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Preparation of vanadium dioxide powders by thermolysis of a precursor at low temperature

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A kind of crystal precursor, $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot 10H_2O$, less than 12×40 μm in dimensions was synthesized by reaction of vanadyl dichloride and ammonium hydrocarbonate in solution. The precursor microcrystals were fined to less than 10 μm with mean size of about 4 μm, by using organic solvents and surfactant in the process of the synthetical technique. Thermolysis of the precursor in a flow of nitrogen gas was investigated by TGA and DTA. The XRD powders patterns for the products from the thermolysis of the precursor show that the VO_2 powder obtained at 350, 365, 380 and 410 °C for 30 min were a noncrystalline phase, a monoclinic one named as B phase, a mixed phase of the B and the usual monoclinic A phase, and the pure A phase, respectively. SEM micrographs of VO_2 powders from the fined precursor demonstrated that the particle sizes of these fine powders were less than 2 μm. DSC curve of the VO_2 obtained at 450 °C for 30 min from the fined precursor showed that there was an endothermic phase transition at 71 °C. *© 2000 Kluwer Academic Publishers*

1. Introduction

VO_2 exhibits a semiconductor to metal transition at about 68 °C accompanied by a crystallographic transition from a monoclinic form to a tetragonal phase. This solid state phase transition is associated with an abrupt change in several physical properties including a decrease by three to four orders of magnitude in electrical resistivity. These properties have been utilized in the fabrication of a number of thermal switching, optical and holographic storage devices [1]. Synthetic techniques for producing pure VO_2 phase have drawn great attention for decades. The main methods have been proposed so far as follows: (a) heating a mixture of V_2O_3 and V_2O_5 corresponding to VO_2 composition in an evacuated silica tube at 700 °C for 2 days [2], (b) reducing V_2O_5 powder in a Pt-crucible in CO_2 atmosphere at 1227 °C for 3 days [3], (c) melting V_2O_5 in a platinum crucible at 1350 °C in a nitrogen atmosphere [4], (d) thin film prepared by sputtering or epitaxial method [5], (e) hydrothermal method of $VOCl_3$ between 800 and 1200 °C [6], (f) vapor deposition method [7] and (g) sol-gel process [8]. Recently Lawton *et al.* [9] synthesized VO_2 powders by evaporative decomposition of solution (EDS) using aqueous solutions of vanadyl sulfate hydrate at $\geq$740 °C in a mixing flow of hydrogen(10%)-nitrogen with a conventional spray-pyrolysis reactor, but a residual sulfur concentration in the powder was as great as 1% of atom ratio.

In this paper, we report a new and simple method to prepare a fine vanadium dioxide powder by thermolysis of a precursor at $\leq$410 °C. The precursor, $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot 10H_2O$, which is a hexanucler oxovanadium(IV) anionic aggregate by a single-crystal X-ray study [10], was synthesized by reaction of $VOCl_2$ and NH_4HCO_3 in solution. The precursor microcrystals could be fined by adding organic solvents and surfactant during crystallizing and then were decomposed in a flow of nitrogen gas to prepare the VO_2 powders with particle sizes of less than 2 μm.

2. Experimental procedures

2.1. Preparation of $VOCl_2$ solution

6 mL concentrated hydrogen chloride and a solution containing 1 g diamide hydrochloride were alternatively added into an aqueous suspension (20 mL) containing 3.5 g V_2O_5. After being warmed up under stirring, a blue solution was formed. The solution was added with a little amount of V_2O_5 or diamide hydrochloride until it contained no VO_2^+ and V^{3+}, then was filtered and a clear $VOCl_2$ solution(pH $\approx$ 1) was obtained.

2.2. The synthesis of the precursor

The above $VOCl_2$ solution was dropped slowly into 30 mL aqueous solution containing 9 g NH_4HCO_3 with stirring while a flow of CO_2 gas was being introduced to prevent VO^{2+} from being oxidized until the addition of $VOCl_2$ solution was completed and violet crystals

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produced. Crystallization in a stoppered Erlenmeyer flask for a little while more, the crystals from the solution were filtered and washed by a saturated NH_4HCO_3 solution until no Cl^- could be detected, finally by a little amount of water and ethanol, respectively. 6 g unfined product was obtained and the yield was about 90%. This product was named as "unfined" because of the comparison with the following fined product.

2.3. The synthesis of fined precursor

The fined precursor could be prepared by a method different from that for unfined precursor. 12 mL $VOCl_2$ solution was dropped into 30 mL aqueous solution containing 9 g NH_4HCO_3, during the process no crystals were produced in the solution. Then a solution of organic solvent and/or surfactant was dropped slowly into the above solution to produce fined precursor.

2.4. The thermolysis of precursor

The precursor was heated in a silica tube at a rate $5\,^{\circ}C\ min^{-1}$ in a flow of nitrogen gas. The composition of products were between $VO_{1.997}$ and $VO_{2.001}$.

2.5. Characterization of the properties

The morphology of the precursor was determined by using an Olympus BH-2 microscope. Differential thermal analysis (DTA) and thermogravimetic analysis (TGA) of the precursor were conducted on a Perkin Elmer DTA-1700 and a Perkin Elmer TGS-2, respectively, with a heating rate at $3\,^{\circ}C\ min^{-1}$ and a nitrogen gas flow at the rate of 45 mL min^{-1}. The morphology of VO_2 powders was determined by scanning electron microscopy (SEM) using a Hitachi s-520 SEM. X-ray diffraction (XRD) was carried out on a Shimadzu XD-3A diffractometer. Differential Scanning Calorimetry (DSC) experiment of VO_2 powders was performed using Pekin Elmer DSC-2C with a heating rate at $10\,^{\circ}C\ min^{-1}$.

3. Results and discussion

3.1. The synthesis of the precursor

In the progress of the synthesis of fined precursor, a few kinds of organic solvents such as ethanol, acetone, isopropanol, propanol and tert-butyl alcohol were used. The experimental results of using the mixture of ethanol and surfactant Op-10 were shown in Table I and Fig. 1. Table I indicates that the yield of fined precursor increased with the increase of ethanol amount, and dramatically increased with a little increase of Op-10 amount in the solution. Ethanol and Op-10 not only could increase the yield of the precursor, but also could reduce the particle size of the precursor and cause the size distribution more homogeneous. The micrographs shown in Fig. 1 corresponds to the typical samples according to the synthesis conditions of No. 4 and No. 7 in Table I and the sample according to the synthesis condition in Section 2.2. It is easy for us to find that the unfined crystals in Fig. 1a were in monoclinic form with particle size less than 12 × 40 μm commonly 6 × 16 μm. However, the fined crystals by ethanol {Fig. 1b} exhibited an incomplete monoclinic form and had a mean size of about 3 × 8 μm. Fig. 1c illustrates that the crystals fined by the mixture of ethanol and Op-10 appear a granular and homogeneous microcrystal less than 4 μm. To observe the fining and homogenization progress of the precursor particles further, the following experiment was conducted. A dilute solution containing a little amount of precursor crystal was divided into three portions, one of them was added ethanol into, one was added mixture of ethanol and Op-10 into, and the other was added nothing into. Then three kinds of as-prepared solutions were allowed to crystallize in stoppered Erlenmeyer flasks for 1 h. The results showed that the size of precursor particles in the original solution, in the solution added ethanol into and in the solution added the mixture of ethanol and Op-10 into were 20 × 150, 5 × 30 and 5–10 μm, respectively. These phenomena can been explained by an adsorption of ethanol and Op-10 on the surface of precursor particles. On the one hand the adsorption of particles lowered the solubility of the precursor in these kinds of solution, resulting in the increase of yield; on the other hand the surface adsorption hindered the growth of crystal, making the crystal grains finer.

TABLE I Effect of ethanol and Op-10 amount on the yields of the fined precursor

Sample no.	Ethanol/H_2O(mL/mL)	Op-10[a](drop)	Yield(%)
1	5/10	0	26
2	10/15	0	42
3	15/30	0	46
4	20/40	0	60
5	10/15	1.5	65
6	20/40	0.2	74
7	20/40	1.5	77

[a] Op-10 = $n\text{-}C_9H_{19}\text{-}C_6H_4\text{-}O\text{-}(\text{-}CH_2CH_2O\text{-})_{10}\text{-}CH_3$.

3.2. Thermoanalysis of the precursor

TG/DTG and DT curves of the precursor are shown in Figs 2 and 3, respectively. The TGA and DTGA data indicate that the weight loss of the precursor began at about 35 °C and ended at about 362 °C. There were four peaks of losing weight on the DTG curve, which demonstrated the formation of four intermediates in the thermolysis process of the compound.

There were three endothermic peaks at 93, 164 and 344 °C on the DT curve of the precursor which were due to thermolysis effects, and an exothermic peak at 387 °C corresponding to the crystallization of VO_2 powders. According to the DT curve in Fig. 3, the crystallization of VO_2 powders began at 370 °C and completed at 415 °C. A thermolysis model is displayed in Fig. 4, which differ from Labonnette's results [11]. The formula, $V_{12}O_{28}H_{14}(CO_3)_8(NH_4)_{10}\cdot 23H_2O$, which can be re-written as $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot 10.5H_2O$,

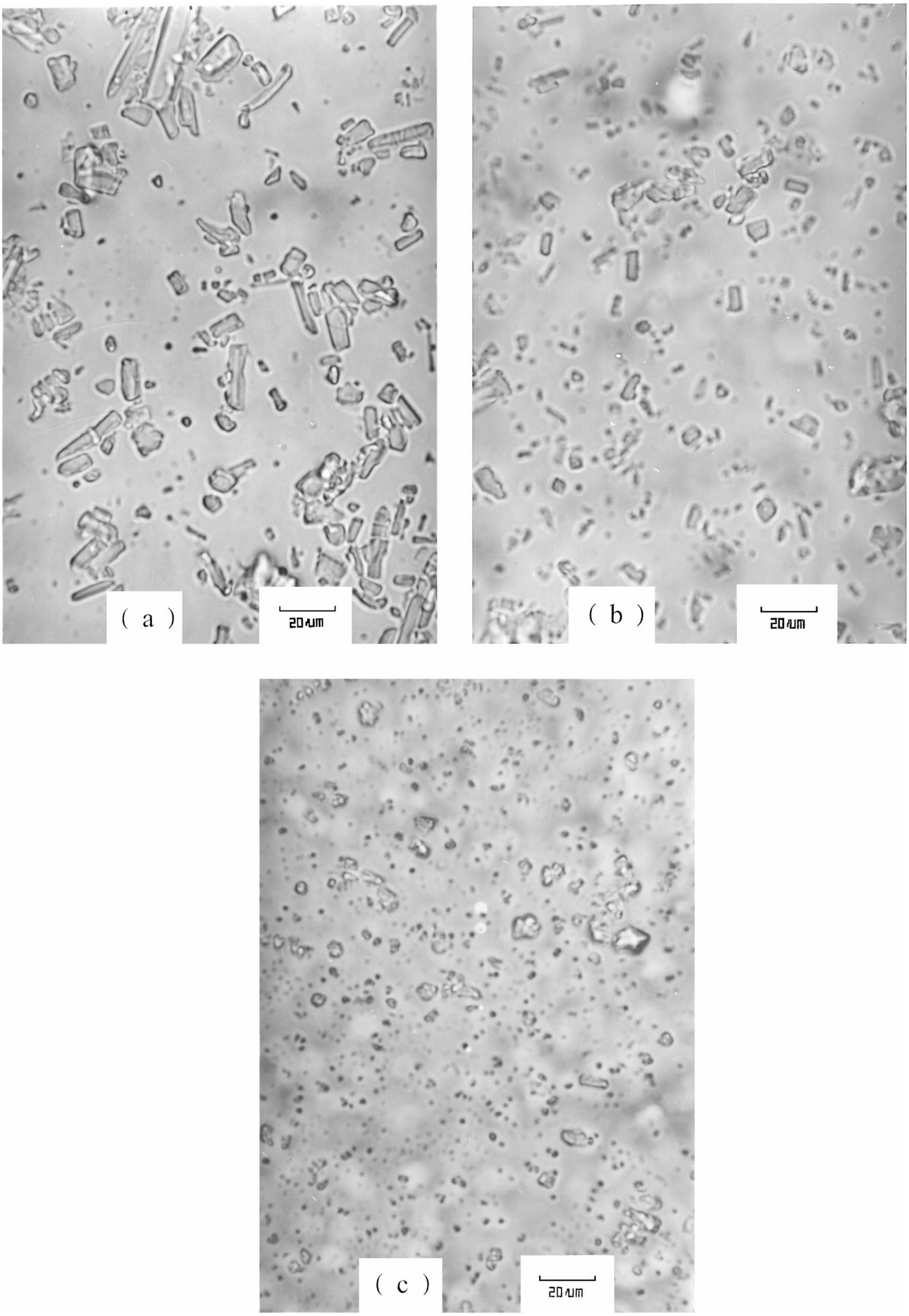

Figure 1 Micrographs of precursor: (a) unfined precursor, (b) precursor fined by ethanol according to the synthesis condition of No. 4 in Table I and (c) precursor fined by the mixture of ethanol and Op-10 according to the synthesis condition of No. 7 in Table I.

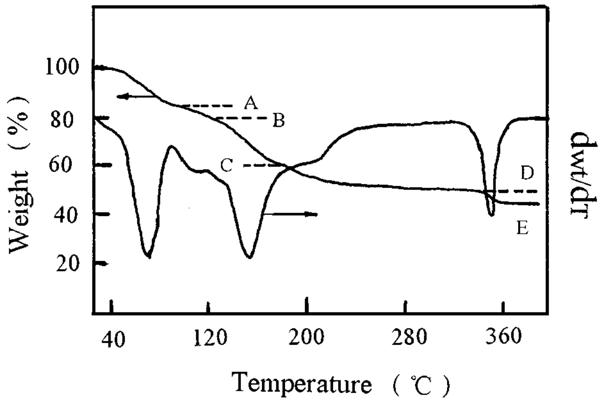

Figure 2 TG and DTG curves of the precursor.

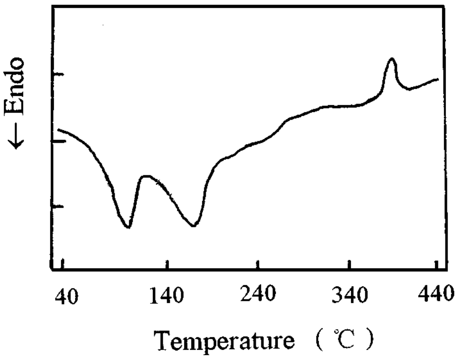

Figure 3 DT curve of the precursor.

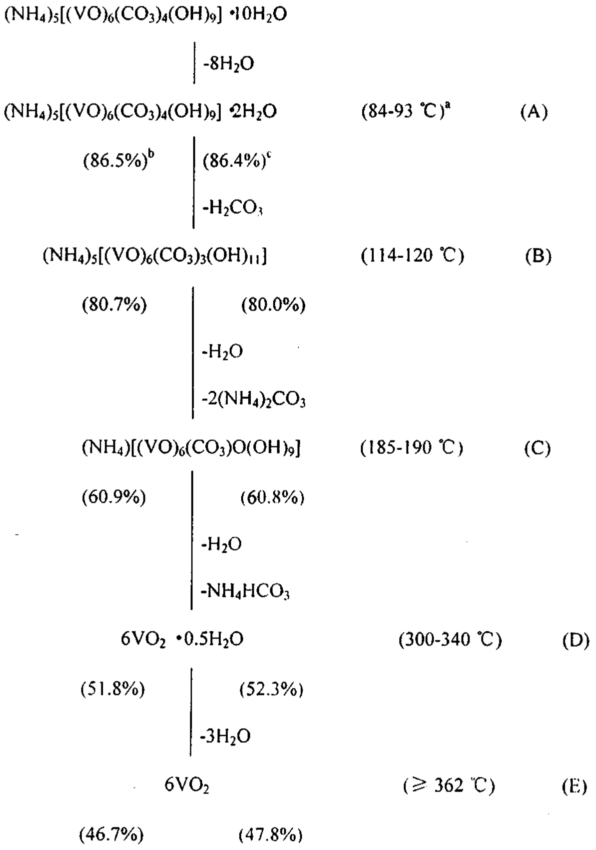

Figure 4 Schematic representation of the thermolysis process of the precursor: a The temperature range of a formation of intermediates; b, c The calculated and experimental value of residual fractional weight, respectively.

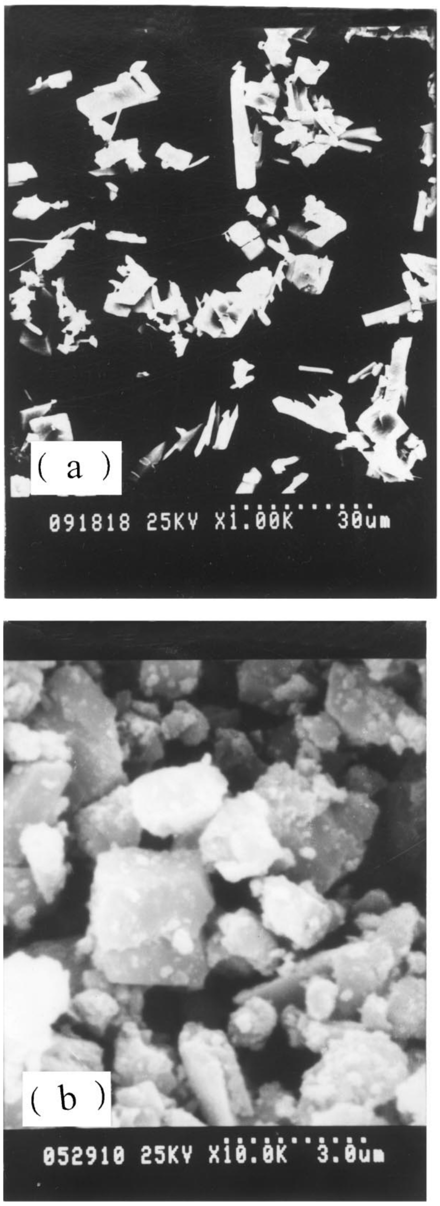

Figure 5 SEM micrographs of VO_2 powders from the unfined (a) and fined precursor (b) produced at 450 °C for 30 min.

was proposed by Labonnette *et al.* when they studied the product of the reaction of $VOSO_4$, NH_3 and $KHCO_3$.

3.3. Characterization of VO_2 powders

The SEM micrographs of VO_2 powder are shown in Fig. 5. The product of VO_2 from the thermolysis of the unfined precursor was still in a monoclinic form with the size of less than 5×30, mainly about 4×10 μm in dimensions, and the product from the thermolysis of the fined precursor appeared granular with the size of less than 2 μm.

The powder X-ray diffraction patterns of VO_2 products from the thermolysis of the precursor are shown in Fig. 6. No crystallization peak was observed for the sample obtained at 350 °C for 30 min, so it could be conclude that the powder was amorphous {Fig. 6a}. The XRD patterns from Figs 6b–e show that the corresponding products formed from the thermolysis of the precursor at 365 °C, 380 °C and 410 °C were the

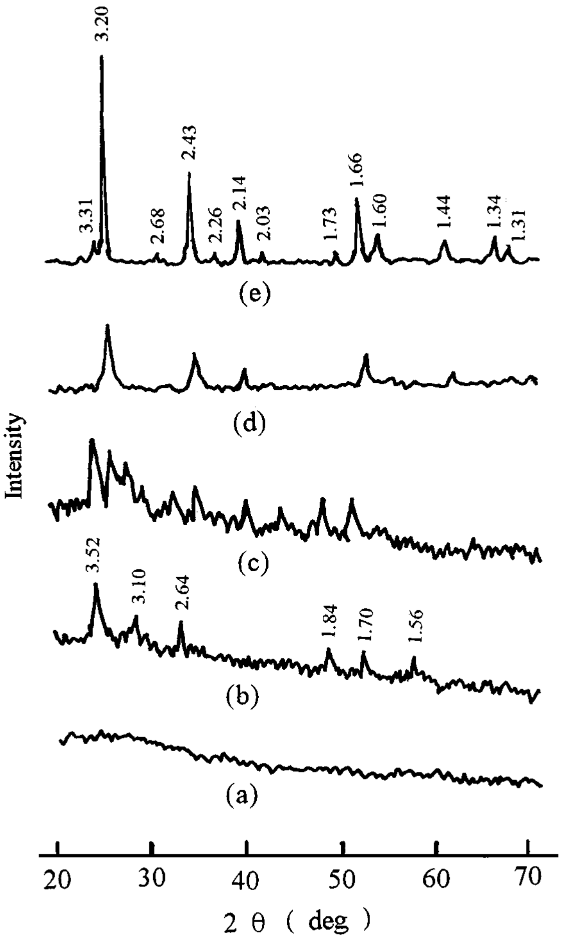

Figure 6 XRD patterns of VO_2 powders from the thermolysis of the precursor: a) at 350 °C, (b) at 365 °C, (c) at 380 °C, (d) at 410 °C and (e) at 450 °C for 30 min.

monoclinic VO_2 (B) phase [12], a mixed phase of the B phase and the usual monoclinic A phase, and the pure A phase [13], respectively. These results demonstrate that amorphous VO_2 at first formed during thermolysis of the precursor and crystallized into the metastable VO_2 (B) phase, and then turned into the stable A phase, finally well crystalline A phase formed completely at 450 °C. This result is in correspondence with that of DTA in Fig. 3.

Fig. 7 shows the DSC curve of the crystallized VO_2 powder produced from the thermolysis of the precursor at 450 °C. It could be found that there was an endothermic phase transition at 71 °C on the DSC curve.

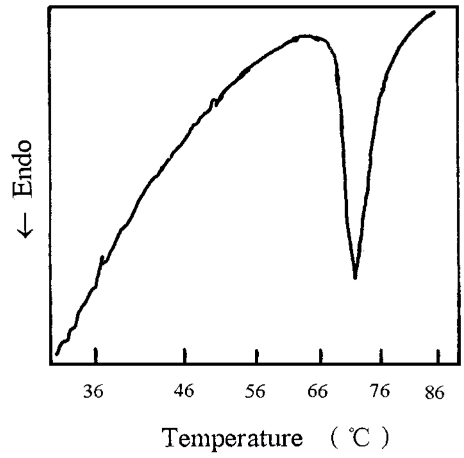

Figure 7 DSC curve of VO_2 powders obtained at 450 °C for 30 min (heating rate at 10 °C min^{-1}).

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