

In Situ Characterization on Thermal Transitions of VO₂(B): Toward VO₂(R) and V₂O₃

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Abstract: VO₂(B) was synthesized via a facile hydrothermal process using V₂O₅ and oxalic acid. The crystal structure and the phase transition of VO₂(B) during elevated temperatures in N₂ 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 VO₂(B) irreversibly transforms into submicron and micron subsphaeroidal tetragonal VO₂(R) between 430 and 700 °C. The as-obtained VO₂(R) starts to decompose and form Magnéli phases V_nO_{2n-1} (3 ≤ n ≤ 9) series compounds at ~1000 °C, and totally transfers into a corundum V₂O₃ 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, V₂O₃, VO₂, and V₂O₅ have been widely studied as optical, electrical, electrochemical, thermochromic and thermal switching materials^[2]. VO₂, 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 VO₂ have been reported^[6], including tetragonal VO₂(R) (P42/mnm)^[7], monoclinic VO₂(M) (P21/c)^[8,9], tetragonal VO₂(A) (P42/nmc)^[10], monoclinic VO₂(B) (C2/m)^[11] and VO₂(C)^[12]. Out of these phases, VO₂(M) is considered to be the most stable and attracts much interest because it undergoes a reversible transition to VO₂(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 VO₂(M/R), VO₂(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, VO₂(B) is usually used as the precursor of VO₂(M/R)^[25-27]. The transformation of VO₂(B) → VO₂(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^[23, 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 VO₂ had significant senses for preparing excellent materials^[31]. Owing to the

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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 V₂O₃.

1 Experiment

All the chemical reagents used in the present experiment were analytical grade. In a typical procedure, 0.9 g vanadium pentoxide (V₂O₅; Tianjin Fuchen chemical reagents factory) and 1.26 g oxalic acid dihydrate (H₂C₂O₄·2H₂O; Jiangsu Qiangsheng Fuctional 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 K $\alpha_{1,2}$ radiation ($\lambda = 0.1540598, 0.1544426$ 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 2 θ 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 μ A 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 ($\lambda = 532.16$ 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° (2 θ), 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].

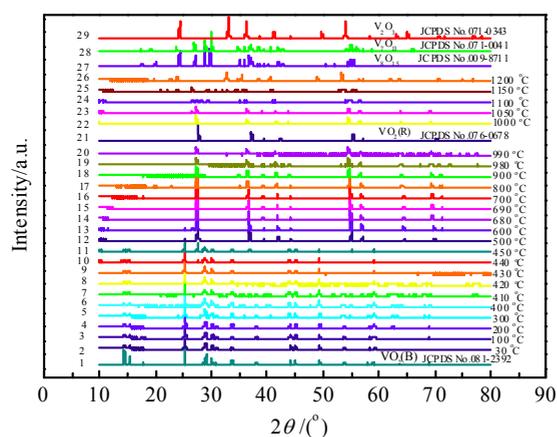


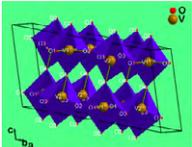
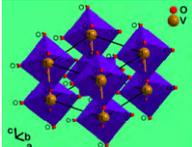
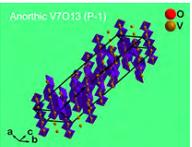
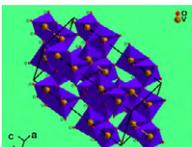
Fig.1 In situ XRD patterns of $\text{VO}_2(\text{B})$ collected at elevated temperature from 30~1200 °C, at 10 °C min^{-1} heating rate, under N_2 flow atmosphere and $\text{VO}_2(\text{B})$, $\text{VO}_2(\text{R})$, V_8O_{15} , V_7O_{13} , V_2O_3 JCPDS simulation patterns. Note the emergence of the $\text{VO}_2(\text{R})$ at 430 °C, which becomes the sole phase at 700 °C; the emergence of Magnéli phases at 1000 °C, V_2O_3 becomes the sole phase at 1200 °C

From 700 to 990 °C, $\text{VO}_2(\text{R})$ phase remains predominant (see Fig.1 curve 16~20). Diffraction peaks other than $\text{VO}_2(\text{R})$ phase emerge at 1000 °C, and the peaks become predominate with the increase of the temperature, and they may be indexed to Magnéli phases $\text{V}_n\text{O}_{2n-1}$ ($3 \leq n \leq 9$) series compounds, such as anorthic V_8O_{15} (JCPDS No. 009-8711), anorthic V_7O_{13} (JCPDS No. 071-0041) and rhombohedral V_2O_3 (JCPDS No. 071-0343). At 1150 °C, $\text{VO}_2(\text{R})$ phase disappears completely. At 1200 °C, all diffraction peaks of the sample are indexed to the rhombohedral phase of V_2O_3 (JCPDS No. 071-0343) (see Fig.1 curve 22~29). From the experiments, we consider that the as-obtained $\text{VO}_2(\text{R})$ is not as stable as that reported in range of 68 to 1540 °C^[27]. It may be attributed to the influence of the microstructure and the morphology of its precursor. In the present work, the rutile $\text{VO}_2(\text{R})$ is originated from nanostructure $\text{VO}_2(\text{B})$, and is prone to decompose to produce series Magnéli phases compounds. The decomposition of $\text{VO}_2(\text{R})$ emerges at 1000 °C.

Thus, from the above in situ XRD experiments analysis, we consider that the as-synthesized sample is monoclinic phase $\text{VO}_2(\text{B})$. 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 $\text{VO}_2(\text{B})$, and rutile structure $\text{VO}_2(\text{R})$ coexists with the monoclinic $\text{VO}_2(\text{B})$ between 430 and 690 °C. The emergence of $\text{VO}_2(\text{R})$ couples with a decrease of $\text{VO}_2(\text{B})$ phase with the increase of the temperature. From 700 °C to 990 °C, $\text{VO}_2(\text{R})$ becomes the sole phase. At 1000 °C, $\text{VO}_2(\text{R})$ starts to decompose to produce series Magnéli phases compounds. At 1150 °C, $\text{VO}_2(\text{R})$ phase disappears completely. Finally, the rhombohedral phase of V_2O_3 is obtained at 1200 °C. The

crystal phase and the structure evolution can be presented in Table 1. Monoclinic $\text{VO}_2(\text{B})$ exhibits a typical layer structure, layers of edge-sharing along the ab plane [VO_6] octahedra are connected by corners to form a three-dimensional crystal structure. V atoms deviate from the center of the oxygen octahedra. It leads to two types of deformed octahedra. Tetragonal $\text{VO}_2(\text{R})$ has a more symmetric structure. V atoms are at the center of the regular oxygen octahedra. With respect to vanadium site it is based on a body-centered tetragonal lattice. [VO_6] octahedra at the corners and the center of a unit cell are rotated by 90° around the c -axis. Adjacent [VO_6] octahedral shares edges to form chains along the c -axis. Corner and center chains are connected via corners. Rhombohedral V_2O_3 is based on a trigonal lattice with space group R-3c. The oxygen atom is arranged qualitatively to be equivalent to the network in VO_2 . V atoms fill only two thirds of oxygen octahedra. Two filled followed by one empty face-sharing octahedra form noncontinuous chains along c -axis. The Magnéli phases can be considered as $\text{V}_n\text{O}_{2n-1} = \text{V}_2\text{O}_3 + (n-2) \text{VO}_2$ ($3 \leq n \leq 9$)^[34]. As is obvious from the stoichiometric relation, their crystal structures comprise dioxide and sesquioxide-like regions, respectively. Clearly, $\text{VO}_2(\text{B})$ and $\text{VO}_2(\text{R})$ have totally different arrangements of [VO_6] octahedra crystal structure. The transition from $\text{VO}_2(\text{B})$ to $\text{VO}_2(\text{R})$ leads a dramatic rearrangement and reshuffling within the structure. It likely is so-called reconstructive solid state phase transformation. It can explain why the $\text{VO}_2(\text{B})$ \rightarrow $\text{VO}_2(\text{R})$ transition

Table 1 Summary of the crystal structure evolution at elevated temperatures

Temperature/°C	Phase indexed	Crystal structure
30~420	Monoclinic $\text{VO}_2(\text{B})$	
430~690	Monoclinic $\text{VO}_2(\text{B})$ + tetragonal $\text{VO}_2(\text{R})$	
700~990	Tetragonal $\text{VO}_2(\text{R})$	
1000~1140	+ Magnéli phases $\text{V}_n\text{O}_{2n-1}$ ($3 \leq n \leq 9$)	
1150~1190	Magnéli phases $\text{V}_n\text{O}_{2n-1}$ ($3 \leq n \leq 9$) + rhombohedral V_2O_3	
1200	Rhombohedral V_2O_3	

undergoes a sluggish process and covers a wide temperature range.

2.2 XRD analysis

The as-synthesized $\text{VO}_2(\text{B})$ (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 $\text{VO}_2(\text{B})$ (JCPDS No. 081-2392), monoclinic phase of $\text{VO}_2(\text{M})$ (JCPDS No. 082-0661) and rhombohedral phase of V_2O_3 (JCPDS No. 071-0343), respectively. According to previous works^[13,14], $\text{VO}_2(\text{M})$ undergoes a reversible phase transition to $\text{VO}_2(\text{R})$ at approximately 68 °C, so the result can further confirm the formation of $\text{VO}_2(\text{R})$. Comparing curves 4 and 5 with curves 1 and 3 in Fig.2, both the spectra of S-450 and S-600 have the $\text{VO}_2(\text{B})$ and $\text{VO}_2(\text{M})$ characteristic diffraction peaks. The result reveals that sample S-450 and S-600 are mixtures of $\text{VO}_2(\text{B})$ and $\text{VO}_2(\text{M})$. 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 $\text{VO}_2(\text{B})$, $\text{VO}_2(\text{M})$ and V_2O_3 , respectively. Thereby, it can be confirmed that $\text{VO}_2(\text{B})$, $\text{VO}_2(\text{R/M})$ and V_2O_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 $\text{VO}_2(\text{B})$ 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 μm 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 μm alongside smaller nanoparticles. Fig.3d reveals that all of the nanostructure

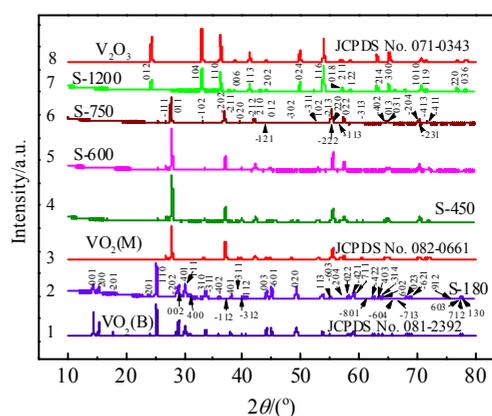


Fig.2 XRD patterns of annealed samples (1: JCPDS No. 081-2392, 2: S-180, 3: JCPDS No. 082-0661, 4: S-450, 5: S-600, 6: S-750, 7: S-1200, 8: JCPDS No. 071-0343)

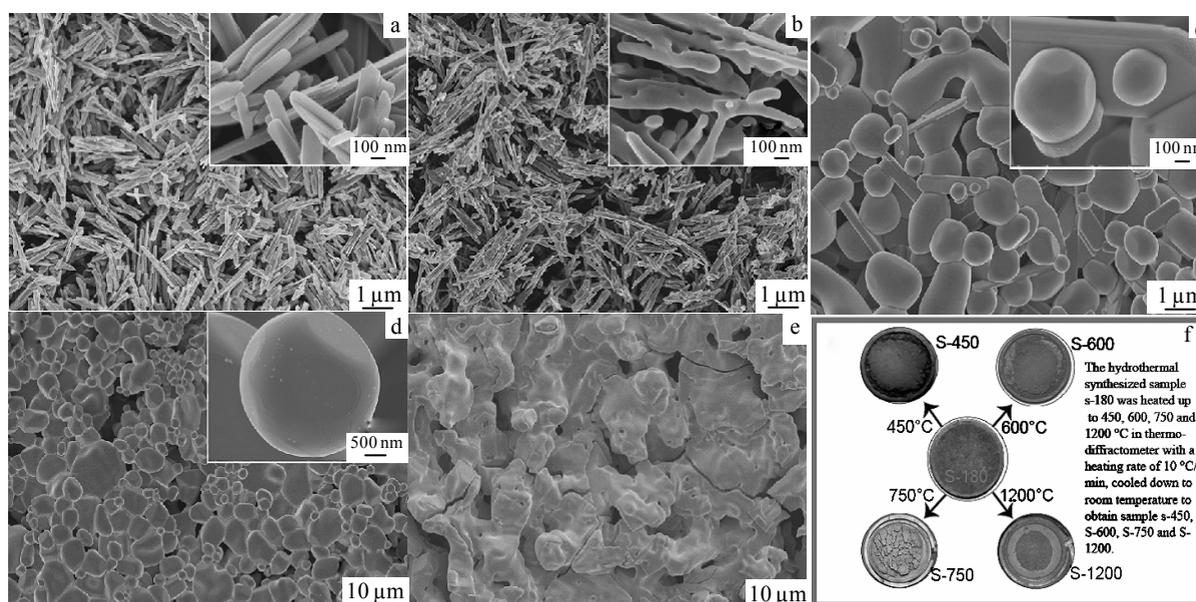


Fig.3 SEM micrograph of $\text{VO}_2(\text{B})$ as-synthesized and annealed at different temperatures: (a) S-180, (b) S-450, (c) S-600, (d) S-750, and (e) S-1200, (f) photo of samples in corundum crucible cooled down in situ

changes into submicron and micron subsphaeroidal morphology in sample S-750, and the particle size keeps polydisperse with $\sim 10 \mu\text{m}$ 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 N_2 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 $4.00 \text{ g}\cdot\text{cm}^{-3}$ [$\text{VO}_2(\text{B})$] to $4.66 \text{ g}\cdot\text{cm}^{-3}$ [$\text{VO}_2(\text{R/M})$] and $4.92 \text{ g}\cdot\text{cm}^{-3}$ (V_2O_3). Large crystallites of $\text{VO}_2(\text{R/M})$ is obtained by heating nanostructure $\text{VO}_2(\text{B})$ in N_2 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 $\text{VO}_2(\text{B})$ drastically change from nano platelet-like $\text{VO}_2(\text{B})$ to submicron and micron subsphaeroidal $\text{VO}_2(\text{R/M})$, finally to a V_2O_3 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 (VO_2). In the wavelength range of $50\sim 1200 \text{ cm}^{-1}$, all spectra are acquired with the same laser power and exposition time except V_2O_3 . The absorption of V_2O_3 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 $\text{VO}_2(\text{B})$ is presented as shown in curve a in Fig.4. It is dominated by the peaks at $104, 185, 257, 400, 464, 666$ and 859 cm^{-1} . All these peaks are assigned to the Raman signature of $\text{VO}_2(\text{B})$ [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 $\text{VO}_2(\text{B})$.

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 $\text{VO}_2(\text{M})$ and highly coincide with those reported in the previous works [39-43] and Thermo Spectral ID Library index 451 VO_2 (Fig.4 curve e). The results further confirm the formation of monoclinic $\text{VO}_2(\text{M})$. 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 $\text{VO}_2(\text{B})$ and $\text{VO}_2(\text{M})$. The emergence of $\text{VO}_2(\text{M})$ is coupled with the decrease of the $\text{VO}_2(\text{B})$. 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 V_2O_3 $\text{E}_g, \text{A}_{1g}, \text{E}_g, \text{E}_g, \text{A}_{1g},$ and E_g phonon modes, respectively. The weak peaks located 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 V_2O_3 predicted by group theory [45]. The result also coincides with the above XRD analysis and further confirms the formation of V_2O_3 .

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 $\text{VO}_2(\text{B})$, $\text{VO}_2(\text{M})$, and V_2O_3 . As seen from Table 2, the present results agree very well with the previous findings. The Raman results also indicate that the obtained $\text{VO}_2(\text{B})$, $\text{VO}_2(\text{M})$, and V_2O_3 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.

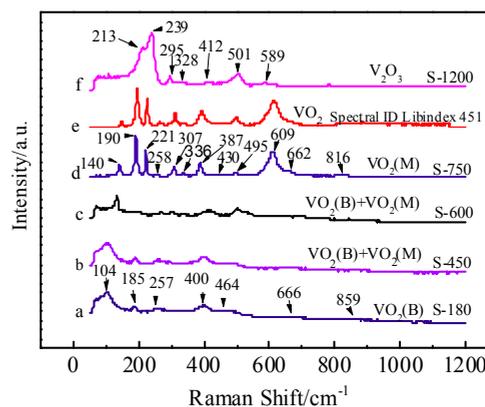


Fig.4 Raman spectra of annealed samples (a: S-180, b: S-450, c: S-600, d: S-750, e: Thermo Spectral ID Library index 451 VO_2 , f: S-1200)

Table 2 Comparison of Raman data for VO₂(B), VO₂(M) and V₂O₃ in previous investigation with those of the present work (cm⁻¹)

VO ₂ (B)			VO ₂ (M)			V ₂ O ₃		
Present work	Ref. [37]	Ref. [38]	Present work	Ref. [39]	Ref. [40]	Present work	Ref. [36]	Ref. [44]
104	103	118	-	-	-	-	-	-
-	-	-	140	142	149	-	-	-
185	195	191	192	191	199	213	203	210
-	-	-	221	223	225	239	231	234
-	-	-	258	262	259	-	-	-
257	295	270	-	-	265	-	-	-
-	-	-	307	310	313	295	290	290
-	-	-	336	-	339	328	-	327
400	391	399	387	392	392	412	-	-
-	-	-	-	-	395	-	-	-
-	-	-	430	443	444	-	-	-
-	-	-	-	-	453	-	-	-
464	-	-	-	-	489	-	-	-
-	-	-	495	500	503	501	500	501
-	-	-	609	613	595	589	590	595
-	-	-	-	-	618	-	-	-
666	662	670	662	-	670	-	-	-
859	-	880	816	-	830	-	-	-

3 Conclusions

1) Platelet-like monoclinic VO₂(B) can be synthesized via a facile hydrothermal process using a vanadium source of V₂O₅ and a reducing agent of oxalic acid.

2) The evolution of the crystal structure and morphology of monoclinic VO₂(B) to tetragonal VO₂(R), monoclinic VO₂(M) and corundum V₂O₃ can be tracked using XRD SEM and Raman spectroscopy.

3) VO₂(B) thermal transition can be obtained via the in situ XRD method, and it undergoes a reconstructive solid state phase transformation. Heating in N₂ flow atmosphere, the as-synthesized VO₂(B) is stable from room temperature to 420 °C, then transforms irreversibly into submicron and micron subsphaeroidal tetragonal VO₂(R) between 430 and 700 °C, and then the as-obtained VO₂(R) starts to decompose to form Magnéli phases V_nO_{2n-1} (3 ≤ n ≤ 9) series compounds at 1000 °C, and finally changes to a corundum structure V₂O₃ sintered block at ca. 1200 °C.

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VO₂(B)热转化为 VO₂(R)和 V₂O₃ 的高温 XRD 原位表征

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摘要:以草酸和V₂O₅为原料,采用水热法制备VO₂(B)。通过高温原位X射线衍射技术研究VO₂(B)在氮气保护下升高温度过程中的相变特性,采用X射线衍射仪(XRD)、场发射扫描电子显微镜(FE-SEM)和激光拉曼光谱技术分析所制备样品及其在不同温度热相变产物的微观形貌、晶体结构和物相组成。结果表明:以草酸和V₂O₅为原料,用水热法可制得单斜晶系VO₂(B),颗粒呈纳米片状;升温至430~700之间,VO₂(B)不可逆转化为四方晶系VO₂(R),形貌由纳米片状变为亚微米及微米近球形;升温至1000左右,VO₂(R)开始分解形成Magnéli相系列化合物(V_nO_{2n-1}, 3 ≤ n ≤ 9);升温至约1200完全转变为具有刚玉结构的V₂O₃烧结块。

关键词:水热法;氧化钒;原位XRD;热相变;拉曼光谱

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