

Crystal Structures of Hydrated Vanadium Oxides with δ -Type V_2O_5 Layers: δ - $M_{0.25}V_2O_5 \cdot H_2O$, $M = Ca, Ni$

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Single crystals of hydrated vanadium oxides with layered structures containing divalent Ca or Ni were hydrothermally grown, and their structural characterization was focused on the interlayer sites. Both compounds are formulated by $M_{0.25}V_2O_5 \cdot H_2O$, $M = Ca, Ni$ and crystallize in the monoclinic system $C2/m$ with $Z = 4$: $a = 11.692(2)$, $b = 3.564(1)$, $c = 10.986(2)$ Å, $\beta = 105.42(1)^\circ$ for $M = Ca$; $a = 11.756(1)$, $b = 3.649(1)$, $c = 10.364(2)$ Å, $\beta = 95.03(1)^\circ$ for $M = Ni$. The structures consist of δ -type V_2O_5 layers stacking along the c axis and interlayer hydrated M^{2+} ions; the δ refers to the V_2O_5 layer of δ - $Ag_{0.68}V_2O_5$ after which the compounds are designated δ - $M_{0.25}V_2O_5 \cdot H_2O$. The M atoms partially occupy interlayer sites of the $2c$ position for $M = Ni$ and the $4i$ position for $M = Ca$, to each of which four water molecules (O_w) are attached forming MO_{w4} rectangles. M and O_w site occupancies indicate that the MO_{w4} rectangles are distributed so that they do not interact with each other, and the above stoichiometric formula correspond to the maximum occupancies. Bonding to three apical oxygens of the V_2O_5 layers, the Ca atom forms a CaO_7 polyhedron, and to two apical oxygens the Ni atom forms a NiO_6 octahedron, due to the Ca^{2+} ion being larger than that of Ni^{2+} ion. This is the first single-crystal study on the structures of hydrated δ -type vanadium oxide bronzes.

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INTRODUCTION

Most vanadium oxide bronzes (VOB) adopt layered structures and sometimes exhibit hydrated phases by accommodating water molecules interstitially. There have been a number of single-crystal structural studies on anhydrous phases of the layered VOBs since the pioneering work on γ - $Li_{1+x}V_3O_8$ (1) and δ - $Ag_{0.68}V_2O_5$ (2), which revealed the interlayer cationic sites as well as the host layer structures. Their structural data were summarized and sorted in a recent review (3). As for hydrated phases, no single-crystal study has been made except for recently reported σ - $Zn_{0.25}V_2O_5 \cdot H_2O$ (4) which consists of a novel-type V_2O_5 layer being somewhat different from the well-known δ -type V_2O_5 layer of δ - $Ag_{0.68}V_2O_5$ (2). The layered VOBs also

occur as natural minerals and interestingly, to our knowledge, they all exhibit hydrated phases. Evans and Hughes (5) recently grouped them into two categories, namely, hewettite group $M_xV_6O_{16} \cdot nH_2O$ and straczekite group $M_xV_6O_{16} \cdot nH_2O$, and claimed that the former is structurally related to γ - $Li_{1+x}V_3O_8$ (γ phase) and the latter to δ - $Ag_{0.68}V_2O_5$ (δ phase). However, their structural details especially concerning interlayer sites have remained unclear. Hydrothermal syntheses are considered to mimic the process of producing natural minerals. Actually, we have synthesized hydrated δ -type VOBs containing alkali metals by using hydrothermal methods (6, 7). Unfortunately the products show highly oriented and thin shapes, which greatly obstructs the way to structural characterization. For this reason we have utilized a series of X-ray 00 l reflections of the alkali-containing δ phases to derive their one-dimensional structures of atomic-sheet models by using the Rietveld method (7). However, owing to the limitations of one-dimensional models, the structural information such as the sites of interlayer atoms and their bonding to the host V_2O_5 layers has remained unknown. In the present study, we have succeeded in synthesizing single crystals of hydrated δ -type VOBs with interlayer divalent cations of Ca and Ni. Single-crystal analyses have been performed to reveal the structures with particular reference to the sites of interlayer cations and water molecules. This is the first study to locate interlayer water molecules as well as cations in the δ -type layered VOBs.

EXPERIMENTAL

Sample Preparation

Hydrothermal synthesis was conducted using starting materials of $VO_2(A)$ powders dispersed in $CaCl_2$ or $NiCl_2$ solutions. $VO_2(A)$ powders were obtained by the hydrothermal treatment of $VO(OH)_2$ powders at $250^\circ C$ for 36 h as described in detail elsewhere (8). Suspensions of 0.3 g $VO_2(A)$ powders in 80-ml solutions of 0.1 mol L^{-1} $CaCl_2$ or $NiCl_2$ were sealed in Pyrex ampoules and treated

hydrothermally in an autoclave at 280°C for 48 h. Products were filtered out and washed with distilled water. Powder X-ray diffractometry revealed that the products had highly-oriented layered phases, a single δ phase for the $\text{VO}_2\text{-CaCl}_2$ system and mixed δ and σ phases for the $\text{VO}_2\text{-NiCl}_2$ system. For the $\text{VO}_2\text{-NiCl}_2$ system, products of single δ phase were obtained when treated below 250°C. Single crystals of black thin plates were separated from the products in both systems. Chemical compositions were determined to be $\text{Ca}_{0.24(1)}\text{V}_2\text{O}_5 \cdot 1.0(1)\text{H}_2\text{O}$ and $\text{Ni}_{0.23(2)}\text{V}_2\text{O}_5 \cdot 0.9(1)\text{H}_2\text{O}$ by using atomic absorption spectrometry, thermogravimetry, and energy dispersive X-ray analysis. As will be discussed later, the two compounds are designated $\delta\text{-Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $\delta\text{-Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ from the structural points of view; the symbol δ is omitted hereafter for simplicity.

Single-Crystal X-Ray Diffraction

Single crystals suitable for structural studies were selected from tens of candidates by Weissenberg camera work since most crystals examined gave many or few elongated diffraction spots. Crystals of $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ were mounted on a Rigaku AFC-7R diffractometer with monochromatized $\text{MoK}\alpha$ radiation. Data collections were made using the $2\theta\text{-}\omega$ scanning method in a 2θ range up to 80°, where three standard reflections were monitored every 150 reflections to give no significant intensity deviations. The two compounds were confirmed to have the C-centered monoclinic system and the statistical treatments

of intensities suggested the centrosymmetric space group $C2/m$. Empirical absorption corrections of the ψ scan method were applied to give transmission factors of 0.803–0.964 for $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and 0.846–0.996 for $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$, and intensity data with $I > 3\sigma(I)$ were used in the structure refinements. Experimental and crystallographic parameters are listed in Table 1. All the data processing and the structure refinements were performed by using the TEXSAN crystal structure analysis package (9).

Crystal Structure Determination

The two compounds obviously consist of V_2O_5 layers and interstitial atoms and hence structures of the V_2O_5 layers were first determined. Atomic parameters for V_2O_5 layers were successfully taken from those of $\text{Rb}_{0.5}\text{V}_2\text{O}_5$ (10) for $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and of $\text{K}_{0.5}\text{V}_2\text{O}_5$ (11) for $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$. Interlayer Ca and Ni atoms were located in differential Fourier maps to reside in $4i$ and $2c$ positions, respectively. Their site occupancies were refined to be 0.24(1) for Ca and 0.44(2) for Ni. Oxygens of interstitial water molecules abbreviated by O_w were subsequently located likewise: $\text{O}_w(1)$ and $\text{O}_w(2)$ in $4i$ positions for $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and O_w in $8j$ positions for $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$. Occupancies of the O_w sites for $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ were checked to be 0.50(3) and thus fixed at 0.5, while that for $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ was refined to 0.47(4). In the course of refinements, the anisotropic temperature factor U_{11} for O(2) and O(3) became close to zero or sometimes negative probably due to poor

TABLE 1
Crystallographic Data and Experimental Parameters
for $\delta\text{-Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $\delta\text{-Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$

	$\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$	$\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$
Chemical formula	$\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$	$\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$
Space group	$C2/m$	$C2/m$
a (Å)	11.679(2)	11.756(1)
b (Å)	3.654(1)	3.649(1)
c (Å)	10.986(2)	10.364(2)
β (°)	105.42(1)	95.03(1)
V (Å ³)	452.0(2)	442.8(2)
Z	4	4
D_c (gcm ⁻³)	3.084	3.218
μ (cm ⁻¹)	43.5	51.8
Crystal size (mm)	0.40 × 0.20 × 0.01	0.50 × 0.10 × 0.01
Radiation	$\text{MoK}\alpha$	$\text{MoK}\alpha$
Scan technique	$2\theta\text{-}\omega$	$2\theta\text{-}\omega$
Scan width $\Delta\omega$ (°)	1.78 + 0.30 tan θ	1.78 + 0.30 tan θ
$2\theta_{\text{max}}$ (°)	80	80
Number of unique reflections ($I > 0$)	2096	1530
Number of reflections ($I > 3\sigma(I)$)	548	784
Number of variables	42	39
R	0.058	0.098
R_w	0.034	0.074

TABLE 2
Atomic Parameters, Isotropic Temperature Factors, and
Occupancies for $\delta\text{-Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $\delta\text{-Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$

Atom	Position	x	y	z	B_{eq} (Å ²)	Occupancy
$\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$						
Ca	$4i$	0.9645(7)	0	0.5184(8)	1.3(2)	0.24(1)
V(1)	$4i$	0.0985(1)	0	0.1381(2)	0.65(4)	1
V(2)	$4i$	-0.1963(1)	0	0.1408(2)	0.68(4)	1
O(1)	$4i$	0.1304(5)	0.5	0.1158(6)	0.8(1)	1
O(2)	$4i$	0.2655(5)	0	0.1008(5)	0.8(1)	1
O(3)	$4i$	-0.0589(5)	0	0.0829(5)	0.8(1)	1
O(4)	$4i$	0.1217(5)	0	0.2890(6)	1.2(1)	1
O(5)	$4i$	-0.1405(5)	0	0.2889(6)	1.4(1)	1
$\text{O}_w(1)$	$4i$	0.587(2)	0	0.491(1)	2.7(3)	0.5
$\text{O}_w(2)$	$4i$	0.670(1)	0	0.497(2)	3.0(4)	0.5
$\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$						
Ni	$2c$	0.0	0	0.5	1.0(1)	0.44(2)
V(1)	$4i$	-0.0555(2)	0	0.1422(2)	0.61(5)	1
V(2)	$4i$	0.2417(2)	0	0.1393(3)	0.74(5)	1
O(1)	$4i$	-0.0920(8)	0.5	0.1183(9)	0.7(2)	1
O(2)	$4i$	0.0860(8)	0	0.0943(9)	0.5(2)	1
O(3)	$4i$	0.2697(7)	0.5	0.1066(9)	0.4(1)	1
O(4)	$4i$	-0.0321(9)	0	0.2989(10)	1.2(2)	1
O(5)	$4i$	0.2396(9)	0	0.2920(10)	1.4(2)	1
O_w	$8j$	0.383(1)	0.892(4)	0.516(1)	2.2(5)	0.47(4)

quality of the crystals as mentioned above; therefore all the oxygens were refined isotropically. The structures were finally refined to $R/R_w = 0.058/0.034$ for $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $0.098/0.074$ for $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$. Atomic parameters, isotropic temperature factors and site occupancies are listed in Table 2.

RESULTS AND DISCUSSION

Description of Structures

Chemical formulas derived from the site occupancies are $\text{Ca}_{0.24(1)}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $\text{Ni}_{0.22(1)}\text{V}_2\text{O}_5 \cdot 0.94(8)\text{H}_2\text{O}$ in good agreement with those from the chemical analyses; stoichiometric formula for the two compounds should be expressed by $M_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (or $M\text{V}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$) as discussed below. Overall views of crystal structures for $M_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ are depicted in Fig. 1, where we note that the monoclinic β angle of $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ corresponds to $-\beta$ of $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$. Both structures are described in a common manner that V_2O_5 layers stack along the c axis and M^{2+} ions as well as water molecules reside in the interlayer space. The layer spacings are $10.591(1)$ Å for $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and $10.326(2)$ Å for $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$. The structures of V_2O_5 layers are built up with $\text{V}(1)\text{O}_6$ and $\text{V}(2)\text{O}_6$ octahedra for which $\text{V}-\text{O}$ distances and $\text{O}-\text{V}-\text{O}$ angles are given in Table 3. The V_2O_5 layers are isostructural with those of δ -type VOBs which have been well described in the preceding papers (10, 11). However, previous single-crystal studies of δ -type VOBs were done exclusively on anhydrous phases. Since this is the first single-crystal characterization of hydrated δ -type VOBs, we focus on the structures of interlayer material of M^{2+} ions and water molecules.

Interlayer sites for the Ca atom and the water ($\text{O}_w(1)$ and $\text{O}_w(2)$) in between the V_2O_5 layers are visualized in Fig. 2a. It is noted that neighboring Ca sites are separated by $1.01(2)$ Å, being so short that they must not be occupied simultaneously. The $\text{O}_w(1)$ and $\text{O}_w(2)$ sites are placed near the midplane ($z = 0.5$) to surround the Ca atom in a way that forms a CaO_{w4} rectangle with $\text{Ca}-\text{O}_w$ distances of $2.38 \sim 2.39$ Å. The Ca atom also bonds to three apical oxygens of the V_2O_5 layer, namely, two apices, $\text{O}(4)$ and $\text{O}(5)$, on one side and one $\text{O}(5)$ on the other. As a whole the Ca atom is coordinated by seven oxygens to form a CaO_7 polyhedron as depicted in Fig. 3a. $\text{Ca}-\text{O}$ distances and $\text{O}-\text{Ca}-\text{O}$ angles in the CaO_7 polyhedron are listed in Table 4. The $\text{O}_w(1)$ and $\text{O}_w(2)$ are apparently coordinated water of the Ca^{2+} ion and the CaO_{w4} rectangles are linked by sharing $\text{O}_w(1)-\text{O}_w(2)$ edges. However, it is unlikely that one coordinated water bonds to two cations. To avoid this situation, the Ca site should be occupied alternatively along the b axis, thereby the CaO_{w4} rectangles become isolated from each other. Figure 4a exemplifies the distribution of CaO_{w4} rectangles. The Ca site occupancy of 0.24 and also the $\text{H}_2\text{O}/\text{Ca}$ ratio of ~ 4.2 are consistent with this isolated CaO_{w4} distribution. The distribution gives an upper-limit Ca occupancy of 0.25 and concomitantly the $\text{H}_2\text{O}/\text{Ca}$ ratio becomes 4, leading to the formula $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$. Interlayer Ca sites in $\text{Ca}_{0.6}\text{V}_2\text{O}_5$, an anhydrous phase relative to $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$, has been determined by Kutoglu (12). There are two kinds of interlayer Ca sites, namely $\text{Ca}(1)$ forming a CaO_8 rectangular prism and $\text{Ca}(2)$ forming a CaO_6 trigonal prism, and they are partially occupied to give the formula as $\text{Ca}(1)_{0.2}\text{Ca}(2)_{0.4}\text{V}_2\text{O}_5$. The Ca site of $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ may correspond to the $\text{Ca}(1)$ site by shifting along the b axis by $y = 1/2$ in order to contact the apical oxygens of V_2O_5 layers and splitting along the a axis.

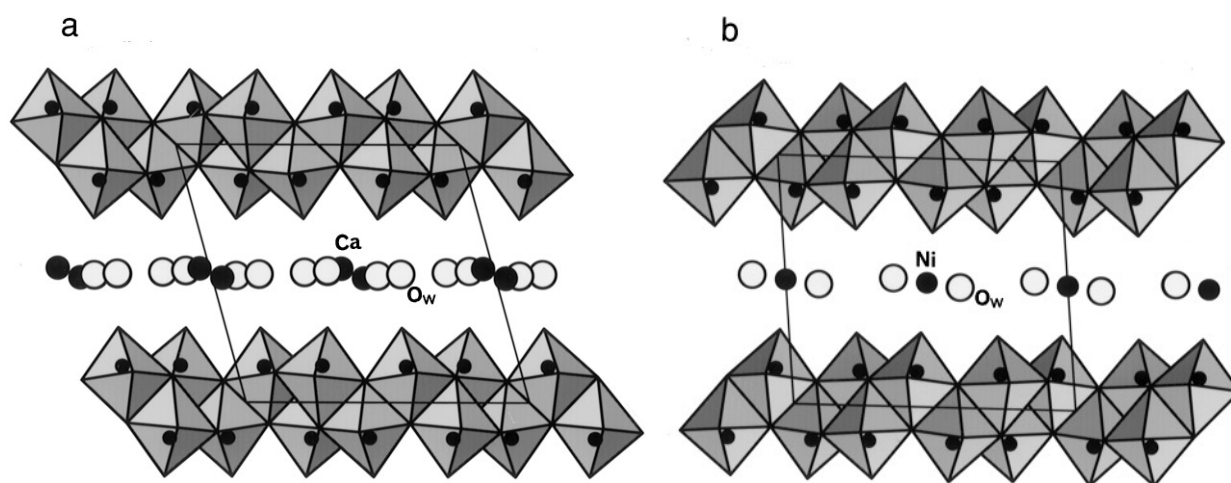


FIG. 1. Crystal structures δ - $M_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ viewed along the b axis for (a) $\text{Ca}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ and (b) $\text{Ni}_{0.25}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$. V_2O_5 layers are represented by corners of polyhedral frameworks. V and M atoms are denoted by small and large closed circles, respectively, and water molecules (O_w) are denoted by shaded circles.

TABLE 3
Bond Distances (Å) and Angles (°) for V–O Polyhedra
in δ -Ca_{0.25}V₂O₅ · H₂O and δ -Ni_{0.25}V₂O₅ · H₂O

Ca _{0.25} V ₂ O ₅ · H ₂ O					
V(1)O ₆ octahedron					
V(1)–O(1) ^{a,b}	1.893(2)	V(1)–O(2) ^a	2.096(6)	V(1)–O(3) ^a	1.776(6)
V(1)–O(3) ^c	2.348(6)	V(1)–O(4) ^a	1.607(7)		
O(1) ^a –V(1)–O(1) ^b	149.5(2)	O(1) ^{a,b} –V(1)–O(2) ^a		75.5(2)	
O(1) ^{a,b} –V(1)–O(3) ^c	100.2(2)	O(1) ^{a,b} –V(1)–O(3) ^c		81.8(2)	
O(1) ^{a,b} –V(1)–O(4) ^d	98.5(2)	O(2) ^a –V(1)–O(3) ^c	149.9(2)		
O(2) ^a –V(1)–O(3) ^c	74.7(2)	O(2) ^a –V(1)–O(4) ^d		107.0(2)	
O(3) ^c –V(1)–O(3) ^c	75.2(3)	O(3) ^c –V(1)–O(4) ^d		103.1(3)	
O(3) ^c –V(1)–O(4) ^d	178.4(3)				
V(2)O ₆ octahedron					
V(2)–O(1) ^d	1.969(6)	V(2)–O(2) ^{e,f}	1.904(2)	V(2)–O(2) ^c	2.561(6)
V(2)–O(3) ^f	1.877(6)	V(2)–O(5) ^a	1.583(7)		
O(1) ^d –V(2)–O(2) ^{e,f}	78.3(2)	O(1) ^d –V(2)–O(2) ^c		80.0(2)	
O(1) ^d –V(2)–O(3) ^f	153.2(2)	O(1) ^d –V(2)–O(5) ^a		105.7(2)	
O(2) ^e –V(2)–O(2) ^f	147.2(2)	O(2) ^{e,f} –V(2)–O(2) ^c		76.7(2)	
O(2) ^{e,f} –V(2)–O(3) ^f	95.2(2)	O(2) ^{e,f} –V(2)–O(5) ^a		104.1(2)	
O(2) ^e –V(2)–O(3) ^f	73.2(3)	O(2) ^e –V(2)–O(5) ^a		174.3(2)	
O(3) ^f –V(2)–O(5) ^a	101.1(3)				
Ni _{0.25} V ₂ O ₅ · H ₂ O					
V(1)O ₆ octahedron					
V(1)–O(1) ^{a,b}	1.886(2)	V(1)–O(2) ^a	1.777(9)	V(1)–O(2) ^c	2.446(9)
V(1)–O(3) ^f	2.056(9)	V(1)–O(4) ^a	1.62(1)		
O(1) ^a –V(1)–O(1) ^b	150.7(5)	O(1) ^{a,b} –V(1)–O(2) ^a		99.9(3)	
O(1) ^{a,b} –V(1)–O(2) ^c	81.7(3)	O(1) ^{a,b} –V(1)–O(3) ^f		76.3(3)	
O(1) ^{a,b} –V(1)–O(4) ^a	98.5(3)	O(2) ^a –V(1)–O(2) ^c		77.2(4)	
O(2) ^a –V(1)–O(3) ^f	153.5(4)	O(2) ^a –V(1)–O(4) ^a		101.5(5)	
O(2) ^a –V(1)–O(3) ^f	76.3(3)	O(2) ^a –V(1)–O(4) ^a		178.7(4)	
O(3) ^f –V(1)–O(4) ^a	105.0(5)				
V(2)O ₆ octahedron					
V(2)–O(1) ^g	1.985(9)	V(2)–O(2) ^a	1.848(9)	V(2)–O(3) ^{a,b}	1.890(32)
V(2)–O(3) ^f	2.540(9)	V(2)–O(5) ^a	1.58(1)		
O(1) ^g –V(2)–O(2) ^a	159.2(4)	O(1) ^g –V(2)–O(3) ^{a,b}		78.0(3)	
O(1) ^g –V(2)–O(3) ^f	81.7(3)	O(1) ^g –V(2)–O(5) ^a		102.2(5)	
O(2) ^a –V(2)–O(3) ^{a,b}	98.0(3)	O(2) ^a –V(2)–O(3) ^f		77.5(4)	
O(2) ^a –V(2)–O(5) ^a	98.6(5)	O(3) ^a –V(2)–O(3) ^f		149.8(5)	
O(3) ^{a,b} –V(2)–O(3) ^f	79.3(3)	O(3) ^{a,b} –V(2)–O(5) ^a		101.4(3)	
O(3) ^f –V(2)–O(5) ^a	176.1(5)				

Symmetry codes. ^ax, y, z; ^bx, y + 1, z; ^c–x, –y, –z; ^dx – 1/2, y – 1/2, z; ^ex – 1/2, y + 1/2, z; ^fx – 1/2, y – 1/2, z; ^gx + 1/2, y – 1/2, z.

The interlayer Ni and water (O_w) sites in between the V₂O₅ layers are depicted in Fig. 2b; the Ni and O_w atoms occupy the 2c and 8j positions, respectively. The O_w sites, in analogy with those in Ca_{0.25}V₂O₅ · H₂O, are placed to form a coplanar NiO_{w4} rectangle with Ni–O_w distances of 2.00 Å. The Ni atom also bonds to two apical O(4) on opposite sides thus forming a NiO₆ octahedron as depicted in Fig. 3b. It is noted that the apical O(5) plays no role in holding the Ni atom. Ni–O distances and O–Ni–O angles in the NiO₆ octahedron are listed in Table 4. The NiO₆ octahedron looks similar to the ZnO₆ octahedron in σ -Zn_{0.25}V₂O₅ · H₂O (2) as both octahedra have the same oxygen coordination exhibiting almost a regular shape. The NiO_{w4} rectangles are not linked directly unlike the CaO_{w4} rectangles, but neighboring rectangles along the b axis lie only 0.78(3) Å apart, which prevents the neighboring of

TABLE 4
Bond Distances (Å) Angles (°) for CaO₇ Polyhedron and NiO₆ Octahedron

CaO ₇ polyhedron					
Ca–O(4) ^a	2.57(1)	Ca–O(5)	2.49(1)	Ca–O(5) ^b	2.53(1)
Ca–O _w (1) ^{c,d}	2.39(1)	Ca–O _w (2) ^{e,f}	2.38(1)		
O(4) ^a –Ca–O(5)	129.6(4)	O(4) ^a –Ca–O(5) ^b		73.7(3)	
O(5)–Ca–O(5) ^b	156.7(4)	O(4) ^a –Ca–O _w (1) ^{c,d}		118.8(4)	
O(4) ^a –Ca–O _w (2) ^{e,f}	70.4(4)	O(5) ^b –Ca–O _w (1) ^{c,d}		91.3(5)	
O(5) ^b –Ca–O _w (2) ^{e,f}	77.9(4)	O(5) ^b –Ca–O _w (1) ^{c,d}		74.0(4)	
O(5) ^b –Ca–O _w (2) ^{e,f}	115.6(4)	O _w (1) ^c –Ca–O _w (1) ^d		99.8(7)	
O _w (1) ^c –Ca–O _w (2) ^f	79.0(5)	O _w (1) ^c –Ca–O _w (2) ^f		169.1(6)	
O _w (1) ^d –Ca–O _w (2) ^f	169.1(6)	O _w (1) ^d –Ca–O _w (2) ^f		79.0(5)	
O _w (2) ^e –Ca–O _w (2) ^f	100.1(6)				
NiO ₆ octahedron					
Ni–O(4) ^{a,g}	2.09(1)	Ni–O _w ^{h,i,j,k}		2.00(1)	
O(4) ^a –Ni–O(4) ^g	180	O(4) ^a –Ni–O _w ^{h,i}		89.3(3)	
O(4) ^a –Ni–O _w ^{h,k}	90.7(3)	O(4) ^a –Ni–O _w ^{h,i}		90.7(3)	
O(4) ^g –Ni–O _w ^{h,k}	89.3(3)	O _w ^h –Ni–O _w ⁱ		91.5(9)	
O _w ^h –Ni–O _w ^j	88.5(9)	O _w ^h –Ni–O _w ^k		180	
O _w ⁱ –Ni–O _w ^j	180	O _w ⁱ –Ni–O _w ^k		88.5(9)	
O _w ^j –Ni–O _w ^k	91.5(9)				

Symmetry codes. ^a1–x, 0, 1–z; ^b2–x, 0, 1–z; ^c1/2 + x, 1/2, z; ^d1/2 + x, –1/2, z; ^e3/2 – x, 1/2, 1–z; ^f3/2 – x, –1/2, 1–z; ^gx – 1, 0, z; ^hx – 1/2, y – 1/2, z; ⁱx – 1/2, 1/2 – y, z; ^j1/2 – x, y – 1/2, 1–z; ^k1/2 – x, 1/2 – y, 1–z.

rectangles. This gives the distribution of NiO_{w4} rectangles as exemplified in Fig. 4b. Since neighboring Ni sites along the b axis must not be occupied simultaneously, upper-limit occupancies for Ni and O_w sites both become 0.5, consistent with the experimental occupancies of 0.44 for Ni and 0.47 for O_w. The upper-limit occupancies again give the formula Ni_{0.25}V₂O₅ · H₂O.

The oxygen coordinations around the M atoms form CaO₇ and NiO₆ polyhedra comprising interlayer water molecules and apical oxygens of the V₂O₅ layers as depicted in Fig. 3. The difference in coordination numbers (CN) is made by the numbers of the apical oxygens. As a larger cation tends to have a higher CN, this difference properly correspond to the ionic radius (13) of Ca²⁺ (1.06 Å for CN = 7) being larger than that of Ni²⁺ (0.69 Å for CN = 6). Interlayer water molecules O_w are essentially water coordinated to M²⁺ ions and take rectangular coordinations for both M = Ca and Ni just like Zn in σ -Zn_{0.25}V₂O₅ · H₂O (2). The MO_{w4} rectangle for M = Ca exhibits an elongated shape, 3.03 (//a axis) × 3.66 Å (//b axis), while that for M = Ni exhibits a square-like shape, 2.80 (//a axis) × 2.86 Å (//b axis). Some hydrogen bonding between the water molecules and the apical oxygens may be anticipated. The distances between O_w and apical O(4) or O(5) are 2.862–3.067 Å for Ca_{0.25}V₂O₅ · H₂O and 2.775–2.930 Å for Ni_{0.25}V₂O₅ · H₂O, which are all substantially longer than 2.7 Å proposed for the critical O–H ··· O distances with strong hydrogen bonding (14). It is thus said that only weak hydrogen bonding exists, if any, between O_w and apical O(4) or O(5) in both compounds.

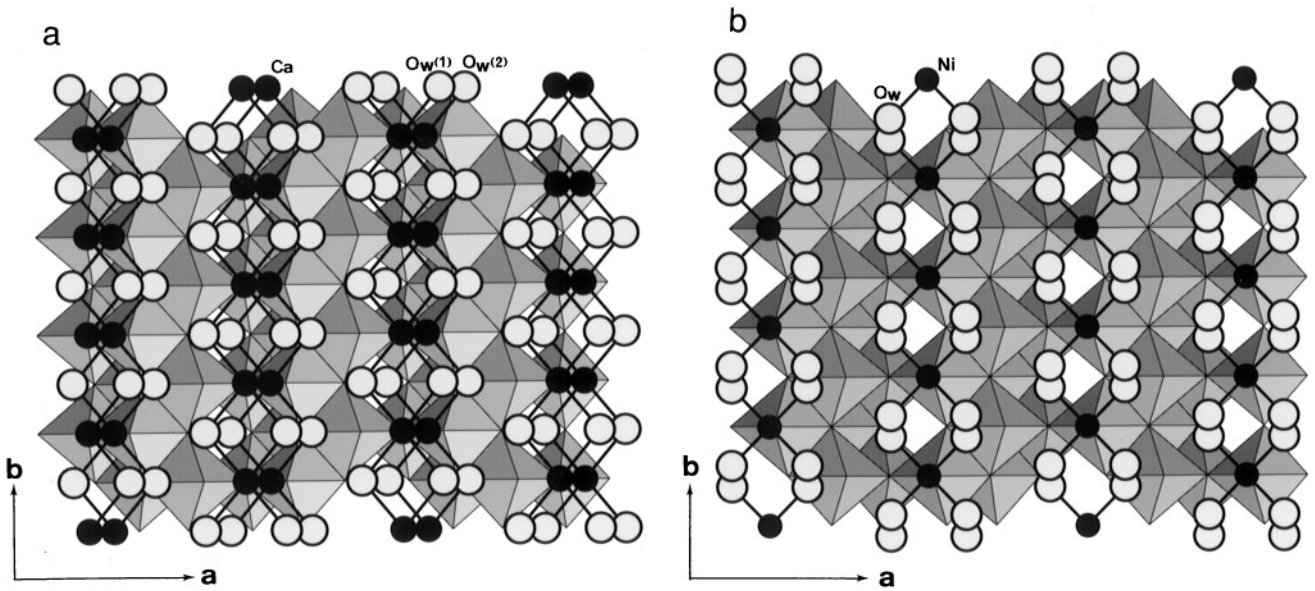


FIG. 2. Locations of M and O_w sites in between the V_2O_5 layers in the ab plane for (a) $M = Ca$ and (b) $M = Ni$. M and O_w sites are denoted by closed and shaded circles, respectively, and $M-O_w$ bonds are indicated by thick lines. V_2O_5 layers below the interlayer sites are drawn by polyhedral representation.

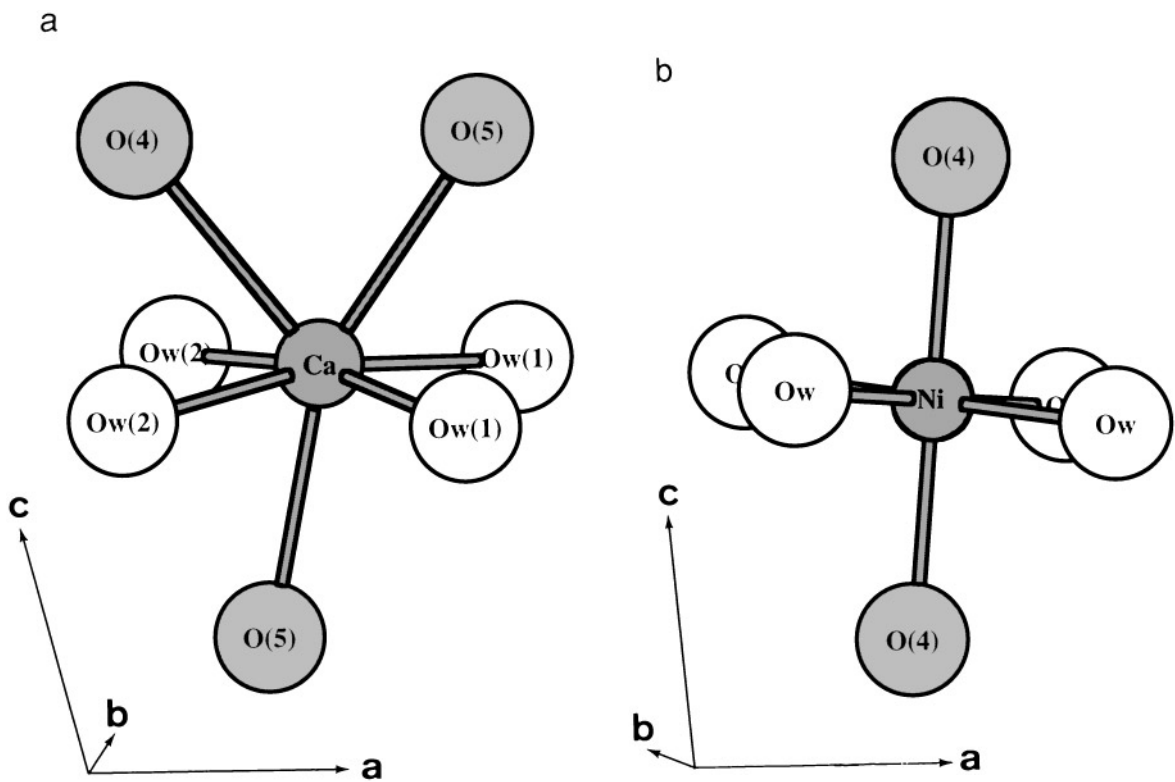


FIG. 3. Oxygen coordinations for (a) CaO_7 polyhedron and (b) NiO_6 octahedron.

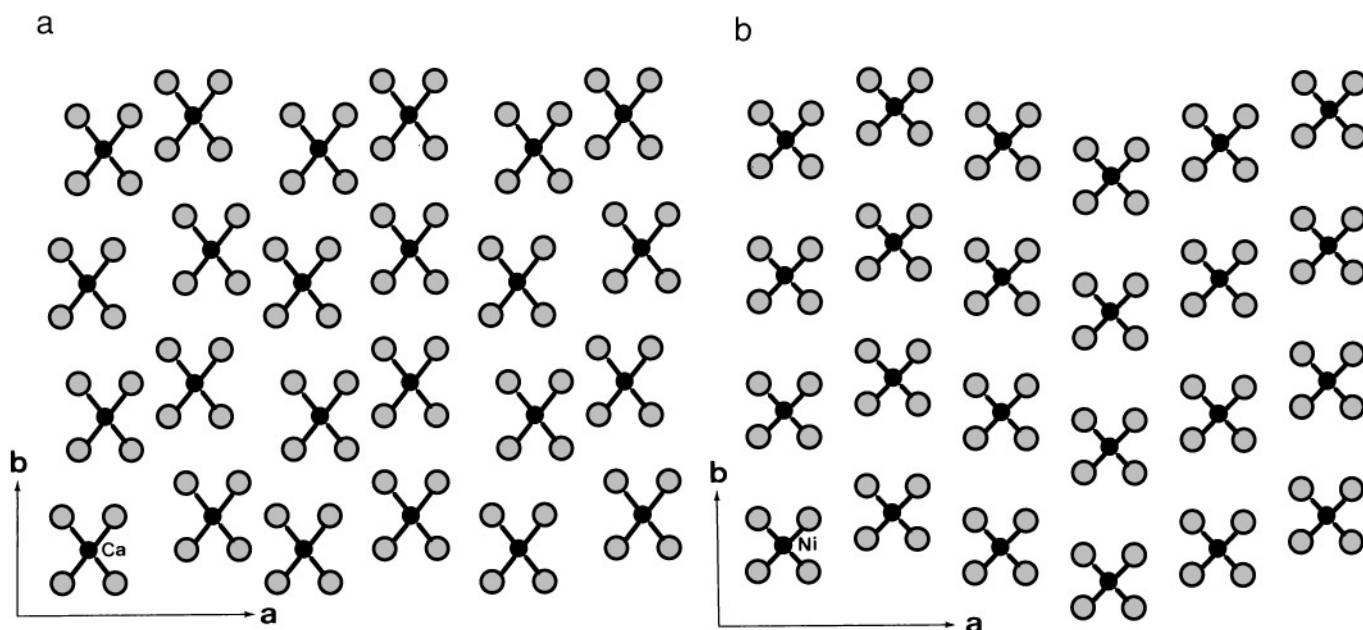


FIG. 4. Demonstrations of distributions of MO_w4 rectangles in the ab plane for (a) $M = \text{Ca}$ and (b) $M = \text{Ni}$. M and O_w atoms are denoted by closed and shaded circles, respectively, and MO_w4 rectangles are represented by $M-O_w$ bonds indicated by thick lines.

Comparison with Natural Minerals

There are a number of mixed-valence vanadium (IV, V) oxide minerals with layered structures. The crystal chemistry of this class of minerals was recently reviewed by Evans and Hughes as natural vanadium bronzes (5). As mentioned above they divided the layered bronzes into two groups, namely, the hewettite group $M_xV_6O_{16} \cdot nH_2O$ ($M = \text{Ca}, \text{Na}$) and the straczekite group $M_xV_8O_{20} \cdot nH_2O$ ($M = \text{Na}, \text{K}, \text{Ca}, \text{Ba}, \text{Al}, \text{etc.}$), and suggested the structural analogy with $\gamma\text{-Li}_{1+x}V_3O_8$ (or $\theta\text{-Li}_3V_6O_{16}$) for the former and with $\delta\text{-Ag}_{0.68}V_2O_5$ for the latter. The present compounds are apparently analogous to the straczekite group or the δ -type bronze. One member of the group designated fernandinite shows $(\text{Ca}, \text{Na}, \text{K})_xV_8O_{20} \cdot 4H_2O$ ($x = 0.9\text{--}1.2$), where the Ca^{2+} ion is a major interlayer cation (15). The formula is well compared to the present $\text{Ca}_{0.25}V_2O_5 \cdot H_2O$. Moreover, fernandinite exhibits the monoclinic system $C2/m$ with $a = 11.680(2)$, $b = 3.6537(4)$, $c = 11.023(2)$ Å, and $\beta = 105.00(2)^\circ$ being close to the lattice parameters of $\text{Ca}_{0.25}V_2O_5 \cdot H_2O$ given in Table 1. Evans *et al.* (14) made an X-ray Rietveld study on natural fernandinite and derived the V_2O_5 layer structure and possible interlayer sites. The atomic parameters for the V_2O_5 layer are similar to those of $\text{Ca}_{0.25}V_2O_5 \cdot H_2O$ but due to the limitation of powder data they failed to locate exact interlayer sites and even to distinguish between metal and water. Their $M(1)$ site at $4i$ ($x = 0.061(2)$, $z = 0.506(3)$) and $M(2)$ site ($x = 0.568(4)$, $z = 0.478(4)$) must correspond to the present Ca and $O_w(1)$

sites, respectively. Consequently $\text{Ca}_{0.25}V_2O_5 \cdot H_2O$ is undoubtedly the synthetic analog of fernandinite. There is no natural mineral in the straczekite group that corresponds to the present synthetic $\text{Ni}_{0.25}V_2O_5 \cdot H_2O$.

CONCLUSION

Single crystals of $\text{Ca}_{0.25}V_2O_5 \cdot H_2O$ and $\text{Ni}_{0.25}V_2O_5 \cdot H_2O$ have been grown hydrothermally. Structural studies revealed V_2O_5 layers of the δ -type layered VOBs and interlayer sites for divalent metals and water. The site occupancies and distributions of the interlayer metals and water confirmed the title formulas to be stoichiometric ones. Both compounds belong to hydrated layered VOBs and thus are denoted $\delta\text{-}M_{0.25}V_2O_5 \cdot H_2O$ ($M = \text{Ca}, \text{Ni}$). The interlayer M^{2+} ions both have four water molecules (O_w) in coplanar MO_w4 rectangular coordinations but show different $M-O$ coordinations with apical oxygens of the V_2O_5 layers depending on the sizes of M^{2+} ions, that is, the CaO_7 polyhedron and the NiO_6 octahedron. $\text{Ca}_{0.25}V_2O_5 \cdot H_2O$ is found to be a synthetic analog of the vanadium oxide mineral fernandinite belonging to the straczekite group.

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