In Situ Characterization on Thermal Transitions of VO\(_2\)(B): Toward VO\(_2\)(R) and V\(_2\)O\(_3\)

Zhang Shaohong, Fu Juan, Su Qiucheng, Wu Liangpeng, Li Xinjun

Abstract: VO\(_2\)(B) was synthesized via a facile hydrothermal process using V\(_2\)O\(_5\) and oxalic acid. The crystal structure and the phase transition of VO\(_2\)(B) during elevated temperatures in N\(_2\) were investigated by in situ X-ray diffraction (XRD). Meanwhile, the morphologies and the crystal structures of the samples obtained by annealing at different temperatures were characterized by Field emission scanning electron microscopy (FE-SEM), XRD and Raman spectroscopy, respectively. The results show that the as-synthesized nano platelet-like monoclinic VO\(_2\)(B) irreversibly transforms into submicron and micron subsphaeroidal tetragonal VO\(_2\)(R) between 430 and 700 °C. The as-obtained VO\(_2\)(R) starts to decompose and form Magnéli phases V\(_n\)O\(_{2n-1}\) (3 ≤ n ≤ 9) series compounds at ~1000 °C, and totally transfers into a corundum V\(_2\)O\(_3\) sintered block at ca. 1200 °C.

Key words: hydrothermal; vanadium oxides; in situ XRD; thermal transformation

Vanadium (V) is the fifth most abundant transition metal in the earth. Unlike its neighboring transitional metals such as Ti, Cr and Mn, V exists with numerous possible valencies and, consequently, has many different oxides \(^1\). Among these compounds, V\(_2\)O\(_3\), VO\(_2\), and V\(_2\)O\(_5\) have been widely studied as optical, electrical, electrochemical, thermochromic and thermal switching materials \(^2\). VO\(_2\), in particular, has attracted tremendous attention as they exhibit different structures with distinctive optical and electrical properties \(^3-5\).

So far, more than ten crystalline phases of VO\(_2\) have been reported \(^6\), including tetragonal VO\(_2\)(R) (P42/mnm) \(^7\), monoclinic VO\(_2\)(M) (P21/c) \(^8,9\), tetragonal VO\(_2\)(A) (P42/mmc) \(^10\), monoclinic VO\(_2\)(B) (C2/m) \(^11\) and VO\(_2\)(C) \(^12\). Out of these phases, VO\(_2\)(M) is considered to be the most stable and attracts much interest because it undergoes a reversible transition to VO\(_2\)(R) at approximately 68 °C \(^13,14\), its conductivity and optical transmittance change abruptly through the phase transition \(^15\), and it can be used in thermochromic coatings \(^16\), temperature sensing devices \(^17\), optical switching devices \(^4,18,19\) and Mott field-effect transistors \(^20\). Except VO\(_2\)(M/R), VO\(_2\)(B) with metastable monoclinic structure is of great interest, owing to its high energy capacity along with moderate work potential, and its promising applications in the field of energy technologies \(^21-24\). Besides, VO\(_2\)(B) is usually used as the precursor of VO\(_2\)(M/R) \(^25-27\). The transformation of VO\(_2\)(B) → VO\(_2\)(R) was first reported at 400–450 °C by Théobald et al. \(^11\). Later, it was studied by thermogravimetry (TG), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and in situ electron microscopy methods \(^25, 27-29\). And it was shown that it was not a first-order transformation occurring at a fixed temperature. It varied from 320 to 500 °C. But, recently, Li and his coworkers have found that the transformation did not complete even when the temperature was kept at 500 °C for 4 h, and they called for a further investigation to confirm the process \(^30\). Meanwhile, they also pointed out that the researches on the phase transition of VO\(_2\) had significant senses for preparing excellent materials \(^31\). Owing to the
complex mechanism and its great importance to VO₂ materials preparation and application, many efforts have been made to investigate the transformation of VO₂(B). However, there is still limited amount of literatures revealing the thermal transition of the VO₂(B) in detail by far.

Thus, the aim of the present work is to present a more detailed characterization of VO₂(B) thermal transition. An in situ XRD method was employed to investigate the as-synthesized VO₂(B) transition during the process of elevated temperature up to 1200 °C in N₂. Our work provided new insights into the VO₂(B) → VO₂(R) transition. We also observed the structure, morphology and Raman spectrum evolution of the sample from monoclinic VO₂(B) to tetragonal VO₂(R)/monoclinic VO₂(M), and to rhombohedral V₂O₅.

1 Experiment

All the chemical reagents used in the present experiment were analytical grade. In a typical procedure, 0.9 g vanadium pentaoxide (V₂O₅; Tianjin Fuchen chemical reagents factory) and 1.26 g oxalic acid dihydrate (H₂C₂O₄·2H₂O; Jiangsu Qiangsheng Functional Chemical Ltd.) were dispersed in 50 mL deionized water. After stirring for 30 min at 60 °C, the resulting yellow suspension was transferred to 90 mL Teflon-lined stainless steel autoclave and hydrothermally treated for 24 h at 180 °C. After cooling down to room temperature, the resulting powder was washed with deionized water and ethanol, and dried at 60 °C for 12 h. The final obtained blue powder was marked as S-180. The samples annealed at 450, 600, 750 and 1200 °C were named as S-450, S-600, S-750 and S-1200, respectively.

Phase identification was carried out via XRD analysis on a PANalytical diffractometer (X’Pert Pro MPD) using Cu Kα1 γ radiation (λ = 0.1 540 598, 0.1 544 426 nm) at 40 kV accelerating voltage and 40 mA. Experiments were performed both at elevated temperatures for in situ XRD study and at ambient temperature for further confirmation of the results. In situ XRD was carried out with an Anton Paar HTK 1200N high-temperature chamber. The chamber was used to heat up the sample with a control accuracy of ± 2 °C in a flow controlled N₂ environment. The sample was heated to 1200 °C at a fixed heating rate of 10 °C·min⁻¹. The diffraction data were obtained in the 2θ range between 10 and 80° with a 0.0167° step size and 10 s dwell time. The identification of the compounds was made by comparing the experimental XRD patterns to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). The alignment was done at ambient temperature with a standard of silicon crystalline powder.

Morphologies and microstructure of the samples were observed by FE-SEM (HITACHI S-4800). Samples were directly deposited on an aluminum stub using double-sided adhesive carbon tape. Images were observed and captured under 2.0 or 3.0 kV accelerating voltage and 10.0 μA emission current.

Raman spectra of samples were recorded on LabRAM HR 800 high resolution spectrometer (Horiba Jobin Yvon). The spectral resolution was about 1 cm⁻¹. Samples were excited by a Nd:YAG laser (λ = 532.16 nm, 50 mW maximum output power) fed through an integral confocal microscope, focused onto the sample with an Olympus MPLN50x micro-objective. The light scattered from the sample was collected with the same objective in backscattering (180°) geometry. To minimize laser irradiate injuring of the sample, the incident beam was attenuated before it entered the microscope. Calibration was performed during measurements with a silicon semiconductor mode at 520.7 cm⁻¹.

2 Results and Discussion

2.1 In situ XRD analysis

The evolution of the diffraction patterns of the as-synthesized sample during elevated temperature in situ XRD is presented in Fig.1, accompanied with JCPDS No. 081-2392, No. 076-0678, No. 009-8711, No. 071-0041 and No. 071-0343. The sample was heated from 30 °C to 100 °C, followed by heating at 100 °C increments to 400 °C, at 10 °C increments to 1000 °C and at 50 °C increments to 1200 °C. At 30 °C, the observed diffraction pattern can be indexed to the monoclinic VO₂(B) (JCPDS No. 081-2392), and this remains predominant phase up to 420 °C (see Fig.1 curve 1~ 8). At 430 °C, a small shoulder appears at 27.5° (20), and as the temperature increases, more other peaks are observed. These peaks become prominent when the heating temperature increases to 700 °C. All the peaks can be indexed to tetragonal VO₂(R) (JCPDS No. 076-0678). No other peaks are observed (see Fig.1 curve 9~ 16 and 21). But, there is a slight shift (−0.2°~0.7°) in the elevated temperature experimental diffraction peak positions, compared with calculated tetragonal VO₂(R) (110), (101), (200), (111), (210), (211), (220), (310), (002), (301), (112) and (311) reflections. The slight shift can be attributed to the thermal expansion [32]. From 430 °C to 690 °C, the emergence of VO₂(R) couples with a decrease of the VO₂(B) phase. At 700 °C, VO₂(B) phase completely disappears and VO₂(R) becomes the sole phase. Thus, we consider that the as-synthesized VO₂(B) shows moderate thermal stability and remains unchanged from room temperature to 420 °C in N₂ atmosphere. The VO₂(B) → VO₂(R) transition undergoes a sluggish process, starting at around 430 °C, and finishing at ~700 °C. Both the onset and offset temperature are lower than that in previous reports [33]. It may be attributed to the lower heating rate and the influence of VO₂(B) synthesis techniques and its initial morphologies [30].
From 700 to 990 °C, VO₂(R) phase remains predominant (see Fig. 1 curve 16–20). Diffraction peaks other than VO₂(R) phase emerge at 1000 °C, and the peaks become predominant with the increase of the temperature, and they may be indexed to Magnéli phases \( V_n O_{2n-1} \) (3 ≤ \( n \) ≤ 9) series compounds, such as anorthic \( V_6 O_{13} \) (JCPDS No. 009-8711), anorthic \( V_9 O_{17} \) (JCPDS No. 071-0041) and rhombohedral \( V_3 O_7 \) (JCPDS No. 071-0343). At 1150 °C, VO₂(R) phase disappears completely. At 1200 °C, all diffraction peaks of the sample are indexed to the rhombohedral phase of \( V_2 O_3 \) (JCPDS No. 071-0343). At 1150 °C, \( V_2 O_3 \) becomes the sole phase at 1200 °C.

Thus, from the above in situ XRD experiments analysis, we consider that the as-synthesized sample is monoclinic phase VO₂(B). During the process of elevated temperature from 30 to 1200 °C in \( N_2 \), there is no obvious change at 30 ~ 420 °C in monoclinic phase VO₂(B), and rutile structure VO₂(R) coexists with the monoclinic VO₂(B) between 430 and 690 °C. The emergence of VO₂(R) couples with a decrease of VO₂(B) phase with the increase of the temperature. From 700 °C to 990 °C, VO₂(R) becomes the sole phase. At 1000 °C, VO₂(R) starts to decompose to produce series Magnéli phases compounds. At 1150 °C, VO₂(R) phase disappears completely. Finally, the rhombohedral phase of \( V_2 O_3 \) is obtained at 1200 °C.

<table>
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<tr>
<th>Temperature/°C</th>
<th>Phase indexed</th>
<th>Crystal structure</th>
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| 30–420         | Monoclinic VO₂(B) | ![Monoclinic VO₂(B)](image)
| 430–690        | Monoclinic VO₂(B) + tetragonal VO₂(R) | ![Monoclinic VO₂(B) + tetragonal VO₂(R)](image)
| 700–990        | Tetragonal VO₂(R) | ![Tetragonal VO₂(R)](image)
| 1000–1140      | Tetragonal VO₂(R) + Magnéli phases \( V_{2n-1} O_3 \) (3 ≤ \( n \) ≤ 9) | ![Tetragonal VO₂(R) + Magnéli phases](image)
| 1150–1190      | \( V_{2n-1} O_3 \) (3 ≤ \( n \) ≤ 9) + rhombohedral \( V_3 O_7 \) | ![\( V_{2n-1} O_3 \) (3 ≤ \( n \) ≤ 9) + rhombohedral \( V_3 O_7 \)](image)
| 1200           | Rhombohedral \( V_3 O_7 \) | ![Rhombohedral \( V_3 O_7 \)](image)
undergoes a sluggish process and covers a wide temperature range.

2.2 XRD analysis

The as-synthesized VO\(_2\)(B) (S-180) and samples annealed at different temperatures were also characterized by XRD at ambient temperature. In Fig.2, all these XRD results are compared with the JCPDS standards. The experimental pattern of samples S-180, S-750 and S-1200 can be indexed to the monoclinic phase of VO\(_2\)(B) (JCPDS No. 081-2392), monoclinic phase of VO\(_2\)(M) (JCPDS No. 082-0661) and rhombohedral phase of V\(_2\)O\(_3\) (JCPDS No. 071-0343), respectively. According to previous works\(^{13,14}\), VO\(_2\)(M) undergoes a reversible phase transition to VO\(_2\)(R) at approximately 68\(^\circ\)C, so the result can further confirm the formation of VO\(_2\)(R). Comparing curves 4 and 5 with curves 1 and 3 in Fig.2, both the spectra of S-450 and S-600 have the VO\(_2\)(B) and VO\(_2\)(M) characteristic diffraction peaks. The result reveals that sample S-450 and S-600 are mixtures of VO\(_2\)(B) and VO\(_2\)(M). It is consistent with the above in situ XRD analysis.

In summary, the results agree with those obtained during the above in situ XRD analysis. The difference is: at high temperature there is a slight shift in the diffraction peak positions, owing to thermal expansion\(^{32}\); nevertheless, at room temperature all peaks are highly coincided with the standard patterns. No peaks of any other phases or impurities are detected in these spectra, revealing that the as-prepared products S-180, S-750 and S-1200 are mainly composed of VO\(_2\)(B), VO\(_2\)(M) and V\(_2\)O\(_3\), respectively. Thereby, it can be confirmed that VO\(_2\)(B), VO\(_2\)(R/M) and V\(_2\)O\(_3\) are formation.

2.3 Morphology and microstructure analysis

All the sizes and morphologies of the samples were examined by FE-SEM. Fig.3a reveals the as-synthesized VO\(_2\)(B) is composed of polydisperse nano platelets. The particle size is 50~250 nm in width, 15~35 nm in thickness and less than 100 nm to more than 1 \(\mu\)m in length. This morphology is attributed to its layer crystal structure\(^{34,35}\). Fig.3b shows the surface and the edge of platelet-like nanostructure get round in sample S-450, but the platelet-like morphology has no prominent change. Fig.3c clearly indicates that most of the nanostructures change from platelet-like morphology to subsphaeroidal morphology in sample S-600, accompanying with a crystal growth. The diameters increase to more than 1 \(\mu\)m alongside smaller nanoparticles. Fig.3d reveals that all of the nanostructure...
changes into submicron and micron subspaheroidal morphology in sample S-750, and the particle size keeps polydisperse with ~10 μm alongside smaller nanoparticles. Fig.3e indicates that the sample S-1200 becomes one sintered compact. Fig.3f demonstrates the macro morphology evolution of the sample annealed at different temperatures under the N2 flow atmosphere. At room temperature, the as-synthesized powder is pressed in the crucible (see Fig.3f S-180). At 450 °C, the gap between the powder and edge of the crucible is observed (see Fig.3f S-450). Up to 600 °C, the gap broadens (see Fig.3f S-600). And to 750 °C, cracks in the sample appear (see Fig.3f S-750). When the temperature is up to 1200 °C, the sample is sintered to one block with pores and flaws (see Fig.3f S-1200). These can be attributed to densification, grain growth and powder agglomeration during thermal transformation and sintering. The heating has a pronounced effect on the morphology. And there is a decrease in specific volume during transformation because the density changes from 4.00 g·cm⁻³ [VO₂(B)] to 4.66 g·cm⁻³ [VO₂(R/M)] and 4.92 g·cm⁻³(V₂O₃). Large crystallites of VO₂(R/M) is obtained by heating nanostructure VO₂(B) in N2 flow atmosphere. The phenomenon is similar to that seen by Corr et al. [33].

Thus, in terms of the above electron microscopy studies, we consider that heating has a pronounced effect on the microstructure and morphology. As temperature increases, the microstructure and the morphology of the as-synthesized VO₂(B) drastically change from nanoplatelet-like VO₂(B) to submicron and micron subspaheroidal VO₂(R/M), finally to a V₂O₃ sintered block.

2.4 Raman spectra analysis

All the Raman spectra of the as-prepared samples are shown in Fig.4, accompanying with the thermo spectral ID library index 451 (VO₂). In the wavelength range of 50~1200 cm⁻¹, all spectra are acquired with the same laser power and exposition time except V₂O₃. The absorption of V₂O₃ at the measure laser wavelength is high, making it necessary to apply more laser power to obtain identifiable Raman peaks [36].

The Raman spectrum of the as-synthesized VO₂(B) is presented as shown in curve a in Fig.4. It is dominated by the peaks at 104, 185, 257, 400, 666 and 859 cm⁻¹. All these peaks are assigned to the Raman signature of VO₂(B) [37,38]. The low-frequency peak at 104 cm⁻¹ is corresponding to its rigid-layer modes. The peaks at 185 and 257 cm⁻¹ are assigned to V-O-V bending modes and external modes (bending/wagging), respectively. The peaks at 400 and 464 cm⁻¹ are attributed to V-O-V stretching modes. The peak at 666 cm⁻¹ is due to coordination of vanadium atoms with three oxygen atoms, while the peak at 859 cm⁻¹ is attributed to V=O stretching of distorted octahedra. These Raman results are in accordance with the above crystal structure analysis, and the results further confirm the formation of monoclinic VO₂(B).

Fig.4 curve d shows the Raman spectrum of sample S-750. There are 12 peaks at 140, 192, 221, 258, 307, 336, 387, 430, 495, 609, 662 and 816 cm⁻¹. All these peaks are the vibration bands of VO₂(M) and highly coincide with those reported in the previous works [39-43] and Thermo Spectral ID Library index 451 VO₂ (Fig.4 curve e). The results further confirm the formation of monoclinic VO₂(M). By the comparison of Fig.4 curve b and c, the Raman spectra of S-450 and S-600, we can find the coexistence of the monoclinic VO₂(B) and VO₂(M). The emergence of VO₂(M) is coupled with the decrease of the VO₂(B). These results are highly in agreement with those obtained in the XRD analysis.

Fig.4 curve f shows the Raman spectrum of sample S-1200. There are seven Raman peaks observed in our experiment. The major peaks at 213, 239, 295, 328, 501 and 589 cm⁻¹ are coincided with literatures [36, 44]. These peaks are assigned to V₂O₃ E_g, A_1g, E_g, A_1g, and E_g phonon modes, respectively. The peaks at 412 cm⁻¹ can be assigned to the other E_g modes. Therefore, our results suggest all two A_1g and five E_g Raman active modes of V₂O₃ predicted by group theory [45]. The result also coincides with the above XRD analysis and further confirms the formation of V₂O₃.

In summary, all the Raman peaks depicted in Fig.4 are presented in Table 2, with the previous alongside the present findings on Raman shifts in VO₂(B), VO₂(M), and V₂O₃. As seen from Table 2, the present results agree very well with the previous findings. The Raman results also indicate that the obtained VO₂(B), VO₂(M), and V₂O₃ have good crystalline quality. They are consistent with the above XRD studies of similar samples as well and further confirm the crystal structure reconstruction during the thermal transition.

![Fig.4 Raman spectra of annealed samples (a: S-180, b: S-450, c: S-600, d: S-750, e: Thermo Spectral ID Library index 451 VO₂, f: S-1200)](image-url)
3 Conclusions

1) Platelet-like monoclinic VO$_2$(B) can be synthesized via a facile hydrothermal process using a vanadium source of V$_2$O$_5$ and a reducing agent of oxalic acid.

2) The evolution of the crystal structure and morphology of monoclinic VO$_2$(B) to tetragonal VO$_2$(R), monoclinic VO$_2$(M) and corundum V$_2$O$_3$ can be tracked using XRD and Raman spectroscopy.

3) VO$_2$(B) thermal transition can be obtained via the in situ XRD method, and it undergoes a reconstructive solid phase transition. Heating in N$_2$ flow atmosphere, the as-synthesized VO$_2$(B) is stable from room temperature to 420 °C, then transforms reversibly into submicron and micron subphaseroidal tetragonal VO$_2$(R) between 430 and 700 °C, and finally the as-obtained VO$_2$(R) starts to decompose to form Magnéli phases V$_n$O$_{2n+1}$ (3≤n≤9) series compounds at 1000 °C, and finally changes to a corundum structure V$_2$O$_3$ sintered block at ca. 1200 °C.

References


2 Tang Qing, Li Fengyu, Zhou Zhen et al. *Journal of Physical Chemistry C*[J], 2011, 115: 11983


8 Andersson G. *Acta Chemica Scandinavica*[J], 1954, 8: 1599

9 Andersson G. *Acta Chemica Scandinavica*[J], 1956, 10: 623


13 Morin F. *Physical Review Letters*[J], 1959, 3: 34


17 Yin Haisheng, Ni Juan, Jiang Wentao et al. *Physica E*[J], 2011, 43: 1720


19 Chen Sihai, Ma Hong, Yi Xinjian *et al. Infrared Physics & Technology*[J], 2004, 45: 239


21 Li Juan, Jiang Wentao, Yu Ke *et al. Electrochimica Acta*[J], 2011, 56: 2122

22 Li Wu, Dahn J R, Wainwright D S. *Chemistry of Materials*[J], 2011, 23: 1720

23 Zhang Shaohong, Fu Juan, Su Quicheng et al. *Rare Metal Materials and Engineering*[J], 2009, 131: 8884


VO₂(B)  VO₂(R)  V₂O₃  XRD

Magnéli  3 ≤ n ≤ 9  1200 °C

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