JOURNAL OF SOLID STATE CHEMISTRY 36, 133–138 (1981)

# Growth of Single Phase, Single Crystals of $V_9O_{17}$[1]

H. KUWAMOTO, N. OTSUKA, AND H. SATO

*School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907*

Received April 7, 1980

Single crystals of Magnéli phase $V_9O_{17}$ were successfully grown for the first time by a vapor transport technique utilizing $TeCl_4$ as a transport agent. No trace of syntactically intergrown $V_8O_{15}$ could be detected in these crystals. The structure is triclinic and is homologous to other Magnéli phase compounds $V_nO_{2n-1}$ ($n = 3 \sim 8$). The lattice parameters (of the reduced cell) measured are

$$a = 7.009\ \text{Å} \quad b = 14.518\ \text{Å} \quad c = 5.418\ \text{Å}$$

$$\alpha = 95.5^\circ \quad \beta = 108.9^\circ \quad \gamma = 83.1^\circ$$

This compound manifests a metal–insulator transition as in other Magnéli phase compounds. The transition temperature has been determined to be 79 K. At and below the transition point down to 16 K, at which an anomalous peak in the resistivity exists, a time dependence of resistivity at fixed temperatures is found. The existence of $V_{10}O_{19}$ was also confirmed by transmission electron microscopy in a material produced under highly nonequilibrium conditions, intergrown in the matrix of $V_9O_{17}$ in a microsyntactoc fashion. The existence of $V_{10}O_{19}$ has never been reported.

## Introduction

The existence of a series of long period compounds (Magnéli phase compounds) $V_nO_{2n-1}$ ($n = 3 \sim 8$) has been known for some time (*1*) and their crystal structures have been investigated in detail between $n = 3$ and 7 (*2*). The structure is basically a periodic modulation of $VO_2$ having the rutile structure where one oxygen layer is removed at every $n$th V layer in the direction perpendicular to the (121) plane of $VO_2$. In other words, $V_nO_{2n-1}$ are a group of homologous long period compounds and the period increases with $n$. The (121) plane, where one oxygen layer is missing, is called the crystallographic shear (CS) plane and is the site for compensation of the nonstoichiometry of this compound.

The stability of a series of long period structures, in general, decreases as the period increases (*3, 4*) and the period cannot become too long. Magnéli phase $V_nO_{2n-1}$ is no exception. Indeed, it has commonly been accepted that $V_9O_{17}$ is the long period limit of these compounds. Moreover, as $n$ becomes large, the difference in the stability among compounds with similar $n$ should become small, and these compounds tend to intergrow in narrow bands (syntactic intergrowth). When this type of intergrowth occurs on a unit cell scale, it is called microsyntactic intergrowth (*5*). The microsyntactic intergrowth indicates that the intergrown components have similar stability.

---

[1] The work was supported in part by the National Science Foundation MRL Program DMR 77 23798.

0022-4596/81/020133-06$02.00/0

Copyright © 1981 by Academic Press, Inc.
All rights of reproduction in any form reserved.

Single crystals of a series of Magnéli phase compounds with $n$ between 3 and 8 are now commonly grown by a vapor transport technique utilizing basically $TeCl_4$ as a transport agent (*6–9*). Because the compound $n = 9$ is at the long period limit, not only is $V_9O_{17}$ difficult to grow, grown crystals of $V_9O_{17}$ are always in a mixed phase, intergrown with $V_8O_{15}$. An example of microsyntactic intergrowth of $V_8O_{15}$ in a matrix of $V_9O_{17}$ as observed by a lattice imaging technique of TEM is shown in Fig. 1. The extremely narrow bands indicated by arrows are $V_8O_{15}$ intergrown in a matrix of $V_9O_{17}$ (stripe width 14.3 Å) (*10*). The stripe width 14.3 Å corresponds to the distance between two CS planes of $V_9O_{17}$ (14.41 Å based on the lattice parameters obtained). Because of this situation, it was generally thought to be impossible to grow single phase $V_9O_{17}$ crystals.

The purpose of the present attempt to grow single phase $V_9O_{17}$ is twofold. The one is to extend the measurements of physical properties of Magnéli phase compounds which depend on the period, especially those on metal–insulator transition and on antiferromagnetic transition, to compounds with periods longer than $n = 8$. The other is to investigate the compensation mechanism for nonstoichiometry in these compounds by observing the change from that due to the CS plane in the region where the existence of the CS plane ceases. The intergrowth of $V_8O_{15}$ and $V_9O_{17}$ is due to the fact that the stability of these two compounds is so similar that the probability of nucleation of either phase is almost identical even under the condition in which the growth of $V_9O_{17}$ is more favorable. According to nucleation theory, however, it should still be possible to increase the degree of preference of $V_9O_{17}$ over $V_8O_{15}$ if the growth rate is decreased. The discrimination of the nucleation of one phase from other phases by reducing the growth rate was well demonstrated, for example, in the selection of orientation in the epitaxial growth of iron on a cleaved surface of rock salt (*11*).

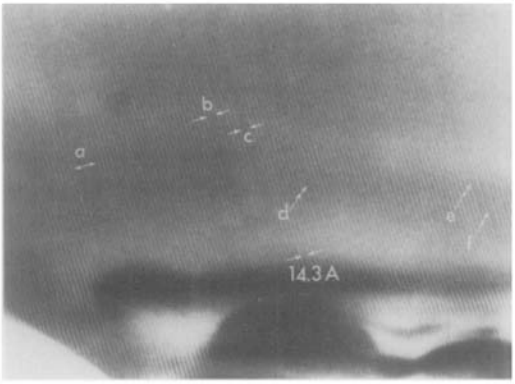

FIG. 1. Syntactic intergrowth of $V_8O_{15}$ in $V_9O_{17}$ on a microscopic scale. The stripes due to $V_8O_{15}$ are indicated by arrows. The stripe width 14.3 Å corresponds to the distance between two CS planes of $V_9O_{17}$.

## Growth Procedures and Morphology

The method adopted for the growth of $V_9O_{17}$ is a vapor transport technique which is essentially the same as those adopted earlier for other $V_nO_{2n-1}$'s (*6–8*). First, appropriate amounts of $V_2O_3$ and $V_2O_5$ in a proportion to make $V_9O_{17}$ are well mixed and heated, sealed in a quartz tube at pressure of $\sim 10^{-3}$ Torr, at 900°C for 3 days. The reacted powder is then sealed in an evacuated ($\sim 10^{-3}$ Torr) quartz tube of 15 mm id and 230 mm in length together with appropriate amount of $TeCl_4$. The tube is then placed in a furnace at the growth temperature of ~950°C under an appropriate degree of temperature gradient.

A special precaution taken this time was to reduce the growth rate of crystals in order to single out the $V_9O_{17}$ phase over $V_8O_{15}$. This can be accomplished at a fixed growth temperature, either by reducing the amount of transport agent or by decreasing the temperature gradient, or a combination of both. First the amount of $TeCl_4$ was reduced to 4 mg or less per cubic centimeter of the closed quartz tube against 8 mg/cm$^3$ specified in earlier attempts (*6–8*). The optimum temperature gradient for growing $V_9O_{17}$ was then determined. After some trials, the optimum temperature gradient to grow $V_9O_{17}$ determined was to make the temperature at the hot zone and at the cool zone to be 1025 and 955°C, respectively. This should be compared to 1050 and 950°C specified in earlier attempts (*6–8*). The quartz tube was placed in a three zone Lindberg furnace under the above condition for one to two weeks. The crystals thus grown generally have equiaxed polyhedron shapes with sizes up to 3–4 mm in diameter like those shown in Fig. 2.

The morphology of the crystals of Magnéli phase produced by vapor transport has been reported to be very similar, needle like (or columnar), and the appearance of smooth, hardly disturbed surface has been rarely observed. It was, however, noticed that the reduction in growth rate resulted in a change of growth habits of crystals from needle-like (or columnar) (*6–8*) to platelet and finally to equiaxed polyhedron with decreasing growth rate. The same tendency for the change of morphology from needle to polyhedron was observed as the rate of growth was decreased in our earlier growth of $V_2O_3$ by a vapor transpor technique (*12*). An earlier attempt of obtaining single phase $V_9O_{17}$ by reducing the temperature gradient of vapor transport, however, ended up in columnar crystals with microsyntactically intergrown $V_8O_{15}$ (*10*). This is probably because a mixture of $TeBr_4$ and $TeCl_4$ instead of $TeCl_4$ alone, was used as the transport agent which eventually increased the growth rate (*10*). In this respect, the equiaxed, polyhedron shape of grown crystals can be taken as proof of sufficient reduction of the growth rate in growing $V_9O_{17}$.

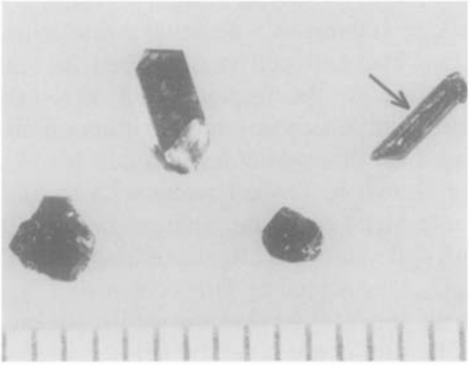

FIG. 2. Some single phase, single crystals of $V_9O_{17}$ grown. A rod crystal indicated by an arrow is a $V_9O_{17}$ crystal with syntactically intergrown $V_8O_{15}$ grown at a faster rate. The scale shown below corresponds to 1 mm.

## Phase Identifications

Crystals of $V_9O_{17}$ thus obtained were examined both by X-ray diffraction and transmission electron microscopy. No trace of inclusion of other phases, especially of syntactically intergrown $V_8O_{15}$, could be detected. Also noteworthy is the absence of twins in these crystals. The abundance of twins in sintered specimens of $Ti_nO_{2n-1}$ which is isomorphous to $V_nO_{2n-1}$ has been reported (*13*). It is also found that the crystal habit plane (the widest exposed plane) of platelet crystals of slowly grown $V_9O_{17}$ corresponds to the (012) plane of $VO_2$, while the corresponding plane of platelets of $VO_2$ grown under the identical condition is found to be the (110) plane with the [001] direction as the direction of growth. Those for $VO_2$ are the same as those reported earlier (*9*). Because growth habit planes for other Magnéli phase compounds have not been reported, comparisons of slowly grown $V_9O_{17}$ with other Magnéli phase compounds with respect to growth habits are now being carried out.

The growth of $V_{10}O_{19}$ and even longer period compounds was attempted but without any success. The existence of $V_{10}O_{19}$ was, however, confirmed by transmission electron microscopy in as-reacted powder of composition corresponding to $V_{18}O_{35}$ prepared at 900°C, $V_{10}O_{19}$ is observed along with $V_8O_{15}$ in the matrix of $V_9O_{17}$ in a syntactic fashion as shown in Fig. 3. This is the first observation of the existence of $V_{10}O_{19}$ ever reported. The existence of $V_{10}O_{19}$ was never observed in specimens carefully prepared by vapor transport by a low growth rate even if the oxygen content is increased beyond the range of $V_9O_{17}$. In the latter cases, obtained crystals are either $V_9O_{17}$ or $VO_2$. Because of this reason, it can safely be said that $V_9O_{17}$ is really the longest period limit of Magnéli phase $V_nO_{2n-1}$ under equilibrium conditions. In Fig. 3, stripes with widths which correspond to $V_{11}O_{21}$ and $V_{12}O_{23}$ are also observed. These are indicted by double arrows.

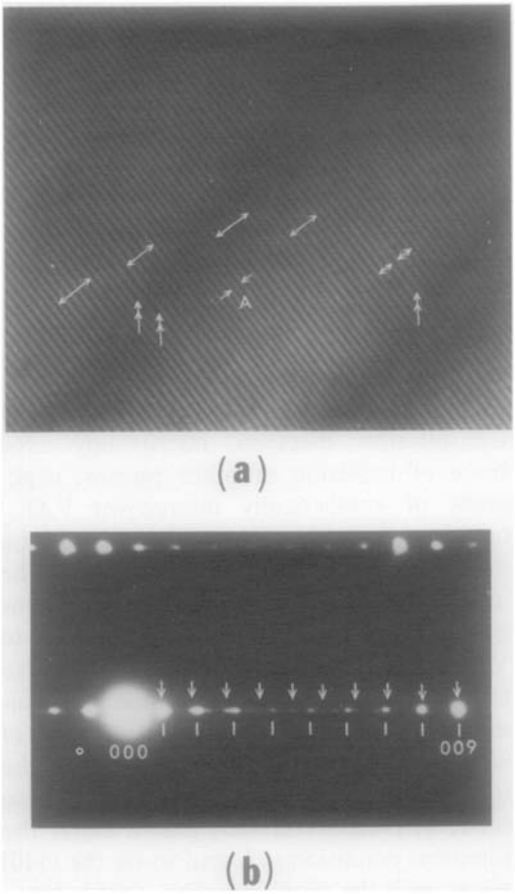

FIG. 3. (a) Syntactic intergrowth of $V_8O_{15}$ and $V_{10}O_{19}$ in the matrix of $V_9O_{17}$ in specimens produced under highly nonequilibrium conditions. The stripes due to $V_8O_{15}$ are indicated by A and stripes due to $V_{10}O_{19}$ are indicated by arrows. Stripes having widths corresponding to $V_{11}O_{21}$ and $V_{12}O_{23}$ are indicated by double arrows. (b) Corresponding diffraction pattern. Diffraction spots from $V_9O_{17}$ are indicated by short lines while those indicated by arrows are those from $V_{10}O_{19}$. The remaining spots are those from $V_8O_{15}$. The diffraction spot indicated as 009 (of $V_9O_{17}$) corresponds to the 121 spot of $VO_2$.

## Unit Cells

The lattice parameters of $V_9O_{17}$ were determined by a least-squares fit from 14 diffraction spots which lie within the Bragg angle of 19 and 25° taken with Mo$K_\alpha$ radiation with the aid of a four circle axis goniometer. The crystal has a triclinic symmetry and there have been two ways of specifying the unit cell of Magnéli phase compounds (*2*, *13*); neither of them, however, is the reduced cell. The reduced cell does not convey the concept that $V_nO_{2n-1}$ are a series of homologous compounds. Among these, that specified by Horiuchi *et al.* (*2*) has an advantage of describing the unit cell of the whole system of $V_nO_{2n-1}$ in a unique fashion as a periodic modulation of $VO_2$. The unit cell is described in Fig. 4 referring to the unmodulated $VO_2$ structure. The lattice parameters thus obtained based on this particular unit cell for $V_9O_{17}$ are shown in Table I along with those for the reduced cell. The relations between the unit cell vectors $\mathbf{a}_H$, $\mathbf{b}_H$, $\mathbf{c}_H$ of Magnéli phase $V_nO_{2n-1}$ specified by Horiuchi *et al.* (*2*) and those for $VO_2$ having the rutile structure, $\mathbf{a}_r$, $\mathbf{b}_r$, and $\mathbf{c}_r$ are given by (*2*)

$$\begin{aligned}\mathbf{a}_H &= \mathbf{a}_r + \mathbf{c}_r\\ \mathbf{b}_H &= \mathbf{a}_r + \mathbf{b}_r + \mathbf{c}_r\\ \mathbf{c}_H &= \frac{2n-1}{2}(\mathbf{b}_r + \mathbf{c}_r)\end{aligned}$$

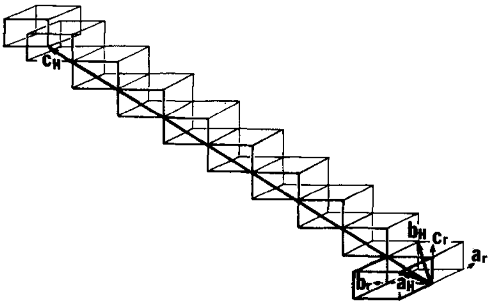

FIG. 4. The relation between the unit cell of $V_9O_{17}$ and that of tetragonal $VO_2$ having the rutile structure. The CS plane corresponds to the plane determined by the unit cell vectors $\mathbf{a}_H$ and $\mathbf{b}_H$.

The relation between the unit cell vectors $\mathbf{a}_H$, $\mathbf{b}_H$, and $\mathbf{c}_H$ and those for the reduced cell $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ is given by the following transformation matrix:

$$\begin{pmatrix} a_H \\ b_H \\ c_H \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 6 & 1 & 5 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}.$$

Refinement of the structure is now under way.

## Physical Properties

Magnéli phase vanadium oxides show metal–insulator transitions and the transition points show an interesting dependence on the period, or $n$. Because of this interest, a preliminary measurement of electrical resistivity $\rho$ of $V_9O_{17}$ was made by a standard four-probe technique. The result is shown in Fig. 5. A distinct metal–insulator transition point is observed at 79 K. This is just between the transition point of $V_8O_{17}$ and that of $VO_2$ ($n = \infty$). At the M-I transition point and below, however, a peculiar time dependence of resistivity at fixed temperatures was observed. The temperature dependence of resistivity between 300 and 80 K was found to be that of normal metal and no specific time dependence of resistivity at fixed temperatures was found. At about 79 K, the resistivity dropped sharply by more than one order of magnitude within the temperature range of less than one degree. After it reached the minimum, without any further observable change of temperature, the resistivity increased with time by more

TABLE I

LATTICE PARAMETERS OF $V_9O_{17}$ BASED ON THE TRICLINIC REDUCED UNIT CELL AND THAT SPECIFIED BY HORUICHI *et al.* (*2*) FOR $V_nO_{2n-1}$[a]

| The Reduced cell parameter | | |
|---|---|---|
| $a = 7.009$ Å | $b = 14.518$ Å | $c = 5.418$ Å |
| $\alpha = 95.5°$ | $\beta = 108.9°$ | $\gamma = 83.1°$ |
| The lattice parameters of the unit cell specified by Horiuchi *et al.* | | |
| $a_H = 5.418$ Å | $b_H = 7.009$ Å | $c_H = 45.213$ Å |
| $\alpha = 39.3°$ | $\beta = 74.5°$ | $\gamma = 108.9°$ |

[a] The obtained values have standard deviations of 0.009 Å and 0.1°.

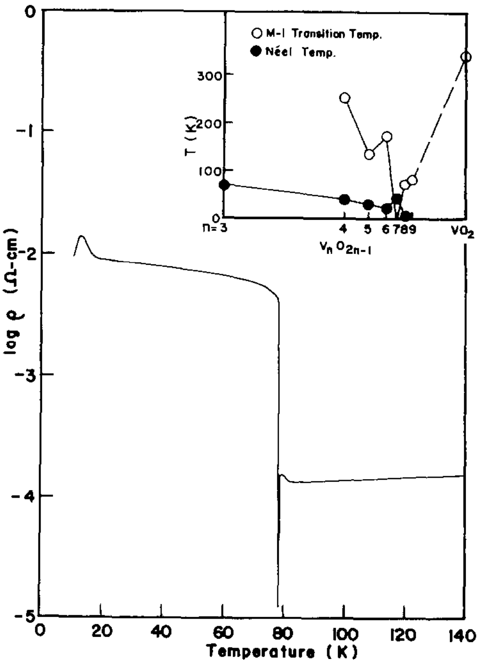

FIG. 5. The temperature dependence of electrical resistivity $\rho$ of $V_9O_{17}$. The dependence on $n$ of the metal–insulator transition point and of the Néel point of Magnéli phase $V_nO_{2n-1}$ are added.

than two orders of magnitude. Below the transition point, the time dependence of resistivity at fixed temperatures (of the order of one hour) was again observed. The increase in the equilibrium value of resistivity with decreasing temperature was, however, relatively small. At about 16 K, an anomalous peak in the resistivity is observed and, below this temperature, the time dependence of the resistivity was found to vanish. No hysteresis in the $\rho$-$T$ curve, however, was found as the temperature was raised back to 300 K. Although the origin of the anomaly at 16 K has not been confirmed yet, it may be connected to the antiferromagnetic transition similar to that observed in other Magnéli phase compounds. The dependence of the metal–insulator transition point and the Néel point on n (*15, 16*) is thus added in Fig. 5. Peculiar behavior in connection with low-temperature transitions is also observed in other Magnéli phase compounds, in particular in $V_7O_{13}$ (*17*) and $V_8O_{15}$ (*15, 16*). A further detailed study of the metal–insulator transition and of the magnetic transition of these compounds is, therefore, in order.

## Acknowledgments

Help of Professor W. R. Robinson in the determination of lattice parameters, and of Mr. S. A. Shivashankar in the measurement of electrical resistivity is highly appreciated.

## References

1. G. Anderssen, Acta Chem. Scand. **8** 413 (1963).
2. H. Horiuchi, N. Morimoto, and M. Tokonami, *J. Solid State Chem.* **17,** 407 (1976).
3. H. Sato and R. S. Toth, *Phys. Rev.* **124,** 1833 (1961); **127,** 469 (1962).
4. H. Sato and R. S. Toth, *In* "Alloying Behavior in Concentrated Solid Solutions" (T. B. Massalski, Ed.), p. 295. Gordon & Breach, New York (1965).
5. Y. Hirotsu and H. Sato, *J. Solid State Chem.* **26,** 1 (1978).
6. K. Nagasawa, *Mat. Res. Bull.* **6,** 853 (1971).
7. K. Nagasawa, Y. Bando, and T. Takada, *J. Crystal Growth* **17,** 143 (1972).
8. K. Kachi, K. Kosuge, and H. Okinaka, *J. Solid State Chem.* **17,** 407 (1976).
9. E. Wolf, H. Oppermann, G. Krabbes, and W. Reichelt, *in* "Current Topics in Materials Science, 1" (E. Kaldis, Ed.), p. 697. North Holland, Amsterdam (1978).
10. Y. Hirotsu, S. Faile, and H. Sato, *Mat. Res. Bull.* **13,** 895 (1978).
11. S. Shinozaki and H. Sato, *J. Vac. Sci. Technol.* **6,** 534 (1969).
12. H. Kuwamoto and J. M. Honig, *J. Solid State Chem.*, in press.
13. O. Terasaki and D. Watanabe, *Japan. J. Appl. Phys.* **10,** 292 (1971).
14. S. Anderssen and L. Jahnberg, *Ark. Kemi.* **21,** 413 (1963).
15. S. Nagata, B. F. Griffing, G. D. Khattak, and P. H. Keesom, *J. Appl. Phys.* **50,** 7575 (1979).
16. S. Nagata, P. H. Keesom, and S. P. Faile, *Phys. Rev.* **20B,** 2886 (1979).
17. B. F. Griffing, S. A. Shivashankar, S. Nagata, S. P. Faile, and J. M. Honig, *Phys. Rev. B.*, submitted for publication.