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Nanocrystalline vanadium dioxide: synthesis and mid-infrared properties

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Abstract

This work describes the first successful synthesis of nanocrystalline thermochromic VO₂ powder using the low temperature irreversible structural transformation of the metastable VO₂(B). At this step, the transformation is associated with a total rearrangement of VO₆ octahedra, and a strong increasing of density. The reversible metal–insulator phase transition (MIPT) of vanadium dioxide ($T_t = 68^\circ\text{C}$) is associated with strong changes in electrical, magnetic and optical properties. The contrast of the optical transition in mid-infrared (MIR) region and the optical transparency are remarkably increased for these nanosized particles. Modifications in coloration are also observed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

This preliminary work consists in studying size-induced modifications of optical properties of thermochromic VO₂. The reversible metal–insulator phase transition (MIPT) of vanadium dioxide ($T_t = 68^\circ\text{C}$) is associated with strong changes in electrical, magnetic and optical properties. The temperature of transition can be easily tailored by cationic and/or anionic substitution. The optical contrast of this transition strongly depends on

stoichiometry, microstructure and surrounding medium of the oxide. Both scientific investigations and technological applications are of great interest due to the temperature range of this structural transition [1–3]. In the past, thermochromic thin films were extensively studied [4–6]; more recently, several works were focused on applications involving pigments in polymeric matrices [7]. In these studies, we investigated the influence of particle sizes on the optical contrast and transparency. Due to the synthesis, the obtained VO₂ grain sizes were micronic (between 0.1 and 10 μm); the optical contrast was shown to increase when the grain size decreased. Recently, we have shown that, making use of the structural transformation VO₂(B) → VO₂(R) [8–11], nanosized

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thermochromic vanadium dioxide powders could be prepared.

2. Experimental

Thermochromic VO₂ is obtained from metastable VO₂(B) powders [12]. The precursor powder was placed in a quartz crucible, heated under inert atmosphere (argon) at 550°C for 2 h, and cooled down to room temperature in the reactor to prevent oxidation of VO₂.

VO₂ (metastable B form) $\xrightarrow{\Delta}$ VO₂(stable rutile form)

VO₂ Aldrich powder (99.9%) annealed at 800°C for 12 h under argon atmosphere has been used as a standard material.

The obtained samples have been characterized by X-ray diffraction, using a Siemens–Brucker D5000 diffractometer, equipped with a copper X-ray source ($\lambda = 1.540 \text{ \AA}$), a secondary monochromator and a rotating sample holder, working in a classical coupled θ – 2θ mode.

Transmission electron microscopy (TEM) observations were carried out on a Philips EM 400 T microscope for grain morphologies and size distributions.

The reversible changes in optical transmittance Tr vs. temperature of thermochromic powders were analysed using a Unicam–Mattson RS-FTIR spectrometer (4000–400 cm^{-1} , resolution = 4 cm^{-1}), and classical KBr pellet technique including pure powdered VO₂ (0.1 wt%). VO₂ and KBr powders were carefully mixed in an agate mortar to obtain reproducible dispersion of thermochromic particles.

3. Results and discussion

The X-ray diffraction measurements reveal the total transformation of metastable VO₂(B) precursor for powders obtained at temperatures higher than 500°C. The X-ray diffraction patterns confirm the monoclinic structure ($P2_1/c$) at room temperature for all samples. Cell parameters of VO₂ (standard and as-prepared) were refined; the

Table 1
Cell parameters of nanocrystalline and standard VO₂ powders

	Nanocrystalline VO ₂	Standard VO ₂ (Å)	Cell parameters variations (%)
<i>a</i>	5.776 (4) (Å)	5.753 (Å)	+0.4
<i>b</i>	4.547 (2) (Å)	4.526 (Å)	+0.5
<i>c</i>	5.400 (4) (Å)	5.383 (Å)	+0.3
β	122.55 (4)°	122.60°	–0.04
<i>V</i>	119.5 (2) (Å ³)	118.08 (Å ³)	+1.2

results are reported in Table 1. As shown in this table, the cell volume V of the as-prepared sample seems to be larger than the cell volume of the standard sample. This increase in volume is often observed for submicronic powders in which surface energy contributions can involve some expansion in cell parameters.

Then, the diffraction profiles of the as-prepared VO₂ powders have been analysed and compared with the standard VO₂ profiles (Aldrich sample). Generally, the determination of the full width at half maximum (FWHM) of Bragg peaks can yield information on crystal sizes. In fact, this observed FWHM is the result of the convolution of an instrumental contribution and a size effect. As a first approximation, mean crystallite dimensions have been calculated using the classical Scherrer formula. The dimension L is given by

$$L = \frac{0.9\lambda}{\Delta 2\theta \cos\theta},$$

where λ is the wavelength, θ the Bragg angle, $\Delta 2\theta$ is the additional broadening due to the size effect.

In the case of low Bragg angles, this broadening can be calculated from

$$(\Delta 2\theta)^2 = (\text{FWHM}_{\text{obs}})^2 - \omega^2,$$

where ω is the standard FWHM obtained from the standard VO₂ sample.

From the analysis of the well defined (011) Bragg peak profiles (with $2\theta = 27.783^\circ$, $\text{FWHM}_{\text{obs}} = 0.195^\circ(2\theta)$ and $\omega = 0.089^\circ(2\theta)$), the mean particle sizes were found to be $L = 45.6 \pm 8$ nm. Fig. 1 shows the superposed (011) Bragg peaks of the two nanosized and standard VO₂ samples; a significant broadening is clearly observed for the nanosized sample.

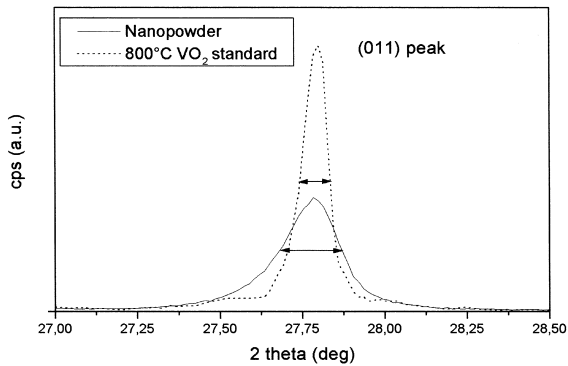


Fig. 1. X-ray diffraction pattern of nanocrystalline thermochromic $\text{VO}_2(\text{M})$ powder (—) and a standard $\text{VO}_2(\text{M})$ powder (···).

The microscopic observations show a specific macroporous morphology that could be described as holed plates with angular shapes (Fig. 2). This is a consequence of the irreversible transformation of $\text{VO}_2(\text{B})$ plate-like particles into thermochromic VO_2 which is accompanied with a drastic increase in density (from 4.03 to 4.67 g cm^{-3}) without any chemical composition change. As it can be seen on Fig. 2, primary particles having sizes ranging between 30 and 80 nm are linked together in accordance with specific orientations; this will be discussed later, in a following paper. Such observed particle sizes are in agreement with the X-ray diffraction analyses reported above.

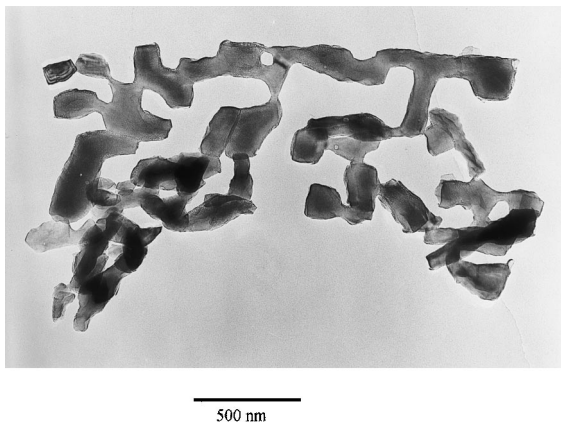


Fig. 2. Transmission electron microscopy micrograph of thermochromic VO_2 nanopowder.

The infrared spectroscopy experiments confirm strong modifications in transmittance upon heating and cooling associated with the reversible MIPT (Fig. 3). The low temperature ($T < T_c = 68^\circ\text{C}$) spectrum shows vibrational bands characteristic of the semiconducting phase. Upon heating, the infrared transmittance drastically decreases due to electron delocalization in the metal phase; as a result of the screening effect, the vibrational bands vanish.

To characterize the transition efficiency of our nanosized powder, we define a contrast factor $\tau(\lambda)$ as follows:

$$\tau(\lambda) = \frac{Tr_{\text{LT}} - Tr_{\text{HT}}}{Tr_{\text{LT}}},$$

where Tr_{LT} and Tr_{HT} are transmittances, respectively for $T < T_c$ and $T > T_c$ and where λ is the IR wavelength.

This contrast factor strongly depends on the volume fraction of VO_2 in the KBr pellet. It is also strongly correlated with the powder morphology, grain sizes and pellet treatment. To evaluate the influence of grain sizes in the KBr pellets, the volume fractions of both micronic and nanosized VO_2 phases have been fixed (see Section 2). In these conditions, the contrast factor τ , reported in Table 2, increases from 0.5 to 0.85 (at $\lambda = 2.5 \mu\text{m}$) for respectively, commercial VO_2 powder annealed at 800°C for 12 h and powder obtained from

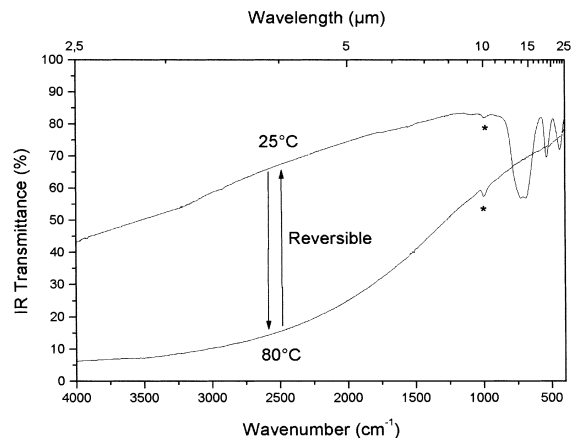


Fig. 3. Fourier transform infrared transmittance spectrum of VO_2 nanopowder.

Table 2
Morphology and contrast factor τ in nanocrystalline and standard VO₂ powders

	Nanocrystalline VO ₂	Standard VO ₂
Color	Brown	Bluish-black
Morphology	Porous grains; nanocrystallized primary particles	Faceted micro-metric grains
Contrast factor τ ($\lambda = 2.5 \mu\text{m}$; 0.1 wt% VO ₂)	0.85	~0.50

metastable VO₂(B) transformation at 550°C. For all samples, this contrast (maximum at $\lambda = 2.5 \mu\text{m}$) decreases in the middle-infrared range with increasing wavelength, and becomes negligible in the vibrational range.

The 995 cm⁻¹ absorption band, is denoted as (*) in the figure, does not disappear upon heating, in contrast to all the other absorption bands. Indeed, some authors have previously observed an additional band at around 1010 cm⁻¹ [13]. It is commonly discussed as a result of the partial oxidation of VO₂ powders. The red shift of this absorption band observed in our samples could be explained by the high specific surface contribution. As a consequence, several explanations can be suggested: surface mode contribution (including adsorbed species) or initial step in the oxidation mechanism related to high surface sensitivity of these powders.

The optical transparency is remarkably increased, and modifications in coloration have been also observed for nanosized particles from bluish-black to brown. The study of these size-induced modifications of optical properties in the visible range is now in progress.

4. Conclusion

A specific synthesis of nanocrystalline vanadium dioxide can be achieved through low temperature irreversible structural transformation of metastable VO₂(B). At this step, thermal energy

transforms the metastable VO₂(B) into nanocrystalline thermochromic VO₂.

The contrast of the reversible optical transition in the mid-infrared (MIR) region is remarkably increased with decreasing size of the thermochromic VO₂ particles. These results are promising for thermochromic composite films in large-scale applications, making use of such nano-pigments with high infrared contrast and optical transparency.

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