Materials Research Bulletin 100 (2018) 243–248

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Hydrothermal synthesis and thermal change in IR reflectance of Al/W co-doped VO_2 powder

Ikuo Yanase*, Yasuaki Mori, Hidehiko Kobayashi

Saitama University, Faculty of Engineering, Department of Applied Chemistry, 255 Shimoohkubo, Sakura-ku, Saitama-shi, Saitama, 338-8570, Japan

ARTICLE INFO

Keywords:
VO_2
Thermochromic
Phase transition
Doping
IR reflectance

ABSTRACT

Al/W co-doped VO_2 with a monoclinic structure, space group $P2_1/c$, was synthesized (hereafter, Al/W-doped VO_2(M1)) and its thermochromic property was investigated. First, to prepare the precursor for Al/W-doped VO_2(M1), V_2O_5, $(NH_4)_{10}W_{12}O_{41}{\cdot}5H_2O$, and $AlCl_3{\cdot}H_2O$ were dispersed in a citric acid solution and then hydrothermally treated in an autoclave. Then, the Al/W-doped VO_2(M1) powders were synthesized by heating the obtained precursor at various temperatures under an Ar gas flow. The Al/W-doped VO_2(M1) has a monoclinic structure with space group $P2_1/c$, similar to undoped VO_2(M1) and W-doped VO_2(M1). The Al/W-doped VO_2(M1) indicated that the monoclinic to tetragonal transition temperature was lowered to approximately room temperature by the Al and W doping. The Al/W-doped VO_2(M1) had the lower optical band gap and showed a larger IR reflectance in the 800–2000 nm range, compared with W-doped VO_2(M1) and pure VO_2(M1).

1. Introduction

Vanadium dioxide (VO_2) has several polymorphs, including VO_2(R), VO_2(M), VO_2(B), VO_2(A), and VO_2(C). Monoclinic rutile-type VO_2, space group $P2_1/c$, (hereafter, VO_2(M1)) transforms at approximately 68 °C to tetragonal rutile-type VO_2, space group $P4_2/mnm$, (hereafter, VO_2(R)) [1]. The first-order metal-to-insulator transition of VO_2(M1) to VO_2(R) [2] causes a reversible change in electric, magnetic, and optical properties [3]. These properties make these materials candidates for many promising applications in diverse fields, such as in gas and temperature sensors [4], optical switching devices [5,6], smart windows [7,8], smart tiles [9], battery materials [10], and capacitors [11].

There have been many reports on various additives [12] for VO_2(M1), including W [13–16], Mo [13,17], Al [18], Fe [13,19], Ti [20], Sn [13], Sb [21], and Mg [22], to control its transition temperature and UV–vis–NIR reflectance. In particular, the doping of W into VO_2 was reported to be effective in lowering its transition temperature [14,23,24]. However, W-doped VO_2(M1) exhibited a smaller increase in IR reflectance after the phase transition caused by the transition of VO_2(M1) to VO_2(R), compared with that of undoped VO_2(M1) [25]. Similarly, Mo-doped [26] and P-doped [27] VO_2(M1) also exhibited a smaller increase in IR reflectance after the phase transition. On the other hand, Al-doped VO_2(M1) [18,27,28] and B-doped VO_2(M1) [28] exhibited a larger increase in IR reflectance after the phase transition. Furthermore, doping rare earth cations such as Ce [29], Gd [30], and Eu [31] for V sites in VO_2 decreases the phase transition temperature.

Therefore, it is expected that the co-doping of smaller trivalent cations and tungsten ions for V sites in VO_2(M1) will be effective for increasing the IR reflectance with lower MI-phase-transition temperature. However, the thermochromic properties of co-doped VO_2(M1) have rarely been reported, except for Mo/W co-doped VO_2 [32] and W/F co-doped VO_2 [33]. Considering that doping of Al increases the IR reflectance and doping of W decreases the phase-transition temperature of VO_2(M1), co-doping of Al and W is of much interest from the two viewpoints of increasing the IR reflectance after the phase transition and decreasing the transition temperature of VO_2(M1). In this study, Al/W-doped VO_2(M1) powders were synthesized via a hydrothermal method for the first time, and the influence of the co-doping of Al and Won the phase-transition temperature and the thermal change in the IR reflectance were investigated.

2. Experimental procedure

First, a V_2O_5 powder was prepared by heating a commercially available V_2O_3 powder (Wako Chemical, 99%) at 400 °C for 10 h in air. Then, the synthesized V_2O_5 powder, commercially available $(NH_4)_{10}W_{12}O_{41}{\cdot}5H_2O$ (Wako Chemical, 99%), and $AlCl_3{\cdot}H_2O$ (Wako Chemical, 99%) powders were dispersed into 40 mL of a citric acid solution to attain a molar ratio of V:W:Al = 1-x-y:x:y (x + y = 0 to 0.02). Here, the total amount of the above powders was 0.4 g. The mixed solution was transferred into a 100-mL stainless steel autoclave with a thermocouple, which was sealed and maintained at 170 °C for

* Corresponding author.
E-mail address: yanase@apc.saitama-u.ac.jp (I. Yanase).

https://doi.org/10.1016/j.materresbull.2017.12.017
Received 15 May 2017; Received in revised form 25 September 2017; Accepted 12 December 2017
Available online 15 December 2017

24 h with stirring, then allowed to cool to room temperature (RT) naturally. The products were filtered, washed with a citric acid solution several times, and dried at RT for 24 h. Finally, the dried products were heated at temperatures of 600 and 1000 °C for 2 h under an Ar gas flow.

The crystalline phase of the products was investigated by X-ray powder diffraction (XRD; D8 ADVANCE with CuKα radiation). The phase transition of products was investigated by high-temperature XRD in the 2θ range of 10–80° with a heating rate of 5 °C/min. The morphology of the products was observed by field-emission scanning electron microscopy (FESEM; S4100, Hitachi). The elements in the products were investigated by energy dispersive X-ray (EDX; XFlash Detector 4010, Bruker AXS). The phase-transition temperature of the products during heating and cooling cycles was measured by differential scanning calorimetry (DSC; EXSTAR 6000, Seiko Instrument). The vis-NIR reflectance properties and band gaps of the products in the range of 20–90 °C were examined by diffuse reflectance ultra violet-visual-near infrared spectroscopy (UV–vis–NIR; V-670, JASCO).

3. Results and discussion

3.1. Synthesis of Al and W-doped VO_2 powder

Fig. 1 shows the XRD patterns of the precursor and the products obtained by heating the precursor at 600–900 °C for 2 h under an Ar gas flow. The precursor VO_2(B) with a brookite structure (JCPDS No. 81-2392) was obtained by reducing V_2O_5 with citric acid ($C_6H_8O_7$) in an autoclave [34,35]. Citric acid reduces vanadium species such as V_2O_5 via the formation of vanadium complexes [36,37,38]. Therefore, VO_2 (B) powders were synthesized in an autoclave in this study. The two crystalline phases, V_6O_{13} [17] (JCPDS No. 75-1140) and VO_2 (M1), were produced at 600 °C, and a single phase of VO_2 (M1) (JCPDS No. 82-0661) was synthesized at temperatures of 700–900 °C.

Fig. 2 shows the XRD patterns of the products obtained by heating the precursor with a chemical composition of $V_{1-x-y}W_xAl_yO_2$ (M1, x = 0.01, y = 0.01) at temperatures of 700–1000 °C for 2 h under an Ar gas flow. Although the V_3O_7 crystalline phase was primarily produced at 700 °C, a single phase of Al/W-doped VO_2 (M1) was produced at 800 °C and 900 °C, while that of Al/W-doped VO_2 (R) (JCPDS No. 76-0675) was produced at 1000 °C. Thus, It was found that the single phase of Al/W-doped VO_2 (M1) was synthesized at higher temperatures than pure VO_2 (M1).

Fig. 3 shows the XRD patterns of the $V_{1-x-y}W_xAl_yO_2$ powders with various chemical compositions synthesized at 800 °C. For $V_{1-x-y}W_xAl_yO_2$ with (x, y) = (0, 0.01) and (0.003, 0.007), a monoclinic phase with a space group of *C*2/*m* (hereafter, M2) was produced. In contrast, the product $V_{1-x-y}W_xAl_yO_2$ (M1) had a monoclinic structure, space group $P2_1/c$, in the cases of (x, y) = (0.005, 0.005) and (0.01, 0.01). The result suggests that doping Al with a smaller ionic size than V was not effective for maintaining a M1 phase. Therefore, a single phase of $V_{1-x-y}W_xAl_yO_2$ (M1) was produced in the cases of (x, y) = (0, 0.01), (0.01, 0.005), and (0.01, 0), including W with a larger ionic radius than Al, as shown in Fig. 4. Thus, it was determined that Al/W-doped VO_2 had a monoclinic structure, space group of $P2_1/c$, similarly to W-doped VO_2.

SEM images of the $V_{1-x}W_xO_2$ (M1; x = 0.01) and $V_{1-x-y}W_xAl_yO_2$ (M1; x = 0.01, y = 0.01) powders are shown in Fig. 5. The particle size of $V_{1-x-y}W_xAl_yO_2$ (M1; x = 0.01, y = 0.01) was smaller than that of $V_{1-x}W_xO_2$

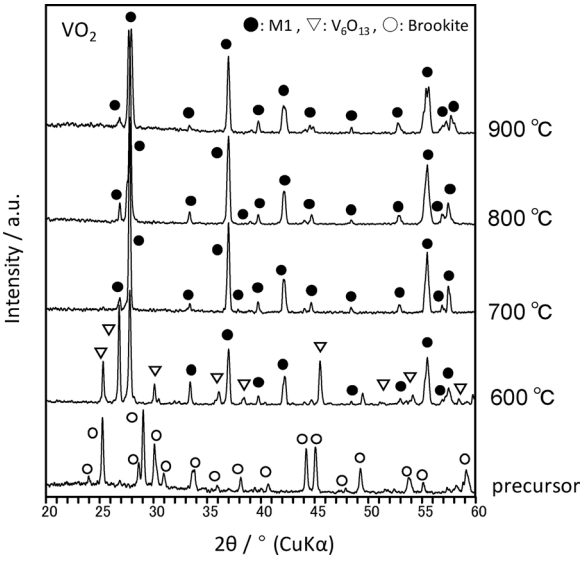

Fig. 1. XRD patterns of products obtained by heating the precursor for VO_2 at temperatures of 600–900 °C under an Ar gas flow. ●: VO_2(M1), ▼: V_6O_{13}, ○: VO_2(B).

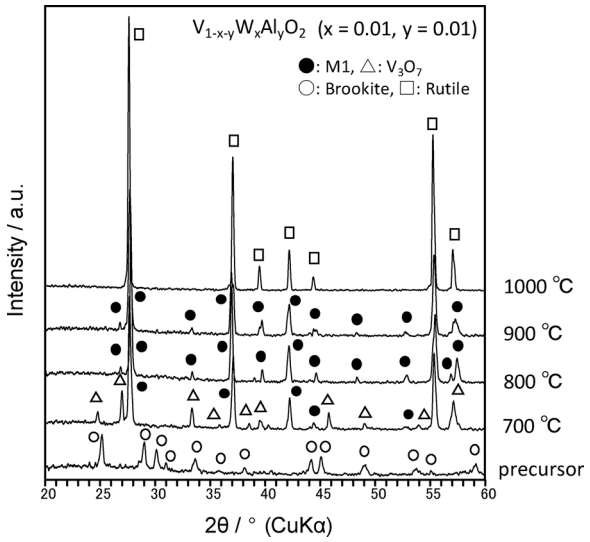

Fig. 2. XRD patterns of products obtained by heating the precursor for $V_{1-x-y}W_xAl_yO_2$ with x = 0.01 and y = 0.01 at temperatures of 700–1000 °C under an Ar gas flow. ●: VO_2(M1), ▲: V_3O_7, ○: VO_2(B), □: VO_2(R).

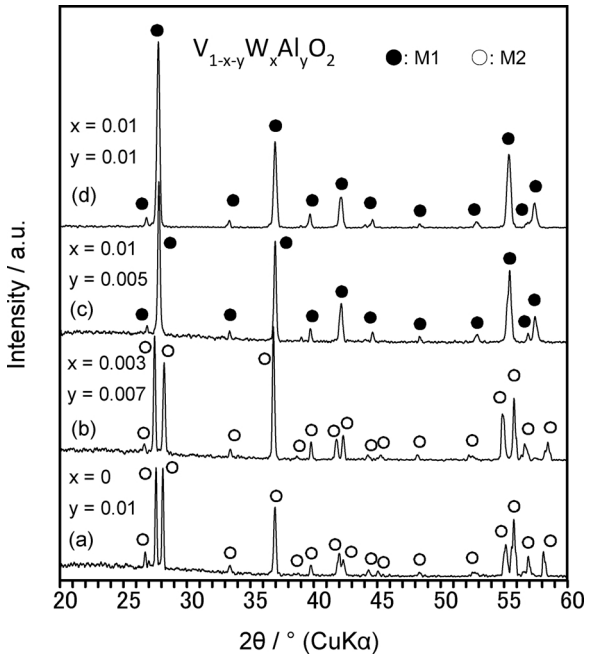

Fig. 3. XRD patterns of products obtained by heating the precursor for $V_{1-x-y}W_xAl_yO_2$ at 800 °C under an Ar gas flow; (a) x = 0, y = 0.01, (b) x = 0.003, y = 0.007, (c) x = 0.01, y = 0.005, (d) x = 0.01, y = 0.01. ●: VO_2(M1), ○:VO_2(M2).