One-step hydrothermal synthesis and characterization of Mg/Mo co-doped VO₂ nanorods

Asratemedhin Bekele Habtemariam^{1,2} · Daniel Manaye Kabtamu¹ · Malik Maaza^{2,3}

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Abstract

This paper reports the successful syntheses of Mg/Mo co-doped thermochromic vanadium dioxide nanorods by hydrothermal technique. In particular, the effect of magnesium and molybdenum co-doping on insulator–metal transition of vanadium dioxide was investigated. The synthesized Mg/Mo co-doped VO₂ nanorods exhibited high purity and crystallinity. X-ray diffraction, scanning electron microscopy, X-ray energy-dispersive spectrometer, transmission electron microscopy, and Fourier transform (FTIR) were used to study the structure and morphology of the as-synthesized rods. X-ray diffraction patterns of the samples show an increase in intensity and a slight shift in the peaks toward lower 2-theta with increasing dopant concentration. The co-doping reduces ΔT_c and has been considered as an effective method for manipulating the phase change in VO₂. The results revealed that smart radiation devices based on Mg/Mo co-doping of VO₂ can be a promising material for thermal control of spacecraft.

Keywords Nanorods · Co-doped VO₂ · Hydrothermal · Smart radiation device · Thermochromic properties

1 Introduction

Vanadium dioxide (VO₂) is one of the intensively studied oxides of vanadium, which undergoes a first-order-type insulator–metal transition (IMT) at a critical temperature (T_c) of about 68 °C [1–5]. The temperature-dependent IMT behavior of VO₂ is reversible from a semiconducting monoclinic structure to a metallic tetragonal structure, accompanied by remarkable changes in electrical and optical properties [1, 3, 5]. During the IMT, the electrical conductivity of VO₂ increases by more than three orders of magnitude [1, 2].

Recently, reducing the phase transition of VO₂ closer to ambient temperature and exploiting this property for applications in diverse areas of technology have been a hot research topic [3, 4]. Lowering the phase transition of VO₂ can be achieved by different driving mechanisms such

as doping [4, 6–8], light illumination [9, 10], and application of electric field [11], which in turn alters the physical properties of VO₂ and exhibits unusual properties in its electrical and optical performances. These remarkable properties bring thermochromic VO₂ to the front line in the manufacturing of future technological devices such as smart window coatings [12–15], smart radiation device (SRD) [16, 17], terahertz (THz) optical devices [18], electronic switches and memories [19–21], Li-ion batteries [22, 23], and thermal sensors [24–26].

To date, various synthesis techniques have been employed to prepare vanadium dioxide nanoparticles. These include thermolysis [6, 14, 27], sputtering [16, 17], spray pyrolysis [28], ion implantation [29, 30], chemical vapor deposition (CVD) [31, 32], pulsed laser deposition (PLD) [33–35], sol–gel [27, 36], and hydrothermal techniques [8, 37–39]. Among these, hydrothermal synthesis

✉ Daniel Manaye Kabtamu, danielmanaye@gmail.com; Asratemedhin Bekele Habtemariam, basrtm@gmail.com; Malik Maaza, likmaaz@gmail.com | ¹Department of Physics, College of Natural and Computational Sciences, Debre Berhan University, P.O. Box 445, Debre Berhan, Ethiopia. ²Nanosciences African Network (NANOAFNET), iThemba LABS-National Research Foundation of South Africa, 1 Old Faure Road, PO Box 722, Somerset West, Western Cape 7129, South Africa. ³UNESCO-UNISA Africa Chair in Nanosciences-Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk Ridge, PO Box 392, Pretoria, South Africa.

technique is environmentally friendly, cost-effective, flexible, does not need complicated setup and can be scaled up easily for mass production [8, 37, 38]. So far, many research works have been conducted using this method for the syntheses of undoped and doped VO₂ nanoparticles [8, 38, 39].

Doping VO₂ with transition metal is a commonly practiced technique to change (increase or decrease) the phase transition temperature [40, 41]. Doping of VO₂ has been observed to appreciably affect the phase transition temperature and improve the electrical and optical properties of the material [4, 7, 8]. Though single-element doping is an important mechanism to alter the phase transition property, better switching of the phase transition of VO₂ was observed by more than one element doping. For instance, Burkhardt et al. [42] prepared tungsten and fluorine co-doping of VO₂ and reported that more than one element doping is effective than single-element doping. Kong et al. [43] synthesized W and Mo co-doped VO₂ microrods via hydrothermal technique. The result showed that the phase transition temperature was decreased using this material.

In this study, we report for the first time the synthesis of Mg/Mo co-doped VO₂ nanoparticles using hydrothermal technique. In this eco-friendly and cost-effective synthesis process, the effective hysteresis loop width of Mg/Mo co-doped VO₂ nanoparticles was reduced to ΔT_c of ~ 8.8 °C, which is an important indication for fast switching application in SRD and smart windows.

2 Experimental section

2.1 Materials and methods

The chemicals used in this experiment were oxalic acid (C₂H₂O₄·2H₂O), vanadium pentoxide (V₂O₅), ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O), magnesium chloride hexahydrate (MgCl₂·6H₂O), and distilled ionized water. All the chemicals were analytical grade and used without further purification. The chemicals were purchased from Sigma-Aldrich, South Africa.

Mg/Mo co-doped VO₂ nanorods were synthesized by a hydrothermal method as described in the previous report [37]. In a typical synthesis procedure, 3.56 g of oxalic acid (C₂H₂O₄·2H₂O) was first dissolved in 100 mL of distilled ionized water with constant magnetic stirring at room temperature. The addition of oxalic acid is to act as a reducing agent to control the electronic valence of vanadium ions and hence control the successive phase transformation into VO₂ (M) [44–46]. Subsequently, 2.0 g of V₂O₅ was added to the solution to reach a yellow suspension (V⁵⁺) while heating at about 60 °C. The solution turned green

and then dark blue (V⁴⁺) with final pH value between 2 and 3. After sufficient reaction, 0.5 at.% of (NH₄)₆Mo₇O₂₄·4H₂O and different concentrations of MgCl₂·6H₂O ($x = 1.0$ at.% Mg, 2.0 at.% Mg, 3 at.% Mg) were added, simultaneously, into the above solution and the suspension was continuously magnetic stirred. An adequate amount of the mixture was transferred into a Teflon-lined autoclave (20 mL) followed by hydrothermal treatment at 240 °C for 6 h. After cooling to room temperature, the resulting blue-black precipitate was separated by centrifugation and then washed with deionized water three times. The product was oven-dried at 80 °C and vacuum-annealed at a temperature of 500 °C to get the less stable polymorph VO₂ (M) [47, 48].

2.2 Characterization of materials

The X-ray diffraction (XRD) patterns of the as-synthesized undoped and Mg/Mo co-doped VO₂ powder were collected on a Bruker D8 ADVANCE GER, X-ray diffractometer recorded in the 2-theta range 15°–90° using CuK α 1 radiation (wavelength = 1.5406 Å). The operating voltage and current were 40 kV and 300 mA, respectively. The XRD characterization was carried out at iThemba LABS, South Africa. The scanning electron microscopy (SEM) images of the synthesized undoped and Mg/Mo co-doped VO₂ powder were obtained using ZEISS, Auriga, Oxford Instruments, field emission scanning electron microscopy. No special sample preparation was required for SEM measurement. The synthesized powder of each sample was carefully spread over the sample holder and was made conducting. The transmission microscopy (TEM) images of the synthesized undoped and Mg/Mo co-doped VO₂ powder were recorded on a TECNAI G2-F20. For TEM, about 0.1 mg of the powder was dispersed in 5 mL ethanol. Then, TEM samples were prepared by placing a drop of the particle solution on a carbon-coated copper grid and dried at ambient temperature. Elemental composition was examined through energy-dispersive X-ray spectroscopy (EDS) on the same high-resolution electron microscopy unit. FTIR spectra of undoped and Mg/Mo co-doped VO₂ powder were recorded on a PerkinElmer Spectrum 100 spectrometer in the 4000–500 cm^{−1} range at the University of the Western Cape (UWC), South Africa. Samples were heated from 20 to 90 °C and cooled back from 90 to 20 °C at a rate of 5 °C/min using STA6000 temperature scan.

3 Results and discussion

The X-ray diffraction (XRD) patterns of Mg/Mo co-doped VO₂ powder with 0.5 at.% Mo and various doping concentrations of Mg (1 at.%, 2 at.%, 3 at.%) are shown in Fig. 1. The peaks of the corresponding XRD pattern are indexed

Fig. 1 XRD patterns of Mg/Mo co-doped VO₂ nanorods

to VO₂ (M) phase (space group: P2₁/c) with lattice constants of $a=5.753$, $b=4.526$, $c=5.383$ Å, and $\beta=122.60^\circ$ (JCPDS No. 44-0252). The XRD patterns of Mg/Mo co-doped VO₂ exhibit diffraction peaks at 26.93° , 27.86° , 33.46° , 37.03° , 39.83° , 42.19° , 44.67° , 52.94° , 55.51° , 57.48° , 65.08° , 70.43° , and 72.03° corresponding to (110), (011), (10-2), (200), (002), (210), (021), (102), (211), (022), (031), (202), and (41-1), respectively, with prominent peak at (011) (JCPDS no. 44-0252). The XRD patterns exhibited that the Mg/Mo co-doped VO₂ nanorods were monoclinic phase. No peaks of any other phase or impurities were detected in the spectra, revealing high phase purity of VO₂ (M) nanorod structure. From the XRD pattern, it is clearly seen that the intensity of the peaks found to exhibit a slight increment with increasing dopant concentration, which means that the crystallinity of VO₂ (M) is increasing with dopant level.

The size and morphology of the Mg/Mo co-doped VO₂ are examined by scanning electron microscopy (SEM). As shown in the magnified SEM image of Fig. 2, the products are rod-shaped particles with a length of about 490 nm and width of 137.6 nm.

Figure 3a–d shows the transmission electron microscopy (TEM) images of Mg/Mo co-doped VO₂ which

Fig. 2 SEM images of Mg/Mo co-doped VO₂ nanorods

provides additional information on the phase of the VO₂ (M) sample. As shown in Fig. 3a, b, the morphology of the Mg/Mo co-doped VO₂ is rod-shaped structure. The SAED patterns in Fig. 3e show the rods exhibited crystalline structures and clear lattice fringes of VO₂ (M) phase. The spacing between two successive crystal planes was

Fig. 3 TEM images (a–d) and SAED (e) ring patterns of Mg/Mo co-doped VO₂ nanorods

calculated to be around 3.21 Å, which is consistent with the distance between two (011) crystal planes of VO₂ (M). With an increase in Mg doping level from 1 at.% to 3 at.%, an increase in aspect ratio of the Mg/Mo co-doped VO₂ nanorods was observed [5, 49]. This reveals that increasing level of dopant concentration promotes the growth of VO₂ (M) nanorods [49].

To determine the chemical composition of Mg/Mo co-doped VO₂ nanorods, energy-dispersive X-ray spectroscopy (EDS) measurements were taken on a representative specimen. The EDS result as shown in Fig. 4 reveals that the nanorods contain V, Mg, Mo, and O. From the EDS spectrum, it is observed that VO₂ was doped with about 1.0 at.% Mg and 1.2 at.% Mo. For all doping concentrations, EDS spectrum was taken and the Mg and Mo elements were observed. The C and Cu peaks observed in the spectrum were from the instrument.

As shown in Fig. 5, the Fourier transform infrared (FTIR) investigations of Mg/Mo co-doped VO₂ nanorods were performed. From FTIR studies, we can determine the

constituting elements and its bonding arrangement, since each specific molecule possesses a unique fingerprint which can reveal its identity [50]. As a result, the absorption band at the vicinity of 989.5, 493.4, and 413.2 cm⁻¹ can be associated with stretching vibrations of V–O and V=O [51]. A small peak at 1608.6 cm⁻¹ was observed which is due to the adsorbed water molecules [51]. No other significant peaks were observed due to the elimination of surfactants if any.

The DSC curve shown in Fig. 6 reveals that the magnitude of effective hysteresis loop width of Mg/Mo co-doped VO₂ is reduced to ΔT_c of ~8.8 °C.

Based on the experimental results, XRD peaks shifting toward lower two-theta is an indication of phase transition due to Mg/Mo co-doping of VO₂. The presence of Mg and Mo atoms in the EDS spectrum reveals that Mg and Mo atoms have been incorporated into the vanadium atom sites. From DSC curve, the phase change between the heating and cooling processes is found to be about 8.8 °C.

Fig. 4 EDS spectrum of Mg/Mo co-doped VO₂ nanorods **Fig. 5** FTIR spectrum of 2 at.% Mg and 0.5 at.% Mo co-doped VO₂ nanorods

Here, we compared our result with formerly reported values from the literature, as listed in Table 1.

Liang et al. [49] carried out a series of cooling DSC measurements and obtained T_c value of 60.6 °C at 0.5

at.% W doping and the T_c decreases with increasing dopant concentration. Zhou et al. [8] reported $T_c \sim 66$ °C at 0.7% Mg doping, which decreases with increasing dopant level. Shen et al. [7] reported T_c value of ~ 68 at

Fig. 6 DCS curve of 2 at.% Mg and 2 at.% Mo co-doped VO₂ nanorods

4.2% Zr doping and 64.3 °C at 9.8 at.% Zr doping. Only the heating or cooling T_c values are recorded, and thus, the ΔT_c value of transition metal doping has not been reported so far. As clearly observed from Table 1, our result includes both the heating and cooling conditions of the sample and the $\Delta T_c \sim 8.8$ °C value is clearly calculated.

In addition to the presence of phase change owing to co-doping, the result revealed that much smaller value in $\Delta T_c \sim 8.8$ °C is achieved in this research work. This implies that the synthesized VO₂ nanorods can be a suitable candidate material for SRD and smart window coatings.

4 Conclusion

In summary, Mg/Mo co-doped VO₂ nanorods were successfully synthesized by hydrothermal technique. The phase transition temperature decreases slightly with increasing level of dopant concentration. The obtained

result indicated that Mg/Mo co-doping could be effectively used to lower the phase transition temperature of VO₂ toward ambient values. Hence, Mg/Mo co-doping of VO₂ is the best candidate material for producing passive thermal control SRD of spacecraft systems as well as for thermochromic smart window coatings. As a follow-up study on these VO₂-doped nanorods, it is tended to carry out investigations on their gas sensing, optical limiting, and plasmonic responses as well as their electrochemical characteristics [1, 52, 53]. Likewise, their deep-space radiation hardness will be investigated via proton irradiations [54].

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Author contribution Prof. Malik Maaza contributed to conceptualization; Asratemedhin Bekele provided the methodology and wrote the original draft preparation; Dr. Daniel Manaye helped in writing, reviewing and editing and performed the formal analysis; Prof. Malik Maaza participated in supervision and funding acquisition.

Compliance with ethical standards

Conflict of interests The authors declare that they have no competing interests.

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Table 1 Comparison of our material with those of previously reported metal doping VO₂

Doping materials for VO ₂	Autoclave temp. (°C), time (h)	Heating temp. (°C)	Cooling Temp. (°C)	ΔT_c (°C)	Reference
W	240, 48		60.6		[49]
Mg	240, 24	~66			[8]
Zr and W-Zr-co-doped	260, 24	~68			[7]
Mg/Mo co-doped	240, 6	64.9	56.1	8.8	This work

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