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Influence of Dimensionality on Phase Transition in VO$_2$ Nanocrystals

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Abstract:

 Hydrothermally synthesized one-dimensional and two-dimensional nanocrystals of VO$_2$ undergo phase transition around 65°C, where temperature and mechanism of phase transition are dependent on dimensionality of nanocrystals. Both nanocrystalline samples exhibit depression of phase transition temperature compared to the bulk material, the magnitude of which depends on the dimensionality of the nanocrystal. One-dimensional nanoribbons exhibit lower phase transition temperature and higher values of apparent activation energy than two-dimensional nanosheets. The phase transition exhibits as a complex process with somewhat lower value of enthalpy than the phase transition in the bulk, probably due to higher proportion of surface atoms in the nanocrystals. High values of apparent activation energy indicate that individual steps of the phase transition involve simultaneous movement of large groups of atoms, as expected for single-domain nanocrystalline materials.
Keywords: _Nanocrystals, Vanadium oxide, Phase transition, Size effects_

1. Introduction

Macroscopic manifestations of electronic and lattice instabilities in VO$_2$ during metal-insulator transition are exceptional in magnitude: changes in electrical conductivity and optical transmittance are up to 5 orders of magnitude at temperatures relatively close to room temperature (67°C in the bulk) [1]. This is also accompanied by changes in magnetic susceptibility, specific heat and Seebeck coefficient [2]. Since its discovery [3], this phenomenon has attracted attention by experimentalists and theorists alike with debate over the microscopic mechanism of this phase transition. In addition, structurally and compositionally more complex system exhibiting similar strong electronic correlations have been discovered, making VO$_2$ a sort of a model system for these systems [4-6]. On its own, VO$_2$ is important for the many potential applications of its near-room-temperature phase transition, due to its tunability with doping, strain and scaling to finite size [7], including "smart windows" [8], Mott field effect transistor [9] and a variety of optoelectronic applications [10, 11]. It is this last aspect that has driven the effort to produce nanostructures of VO$_2$ and to achieve as much control as possible of their size and morphology. In addition, nanosized materials offer the opportunity to study VO$_2$ phase transition in a single-domain material, as opposed to many-domain composition of a typical macro- or micro-sized material [12].

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Structural phase transition, which accompanies metal-insulator transition in VO_2, occurs with transformation from tetragonal rutile ($P_4/2mn$) to monoclinic M_1 phase ($P2_1/c$) [13]. Latent heat of this first-order transition is around 4.27 kJ/mol. Tetragonal structure contains equidistant vanadium atoms (with interatomic distance of 2.85Å), while monoclinic structure contains distinct pairs of vanadium atoms (interatomic distance 2.65Å) separated by 3.12Å. Recent studies have shown that this phase transition exhibits size dependence in nanocrystalline VO_2 [14] indicating that the temperature of phase transition depends on the size of the smallest dimension of the nanocrystal. Here we present a study of the effect of dimensionality of VO_2 nanocrystals on structural phase transition temperature and kinetics.

2. Experimental

Synthesis of VO_2 nanocrystals was performed using previously developed hydrothermal reaction [15] to obtain nanoribbons and nanosheets of VO_2. The as-prepared samples were washed with distilled water and acetone and dried first at room temperature for 72h and then vacuum-dried at 50^oC for 1h.

DSC measurements were performed using DSC-50 analyzer (Shimadzu, Japan) under nitrogen atmosphere, at constant heating rates of 2, 5, 10 and 20 $^oCmin^{-1}$, in the temperature range from room temperature to 120^oC. Calibration of the instrument was performed, for corresponding heating rate, prior to each of the measurements and the DSC curves shown were obtained by deducting the baseline from the experimental curve. DTA measurements were conducted on TA SDT 2960 instrument under nitrogen atmosphere, at constant heating rates of 2, 5, 7.5 and 10 $^oCmin^{-1}$. Gas flow rate of nitrogen in all experiments was $50mlmin^{-1}$. Due to technical limitations, DSC measurements on cooling were performed only at a cooling rate of 2 $^oCmin^{-1}$.

X-ray diffraction measurements were performed on Inel X-ray diffractometer with scintillating gas detector in a range of 2θ of $15-90^o$. TEM images were obtained using Philips 430 transmission electron microscope (TEM) with 200kV acceleration voltage using a CCD camera.
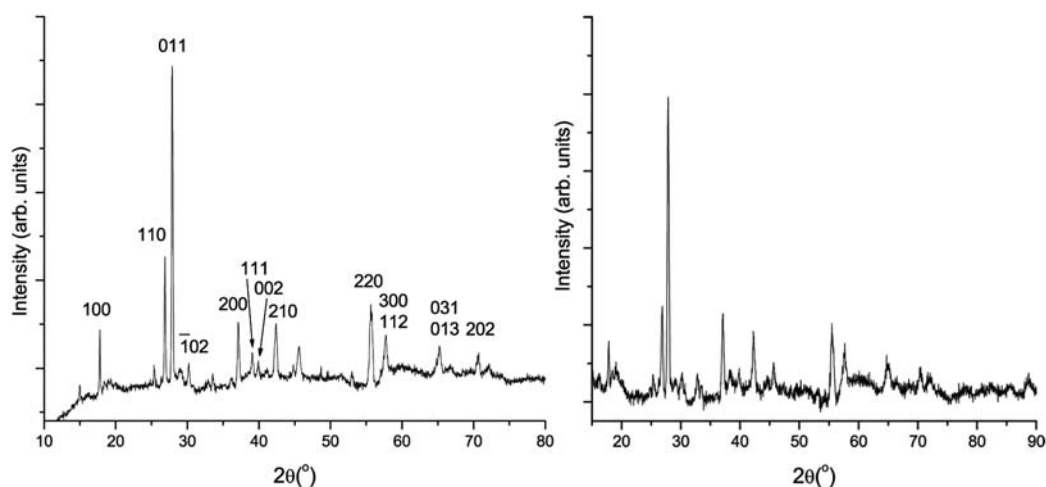
3. Results and discussion

Fig. 1. XRD spectra of VO_2 nanoribbons (left) and nanosheets (right).

XRD spectra of VO_2 nanoribbon and VO_2 nanosheet samples show that they can be characterized as monoclinic M1 phase of VO_2 [JCPDS 43-1051] (Fig. 1). There is high degree of crystallinity, consistent with high yield of the reaction and high aspect ratios of the products. TEM images show the difference in dimensionality of the two samples (Fig. 2). It was estimated that the shortest dimension of nanoribbons was 10-20nm, while the shortest dimension of nanosheets was 20-30nm.
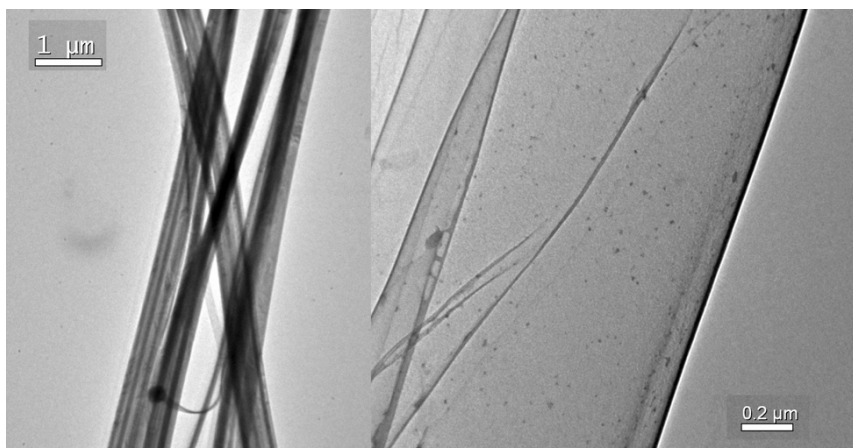

Fig. 2. TEM images of VO_2 nanoribbons (left) and nanosheets (right).

DTA measurements (Fig. 3) show a peak around 66°C, which shifts to higher temperatures with increase in heating rate, indicating a thermally activated process. The asymmetry of the peak increases with increase in heating rate – at heating rate of 2 °C/min the peak is relatively symmetric and exhibits increases asymmetry on the right half with increase in heating rate, suggesting a complex process containing several individual steps. One of the processes that is present, beside phase transition, is adsorption/desorption of nitrogen from VO_2 surface. This process was found to be continuous over the entire temperature region of DTA measurements, without any discontinuity around the phase transition temperature. However, its exact effect and contribution is still unclear.
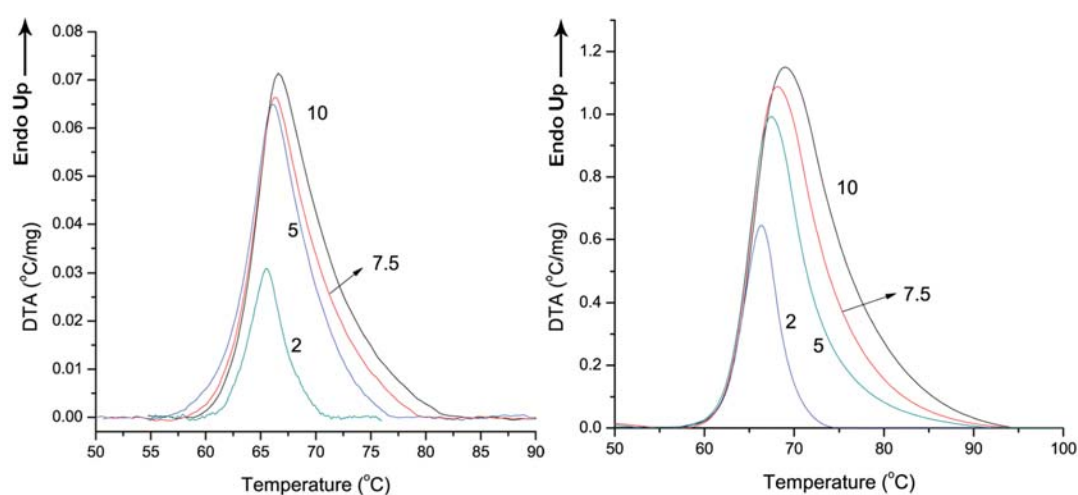

Fig. 3. DTA of VO_2 nanoribbons (left) and nanosheets (right).

DSC measurements (Fig. 4) show an asymmetric peak around 65 °C on heating and 57°C on cooling. This hysteresis width is consistent with the hysteresis width obtained in macroscopic samples and in other VO_2 nanoribbon samples [16]. The peak shifts to higher

temperatures with increase in heating rate, indicating a thermally activated process. ΔH on heating is 33.5 J/g, which is equivalent to 2.78 kJ/mol of VO_2, which somewhat lower than previously reported latent heat for a macroscopic system (4.27 kJ/mol), even when taking into account that latent heat also includes contribution from entropy change. This is expected as nanocrystalline systems have significantly higher surface-to-volume ratio, which reduces the energy required for structural transformation, due to higher proportion of surface atoms, which experience less constraints than atoms in the bulk, requiring less energy to change position in the lattice.
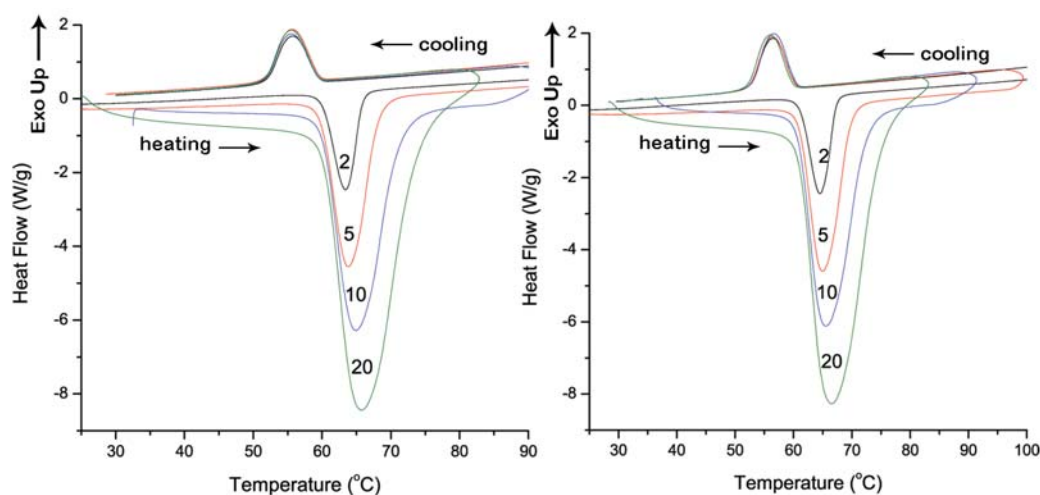

Fig. 4. DSC of VO_2 nanoribbons (left) and nanosheets (right).

Both DTA and DSC measurements show that the phase transition occurs at higher temperature for nanosheets than it does for nanoribbons, with the difference in phase transition temperatures of around 1°C (Tab. I). The difference between nanoribbons and nanosheets is indicative of their different morphology and, it shows that, since the phase transition temperatures in nanosheets are closer to the value in bulk material (67 °C), reduced size leads to depression of phase transition temperature. However, since nanoribbon size is only 10-20nm on the shortest dimension, this also indicates that the depression of phase transition temperature in 1-dimensional or 2-dimensional VO_2 nanostructures that can be achieved in pure VO_2 is relatively marginal and much smaller than anything needed for practical application.

Tab. I. DSC and DTA peak positions and difference in phase transition temperatures between nanoribbons and nanosheets.

β (°C/min)	DSC nanoribbons (°C)	DSC nanosheets (°C)	difference (°C)	DTA nanoribbons (°C)	DTA nanosheets (°C)	difference (°C)
2	63.48	64.50	1.02	65.41	66.39	0.98
5	64.15	65.01	0.86	66.01	67.39	1.38
10	64.96	66.34	1.38	66.37	68.88	2.51

In order to investigate the kinetics of phase transition in VO_2 nanostructures, the effective values of E_a for different conversion degrees were determined using Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose isoconversional methods [17-20], using DTA measurements. The conversion degree of reaction, α, at temperature T is equal to the ratio of S_T to S, where S is the total peak area, and S_T is the area between the initial crystallization temperature and temperature T. The dependence of α on temperature shows that at heating

rate of 2 °C/min the reaction has a completely different mechanism (Fig. 5). Therefore, only the measurements at heating rates 5, 7.5 and 10 °C/min were taken into consideration for calculation of kinetic parameters.
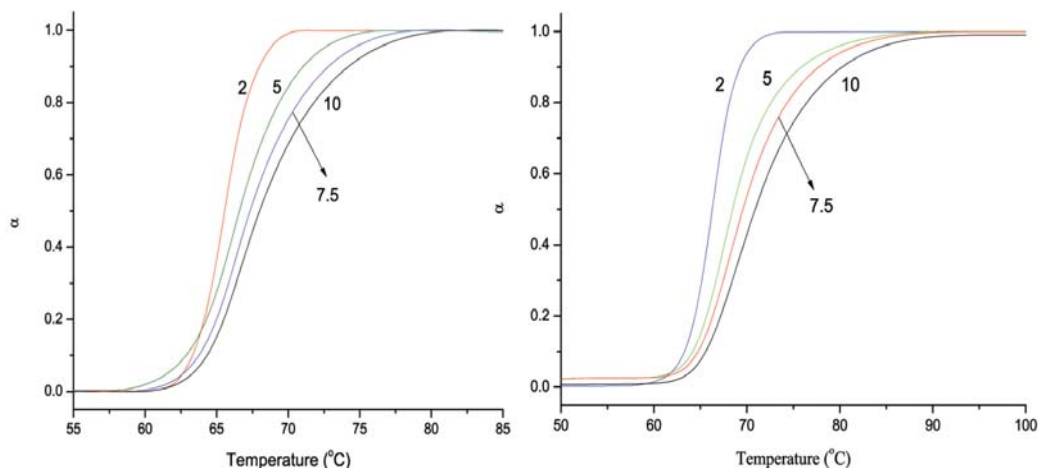

Fig. 5. Dependence of conversion degree α on temperature for DTA of nanoribbons (left) and nanosheets (right).

Dependence of effective activation energy on α for nanoribbon and nanosheet samples shows that the structural phase transition of VO_2 is a complex process containing at least two separate single-step processes (Fig. 6). It was not possible to deconvolute the data to isolate individual single-step processes. The initial part of the reaction exhibits much higher activation energy than the final part and the nanoribbons exhibit both higher activation energy and somewhat different mechanism than the nanosheets. The values of activation energies for both samples are high (570 and 450 kJ/mol, respetively), indicating high complexity of the process involving simultaneous movement of large number of atoms. If the calculated value of ΔH of the phase transition, of 2.78 kJ/mol, is used to calculate the approximate number of VO_2 units involved in elementary step of phase transformation, by dividing the activation energy with it, it can be estimated that at least several hundred atoms are involved in each elementary step of phase transformation. Since nanocrystals represent single domain crystals, this high level of complexity is expected, as the entire domain would undergo structural transformation simultaneously.
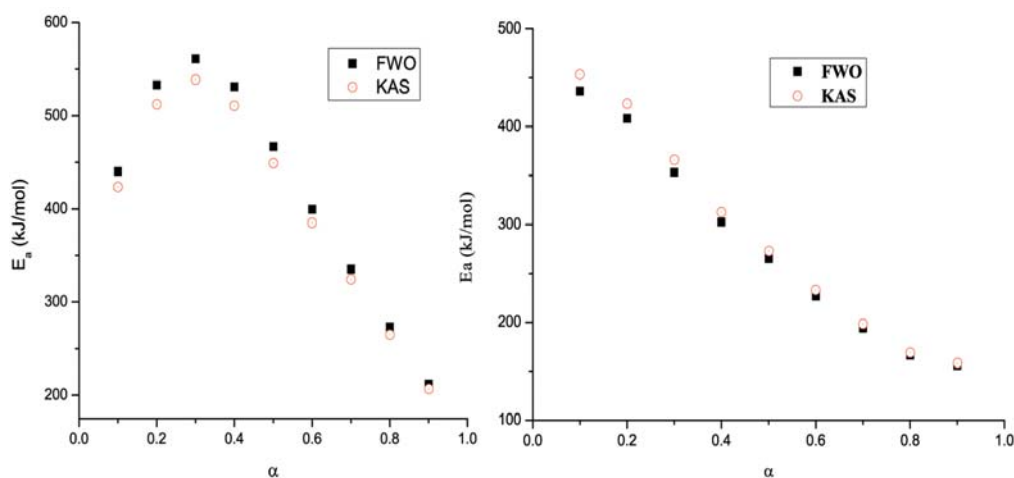

Fig. 6. Dependence of apparent activation energy E_a on α using isoconversional methods for VO_2 nanoribbons (left) and nanosheets (right).

4. Conclusions

Hydrothermally synthesized nanocrystals of VO_2 undergo structural phase transition around 65 ^oC. The phase transition mechanism shows some dependence on heating rate and the enthalpy of phase transition is somewhat lower than in the bulk, probably due to much higher proportion of surface atoms in the nanocrystals. Analysis of the kinetics of the process shows that it is a complex process involving several individual single-step processes, which exhibit apparent activation energies of 150-570 kJ/mol. Morphology of nanocrystals has significant effect on the process of structural phase transition. 2-dimensional nanosheets exhibit higher phase transition temperature and lower values of apparent activation energy. Although nanocrystals of VO_2 exhibit depression of phase transition temperature, its magnitude is too low to be of any practical importance for possible application.

Acknowledgments

5. References

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Садржај: *Једнидимензионални и дводимензионални нанокристали ванадијум-диоксида синтетисани су хидротермалним процесом и испољавају фазни прелаз око 65°C. Температура и механизам фазног прелаза показују зависност од димензионалности нанокристала. Оба нанокристална узорка показују нижу температуру фазног прелаза у односу на макроматеријал и разлика у температури фазног прелаза зависи од димензионалности нанокристала. Једнодимензионалне нанотраке испољавају нижу температуру и вишу енергију активације фазног прелаза у односу на дводимензионалне нанолистиће. Фазни прелаз у нанокристалу испољава се као сложени процес са нешто нижом вредношћу енталпије од фазног прелаза у наноматеријалу, што је вероватно последица значајно већег удела површинских атома у наноматеријалу. Високе вредности енергије активације фазног прелаза указују на висок степен сложености процеса и учешће великог број атома у сваком појединачном кораку фазне трансформације. Ово је очекивано, пошто су наноматеријали састављени од само једног домена.*
Кључне речи*: Нанокристал, ванадијум-оксид, фазни прелаз, утицај величине кристала*