Crystal Chemistry of V3O5 and Related Structures

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V_2O_3 single crystals have been grown by chemical vapor transport with HCl and $TeCl_4$. Crystals grown with $TeCl_4$ contain V_3O_5, as verified by X-ray analysis, and this affects the low temperature transition. Polycrystalline V_2O_3 has also been prepared containing various amounts of V(IV). Magnetic data for these samples demonstrate the sensitivity of V_2O_3 to small substitutions of V(IV) for V(III). A similar substitution of Ti(IV) into V_2O_3 does not result in any change in the transition temperature, although the magnitude of the transition decreases. © 1986 Academic Press, Inc.

Introduction

Several investigators have reported that the slight oxidation of V_2O_3 greatly affects the low temperature transition and stabilizes the metallic phase (1–4).

Otsuka (5) oxidized single crystals of V_2O_3 by heating them in varying concentrations of CO/CO_2. Electron diffraction studies indicated that single crystals of V_2O_3 which had been oxidized beyond the homogeneity range for V_2O_3 contained V_3O_5. The isostructural compound, V_2TiO_5, was first reported by Magnéli (6). Åsbrink and Savborg (7) determined from a refinement of the structure and from neutron powder diffraction data that all the vanadium atoms in the rutile-like units were in the V(III) state. It was concluded that this was also true for the V_3O_5 phase.

Despite these studies, there still appears to be some question concerning the relationship among the structural, electrical, and magnetic properties of the V_3O_5, the V_2TiO_5, and the corundum V_2O_3 phase containing either V(IV) or Ti(IV). In this study, single crystals of V_2O_3 containing V_3O_5 will be characterized as well as polycrystalline samples of V_2O_3 which contain VO_2 or TiO_2 to form the phases V_3O_5 and V_2TiO_5. Within the homogeneity range for V_2O_3, it is proposed that the structure of V_3O_5 is compatible with the corundum structure and can alter its electrical and crystallographic properties.

Experimental

Preparation

All vanadium compounds were prepared from reagent grade ammonium metavanadate which was purified by recrystallization

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as described by Brauer (8). The purified ammonium metavanadate was heated in a covered platinum crucible for 4 days at 450°C to yield pure V_2O_5. The V_2O_5 was reduced to V_2O_3 in an Ar/H_2 (85%/15%) atmosphere at 1000°C. Polycrystalline vanadium oxides were prepared by reacting appropriate quantities of V_2O_3 and VO_2 in evacuated silica tubes at 800°C for 72 hr. Polycrystalline TiO_2 was prepared from titanium isopropoxide as described by Sprague (9). The product was heated to 600°C to yield rutile TiO_2. V_2TiO_5 was obtained by reacting an equimolar mixture of V_2O_3 and TiO_2 in an evacuated silica tube at 1000°C for 2 weeks. Polycrystalline samples of the system V_2O_3–TiO_2 were obtained by reacting appropriate quantities of V_2O_3 and TiO_2 in evacuated silica tubes at 1000°C for one week.

Single crystals of V_2O_3 were prepared by chemical vapor transport using either hydrogen chloride or tellurium(IV) chloride as transport agents (600 Torr of hydrogen chloride and a concentration of 4 mg/cm³ of tellurium(IV) chloride were used). Single crystals of V_2O_3 were also grown by chemical vapor transport with $TeCl_4$ and an excess of Cl_2 (10 mg of Te and 585 Torr of Cl_2 were used). For all single crystal growth, the temperature of the charge zone was 1000°C and the growth zone was maintained at 900°C. Crystal growth was allowed to proceed for 1 week with $TeCl_4$; a duration of 2 weeks was required to obtain suitable crystals using HCl as the transport agent. All crystals were removed from the transport tubes, washed in dilute HCl, then washed with distilled water and dried. The average dimensions of the crystals were 3–8 mm on an edge. No detectable quantity of Cl^- was found to be present in the crystals grown.

X-Ray Analysis

Powder diffraction patterns were obtained with a Philips–Norelco diffractometer using monochromatic high-intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). For qualitative identification of the phases present, the patterns were taken from $12° < 2\theta < 100°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in./hr. The scan rate used to obtain X-ray patterns for precision cell constant determination was 0.25° 2θ/min with a chart speed of 30 in./hr. Cell parameters were determined by a least-squares refinement of the reflections.

Slow-scanned peaks were digitized on a Hewlett–Packard 7225A plotter and were integrated by the Gaussian method to determine their areas from which the relative intensities of the various reflections were obtained.

Single crystals were X-rayed with Cr$K\alpha$ radiation (λ = 2.2896 Å), using a Gandolfi camera (10). Polycrystalline samples of V_2O_3 containing VO_2 and TiO_2 were X-rayed with Cr$K\alpha$ radiation using a Debye–Scherrer camera.

Electrical Measurements

The resistivities of various single crystals were measured using the van der Pauw four-probe method (11) from room temperature to 77 K. Contacts were made by attaching copper wire to the samples with Electrodag (a dispersed colloidal graphite) and allowed to dry. The ohmic behavior of the contacts was established by measuring their current–voltage characteristics.

Magnetic Measurements

Magnetic data were obtained over the temperature range 77–300 K using a Faraday balance. Measurements were performed at field strengths between 6.1 and 10.4 kOe. The balance was calibrated using platinum wire (χ_g = 0.991 × 10^{-6} emu/g at 273 K) as a standard; temperatures were measured with a Ga–As diode. The core diamagnetic correction reported by Selwood (12) was applied to these measurements.
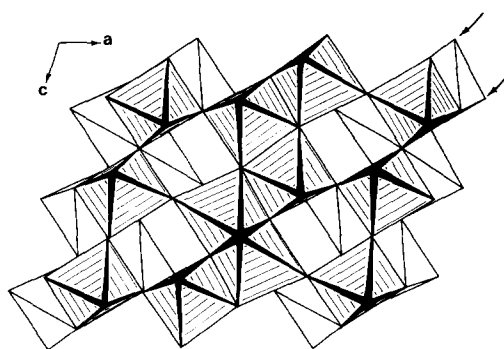
FIG. 1. Crystal structure of V$_3$O$_5$.

Results and Discussion

The crystal structure of V$_3$O$_5$ was first reported by Andersson (*13*). A single crystal structural refinement was later determined by Åsbrink (*14*); the symmetry of V$_3$O$_5$ is monoclinic (space group *P2/c*). The structure is shown in Fig. 1; it can be seen that the oxygen atoms are hexagonal close packed and that $\frac{2}{3}$ of the octahedral sites are occupied. The structure contains two distinct chains of octahedra which are directed along the *c* axis. One chain contains pairs of face-shared octahedra which are linked together via edge-sharing. The second chain is composed of corner-sharing octahedra. These two chains are connected by corner-sharing in the *ac* plane, and by edge-sharing in the *b* direction. The cell parameters obtained at room temperature were $a = 9.852(2)$ Å, $b = 5.036(2)$ Å, $c = 6.985(2)$ Å, and $\beta = 109.5°$ and are in agreement with those previously reported by Åsbrink (*14*). It was reported by Nagasawa *et al.* (*2*) that V$_3$O$_5$ single crystals can be obtained with TeCl$_4$ as a transport agent. However, under the same conditions reported by Nagasawa, both V$_3$O$_5$ and V$_4$O$_7$ phases were found in this study to coexist in some of the crystals grown with TeCl$_4$.

The electronic transitions in most vanadium oxides are evident in the variations of both resistivity and magnetic susceptibility with temperature. The transition temperatures are sensitive to the valencies of the
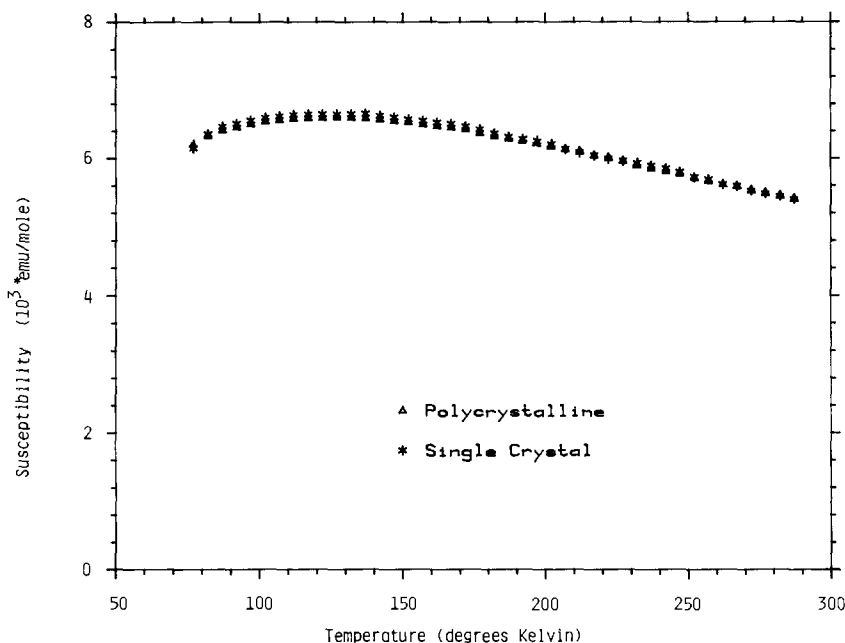

FIG. 2. Magnetic susceptibility as a function of temperature for a single crystal and polycrystalline sample of V$_3$O$_5$.

vanadium ions. Since its magnetic suscepti-
bility data (Fig. 2) shows no observable
transition below room temperature, the
presence of a small additional amount of
V(IV) in V_3O_5 cannot be readily deter-
mined. This study was therefore extended
to the preparation of V_2O_3 single crystals
grown with $TeCl_4$ as the transport agent.
Small amounts of V(IV) have been shown
by Ueda (3) and Shivashankar (4), among
others, to affect markedly the electronic
transition observed in V_2O_3. It was of inter-
est to also observe the nature of V_3O_5 crys-
tal growth in a V_2O_3 single crystal matrix.

Three samples of V_2O_3 crystals were pre-
pared with HCl, $TeCl_4$, and $TeCl_4/Cl_2$ (ex-
cess) as transport agents. Single crystals of

V_2O_3 grown with HCl exhibited a first-order
electrical transition from a metal to a semi-
conductor at 158 K on cooling, in agree-
ment with the results first reported by
Morin (15). However, single crystals which
were prepared by chemical vapor transport
using $TeCl_4$ as the transport agent remained
metallic to 96 K on cooling (Fig. 3). The
suppression of the semiconducting phase
had previously been reported by Pouchard
(16) and was attributed to the oxidation of
V(III) to V(IV) by Cl_2. In an attempt to ver-
ify that the V_2O_3 was being oxidized by Cl_2,
a transport tube was prepared which con-
tained $TeCl_4$ with an excess of Cl_2. The re-
sistivities of these crystals were measured
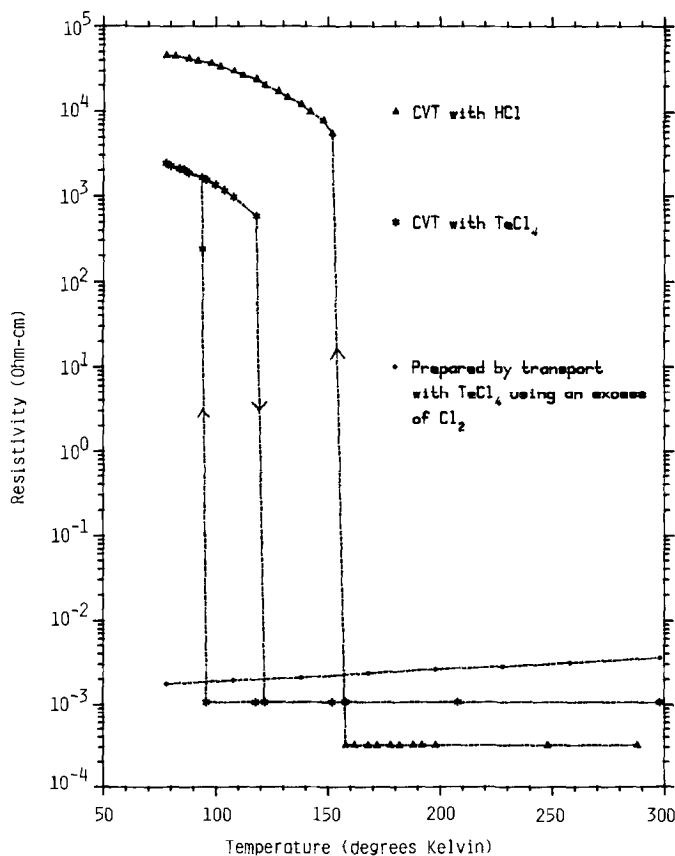and they remained metallic to 77 K. In or-

FIG. 3. Resistivity versus temperature for various crystals of V_2O_3, showing the dependence of the
V_2O_3 electronic transition temperature upon the transport agent used for crystal growth.
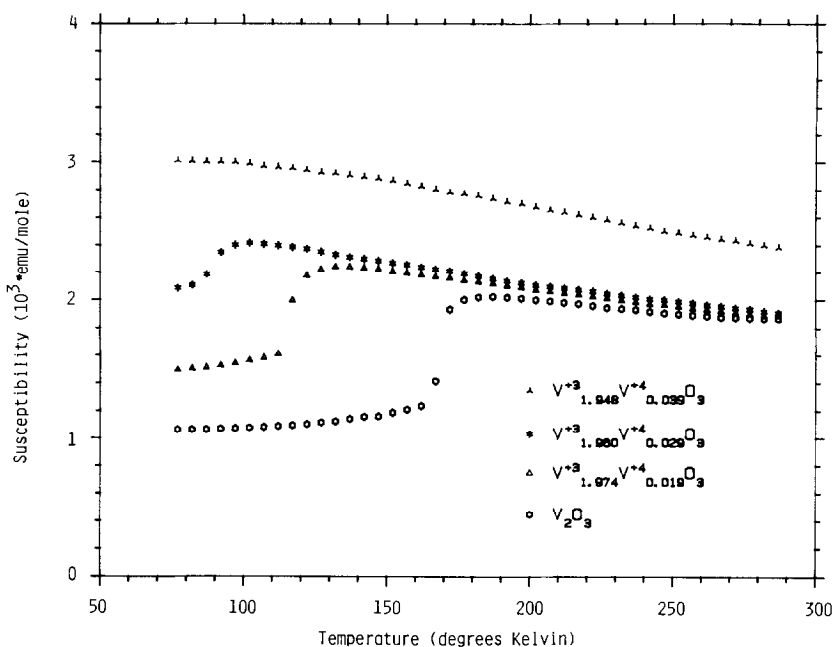
FIG. 4. Warming curves of magnetic susceptibility versus temperature for several polycrystalline samples of $V_{2-x}O_3$, showing the dependence of the electronic transition temperature upon V(IV) concentration.

der to determine if the oxidized crystals contained V_3O_5, a single crystal was mounted on a Gandolfi camera and X-rayed with $CrK\alpha$ radiation. X-Ray diffraction data from this crystal could be partially indexed on the basis of a V_2O_3 unit cell; however, additional reflections appeared which could be accounted for by the presence of V_3O_5. These additional reflections were seen when the c axis of the crystal was positioned perpendicular to the X-ray beam.

Since the low temperature transition for V_2O_3 can be observed magnetically (17), polycrystalline samples of V_2O_3 containing VO_2 were prepared and their molar susceptibilities were obtained as a function of temperature. These results are plotted in Fig. 4. It can be seen that with increasing V(IV) content the magnitude and temperature of the transition decrease. Upon the addition of 0.04 mole of VO_2, the transition for V_2O_3 has disappeared. This is in agreement with

the results obtained by Ueda (3), Shivashankar (4), and others. The susceptibility continually increases for V_2O_3 with the addition of VO_2. X-Ray diffraction patterns taken with a Debye–Scherrer camera were obtained for these polycrystalline samples of V_2O_3 containing V(IV). For the sample with 0.04 mole of VO_2, the monoclinic reflections associated with V_3O_5 were visible.

An analogous study was carried out on V_2TiO_5 and on V_2O_3 containing TiO_2. The cell parameters for V_2TiO_5 were $a = 9.962(2)$ Å, $b = 5.062(2)$ Å, $c = 7.011(2)$ Å, and $\beta = 109.7°$ and are in agreement with those reported by Savborg (18) and Brach (19).

The molar susceptibilities versus temperature for polycrystalline samples of V_2O_3 containing Ti(IV) were obtained and are shown in Fig. 5. It can be seen that the low temperature transition for V_2O_3 remains ap-
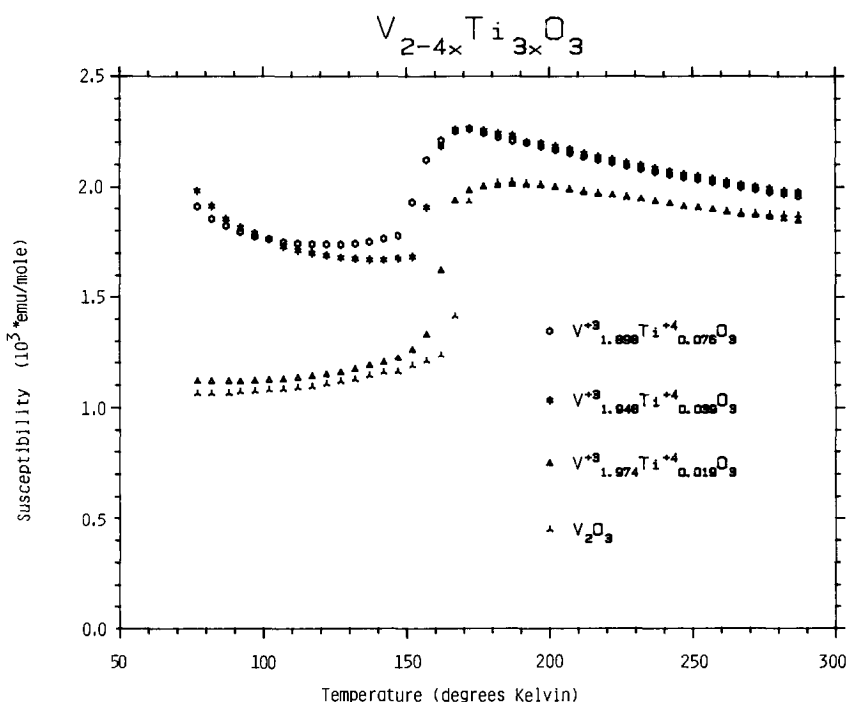
FIG. 5. Warming curves of magnetic susceptibility versus temperature for several polycrystalline samples of Ti(IV)-substituted V_2O_3 showing the absence of any change in the electronic transition temperature with composition.

proximately at 160 K for all samples. This is consistent with the previous study on ceramic samples by McWhan (20). However, the magnitude of the transition decreases with increasing Ti(IV) and is absent in V_2TiO_5. The susceptibility of V_2O_3 also increases upon the addition of TiO_2. Debye–Scherrer powder patterns were obtained for these samples, and the monoclinic phase, V_2TiO_5, could be seen for the sample with 0.04 mole of TiO_2. These results are in contrast to the studies reported by Chandrashekhar (21) and Shivashankar (4) which indicated that the addition of Ti(III) to V_2O_3 lowered both the magnitude and temperature of the transition.

It can be concluded that oxidized single crystals of V_2O_3 contain V_3O_5, and that the structural similarities which exist between these two compounds allow the V_3O_5 to become an integral part of the corundum

structure. The results reported in this study support the crystallographic data of Åsbrink concerning the valency distribution for V_3O_5. The structural refinement of V_3O_5 by Åsbrink (14) indicates that the V(IV) resides in the corundum-like units of V_3O_5 while the V(III) is situated in the rutile-like units. Upon substitution of V(IV) ($3d^1$) for V(III) ($3d^2$) the temperature and magnitude of the transition for V_2O_3 are lowered. The attempted substitution of Ti(IV) ($3d^0$) in the corundum structure results in a decrease in the magnitude but not in the temperature of the transition.

Acknowledgments

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