

Crystal Growth, Structural and Electrical Properties of Rubidium and Cesium Vanadium Oxide Bronzes

PIERRE STROBEL

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'U.S.M.G., 166X, 38042 Grenoble Cédex, France

Received October 17, 1985; in revised form February 4, 1986

Crystals of the following compounds were grown by cathodic reduction of Cs-V⁵⁺-O or Rb-V⁵⁺-O metls: Cs_{0.3}V₂O₅ (A), Cs₂V₅O₁₃ (B), CsV₂O₅ (C), Rb_{0.4}V₂O₅ (D), Rb_{0.37}V₂O_{-4.8} (E) (a new orthorhombic compound) and Rb_{2-x}V_{3+2x}O_{8+2x} (F). The crystal symmetry and cell parameters of the Rb compounds (which were known for F only) were determined, as well as those of Rb_{0.3}V₂O₅, which has the structure of A. Magnetic susceptibility and ESR measurements confirm the intermediate valence in E. A, C, and E are semiconductors with activation energies in the range 0.07-0.2 eV. Cs_{0.3}V₂O₅ (A), in which V⁴⁺ and V⁵⁺ do not occupy distinct crystallographic sites, has the highest electrical conductivity. © 1987

Academic Press, Inc.

Introduction

Vanadium oxide bronzes (VOB's), i.e., ternary vanadium oxides containing vanadium with an oxidation state between +4 and +5, are known to exist with various univalent or divalent metal cations (1, 2). Those formed by rubidium and cesium have been much less studied than their lighter alkali metal or IB metal counterparts (1, 2). Fotiev *et al.* (3-5) reported a number of M₂V₂O₅ compounds with M = Rb or Cs, but did not publish any structural data or physical properties; the nomenclature used in their papers is rather confusing (the compound later identified as Cs₂V₅O₁₃, for instance, was named "ζ-phase" (3), "ν-phase" (4), and "σ-phase" (5), successively). The only well-characterized rubidium compound is Rb_{2-x}V_{3+2x}O_{8+2x} (6), which is isostructural of the potassium "φ-VOB" (7, 8). Cesium VOB's have been bet-

ter characterized, because single crystals were prepared by either electrolysis (Reid and Watts (9), two compounds) or a flux method under controlled oxygen pressure (Forslund and Jelinski (10), four compounds). The structures of these four cesium VOB's have been determined (11, 12), and their electrical and magnetic properties have been recently reported (13).

These heavy alkali metal VOB's are interesting because they adopt structures differing from VOB's containing light univalent cations, which form a fairly homogeneous family (1). In particular, the very common β-VOB structure (14), which can accommodate various cations with octahedral ionic radii (15) up to ~140 pm (Ba²⁺, K⁺), does not occur for Rb⁺ and Cs⁺ (ionic radius 152 and 167 pm, respectively). Cesium VOB's crystallize with either a layer or channel structure. The former are insulating, while the latter are semiconduc-

tors with activation energies of conductivity near 50 meV and unexplained slope changes in their $\log \sigma$ vs T^{-1} curves (13).

Chemically, Rb- and Cs-VOB's do not resemble the typical tungsten oxide bronzes, which were early noted for their remarkable chemical inertness. In a study of electrolytic crystal growth of potassium VOB's, Babenko *et al.* (16) were able to wash the bronze crystals in a 50% NaOH solution. On the contrary, Fotiev *et al.* (3) noted that Rb- and Cs-VOB's are readily decomposed in alkalis, as well as in acids. This property, which is confirmed by the present work, makes difficult the recovery and washing of crystals. For flux growth, Forslund and Jelinski had to build a movable suction tube to pick up crystals before melt cooling (10).

The present paper reports a systematic investigation of single-crystal synthesis of Rb- and Cs-VOB's by electrolysis, the structural and ESR characterization of Rb-VOB's, and electrical conductivity measurements on single crystals. Preliminary results of crystal growth have been discussed in Ref. (17). A new orthorhombic structure, which is not known in either the potassium or cesium VOB's system, was found in the Rb-V-O system and obtained as single crystals up to 3 mm long.

Experimental

The electrolytic arrangement used in this work has been described previously (17, 18). Starting materials were reagent grade Rb_2CO_3 , Cs_2CO_3 , and V_2O_5 (Alfa-Ventron or Prolabo), heated in high-purity alumina crucibles (McDaniel Co.). In a typical run, the sample charge was first intimately mixed and heated slowly to 400°C in air, allowing the carbonates to decompose. The temperature was then increased to the melting point and melting was checked visually. The temperature was finally stabilized at

20–30°C above the melting point, and the cathode was lowered down to the surface of the melt. The electrolysis was carried out for several days with a stabilized current (usually <20 mA). Preliminary attempts carried out in argon atmosphere (in the rubidium system) gave results similar to those carried out in air. Detailed experimental conditions are given in Table I. At the end of the process, the cathode was raised above the melt before cooling. Recovery of the crystals was difficult because the cathode tip frequently carried a group of crystals imbedded in solidified vanadate. The vanadate block had to be broken and washed out with water or dilute ammonia. As noted by Fotiev *et al.* (3), the use of acids, even dilute, resulted in the loss of the crystals.

Crystals were identified by X-ray diffraction (precession camera) and electron diffraction (PHILIPS 400T electron microscope). Accurate cell parameters were obtained by a least-squares refinement from room-temperature powder X-ray diffraction in a Guinier camera ($\text{FeK}\alpha$ radiation, internal silicon standard). The composition of crystals of rubidium VOB's was determined by microprobe analysis of Rb and V, using pure vanadium as a primary standard and $\text{Rb}_2\text{V}_3\text{O}_8$ as a secondary standard. An average of 25 countings was made with the electron beam scanning across the surface of cut and polished samples. The standard deviation was in each case within 2%, with the exception of the Rb determination in the rubidium “ ν ” compound, for which the scattering reached 5%.

Magnetic susceptibilities were measured in the range 4–300 K using a Faraday balance with a 660 kA/m field. The observed susceptibilities were corrected for diamagnetism (19) and for V_2O_5 temperature-independent paramagnetism (see below). ESR spectra of the new rubidium phase were recorded down to 8 K at X-band frequencies with a Thompson THN 251

TABLE I
EXPERIMENTAL CONDITIONS AND RESULTS OF ELECTROLYTICAL CRYSTAL GROWTH

Run	Melt composition (mole% M_2CO_3)	Temp. ($^{\circ}C$)	I (mA)	Time (Days)	Crystals recovered	Identification
(A) Cs-V-O system						
1, 2	12-13	600	25-50	8-14	(V_2O_5 + Pt dendrites)	
3		570	9.0	7	Dark needles 2-3 mm long	$Cs_{80.3}V_2O_5$ (12)
4	15.0	500	10.1	11	Black plates $2 \times 2 \times 0.2$ mm	$Cs_2V_5O_{13}$ (9, 12)
5	30.0	460	7.0	12	Black plates $2 \times 2 \times 0.2$ mm	CsV_2O_5 (9, 11)
	37.0					
(B) Rb-V-O System						
6		600	20.4	5	Yellow needles	V_2O_5
7	9.8 ~20.7	535	10.0	5	Brown blocks (cathode) $5 \times 3 \times 2$ mm ^a + black needles up to 3 mm long ^b	" ν' -VOB" monoclinic (22) New orthorhombic phase
8		510	15.0	8	As in run 7	
9	21.9 22.0	~500	60.0	8	Black blocks or plates	" ν' -VOB"
10, 11	27.0 - 29.2	490-540	10-17	6-10	As in run 9	" ν' -VOB"
12, 13	40.0	500	6.6	10	Brown blocks $5 \times 3 \times 3$ mm	~ $Rb_2V_3O_8$ ("' ϕ -VOB'") (6)

^a Cleave easily as thin platelets.

^b Recovered from solidified melt surface or crucible walls.

spectrometer calibrated with P-doped silicon ($g = 2.0038$).

Electrical resistivities were determined in the temperature range 77-300 K using a four-probe arrangement. The voltage drop across the samples was measured by a Keithley 610 electrometer. Electrical contacts were made of evaporated or ultrasonically applied indium. Dimensions of the samples were measured with a microscope using a calibrated grid. Uncertainties about the absolute values of the resistivity were estimated to be about 20% due to the irregular shape of the samples; the error in the relative values and in the slope of the temperature dependence was much smaller.

Results and Discussion

1. Crystal Growth and Characterization

The conditions and results of electrochemical synthesis are summarized in Table I. Three rubidium phases and three cesium phases were obtained, depending on the composition of the melt.

1.1. Cesium compounds. In the Cs-V-O system, electrolysis yielded crystals of $Cs_2V_5O_{13}$ and CsV_2O_5 previously obtained by Reid and Watts (9). The alkali contents required, however, were lower than those reported by Reid and Watts. A decrease in this content below 22 mole% leads to a markedly higher liquidus temperature (20,

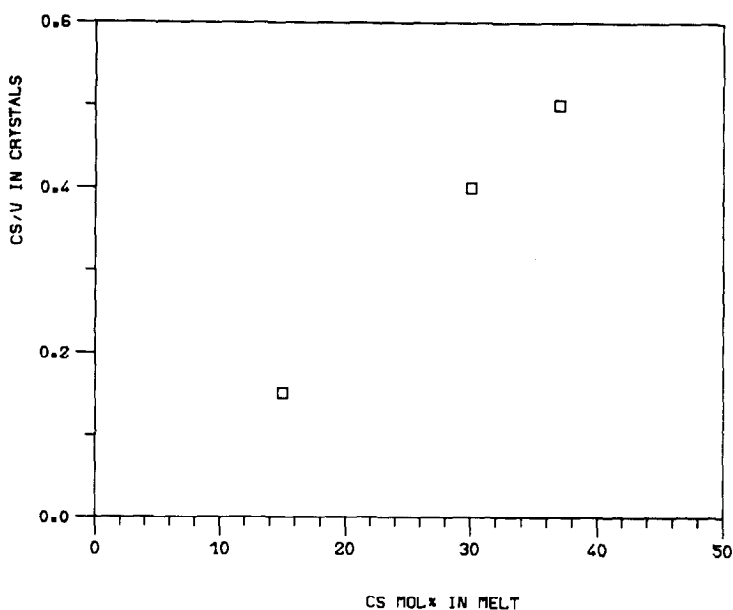


FIG. 1. The relationship between melt and cathodic deposit composition in the Cs-V-O system.

21), making more difficult the synthesis of the oxide bronzes, which have limited thermal stability. Crystals of $\text{Cs}_{0.3}\text{V}_2\text{O}_5$ were grown in this composition range at 570°C . There is an obvious relationship between the Cs/V ratio in the crystals deposited and the composition of the melt (see Fig. 1). However, further attempts at low alkali content, which required temperatures in excess of 600°C , produced no oxide bronze crystals; platinum dendrites formed on the cathode in several runs, indicating partial dissolution of the platinum anode in the melt.

$\text{Cs}_2\text{V}_5\text{O}_{13}$ and CsV_2O_5 grow as thin plates, whereas $\text{Cs}_{0.3}\text{V}_2\text{O}_5$ gives acicular crystals. The habits and structures of these compounds confirm the results of Forslund *et al.* (12, 13). $\text{Cs}_{0.35}\text{V}_3\text{O}_7$, which was prepared by solid state reaction at 500 – 600°C (10), could not be obtained electrochemically, probably because of the high temperatures required to melt the mixtures with low Cs/V ratios.

1.2. Rubidium compounds. Although Fottiev and co-workers (3–5) reported no less

than six rubidium VOB's (characterized only by unindexed powder X-ray diffraction patterns), only three compounds were found in the present work. The critical temperature for bronze deposition on the cathode seems to be about 600°C . A quite surprising result was the reproducible formation of two oxide bronzes simultaneously in melts with ~ 21 mole% Rb_2CO_3 (see Table I). Cathodic reduction yielded $\text{Rb}_{-0.4}\text{V}_2\text{O}_5$ platelets, while crystals several millimeters long of a new compound grew on the crucible walls or at the surface of the solidified melt. $\text{Rb}_{-0.4}\text{V}_2\text{O}_5$ was formed from a rather wide range of melt compositions (20 to 27 mole% Rb) and was found to exist with a range of compositions: the crystals grown from a 27 mole% melt have a larger Rb content and a smaller O/V ratio (see Table II). At higher rubidium concentrations, the known compound $\text{Rb}_2\text{V}_3\text{O}_8$ (actually slightly nonstoichiometric) grew. It has a typically layered morphology and cleaves easily into very thin plates.

The results of chemical analysis and structural characterization are given in Ta-

TABLE II
CHEMICAL COMPOSITION AND STRUCTURAL CHARACTERIZATION OF
Rb-VANADIUM OXIDE BRONZES

Run	Composition	Phase	Crystal system	Space group	Cell parameters (pm)
8	Rb _{0.365(6)} V ₂ O _{4.8(1)}	ν'	Monoclinic	<i>C2/m</i>	$a = 1163(4)$
9	Rb _{0.38(2)} V ₂ O _{4.8(2)}				$b = 366.4(8)$
10	Rb _{0.40(2)} V ₂ O _{4.6(3)}				$c = 975(3)$
					$\beta = 101.2(5)$
7	Rb _{0.383(7)} V ₂ O _{4.65(15)}	New	Orthorhombic	<i>C222</i> or	$a = 1522.1(5)$
8	Rb _{0.375(4)} V ₂ O _{4.99(8)}			<i>Cmm2</i> or	$b = 361.8(1)$
				<i>Cmmm</i>	$c = 1499.7(4)$
12	Rb _{1.88(2)} V _{3.24} O _{8.24}	ϕ	Tetragonal	<i>P4/*b*</i>	$a = 892.0(1)$
13	Rb _{1.85(4)} V _{3.30} O _{8.30}				$c = 553.9(1)$
	Rb _{0.3} V ₂ O ₅ or RbV ₆ O ₁₅ ^a	Cs _{0.3} V ₃ O ₅	Hexagonal	<i>P6₃/m</i>	$a = 1415.1(6)$ $c = 358.6(1)$

^a Not found in this work; cell parameters obtained by indexing X-ray data from Ref. (4) in the Cs_{0.3}V₂O₅ cell.

ble II. The two compounds obtained simultaneously in Runs 7 and 8 have very close Rb/V ratios, but they differ by their crystal habit and unit cell as shown by powder and single-crystal X-ray diffraction. Both, however, exhibit a short *b* parameter (~365 pm) which is typical of structures derived from V₂O₅. This parameter represents the double of a VO₅ square-pyramid height in V₂O₅; it is found in the oxides V_{*n*}O_{2*n*+1} and in many VOB's (22) (but in none of the cesium VOB's).

Monoclinic Rb_{-0.4}V₂O₅ appears to be the rubidium homolog of the " ν' phase" K_{-0.6}V₂O₅ (23). Its structure is not known; precession photographs show that all crystals obtained are badly twinned. The Rb_{-0.4}V₂O₅ unit cell (Table II) is very similar to that of Ca_{0.6}V₂O₅ (24), which contains zig-zag chains of edge-sharing distorted VO₅ pyramids (described in Ref. (24) as distorted octahedra). Such a framework, in which there are no specific sites for V⁴⁺ ions, is characteristic of VOB's (22).

The new compound is C-centered orthorhombic. Its unit cell (Table II) does not present any simple relationship with

that of other known VOB's. Because of twinning, a single-crystal structural study could not be carried out. The unit cell was confirmed by electron diffraction. The needle axis is the shortest cell axis *b*. Indexed powder patterns of Rb_{-0.4}V₂O₅ and Rb_{0.37}V₂O_{4.8} are given in Table III.

The third rubidium VOB obtained here is the tetragonal " ϕ -phase," which is slightly nonstoichiometric (Rb_{2-*x*}V_{3+2*x*}O_{8+2*x*} with *x* = 0.13) and grew as plates perpendicular to *c*. The previously reported compound Rb_{0.3}V₂O₅ (or RbV₆O₁₅) (3, 4) was not found in the present study, possibly because it would require a melt composition with too high liquidus temperature. An examination of its powder pattern (JCPDS n° 30-1098) reveals a striking resemblance to that of the hexagonal cesium VOB Cs_{0.3}V₂O₅ and corresponds to the cell parameters given in Table II. The few powder diffraction lines previously attributed to two compounds Rb_{*x*}V₂O₅ with *x* ~ 0.4 (3-5) are mostly included in the powder patterns of Rb_{0.37}V₂O_{4.8} and Rb_{-0.4}V₂O₅ (see Table III). Note that previous synthesis in the Rb-V-O system was carried out by solid state reactions (3-6).

As discussed by Nygren *et al.* (13), it is difficult to reach homogeneous phases by this technique.

2. Physical Properties

2.1. Magnetic properties. The magnetic susceptibilities of the tetragonal and orthorhombic rubidium VOB's have been measured. The former follows a Curie-Weiss law down to 10 K with $\theta = -16$ K and $C = 0.590$ emu K/mole, corresponding to a magnetic moment of 1.718 Bohr magnetons for V^{4+} in $Rb_{1.88}V_{3.24}O_{8.24}$ (theoretical spin-only value: 1.732). This behavior is very similar to that of the potassium homolog (25). On the contrary, the variation of the reciprocal susceptibility of the new orthorhombic bronze $Rb_{0.37}V_2O_{4.8}$ (which could be measured up to 180 K only) exhibits a strong curvature towards the T axis below ~ 90 K (see Fig. 2). No meaningful magnetic moment was extracted from the data. It was checked that the curvature of

TABLE III
X-RAY POWDER DIFFRACTION
PATTERNS OF RUBIDIUM
VANADIUM OXIDE BRONZES

d_{obs} (pm)	d_{calcd} (pm)	$h k l$	I_{obs}
(a) $Rb_{-0.4}V_2O_5$ ("v'-phase")			
345 ^a	348.5	1 1 0	60
336	336.2	2 0 2	100
331 ^a	333.8	$\bar{1}$ 1 1	<10
323.7 ^a	321.5	1 1 1	20
306.9	304.5	$\bar{2}$ 0 3	40
284.4	284.7	4 0 0	40
264.0 ^a	263.5	3 1 0	60
259.7	259.7	4 0 1	40
226.6	226.4	4 0 2	<10
202.8	203.0	$\bar{1}$ 1 4	40
195.9	195.8	$\bar{5}$ 1 1	10
193.0	193.1	$\bar{2}$ 0 5	40
184.5	183.9	5 1 1	60
180.1	179.8	0 2 1	40
	179.7	6 0 1	

TABLE III—Continued

d_{obs} (pm)	d_{calcd} (pm)	$h k l$	I_{obs}
(b) $Rb_{0.37}V_2O_{4.8}$ (new phase)			
760	761.0	2 0 0	20
682	678.7	2 0 1	20
535 ^b	534.1	2 0 2	40
500 ^b	499.9	0 0 3	<10
417.6 ^b	417.8	2 0 3	60
374.9	374.9	0 0 4	20
368.6 ^b	368.8	4 0 1	60
342.8	342.7	1 1 1	100
339.1 ^b	339.3	4 0 2	100
336.4	336.3	2 0 4	40
318.6	318.6	1 1 2	60
302.9 ^b	302.8	4 0 3	60
299.8	299.9	0 0 5	60
294.5	294.6	3 1 0	40
288.9 ^b	289.0	3 1 1	60
287.9	287.8	1 1 3	60
279.2 ^b	279.1	2 0 5	40
274.4	274.2	3 1 2	40
267.4 ^b	267.1	4 0 4	20
256.5	256.6	1 1 4	60
253.8 ^b	253.8	3 1 3	40
237.5 ^b	237.5	2 0 6	40
233.0 ^b	232.9	5 1 0	10
230.1	230.2	5 1 1	10
228.1	228.3	1 1 5	40
226.1	226.2	6 0 3	20
211.2	211.1	5 1 3	10
210.0	210.1	6 0 4	40
209.2	208.9	4 0 6	40
203.7	203.8	1 1 6	40
198.2	197.9	5 1 4	20
190.5	190.6	3 1 6	40
186.4	186.37	7 1 0	10
185.05	194.95	7 1 1	10
183.95	183.97	5 1 5	20
180.9	180.90	0 2 0	80
169.9	170.10	0 2 3	10
	169.67	8 0 4	
159.6	159.63	4 2 2	20
157.8	157.64	5 1 7	20
154.9	154.91	0 2 5	20
152.6	152.64	4 0 9	20

^a Lines of Volkov's "δ" phase (4); also at $d = 241, 182.6$.

^b Lines of Fotiev's "δ'"-phase (3); also at $d = 560, 306, 270, 249, 240$ (all very weak).

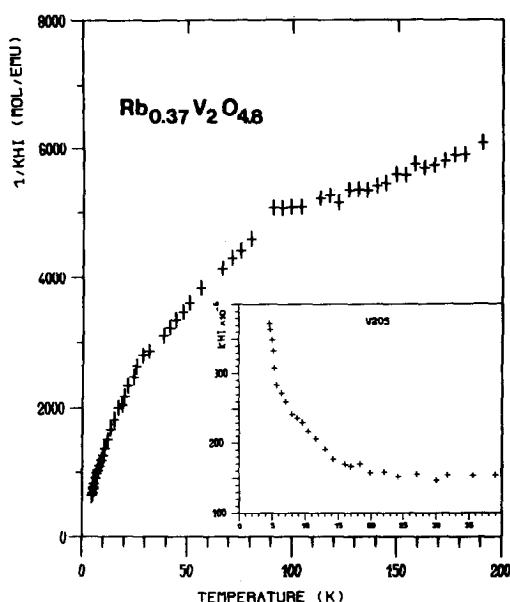


FIG. 2. Low-temperature magnetic susceptibility of $\text{Rb}_{0.37}\text{V}_2\text{O}_{4.8}$ (plotted as χ^{-1} vs T).

$\chi^{-1}(T)$ is not due to the contribution of V_2O_5 , which is a temperature-independent paramagnet above ~ 80 K, but often exhibits impurity paramagnetism at low temperature (26), as shown in "Prolabo" V_2O_5 (see Fig. 2, inset). The temperature dependence of $\text{Rb}_{0.37}\text{V}_2\text{O}_{4.8}$ reverse susceptibility (after correction for the V_2O_5 contribution) probably indicates short-range antiferromagnetic interactions.

ESR spectra were recorded on bunches of twinned acicular crystals with a common needle axis b at variable (H , b) angle. A single resonance line is observed (Fig. 3) with $g = 1.982 \pm 0.002$ ($b \parallel H$) and $g = 1.933 \pm 0.005$ ($b \perp H$). These g -values are typical of oxide lattices with V^{4+} centers in an axially distorted crystal field (26–28). The peak-to-peak linewidth ΔH shows a broad plateau in the range 8–25 K (~ 42 G), then increases with temperature (82.5 G at 80.1 K). No low-temperature decrease of ΔH with T , such as that occurring in copper VOB's (and ascribed to motional narrowing by hopping $3d^1$ electrons (26)), was ob-

served. The lack of hyperfine structure in $\text{Rb}_{0.37}\text{V}_2\text{O}_{4.8}$ indicates that the hopping frequency of the $3d^1$ electron is larger than the hyperfine coupling constant (in frequency units).

2.2. Electrical properties. The resistivities of crystals of five VOB's were measured (crystals of the ν' -phase were too brittle for the attachment of contacts). For $\text{Cs}_{0.3}\text{V}_2\text{O}_5$, contacts deposited by evaporation–condensation of indium were used and particular care was given to the acquisition of data points in the range 90–100 K, where a semiconductor–semiconductor transition with a jump in resistance by a factor ~ 2 was reported (13). There is a slight curvature in $\log \sigma = f(T^{-1})$ in that temperature range (see Fig. 4a), but no transition was found in any of the three crystals examined (measurements were made parallel to the c axis). Activation energies are comparable with those reported by Nygren *et al.* (13) (see Table IV). It should be noted that the magnetic susceptibility curve of $\text{Cs}_{0.3}\text{V}_2\text{O}_5$ exhibits no anomaly near 97 K (13), and that similar unexplained jumps in σ at 98–115 K were found on other compounds by Nygren *et al.* (Fig. 6 in Ref. (13)), which may indicate some instrumental effect in their measurements. The fairly good electrical conductivity of $\text{Cs}_{0.3}\text{V}_2\text{O}_5$ and its low activation energy (which is of the same order of magnitude as those of semiconduct-

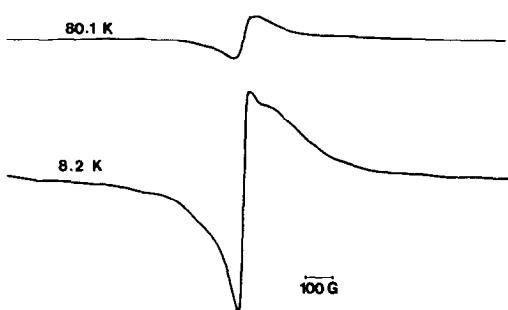


FIG. 3. ESR spectrum of polycrystalline $\text{Rb}_{0.37}\text{V}_2\text{O}_{4.8}$.

ing sodium VOB's (1)) are consistent with its structure, which contains V^{4+} ions statistically distributed among the vanadium sites. This feature is characteristic of an oxide bronze, and favors conduction by small-polaron hopping through the framework vanadium sites (27, 29).

The new orthorhombic compound $Rb_{0.37}V_2O_{4.8}$, which exhibits comparable structural features (see Section 1.2), is a fairly

good electrical conductor, with a small activation energy (see Fig. 4b). The alkali metal-richer compounds, however, are much poorer conductors (Table IV). The temperature variation of the resistivity could be measured for CsV_2O_5 only (see Fig. 4c), while $Cs_2V_5O_{13}$ and the rubidium ϕ -phase can be practically regarded as insulators. These three compounds share similar structural features, departing from typi-

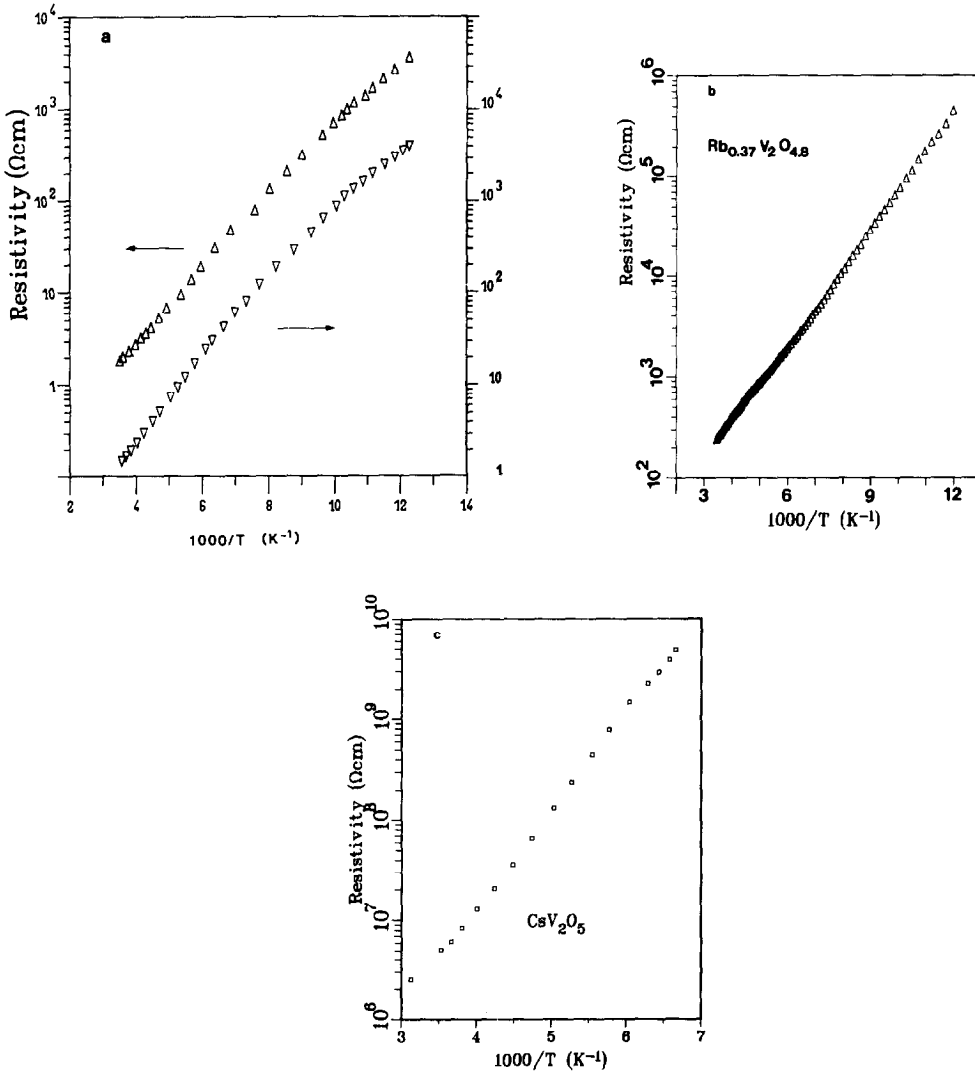


FIG. 4. Electrical resistivity of bronze phases versus reciprocal temperature: (a) $Cs_{0.3}V_2O_5$ (two single crystals, measurement along the c axis); (b) $Rb_{0.37}V_2O_{4.8}$ (block of twinned crystals, measurement along the b axis); (c) CsV_2O_5 (single crystal).

TABLE IV
ELECTRICAL PROPERTIES OF Rb AND Cs VOB'S

Formula	Sample origin	Approximate RT conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	Activation energy of conductivity (meV)		Shortest V-V distance (pm)
			100-300 K	80-95 K	
$\text{Cs}_{0.3}\text{V}_2\text{O}_5$	Ref. (13)	~5	62	53	304 ^a
	Run 3	~2	73	55	
$\text{Rb}_{0.38}\text{V}_2\text{O}_{4.8}$	Run 8	0.5	-75-		?
CsV_2O_5	Run 5	$5 \cdot 10^{-5}$	190		307 ^b
					335 ^c
$\text{Rb}_{1.88}\text{V}_{3.2}\text{O}_{8.2}$	Run 12	$<10^{-9}$			348 ^c
$\text{Cs}_2\text{V}_5\text{O}_{13}$	Run 4	$<10^{-9}$			348 ^c

^a Sites statistically occupied by V^{4+} or V^{5+} .

^b Distance $\text{V}^{4+}-\text{V}^{4+}$ (isolated pairs).

^c Distance $\text{V}^{4+}-\text{V}^{5+}$.

cal oxide-bronze character, which can explain their insulating character. They are built up of layers containing V^{4+} and V^{5+} on distinct crystallographic sites with different oxygen coordination (square pyramidal for V^{4+} , tetrahedral for V^{5+} (8, 12)). Moreover, in each of these compounds, the single V^{4+} atom is more strongly bonded to one oxygen atom, with one $\text{V}^{4+}-\text{O}$ distance 158-160 pm, typical of the vanadyl ion VO^{2+} . Thus they can be written as $\text{Cs}(\text{V}^{\text{IV}}\text{O})(\text{V}^{\text{VO}}\text{O}_4)$, $\text{Cs}_2(\text{V}^{\text{IV}}\text{O})(\text{V}^{\text{VO}}\text{O}_3)_4$, and $\text{Rb}_2(\text{V}^{\text{IV}}\text{O})(\text{V}_2^{\text{VO}}\text{O}_7)$, and should be considered as ionic mixed oxides rather than oxide bronzes. (The $\text{M}_2\text{V}_3\text{O}_8$ structure is actually that of the ionic mineral fresnoite, $\text{Ba}_2(\text{TiO})(\text{Si}_2\text{O}_7)$ (30)). No electronic conduction is to be expected in this case; hopping between V^{4+} and V^{5+} sites is hampered by the important differences in size and environment geometry of the V^{4+} and V^{5+} sites and by prohibitively long V-V distances, except in CsV_2O_5 (see Table IV).

Conclusion

Crystals of three rubidium and three cesium vanadium oxide bronzes were prepared. This proves the usefulness of molten salt electrolysis in the synthesis of interme-

diate-valence compounds, as an alternative to chemical reactions under controlled oxygen pressure. The crystallographic cells of four rubidium VOB's were determined. Two of these (the ν' and ϕ -phases) are isostructural with known potassium compounds; one has an orthorhombic cell which is new among VOB's, while the previously reported $\text{Rb}_{0.3}\text{V}_2\text{O}_5$ (or $\text{RbV}_6\text{O}_{15}$) is found isostructural with a cesium compound. In the Cs-V-O system, this study fully confirms the results of Waltersson and Forslund (12). Electrical measurements on $\text{Cs}_{0.3}\text{V}_2\text{O}_5$, however, do not support a previously reported jump in conductivity, which was attributed to a semiconductor-semiconductor transition (13). Rb- and Cs-VOB's are interesting examples of mixed-valence oxides with widely different electrical properties connected to localization of V^{4+} ions in specific crystallographic sites in the structures, as expected from Robin and Day's mixed-valence compound classification (31).

Acknowledgments

This work was initiated during the author's stay in the Solid State Chemistry section, National Research Council, Ottawa, Canada, with the help of A. D. In-

glis. Physical measurements were carried out with the help of M. Maeder (Lab. Louis Néel, CNRS Grenoble) and R. Buder (LEPES, CNRS Grenoble). Special thanks to J. Dumas (LEPES, CRNS Grenoble) for practical help in ESR and electrical measurements and for fruitful discussions.

References

1. P. HAGENMULLER, *Progr. Solid State Chem.* **5**, 71 (1971).
2. P. B. DICKENS AND P. J. WISEMAN, *MTP Int. Rev. Sci. Inorg. Chem., Ser. Two* **10**, 211 (1975).
3. A. A. FOTIEV AND B. G. GOLOVKIN, *Russ. J. Inorg. Chem.* **17**, 691 (1972).
4. V. L. VOLKOV, L. L. SURAT, AND A. A. FOTIEV, *Inorg. Mater.* **10**, 155 (1974); L. L. SURAT, V. L. VOLKOV, AND A. A. FOTIEV, *Russ. J. Inorg. Chem.* **19**, 1570 (1974).
5. A. A. FOTIEV AND L. L. SURAT, *Russ. J. Inorg. Chem.* **24**, 735 (1979).
6. J. TUDO AND B. JOLIBOIS, *C. R. Acad. Sci. (Paris), Sér. C* **273**, 1526 (1971).
7. M. POUCHARD, J. GALY, L. RABARDEL, AND P. HAGENMULLER, *C. R. Acad. Sci. (Paris), Sér. C* **264**, 1943 (1967).
8. J. GALY AND A. CARPY, *Acta Crystallogr. Sect. B* **31**, 1794 (1975).
9. A. F. REID AND J. A. WATTS, *J. Solid State Chem.* **1**, 310 (1970).
10. B. FORSLUND AND B. JELINSKI, *Mater. Res. Bull.* **19**, 1031 (1984).
11. W. G. MUMME AND J. A. WATTS, *J. Solid State Chem.* **3**, 319 (1971).
12. K. WALTERSSON AND B. FORSLUND, *Acta Crystallogr. Sect. B* **33**, 775, 780, 784, 789 (1977).
13. M. NYGREN, B. BLOM, B. FORSLUND, AND M. WOLCYRZ, *J. Solid State Chem.* **59**, 201 (1985).
14. A. D. WADSLEY, *Acta Crystallogr.* **8**, 695 (1955).
15. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
16. E. V. BABENKO, A. A. FOTIEV, A. N. BARABOSHKIN, AND K. A. KALIEV, *Russ. J. Inorg. Chem.* **23**, 1241 (1978).
17. P. STROBEL, "7th Int. Congress on Crystal Growth, Stuttgart (Germany) 1983."
18. P. STROBEL AND M. GREENBLATT, *J. Solid State Chem.* **36**, 331 (1981).
19. LANDOLT-BORNSTEIN, in "Numerical Data and Functional Relationships in Science and Technology," New Series (K. H. Hellwege, Ed.), Vol. II/8, Suppl. 1, p. 27, Springer, Berlin (1976).
20. N. BELYAEV AND T. G. GOLOVANOVA, *Russ. J. Inorg. Chem.* **9**, 126 (1964); see also E. M. LEVIN, C. R. ROBBINS, AND H. F. McMURDIE, "Phase Diagrams for Ceramists," Amer. Ceramic Soc., Columbus, Ohio, Suppl. 1969, diagram n° 2276.
21. J. PERRAUD, *Rev. Chim. Miner.* **11**, 302 (1974).
22. A. F. WELLS, "Structural Inorganic Chemistry," pp. 568-569, Clarendon Press, Oxford (1982).
23. M. POUCHARD AND P. HAGENMULLER, *Mater. Res. Bull.* **2**, 799 (1967).
24. A. KUTOGLU, *Z. Kristallogr.* **162**, 263 (1983).
25. M. POUCHARD, A. CASALOT, AND G. VILLENEUVE, *Bull. Soc. Chim. Fr.* **81** (1968).
26. F. Y. ROBB AND W. S. GLAUNSINGER, *J. Solid State Chem.* **30**, 89, 107 (1979).
27. C. SANCHEZ, F. BABONNEAU, R. MORINEAU, J. LIVAGE, AND J. BULLOT, *Philos. Mag. B* **47**, 279 (1983).
28. F. THEOBALD AND J. G. THEOBALD, *J. Phys. Chem. Solids* **45**, 581 (1984).
29. J. B. GOODENOUGH, *J. Solid State Chem.* **1**, 349 (1970).
30. R. MASSE, J. C. GRENIER, AND A. DURIF, *Bull. Soc. Fr. Mineral. Cristallogr.* **1**, 20 (1967).
31. M. B. ROBIN AND P. DAY, *Adv. Inorg. Chem.* **10**, 247 (1967).