Phase Transition and Electrical Properties of VO$_2$(A)

Yoshio OKA, Tsukio OHTANI*, Naoichi YAMAMOTO and Toshio TAKADA*

Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University,
Yoshidainohmonnatsu-cho, Sakyo-ku, Kyoto-shi, 606
*Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho, Okayama-shi, 700

VO$_2$(A) の相転移と電気的性質

岡 与志男・大 谷 榊 男*・山 本 直一・高 田 利 夫*

*京都大学教育学部化学教室, 606 京都市左京区吉田二本松町
**岡山理科大学理学部化学教室, 700 岡山市中区

VO$_2$(A), a metastable phase of VO$_2$, was prepared by hydrothermal treatment of an aqueous VOSO$_4$ solution. (VO$_2$(A) has tetragonal symmetry but the crystal structure remains unknown. DTA and magnetic susceptibility measurements revealed a transition at 162°C which was detectable on heating but not on cooling. Semiconducting behavior was observed and the high-temperature phase was characterized by lower electric resistivity. The transition on heating expanded the a-axis and contracted the c-axis. It was also observed that the lattice spacing along the c-axis was reduced to the half at the transition. The transition was found to be similar to the metal-insulator transition in the rutile-type VO$_2$.

[Received May 23, 1989; Accepted July 14, 1989]

Key-words: Vanadium dioxide, Hydrothermal synthesis, Metastable phase, Polymorph, Phase transition

1. Introduction

VO$_2$(A) is a metastable phase of vanadium dioxide in which the rutile-type structure (VO$_2$(R)) is adopted as a stable phase. The formation of VO$_2$(A) was first reported by Théobald$^1$ in the extensive study of the hydrothermal synthesis of vanadium oxides and oxyhydroxides using mixtures of V$_2$O$_5$ and V$_2$O$_3$ as starting materials. He also obtained metastable VO$_2$(B), whose structure has been determined to be layer-type one related to the structures of V$_2$O$_5$ and V$_6$O$_{13}$.$^2$ He showed that VO$_2$(A) had tetragonal symmetry with lattice parameters; $a=11.90$ Å and $c=7.68$ Å.$^1$ But the structure of VO$_2$(A) remains unknown and also its physical properties have not been studied. To our knowledge VO$_2$(A) has not yet been obtained by any method other than the hydrothermal synthesis, while VO$_2$(B) has been prepared as an intermediate product in the thermal reduction of V$_2$O$_5$ by H$_2$, SO$_2$ and NH$_3$ gases.$^2$-$^4$

Among the polymorphs of VO$_2$, VO$_2$(R) is well known for the metal-insulator transition at 68°C accompanied by the lattice distortion from the rutile-type tetragonal structure of the high-temperature metallic phase to the monoclinic structure of the low-temperature insulating phase.$^5$-$^7$ The mechanism of the transition has been clarified that the paring of V$^{4+}$ ions (V$^{4+}$-V$^{4+}$ pair) along the c-axis of the rutile type takes place at the transition from metallic to insulating phase.$^8$ As a result of the pairing, the lattice spacing of the c-axis of the rutile type doubles and the magnetic moment of V$^{4+}$ disappears. With reference to the phase transition of VO$_2$(R), stable phase VO$_2$, described above, it is worthwhile to investigate the structures and properties of metastable VO$_2$.

In the present work, VO$_2$(A) was prepared by the hydrothermal reaction starting from VOSO$_4$ aqueous solutions. The physical and structural properties of VO$_2$(A) were studied and it was found that VO$_2$(A) exhibited a phase transition which showed behavior similar to that of VO$_2$(R).

2. Experimental

The hydrothermal synthesis was conducted as follows. A VOSO$_4$ aqueous solution with a certain concentration was sealed in a pyrex tube and was treated at 200° to 280°C for various hours. Precipitates were separated by filtration and dried in air. Crystalline phases in the samples were identified by an X-ray diffraction method using Cu K$_{α}$ radiation. DTA were carried out in air at a rate of 10°C min$^{-1}$ by using an ULVAC TA-1500 thermal analyzer. Magnetic susceptibility was measured by a Faraday-type torque balance and electric resistivity by a dc four-probe method on powdered pressed pellets. High-temperature X-ray measurements were carried out using a JEOL
high-temperature attachment to control temperature within ±1°C.

3. Results and discussion

Figure 1 shows an X-ray diffraction pattern of VO₂(A) which is indexed based on the tetragonal symmetry as revealed by Théobald. The particle shape of VO₂(A) is of flat rectangular rod as shown in an SEM picture of Fig. 2. The flat surface of the rod is assigned to the a-plane, since h00 peaks became considerably higher for samples with well-grown particle. Figure 3 shows DTA curves of VO₂(A) on heating and cooling. An endothermic peak was observed at 162°C on heating while a corresponding exothermic peak was absent on cooling. This was reproducible for repeated heating cycles, indicating that some transition exists in VO₂(R) which is observable in the heating process. To confirm the existence of the transition in VO₂(A), the magnetic susceptibility was measured as shown in Fig. 4, where that of VO₂(R) is given in the inset for comparison. On heating the magnetic susceptibility showed sudden increase at 162°C and on cooling it gradually decreased to the starting value with a large hysteresis. It is noted that the change in the magnetic susceptibility on heating shows a striking resemblance to that of VO₂(R) shown in the inset of Fig. 4. Figure 5 shows the electric resistivity of VO₂(A). VO₂(A) exhibited semiconducting behavior over the temperature range of the measurement. It should be noted that the resistivity appeared rather high because it was measured on an as-pressed pellet of powder sample not sintered. The resistivity curve on heating showed a clear deflection at the transition indicating that the high-temperature phase becomes more conductive than the low-temperature phase. Also the activation energy estimated from the Arrhenius plot was lowered from 0.8 eV for the low-temperature phase to 0.65 eV for the high-temperature phase in the heating process.
This trend corresponds to the transition of \( \text{VO}_2 \) (R) on heating from insulator to metal. Consequently the presence of phase transition has been confirmed in \( \text{VO}_2 \) (\( \text{A} \)) and the changes in the magnetic and electric properties at the transition are quite similar to those of \( \text{VO}_2 \) (R) at the metal-insulator transition.

The transition from metallic to insulating phase in \( \text{VO}_2 \) (R) gives rise to the lattice distortion from tetragonal to monoclinic, and thus some structural change at the transition should be expected in \( \text{VO}_2 \) (\( \text{A} \)). Figure 6 shows the high-temperature X-ray diffraction patterns of \( \text{VO}_2 \) (\( \text{A} \)) on heating.
The X-ray patterns below and above the transition temperature were almost the same except that the $hkl$ reflections with odd $l$, e.g., 131 and 241 marked by arrows in Fig. 6, disappeared in the high-temperature phase. It indicates that the crystal structure does not change drastically but the lattice spacing along the $c$-axis becomes the half through the transition. Another feature appeared in the peak profile of $h00$ reflections as shown in Fig. 7 for 600 peak. That is, the top of the peak became flat around the transition temperature suggesting that the array of $V^{4+}$ ions along the $a$-axis becomes somewhat irregular at the transition. Figure 8 shows the temperature dependence of the lattice parameters of VO$_2$(A), where that of VO$_2$(R) is presented in the inset for comparison. In Fig. 8 the $c$-axis of the high-temperature phase is assumed to be unchanged from that of the low-temperature phase for convenience. At the transition on heating, the $a$-axis expands while the $c$-axis contracts. It is also seen that the $c$-axis tends to decrease above the transition temperature. Let the $a$- and $c$-axis of VO$_2$(A) correspond to the $a$- and $c$-axis of the rutile structure of VO$_2$(R), respectively, we find that this behavior through the transition appears to be quite similar to that of VO$_2$(R). As is seen in the inset of Fig. 8, the $a$- and $c$-axis of the rutile structure expands and contracts, respectively, at the transition. The $a$-axis of the monoclinic structure becomes the half through the transition connecting to the $c$-axis of the rutile structure. Moreover the $c$-axis of the rutile structure tends to decrease above the transition temperature.

The present study has revealed the transition in VO$_2$(A) which exhibits behavior similar to that of the metal-insulator transition of VO$_2$(R) in both physical and structural properties. Thus it is considered, in analogy with the case of VO$_2$(R), that the $V^{4+}$-$V^{4+}$ paring along the $c$-axis may occur in the low temperature phase of VO$_2$(A) resulting in the non-magnetic and lower conductive phase. The features of the transition in VO$_2$(A) in contrast to that in VO$_2$(R) are that the transition is observable on heating not on cooling, the transition is not accompanied with lattice distortion, and the high-temperature phase does not become metallic. Since the DTA peak of VO$_2$(A) is considerably smaller than that of VO$_2$(R), the transition of VO$_2$(A) seems to be so faint that the lattice distortion and the change into the metallic phase are difficult to occur. Unfortunately, the crystal structure of VO$_2$(A) still remains unknown. Further study to determine the crystal structure of VO$_2$(A) is in progress to elucidate the exact mechanism of the transition with reference to the metal-insulator transition of VO$_2$(R).

Acknowledgement The authors wish to thank Professor K. Kosuge and Dr. Y. Ueda of Kyoto University for helpfull discussions. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References