Phase, Microstructure, Thermochromic, and Thermophysical Analyses of Hydrothermally Synthesized W-Doped VO₂ Nanopowder

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Received 4 June 2021; Accepted 28 August 2021; Published 13 September 2021

Energy-saving methods are important in curbing the problem of global climate change. One way to conserve energy is by enhancing energy efficiency, i.e., minimizing avoidable energy losses while maximizing its output [1]. Consequently, one of the areas where efficiency can be greatly improved is in built environments or buildings as they use up a significant amount of energy. In fact, buildings consume about 30–40% of the world’s primary energy, mainly for heating, ventilation, and air conditioning (HVAC), lighting, and appliance usage [2]. However, the majority of this energy is wasted due to the inefficiencies of windows. Since windows easily allow heat to go in or out of a building, more energy is required to use cooling or heating systems to balance the increase or decrease in temperature [3].

A promising avenue in reducing energy expenditure and losses in buildings is the fabrication of energy-efficient windows with the ability to control the throughput of light, heat-carrying infrared (IR) radiation, and solar energy. One way to do this is by coating spectrally selective materials on the surface of windows [4]. By blocking unwanted and regulating solar radiation, usage of HVAC and lighting can

1. Introduction

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A promising avenue in reducing energy expenditure and losses in buildings is the fabrication of energy-efficient windows with the ability to control the throughput of light, heat-carrying infrared (IR) radiation, and solar energy. One way to do this is by coating spectrally selective materials on the surface of windows [4]. By blocking unwanted and regulating solar radiation, usage of HVAC and lighting can
be minimized, which can translate into reductions in energy use and greenhouse gas (GHG) emissions.

A prime candidate for this application is the thermochromic compound vanadium dioxide (VO$_2$), as it has the ability to reversibly change from a semiconductor with a monoclinic structure (M-phase) to a metal with a tetragonal rutile structure (R-phase) at a phase transition temperature ($\tau_c$) of 68°C [5]. As the material undergoes a phase shift, its optical properties also change; i.e., when it is in the VO$_2$ (M) phase, it is transparent to IR radiation, whereas when it is in the VO$_2$ (R) phase, it becomes IR reflective [6]. Meanwhile, the transmission of visible light does not change in both phases [7]. Hence, VO$_2$ has great potential in the fabrication of smart windows.

However, the industrial and commercial use of VO$_2$ have yet to be realized due to some limiting factors [8]. For instance, the $\tau_c$ of VO$_2$ is still too high for near room temperature usage in buildings. Ideally, VO$_2$-based windows should reflect heat-carrying IR rays at room temperature (~25°C) to achieve people’s thermal comfort [9]. Doping VO$_2$ has been reported to be the most effective way of lowering the $\tau_c$ value of VO$_2$ [10]. Cations such as niobium (Nb$^{5+}$), tantalum (Ta$^{5+}$), molybdenum (Mo$^{6+}$), and tungsten (W$^{6+}$), which have a larger radius than V$^{4+}$ ion and high valency, are primary candidates for such task [11].

For instance, in the case of tungsten, Long et al. comprehensively discussed the effects of W dopant on the atomic structure of VO$_2$ and the reduction of $\tau_c$ by employing X-ray absorption spectroscopy using synchrotron radiation coupled with first-principle calculations [12]. Accordingly, there is intrinsic symmetry around the local structure of the W atom with a seemingly tetragonal configuration. This propels the distortion and twisting of the asymmetric VO$_2$ lattice forming rutile-like nuclei that cause a reduction in the thermal activation energy of the phase transition. This is evident in the works of Chen et al. (2012) and Blackman et al. when both groups doped VO$_2$ with W and reported a reduced $\tau_c$ of 35°C and 20°C, respectively [13, 14]. Most recently, W doping was done by Zou et al. (2018) by a combined sol-gel-hydrothermal-annealing process that further reduced $\tau_c$ to 27°C with a temperature reduction rate of ∼22 °C/at% W [15]. Meanwhile, Hanlon et al. used molybdenum as VO$_2$ dopant and found that the phase transition temperature of VO$_2$ decreases to 24°C with a rate of 5 °C/at% Mo [16]. Moreover, codoping of W and Mo was conducted by Lv et al. (2014), using microwave-assisted HT synthesis, which led to further reduction of $\tau_c$ to as low as 17°C [17].

Overall, these studies have mostly reported on the reduction of the transition temperature of VO$_2$ to near room temperature by elemental doping. However, very few studies have analyzed the effects of doping on the phase transition performance of VO$_2$. Additionally, there is a notable paucity of studies assessing the effects of doping on the thermophysical properties of VO$_2$, particularly across its phase transition temperature. Hence, in this work, the effects of tungsten as dopant on the structural and thermochromic properties of VO$_2$ were examined. In particular, the phase transition performance of doped VO$_2$ was evaluated by measuring its enthalpy and hysteresis. Further, the effects of the dopant on the thermophysical properties of the prepared nanostructured VO$_2$ were investigated.

### 2. Materials and Methods

#### 2.1. Sample Preparation

All chemical reagents in this study were of analytical grade and used without further purification. Differing weight percentages (wt%) of metallic tungsten powder relative to the V precursor were prepared. This was done by dissolving the requisite amount of W in 2 mL hydrogen peroxide ($\text{H}_2\text{O}_2$, 30%). The concentration of the dopant relative to the V precursor, wt% (W), was calculated using the following equation:

$$\text{wt}\% (W) = \frac{m(W)}{m(W) + m(V)} \times 100\%, \quad (1)$$

where $m(W)$ is the mass of the dopant and $m(V)$ is the mass of the V precursor. W concentrations of 1, 1.5, 2, and 3 wt% were prepared for the hydrothermal process, and the respective powder products were labeled as VMW1%, VMW1.5%, VMW2%, and VMW3%. Also, the undoped sample was labeled VMW0% to denote the absence of dopant.

The preparation of the undoped sample is reported elsewhere [18]. Meanwhile, to begin the synthesis of the doped samples, 2.4750 g of V$_2$O$_5$ was dissolved in 148 mL deionized water under magnetic stirring. $\text{H}_2\text{C}_2\text{O}_4$ with a mass of 4.9502 was then added while vigorous stirring continued. When the V$_2$O$_5$.H$_2$C$_2$O$_4$.H$_2$O system turned blue-black, the W-$\text{H}_2\text{O}_2$ solution was added to it. Afterwards, the solution was transferred into a 240 mL Teflon-lined autoclave when it changed into a reddish color. It was then heated inside an electric oven at a temperature and processing time of 180°C and 24 h, respectively. Then, the blue-black precipitate was collected after cooling it to ambient temperature. Then, it was centrifuged and washed with ethanol and water several times. Finally, the powder was dried at 60°C overnight. Since the produced VO$_2$ particles were in a metastable state, further heat treatment was employed to obtain the desired thermodynamically stable phase. Hence, the samples were calcined at 650°C in 2 hours under an N$_2$ environment with heating and cooling rates of 5°C/min.

#### 2.2. Sample Characterization

The phase and crystal structures of the prepared samples were analyzed by X-ray diffraction using the X’pert Pro PANalytical MPD diffractometer at 2θ values ranging between 20° and 80° at a scanning step rate of 0.017° s$^{-1}$. Additionally, the morphology of the samples was examined by field-emission scanning electron microscopy (FESEM) using a JEOL-JSM7600F scanning electron microscope at an acceleration voltage of 5 kV. Meanwhile, differential scanning calorimetry (DSC) was employed to measure the obtained powder’s thermochromatic properties. This was done by placing an amount of nanopowder in a DSC822e (Mettler Toledo) specimen pan with a temperature accuracy of ±0.20°C. As the temperature
was increased from 30°C to 200°C and then decreased from 200°C to 30°C, the heat flow on the sample was measured. Finally, thermal diffusivity was measured using a Netzsch LFA457 light flash apparatus (LFA). This was done by molding the nanopowder samples into pellets with a thickness of 1 mm and a diameter of 10 mm using a hydraulic press.

3. Results and Discussion

3.1. Phase and Structural Analysis. The XRD scans of the hydrothermally prepared undoped and W-doped VO₂ powders after annealing are illustrated in Figure 1. The appearance of a non-VO₂ compound was observed from sample VMW1%, as shown in the presence of V₆O₁₃. These crests gradually diminish as the concentration of the dopant was increased. However, peaks belonging to V₂.₄W₀.₆O₇ began to appear at wt. percentage of 1.5 wt%. Interestingly, when the concentration of W reached 2 wt%, peaks associated with the tetragonal rutile VO₂ (R) were detected with ICSD code 98-007-1662 of space group P42/mnm. As found in literature, replacing a V site in the VO₂ crystalline structure with the larger W atom causes strong interactions. Subsequently, the asymmetric atoms in the VO₂ lattice rearrange themselves, which leads to the transformation from monoclinic to tetragonal configuration.

Moreover, an enlarged view of the preceding XRD patterns is illustrated in Figure 2 to provide a magnified look at the effects of the doping concentration on the phase formations in VO₂ (M). At 2θ values between 26° and 35°, as many as four events or changes (labeled I, II, III, and IV) in the XRD plots can be observed. Firstly, in event I, the (0 1 1) peak of VO₂ (M) at 26.90° deteriorated, and a new peak at 27.11°, which belongs to V₂.₄W₀.₆O₇, appeared. In event II, the VO₂ (M) peak at 27.86° shifted position gradually to 27.65°, which can be indexed to the VO₂ (R) peak with Miller indices (hkl) of (1 1 0). Also, the appearance and abrupt disappearance of the peak associated with V₆O₁₃ can be seen in event III. The presence of V₆O₁₃, which signified the occurrence of oxidation in an otherwise inert nitrogen atmosphere, may have stemmed from the residual H₂O₂ molecules, which were not fully dissolved during the hydrothermal synthesis nor removed through the washing and centrifugation processes. Potentially, these molecules were adsorbed in the VO₂ (B) molecules and tended to reoxidize the VO₂ particles into V₆O₁₃ during the heating treatment. Finally, in event IV, a VO₂ (M) peak gradually diminished while a new peak belonging to VO₂ (R) emerged. This shifting of peak to lower 2θ value is mainly due to the replacement of W atoms on the V sites. Considering that tungsten has a greater atomic radius (1.37 Å) compared with vanadium atom (1.34 Å), this can potentially result in the increase of adjacent interplanar distance (d-spacing). Hence, the peak position movement is towards the left because there is an inverse proportionality relationship between the d-spacing and 2θ values based on Bragg’s law.

Additionally, the samples’ full width at half maximum (FWHM) and lattice properties at the peak with the greatest intensity were measured and summarized in Table 1. It can be observed that the quality of crystallization diminished as the W content was increased to 2 and 3 wt%. Specifically, the FWHM widened from 0.1299° to 0.1948° with increasing W concentration. A factor that affected the FWHM was the crystallite size which significantly decreased from 81.5 nm (for the undoped sample) to 50.1 nm (for sample VMW3%).
Based on the transformation of \( \text{VO}_2 \) (B) to \( \text{VO}_2 \) (R) during the annealing process, the increase in temperature resulted in the breakage of the interconnections between the edge-sharing and corner-sharing octahedra in the \( \text{VO}_2 \) (B) crystal lattice. Then, the octahedra underwent reorientation to form the rutile tetragonal structure, which has a smaller crystallite size. Moreover, the addition of tungsten accelerated this process. As elucidated in the work of Zhang et al. (2015), distortions caused by the tungsten atoms in the doped \( \text{VO}_2 \) (B) hasten the breakage of the interconnecting V-O octahedra [19]. With prolonged heating during the annealing stage, the \( \text{VO}_2 \) (B) transformed to \( \text{VO}_2 \) (R) at a faster rate, which resulted in the growth of \( \text{VO}_2 \) (R) with reduced crystallite size.

Another factor that caused the broadening of peaks was the internal strain in the \( \text{VO}_2 \) lattice which increased from 0.196 to 0.322. This increase is mainly due to the difference in the atomic radius of W and V. By replacing V sites with W atoms, which have a greater radius, distortions in the V-V and V-O bonds in the \( \text{VO}_2 \) (M) crystals transpire. With increasing dopant concentration, more V sites were replaced with W atoms, thus resulting in greater lattice strain. This finding is further supported by the measurement of the interplanar spacing in the undoped and W-doped samples. As shown in the rightmost column of Table 1, the d-spacing increased with increasing W weight percentage. Indeed, this shows the successful partial substitution of V atoms with W atoms in the \( \text{VO}_2 \) (M) crystal structure.

Additionally, the morphologies of the synthesized W-doped \( \text{VO}_2 \) were examined using field-emission scanning electron microscopy analysis. The FESEM scans of the samples are given in Figure 3. Similar to sample VMW0%, all the doped samples showed the formation of spherical shapes, albeit at larger sizes. Grain growth mechanism may have caused these changes in the morphology during the heat treatment process. Correspondingly, dissociation of the vanadium and oxygen atoms causes the disordering and breakage of the \( \text{VO}_2 \) (B) nanobelts. Then, the crystalline structure is reconfigured and transformed into the monoclinic \( \text{VO}_2 \) (M) or into the tetragonal \( \text{VO}_2 \) (R) with the addition of tungsten. After 2 hours of annealing, coalescing of the nanoparticles occurs. Agglomeration stage follows, whereby oblate, spherical, and/or plate-like shaped particles are formed. For samples VMW0%, VMW1%, VMW1.5%, VMW2%, and VMW3%, the measured average diameters of these spheroids were 0.24, 3.08, 2.17, 1.51, and 0.89 \( \mu \text{m} \), respectively. According to Chen et al. (2014), this increase in grain size is a prominent feature of W doping on \( \text{VO}_2 \) [20]. Seemingly, samples with wt.% of 1% and 1.5% had rough surfaces compared with the undoped and the other doped samples. This may be due to the presence of \( \text{V}_6\text{O}_{13} \) based on their XRD scans. Meanwhile, the formation of nanorods can be noticed in Figures 3(c) and 3(d) when the doping reached 2 and 3 wt%. The widths of these rods were as low as 161 nm for VMW2% and 101 nm for VMW3%. Based on the diffractograms of these samples, these rods may contain the compound \( \text{V}_2\text{.3W}_0\text{.6O}_7 \).

### Table 1: FWHM and lattice properties of the undoped and W-doped \( \text{VO}_2 \) samples.

| Sample   | W conc. (wt.%) | FWHM (°) | Crystallite size, (nm) | Lattice strain LS (%) | d-Spacing (Å) |
|----------|----------------|----------|------------------------|----------------------|---------------|
| VMW0%    | 0              | 0.130    | 81.5                   | 0.196                | 3.203         |
| VMW1%    | 1              | 0.130    | 81.5                   | 0.216                | 3.205         |
| VMW1.5%  | 1.5            | 0.130    | 81.5                   | 0.197                | 3.206         |
| VMW2%    | 2              | 0.195    | 50.1                   | 0.321                | 3.214         |
| VMW3%    | 3              | 0.195    | 50.1                   | 0.322                | 3.225         |

3.2. Influence on Thermochromic Properties. The thermo-chromic behavior of W-doped \( \text{VO}_2 \) can be evaluated using the DSC curve of the samples in Figure 4. As seen, a change in the position of the peaks can be readily observed as the concentration of W was increased. Particularly, the peaks shifted to the left, indicating the reduction of the phase transition temperature. As elaborately discussed by Tan et al. (2012), the local structure of the tungsten atom has intrinsic symmetry with a tetragonal-like configuration [21]. When added to a \( \text{VO}_2 \) (M), W propels the distortion of the \( \text{VO}_2 \) lattice and twisting of the asymmetric V-V bonds, resulting in the formation of rutile-like nuclei. Consequently, this lowers the thermal activation energy, thereby causing the reduction of the phase transition. Also, sample VMW3% exhibited two sharp peaks at 31.64°C and 51.99°C. These lower phase transition temperatures may be caused by the increase in \( \text{VO}_2 \) (R) contained in the sample compound as evidenced in the sample’s XRD scan in Figure 1. Also, as reported by Xu et al. (2020), the presence of different-shaped \( \text{VO}_2 \) nanoparticles can lead to multiple phase transition peaks [22]. Indeed, nanoparticles with differing shapes and sizes can be observed in sample VMW3% in Figure 3(e). However, in the cooling direction, only a single peak was observed. This can be explained through the work of Zou et al. (2018). Accordingly, heating a W-doped \( \text{VO}_2 \) (M) nanoparticles causes recrystallization which may transform the nanoparticles into larger-sized \( \text{VO}_2 \) [15]. By heating the sample to 200°C during the heat flow measurement in the DSC, larger-sized \( \text{VO}_2 \) may have formed. Subsequently, this resulted in higher phase transition temperature in the cooling direction with a single peak.

Furthermore, the measured values of the phase transition temperatures of the samples based on the DSC curve are recorded in Table 2. Correspondingly, \( \tau_c \) significantly decreased from 66.47°C to 47.35°C when the W concentration was increased to 3%. The decrease in the phase transition temperature can be attributed to the increase in lattice strain (Table 1) as well as the growth of \( \text{VO}_2 \) (R), as evidenced by the XRD scan (Figure 1). Meanwhile, to determine the heat of metal-to-semiconductor transition and strength of phase change, the enthalpies and hysteresis of the samples were...
measured (see Table 2). As seen, a large increase in hysteresis is observed as the doping wt.% increases. Since hysteresis is mainly affected by crystallinity and grain size, the high hysteresis in the doped samples may have resulted from the low quality of crystallization due to the presence of impurities in the forms of $V_6O_{13}$ and $V_{2.4}W_{0.6}O_{7}$ (see Figure 2) as well as their large grain size (refer to Figure 3).

Meanwhile, a decrease in enthalpy can be observed when 1 wt% W was added to the VO$_2$ sample. Then, an increasing trend occurred when the wt% of the dopant was increased to 2%. Finally, the heat of metal-semiconductor phase transition (MST) decreased when the W was at 3 wt%. The trends in $\tau_c$ and $\Delta H$ of the samples are summarized in Figure 5. As seen, both the phase transition temperatures

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**Figure 3**: FESEM scans of W-doped VO$_2$ at differing dopant weight percentages of (a) 0, (b) 1, (c) 1.5, (d) 2, and (e) 3 wt%.
enthalpies of all doped samples were lower compared to the undoped sample. This is primarily due to the decrease in the thermal activation energy when W was introduced in the VO₂ (M) lattice. Based on the work of Liang et al. (2016), the V-V bonds in VO₂ (M) are arranged with interval distances of 2.65 and 3.12 Å, while in VO₂ (R), the V-V intervals are equidistant at 2.87 Å [23]. Accordingly, partial substitution of V atoms with W atoms, whose radius is greater, results in the shrinking of the V-V bond intervals. Thus, a decrease in the structural difference between the M- and R-phases of VO₂ emerges. Consequently, the activation energy of the metal-to-semiconductor transition decreases; hence, τ_c and ΔH of the doped sample are lower compared with the undoped VO₂ (M). Nonetheless, the values of the enthalpies in this work are closer to the values for bulk VO₂ (37.38 J/g – 51.85 J/g) [24]. Moreover, the decreasing trend in τ_c is mainly due to the increase in lattice strain, as shown in Table 1. Meanwhile, an increase in the enthalpy from 1 to 2 wt.% may be due to the removal of impurity in the form of V₆O₁₃, as displayed in the XRD pattern in Figure 2. Meanwhile, the decrease in enthalpy when the W concentration was changed from 2 to 3 wt.% can be potentially caused by the grain size effect considering that sample VMW3% has a greater grain size than VMW2%. Reasonably, the large grain size of VMW3% may contain structural defects or more oxygen vacancies, which have been reported to cause a decrease in the phase transition temperature and the rate of phase transition [25].
3.3. Influence on Thermophysical Properties. The effects of introducing a tungsten dopant on the thermophysical properties of VO2 were carried out using the microflash method. Specifically, the thermal diffusivity ($\alpha$) of the samples at temperatures of 25, 50, 100, and 150°C was measured, and the results are plotted in Figure 6. Accordingly, the changes in $\alpha$ from 25 to 50°C, 50 to 100°C, and 100 to 150°C were 0.091, 0.210, and 0.027 mm$^2$/s. Hence, it can be inferred that the heat transferring ability of the highly pure VO2 (M) significantly increased across the phase transition temperature. Apart from sample VMW1%, an increase in $\alpha$ was still discernible across the metal-to-semiconductor transition temperature of the doped samples. Specifically, the measured $\Delta \alpha$ from 50 to 100°C were 0.113, 0.157, and 0.07 for samples with W concentrations of 1.5, 2, and 3 wt%. Meanwhile, doping generally resulted in a decrease in thermal diffusivity at a temperature above 25°C. As shown in Table 1, the d-spacing of the doped samples increased, which could result in the decrease of the transfer of heat in the VO2 lattice.

Moreover, the thermal conductivity ($\kappa$) of the samples was calculated using the following equation:

$$\kappa = \rho \alpha C_p,$$  \hspace{1cm} (2)

where $\rho$ is the material’s density and $C_p$ is the heat capacity. The measured densities of the pelletized samples, namely, VMW0%, VMW1%, VMW1.5%, VMW2%, and VMW3%, were 2.75, 3.20, 3.23, 3.23, and 3.31 g/cm$^3$, respectively. Inasmuch as these pellets were obtained by the hydraulic pressing of porous nanopowder samples, their densities were lower than the theoretical density of VO2 (M), which is 4.67 g/cm$^3$. The heat capacities, on the other hand, were determined from the DSC data in Figure 4, using the following equation:

$$C_p = \frac{Q/m}{dT/dt},$$  \hspace{1cm} (3)

where $Q/m$ is the measured heat flow in the DSC curve and $dT/dt$ is the temperature gradient employed in the DSC scan. The resulting measurements of $\kappa$ are plotted in Figure 7.

Correspondingly, the profiles of these plots are similar to the results of Oh et al., albeit with lower values, which is primarily due to the low densities used in calculations [26]. Accordingly, a considerable increase in thermal conductivity across $\tau_c$ can be observed. Particularly, for the undoped VO2, $\kappa$ increased from 2.140 to 3.163 W/m$\times$K as the temperature was increased from 50 to 100°C. This corresponded to a $\Delta \kappa$ of 1.023 W/m$\times$K, which is greater than $\Delta \kappa$ from previous results on VO2 bulk and nanobeams [27]. Meanwhile, for W-doped samples, the thermal conductivities at 25°C were very close to that reported by Oh et al. for VO2 bulk. Also, an incremental change in $\kappa$ occurred from 25 to 50°C. Then, a bigger jump can be observed across the phase transition temperature. Specifically, $\Delta \kappa$ with values of 0.297, 1.424, 1.329, and 1.288 W/m$\times$K were recorded. In general, these values are greater compared to previous findings [13, 27].

This increase in thermal conductivity is possibly caused by the absence of grain boundary defects, which tend to decrease the thermal conductivity of a material.

4. Conclusions

Investigation of the influences of elemental doping on the structural, morphological, thermochemical, and thermophysical properties of VO2 nanoparticles was carried out. Accordingly, the introduction of W shifted some of the peak locations in the XRD scans of the samples, which indicated a phase transformation from VO2 (M) to VO2 (R). This shift in phase was caused by the increase in the lattice strain of the VO2 crystal structure. Also, an increase in grain size was observed in the doped sample. More importantly, doping resulted in the decrease of the phase transition temperature of VO2 from 66.47°C to as low as 31.64°C. However, a decrease in the enthalpy was observed, which signified a decrease in the transition strength. This was potentially caused by many factors such as lower crystallinity, an increase in lattice strain, and the presence of impurities. In addition, W doping was found to influence the thermophysical
properties of VO₂. In particular, the thermal diffusivity and thermal conductivity of the doped VO₂ increased noticeably across its phase transition temperature.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors would like to thank the Universiti Putra Malaysia for the financial support of this research under Putra Grant GP-IPS (Grant no. 9501500).

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