepared at 350°C appears particularly well ordered and when heated at a higher temperature, around 650°C, it yields the δ phase ($x \leq 0.50$) which disproportionates partially into the two phases β ($x \leq 0.33$) (21) and ν ($x \leq 0.75$). These phases were observed by the X-ray powder diffraction technique in the bulk resulting from the heating process. Figure 4 shows, for increasing temperatures, these idealized ρ-, δ-, β-, and ν-K$_x$V$_2$O$_5$ phases and allows an easy comparison.

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