Phase transition in hydrothermal synthesized VO_2(M) nano-crystals: An X-ray diffraction study

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Abstract. We report on the phase transition of VO2(M) nano-particles synthesized by hydrothermal processing. The study was carried out by X-ray diffraction with a focus on the major Bragg peaks located at 37.1 and 36.9 deg. The reversible crystallographic transition from monoclinic to tetragonal phase at about 67°C is close to the bulk value. It was observed that the dynamic of the tetragonal and monoclinic one are complementary. This structural phase transition studies were complemented by elemental composition, selected area electron diffraction and Fourier transform attenuated total reflection infrared spectroscopy.

1. Introduction

The unusual properties of the metallic state near the insulating transition have been most extensively studied in d-electron systems. Among these materials, the Vanadium dioxide (VO_2) has intrigued researchers for five decades since its discovery by Morin in 1959, especially with regard to its thermochromic properties in the Infrared spectral range [1]. This latter peculiar behavior determines the ability of VO_2 based coatings to regulate the infrared radiations and so acting as an intelligent reversible window filter. In addition, it has potentialities in thermal sensing and switching devices [2]. VO_2 is considered as an archetypical system with a conductivity change of several orders at the critical temperature T_c (341.1K) accompanied by a transition in lattice structure from a monoclinic to a tetragonal phase and a dramatic increase of the infrared modulation [3]. Various micro/nanostructures of VO_2 such as nanoribbonds, nanobelts, nanorods, nanowires, hollow microspheres by facile template-free process have been prepared [4]. Few reports are available to date on direct synthesis of pure VO_2 (M) micro-nano radiative platelets with high crystallinity without thermal annealing due to the abscence of propagation of the transition across the grain boundaries and the dissipation of the intrinsic stress. Grain size is widely believed to determine the structure-dependent hysteresis curve in the phase transition [5]. Figure 1 presents structural information during VO_2 metal insulator transition (MIT) with an increase in symmetry both in the VO_6 octaedron and in the V atomic chains where the V-V pairs undergo the elongation, shortening and twist from the zigzag-type to a linear chain.

Different techniques have been used to investigate the kinetics of the transition via electron – correlation-driven Mott transition, structure-driven Peierls transition or the cooperation of the two mechanisms [3] and synchrotron X-ray scattering in conjunction with real space analysis showing that the transition from low temperature monoclinic to high temperature occurs in a first order manner with coexistence of the two phases [6]. It has been shown that the phase of electronic property occur simultaneously suggesting for the MIT of VO_2 a cooperative mechanism of a structural driven and electron correlation mechanisms.

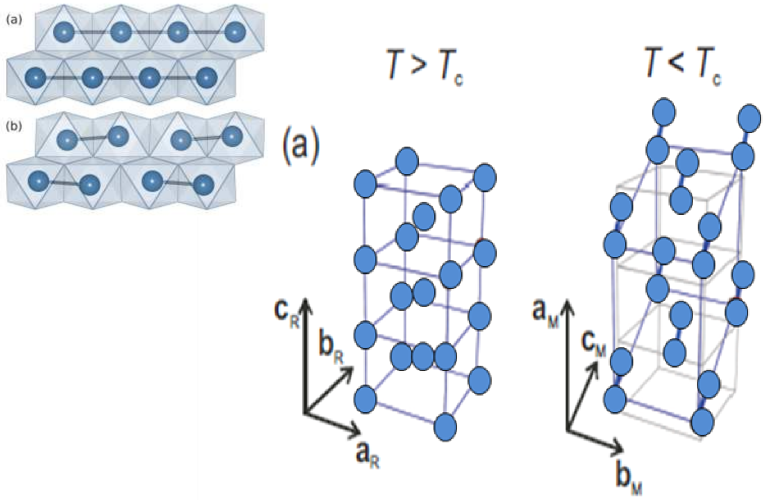

Figure 1: (a) the metallic high temperature tetragonal rutile form of VO_2 with a single V-V distance and (b) the insulating low-temperature monoclinic form showing dimerized chains of alterning short and long V-V distances along the c-axis. [6]

This contribution reports on in-situ x-ray diffraction versus temperature within a thermal range of 25-110°C on highly crystalline VO_2(M) nano-crystals. It has been reproducibly observed that such hydrothermal synthesized nano-crystals exhibit an average transition temperature at around ~68°C equivalent to the bulk value pointing out that the investigated snow-flake type nano-crystals could be stress/strain free.

2. Experimental techniques

All the reagents were of analytical grade and used without further purification. 0.75ml of Sulfuric acid H_2SO_4 (Kimix, 98%) followed by the drop-wise addition of 0.25ml of $N_2H_2{\cdot}2H_2O$ (Merck) were added into an aqueous suspension (10 mL) containing 0.45g of V_2O_5 (Alfa Aesar). After being warmed at 95˚C while stirring, the solution changes from yellow to green, then green to blue, characteristic of the presence of V^{+4} ions in the solution, finally blue to gray depending on the concentration of NaOH used to stabilize the dissolved precipitates. Hydrothermal synthesis was carried out in a Teflon-lined autoclave at ~230˚C for ~48h. Then the content was air-cooled at room temperature followed by the filtration of the formed precipitates. The final black product was washed thorougthly with water and ethanol for the exfoliation of bulk layered V_2O_5 and then dried at about 60˚ C for 12h in an oven.

3. Results and discussion

3.1. Morphological studies and elemental analysis

The morphology of the synthesized crystals was observed by a scanning electron microscopy Nova NanoSEM 230 equipped with an elemental EDAX system. As typically reported on figure 1, the surface morphology of the samples exhibit snowflake radiative platelike aggregates in 3-D structures, with an anisotropic orientation in shape. This was found to be correlated to the V_2O_5 initial concentration and the high surface-energy liable with chemical reactions of the medium. The dimension of the crystallites is in the range of ~400 nm to 3μm. The elemental composition of the material acquired from the X-rays emitted is shown in figure 2. The snow-flake crystals consist of ~35.24 and ~64.76 wt% of oxygen and vanadium respectively demonstrating that the stoichiometry of the compound is almost VO_2.

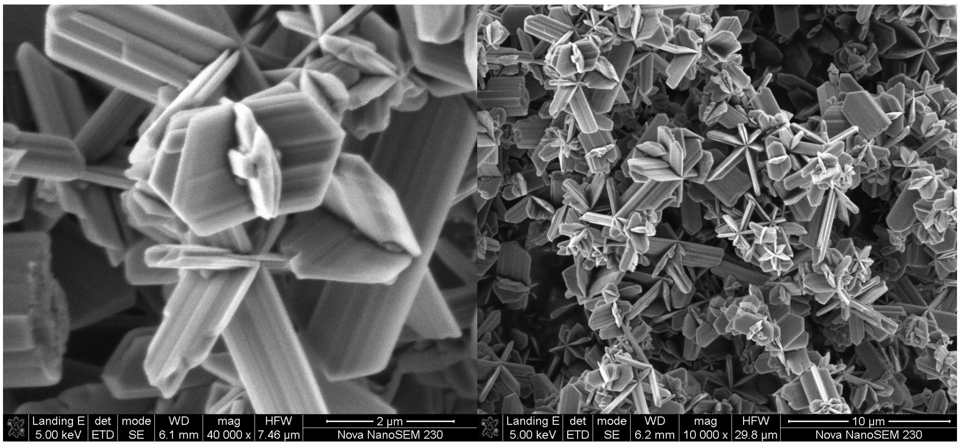

Figure 1: High and low magnification scanning electron microscopy images of a typical VO_2 synthesized crystal.

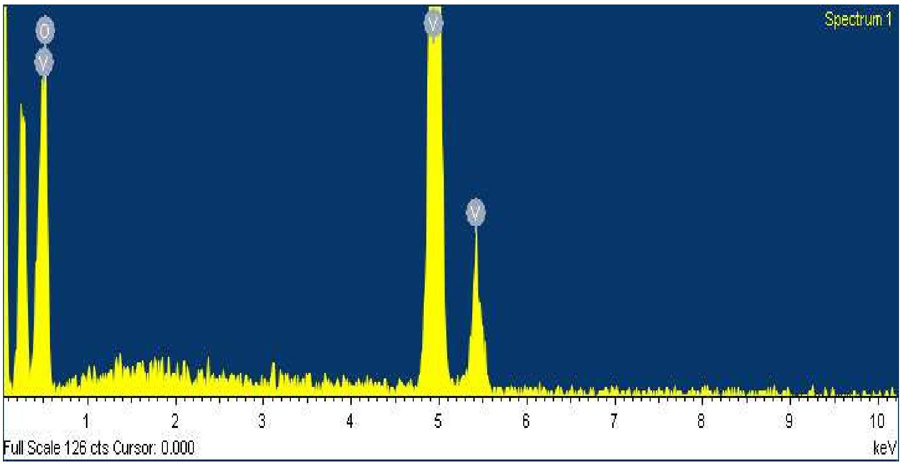

Figure 2: Elemental composition of a typical VO_2 synthesized crystal.

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3.2. Vibrational spectroscopy studies

Chemical and kinetic information related to band absorption for multiple internal reflections have been performed by attenuated IR total reflection spectroscopy using a Perkin Elmer Spectrum 1000 FTIR-ATR spectrometer. Initially and as a reference, V_2O_5 powder was investigated. Its IR spectrum exhibited the 1000.703cm^{-1} and 782.392 cm^{-1} bands, characteristic of the intermediate oxidation state V^{+5} to V^{+4} of V=O bond. The snow-flake synthesized nano-crystals exhibited 4 mainly bands; at 840.65 cm^{-1} describing the coupled vibration V=O and V-O-V (Figure 3). This concurs with the transition from VO_2 (amorphous) to VO_2 (M). The 420cm^{-1} band is a weak vibration of the absorption band of V-O bond while 544.5cm^{-1} is assigned to the V-O-V octahedron bending modes. In accordanceto the previous IR studies of with Sorapong et al [9], such a spectrum is a characteristic of pure VO_2(M) phase.

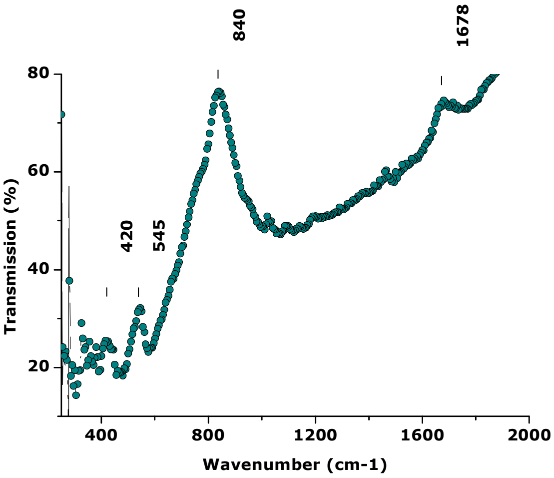

Figure 3: Typical room temperature ATR-FTIR of the snow-flake like synthesized nano-crystals.

3.3. Phase transition and in-situ x-rays diffraction studies

The crystalline structure was determined by X-ray diffractometry in a θ-2θ mode with CuKa 1 (AXS Bruker, λ=1.54056Å). Figure 4 reveals sharp peaks and intense diffraction which demonstrate that the sample is well crystallized without any additional phases and any presence of the reference. All peaks are indexed as VO_2 (M) according to a JCPDS card 00-043-1051 with the lattice constants a, b and c are of 5.75170 Å, 4.53780 Å and 5.38250 Å respectively, β=122.64˚C. XRD analysis shows that VO_2 (M) with a space group of $P2_1/c$ has a strong preferential orientation along (011) plane which agrees with Shidong et al's investigations [8]. The different peaks are indexed as: (011) with a preferred orientation, (200) the 2nd main Bragg peak serie, (002), (012), (210), (-302), (102), (211) the 3rd main Bragg peak series. To investigate the Mott phase transition of the synthesized snow-flake like crystals which exhibit a priori pure VO2(M) phase, in-situ x-rays diffraction were conducted on powder samples. The heating of the samples during the x-ray measurement were performed using a Peltier thermoelectric heat pump with a regulation module of ~0.1°C. The ability to automate the scattering intensity and particle size trend measurements is a major advantage in many applications in this set up. Processes as aggregation, solubilisation, sedimentation and change in molecular conformation can be followed by the scattering of the intensity of the samples as a function of temperature. Figure 5 depicts the evolution of the major Bragg peaks such as the one with a preferential orientation i.e (011) one versus temperature. More accurately, and in the range of 50 °C to 75 °C , the intensity of two different diffraction peaks at 37, 1° corresponding to (200) monoclinic and his equivalent at 36.9° (middle) were followed.

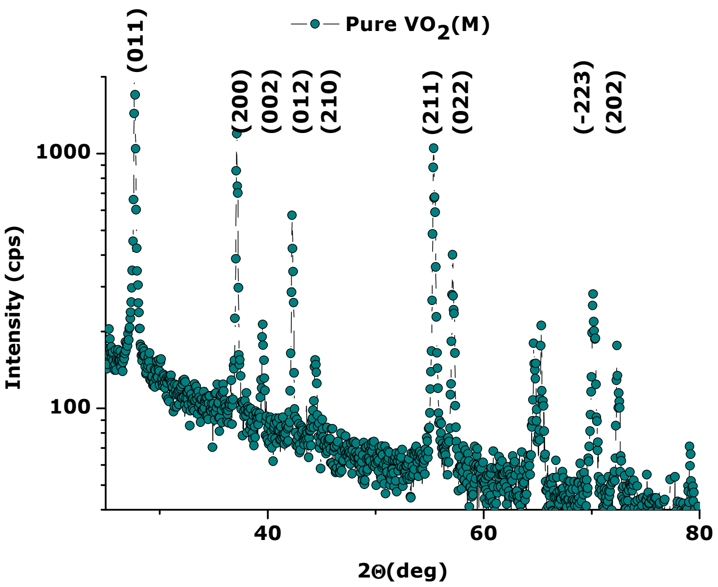

Figure 4: Typical room temperature indexed X-rays diffraction of the snow-flake like synthesized nano-crystals.

Figure 5.a. reports the isoline3-D view of the X-ray spectra (left) showing the shifting of the entire transition monoclinic-tetragonal with temperature. The evolution is continuous at the operationa time scale. While there is net decrease of the monoclinic Bragg peak intensity (situated at about 27.1 deg), there is a steady increase of the intensity of the Bragg peak corresponding to the tetragonal peak located at about 2θ of 36.9 deg. This trend concurs with Joyeeta et al's predictions [11]; the area under the monoclinic peak decreases as the tetragonal fraction grows. Both phases coexist in equal fractions at around 64°C as substantiated by Figure 5.b. The VO_2 (M) nano-crystals are entirely tetragonal at 70°C. naturally, the Bragg peak shift during the transition is attributed to thermal expansion and VO_2 lattice. One can notice that the transition seems to start as early as 55°C. At around

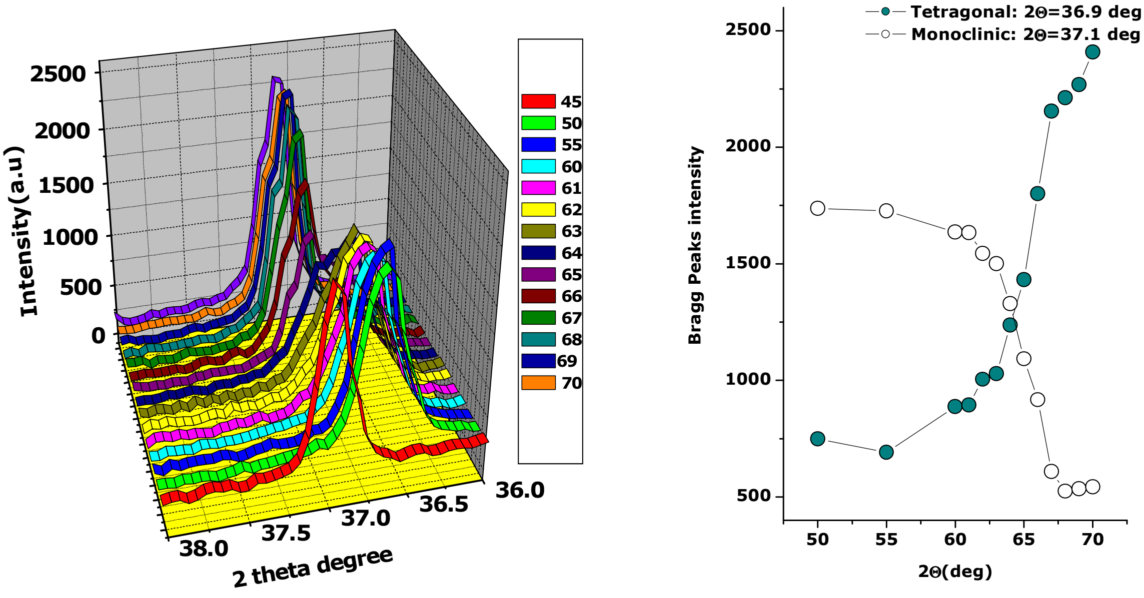

Figure 5: Evolution of the main Bragg angular positions of the monoclinic and tetragonal phases versus temperature.

64°C, the intensity of both monoclinic and tetragonal main Bragg peaks are quasi equal. Thermal evolution of the intensity of the 37.1° Bragg peak reflection increases continuously between 55 and 70 ° C due to the rearrangement of the structure while the monoclinic one seems to stabilize at about 68°C as per reported on Figure 5.b.

Conclusions

In summary, snow-flakes aggregated VO_2(M) nano-crystals have been demonstrated to be synthesized by hydrothermal process. Their phase transition from monoclinic to tetragonal phase with temperature was followed using in-situ x-rays diffraction. It was found that the crystallographic phase transition induced thermally is not sharp and ultrafast in the case of investigated VO_2(M) hydrothermally engineered nano-crystals. It was clearly observed that the tetragonal phase grows in favor of the monoclinic one.

Acknowledgements

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