High efficiency thermochromic VO$_2$(R) resulting from the irreversible transformation of VO$_2$(B)

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Abstract

The metastable VO$_2$(B) transforms irreversibly into thermochromic VO$_2$(R) between 400 and 500°C. Differential scanning calorimetry (DSC) of this transition shows a broad transformation starting with a first endothermic step at 420°C followed by a second exothermic step at 455°C. During this process, the initial platelet like VO$_2$(B) morphology leads to a submicronic VO$_2$(R) powder. This low temperature thermal treatment avoids the grain growth commonly observed in the case of classical routes at higher temperatures. This transformation with constant mass and high increases of density has been studied by XRD, IRTF spectroscopy, thermal analyses and electronic microscopies. The structure and properties of the VO$_2$(R) issued from this irreversible transition are very similar to those of the VO$_2$(R) obtained by the powder metallurgy process, except the optical properties. Indeed, this thermochromic VO$_2$(R) powder shows an unexpected transition contrast in the IR spectral range during the insulator–metal transition at 68°C. Experimental observations by scanning electron microscopy (SEM) correlated with calculations could explain this high efficiency by the unusual morphology of the submicronic particles. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Rutile vanadium dioxide shows a reversible first-order metal–insulator phase transition VO$_2$(M) → VO$_2$(R) associated with drastic changes in the optical properties, like a rapid decrease in optical transmittance in the near-IR region when heated at $T_c = 68°C$. For the first time, to the best of our knowledge, we have applied the thermochromic pigment of VO$_2$ as a polymer composite coating [1]. Submicronic powders of VO$_2$ show radical changes in the optical transmission compared with larger particles (i.e. a few microns) as the efficiency of the optical transition increases with decreasing particle size. Hence, the polymer/submicron powder composites are a new approach for preparing such coatings. Most of the work carried out on this thermochromic phase transition has been done on thin films of VO$_2$. However, it is extremely difficult to control the stoichiometry of this material in the thin film form for large area applications. Polymer/powder composites are in retro-spect inexpensive and very simple for coating applications.

Various methods have been used for the deposition of VO$_2$ thin films. Some of the techniques reported in the literature include ion-beam sputtering [2], electron beam evaporation [3,4], chemical vapour deposition [5,6], sol–gel [7,8], powder metallurgy (PM) [9], reactive decomposition [10,11], evaporative decomposition of solution [12], etc. Most methods used to produce the thermochromic VO$_2$ involve an intermediate reduction step. We previously showed that during this reduction step, the VO$_2$(B) metastable allotropic phase could be formed as an intermediate compound [10,11]. For example, in the case of thermal decomposition of ammonium hexavanadate at 600°C, the initial vanadium V$^{5+}$ is totally reduced into V$^{4+}$ with the formation of the submicronic powder thermochromic VO$_2$(R). During this transformation, pure metastable VO$_2$(B) appears at low temperatures ($T < 400°C$). The transformation of this black/bluish non-thermochromic powder into rutile VO$_2$ is a crucial step for the determination of the final morphology that influences optical properties.
The aim of this work was to study the mechanism involved in the irreversible transition VO₂(B)→thermochromic VO₂(R). Thus, VO₂(B) powder and intermediate compounds were fully characterized by X-ray diffraction and IR spectroscopy. The transition was studied by using thermal analyses and in situ TEM. The results of electron microscopy experiments obtained by our laboratory have been recently published [13].

2. Experimental

The VO₂(B) powder was obtained by thermal decomposition of ammonium hexavanadate (NH₄)₂V₆O₁₆ in static N₂ atmosphere, at 380°C and large heating rates (250°C min⁻¹). The synthesized VO₂(B) powder had a specific surface of 30 m² g⁻¹, and a density of 4.03 g cm⁻³, which is lower than the density of the rutile structure (4.67 g cm⁻³).

The X-ray diffraction patterns were obtained from a classical D5000-Siemens θ–2θ diffractometer using the Cu–Kα radiation and Ni filter. For the IR spectroscopy study of the VO₂(B)→VO₂(R) transformation, the initially prepared VO₂(B) powders were placed in a quartz tube under Ar atmosphere and heated separately at different temperatures ranging from 400 to 600°C. Characterizations of the powder were carried out after each heat treatment with KBr pellets by transmission with a Mattson Research Series IRTF spectrometer. Thermogravimetric analysis (TG) was performed using a Setaram TGA apparatus. VO₂(B) samples were initially placed in a platinum crucible in N₂ atmosphere. Differential scanning calorimetry (DSC) measurements (using a Setaram DSC-92 apparatus), were also performed under inert atmosphere (Ar) using an open stainless crucible and an N₂ flux, from 100 to 600°C at the heating rate of 5°C min⁻¹.

3. Results and discussion

The cell parameters of the so prepared VO₂(B) powder are found to be very similar to those obtained by Theobald et al. [12] for VO₂(B) obtained by reduction of V₂O₅ (a = 12.03, b = 3.693, c = 6.42 Å; β = 106.0°).

3.1. IR spectroscopy

The transmission IRTF spectrum of VO₂(B) is similar to those of V₆O₁₃ (or V⁵⁺₂V⁴⁺₄O₁₃) The absorption bands of both compounds are reported below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavenumbers (cm⁻¹)</th>
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<tbody>
<tr>
<td>V₆O₁₃</td>
<td>1010, 995, 950, 895, 861, 770, 543</td>
</tr>
<tr>
<td>VO₂(B)</td>
<td>997, 931, 875, 771, 534</td>
</tr>
</tbody>
</table>

Their structures are locally very similar but differ by their oxygen octaedra long range arrangement. In the following, we propose an assignment of the absorption bands to vibrational modes related to the differences between the two structures. The 1010 and 995 cm⁻¹ bands of V₆O₁₃ are, respectively, attributed to the V⁵⁺
–O bonds in the isolated octahedra and to $V^{4+}$ O bonds in double octahedra. The 534/545 cm$^{-1}$ bands can then be associated with angle deformations of the octahedra in both compounds.

During the transition VO$_2$(B) $\rightarrow$ VO$_2$(R), the transmission spectra of the intermediates show strong and spread modifications. In Fig. 3, we have reported the various vibrational FTIR spectra corresponding to the following preparation conditions. During the pyrolysis, the 534 cm$^{-1}$ vibrational band, attributed to the V–O–V octahedra bending modes, remains unaltered from the spectra in Fig. 3(a)–(c), although its relative intensity decreases. This is significant of an invariant local arrangement of the octahedra during the first step of the transformation. After this first step, this band at 534 cm$^{-1}$ becomes thinner, and a new band appears at 440 cm$^{-1}$ very similar to the previous one. In Fig. 3(b), it can be observed that the 880 cm$^{-1}$ band disappears, while a broad and weak undulation appears at 920 cm$^{-1}$. These two last features are attributed to some disordering in the initial VO$_2$(B) octahedra arrangements: The stretching modes associated with the corner and edge sharing of octahedra are broadened, giving rise to intermediate vibrational states, mixing 1000 and 880 cm$^{-1}$ modes. Such an intermediate band slowly disappears up to the final VO$_2$(M) spectrum (Fig. 3(e)). It should be noted that the specific VO$_2$(M) bands appear in the spectrum in Fig. 3(c). Indeed, the broad double band at 680–730 cm$^{-1}$ is characteristic of the first ‘rutile packing’ of octahedra. In fact, it appears at 630 cm$^{-1}$ (Fig. 3(a)) to reach the value of 690 cm$^{-1}$ at the end of the transformation. The 995–1000 cm$^{-1}$ band observed for VO$_2$(B) is present in many vanadium oxide compounds with intermediate oxidation state between V$^{5+}$ and V$^{4+}$. It is attributed to the stretching of short V–O bonds that are also present in VO$_2$(B). This band strongly decreases during upon transformation.

At the end of the irreversible transition (600°C), a weak band is still present at approximately the same position (995–1000 cm$^{-1}$). This could result from some adsorption of oxygen on the surface of VO$_2$(R), providing V–O bonds enhanced by the high specific surface area of this powder. Indeed, when samples are annealed at higher temperatures (e.g. at 800°C under the same inert atmosphere), we observe a rapid grain growth and this weak band at 995–1000 cm$^{-1}$ disappears.

We recall that, above the transition temperature $T_c$ = 68°C, all bands of the insulator VO$_2$(M) reversibly disappear due to the delocalization of the electron of the metallic state of the rutile phase VO$_2$(R). The unusual profile of the baseline (Fig. 4) shows a maximum of transmitted radiation at around 900 cm$^{-1}$, just before the strongest absorption band of VO$_2$(M). This strong deformation is due to the modification of the light scattering that is also called the Christiansen ef-
fect. It is both correlated with grain size of VO₂ and the strong modification of the refractive index of VO₂ at around the absorption frequency.

3.2. Thermal analyses

TG analyses show a very weak weight loss (< 1%); this rules out the presence of any lattice water that could have been at the origin of the stabilization of the VO₂(B) intermediate structure. The DSC of the VO₂(B) samples shows (Fig. 5) a strong and spread irregularity of the measured heat flux. During the transformation, a first step (390–430°C) is observed, characterized by an endothermic broad peak with a minimum at 410°C. This first step could be attributed to some disordereding between the VO₂(B) octahedra as previously discussed in the case of IR experiments. At the minimum of this endothermic peak we associate the first modifications of the absorption bands (Fig. 3(b)). A second step appears in the range 430–470°C, which is exothermic with a maximum at 450°C. It could be associated with the progressive ordering of the VO₂(R) octahedra, as previously observed in the IR spectroscopy analysis. At 450°C, most of the initial VO₂(B) is changed into the rutile phase. It should be noted that the shifts in temperature observed with DSC analysis (continuous acquisition) and FTIR spectroscopy (performed step-by-step) could be related to the rate of structural transformation in each method. During the cooling, one exothermic peak is observed at 65°C (associated with the reversible insulator–metal phase transition VO₂(R) → VO₂(M)), which confirms the formation of thermoelastic VO₂ during the thermal treatment.

It can be concluded, from these FTIR and DSC analyses, that two main steps in the VO₂ transformation have been clearly evidenced: the first step corresponds to the disordereding of the initial octahedra arrangement; the second step corresponds to the formation of the final rutile arrangement.

These two steps also correspond to a strong change in morphology.

3.3. Microstructure

From micrographic analyses, the first disorder step has been shown to give rise to a modification of the initial crystals into small microcrystals with a glassy surface aspect, as if a liquid was in formation on the surface of the grains. Then, the second step corresponds to the crystal growth of the final phase. For samples annealed at low temperatures (< 600°C), the morphology of the thermoelastic powder (Fig. 6) shows submicronic grains clustered together in a specific plane. This morphology is similar to the thermally decomposed gibbsite Al(OH)₃, that also involves an increase in crystallographic density. Depending on the heating rate, the obtained grain sizes can be more or less in size. Generally, the major part of these grains are submicronic, which is very promising for optical applications.

3.4. Optical properties

Optical switching properties have been characterized using a pyranometer and a multimeter in a home made device as indicated in our previous work [1]. The optical absolute efficiency ρ was defined as
Fig. 6. SEM micrograph of thermochromic VO$_2$ powder obtained by heating metastable VO$_2$(B) at 600°C under inert atmosphere (N$_2$).

\[ \tau = \Delta I = (I_{\text{low}} - I_{\text{up}}) \]

where \( \Delta I \) is the difference between the transmitted intensities \( I_{\text{low}} \) (at \( T < T_c \)) and \( I_{\text{up}} \) (at \( T > T_c \)). The measured \( I \) values are obtained through composite samples (polymer/VO$_2$) having variable volume fractions of oxide pigments; the thermochromic VO$_2$ grains present variable mean sizes \( d^* \), determined from usual laser granulometry measurements. To optimize the efficiency of the optical switching, the VO$_2$(R) grains must present mean linear dimensions smaller than the incident wavelength \( \lambda \), i.e. smaller than 1–5 \( \mu \)m, in the case of solar and near-IR applications [1]. Various types of composite samples were tested: the volume fraction \( \Phi \) of VO$_2$(R), and the grain size \( d^* \) are the two main parameters. In Fig. 7, the absolute efficiencies \( \tau \) associated with two distributions of pigments (\( d^* = 2.1 \mu \text{m} \) and \( d^* = 4.2 \mu \text{m} \)) have been reported; it can be clearly observed that the efficiency of the optical switching can present a maximum contrast for specific values of \( \Phi \) and \( d^* \). The lower curve was obtained from VO$_2$ grains obtained after a too long heat treatment (6 h at 590°C), while the upper curve, which presents a maximum, was obtained from a limited heat treatment (1 h at 590°C).

4. Conclusion

The mechanism of the transformation: metastable VO$_2$(B) \( \rightarrow \) thermochromic VO$_2$(R) is complex and involves two main steps:

(a) disordering of the oxygen octaedra of the VO$_2$(B) lacunar monoclinic structure associated with endothermic effects,

(b) rearrangement of the octaedra in the rutile-type structure associated with exothermic effects, strong increase in crystallographic density and formation of submicronic grains.
Finally, we have to keep in mind that the kinetics of VO₂ modifications and the associated mechanisms directly condition the final grain size and therefore, the switching optical properties. In the case of low temperature heat treatment, very small particles of thermochromic VO₂ have been obtained showing a high efficiency optical switching. These results could be extended for all processes involving a slow reduction transformation of V⁵⁺ oxide that produce the metastable VO₂(B). Indeed, the microstructure of stable VO₂(R) powder (or thin films) can be controlled by the rearrangement of the metastable lacunar structure of VO₂(B). This transformation appearing at low temperature is a very interesting new method for limiting the crystal growth of thermochromic VO₂(R).

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References