

Thermochromism of vanadium–titanium oxide prepared from peroxovanadate and peroxotitanate

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Abstract Vanadium–titanium complex oxides were prepared through a new synthetic route from peroxovanadate and peroxotitanate solutions, and their thermochromism were investigated. Reflectance spectra for $V_{0.48}Ti_{0.52}O_2$ pellet showed a reversible reflectivity increase in the wavelength region of 700–1,000 nm above 45 °C. The reflectivity was increased gradually from 45 °C to ca. 80 °C unlike the conventional VO_2 which shows an abrupt increase at 67 °C. The mechanism was discussed using powder XRD patterns, SEM images and element distribution maps.

Introduction

Thermochromic smart windows, which automatically shade the sunlight at high temperature have attracted much attention from the viewpoint of energy saving. Many researchers have tried to apply the semiconductor-to-metal transition of some metal transition oxides to the smart windows, because it accompanies an abrupt reflectivity change [1]. For example, the monoclinic form of VO_2 is transformed into the rutile form at $T_c = 67$ °C [2], and this semiconductor-to-metal transition brings about an abrupt reduction of transmittance at near-infrared region [3]. On the other hand, we have found a new nonstoichiometric orthorhombic titanium oxide (TiO_x , $x = 1.85$ – 1.94) [4] and

have investigated its thermochromic properties in near-infrared region [5]. In this study, we focus on the preparation of vanadium–titanium complex oxides and their thermochromism.

Doping tungsten or molybdenum in VO_2 lowers the T_c of the phase transition [6, 7], and the switching performance of double-doped films in the $V_{1-x-y}W_xMo_yO_2$ and $V_{1-x-z}W_xTi_zO_2$ systems has been precisely investigated [8]. Phase transitions of $V_{1-x}Ti_xO_2$ system have been also investigated using the conductivity and DTA measurements [9, 10]. The DTA measurement suggested that the transition temperature of $V_{0.60}Ti_{0.40}O_2$ was 48 °C. Their optical switching properties at 2.5 μm have been reported using thin films deposited from alkoxides [11]. From the practical point of view, a wet process using solutions is suitable for fabricating thin films because it is feasible to produce a large-area film at a low cost. It is highly desirable to develop a vanadium–titanium solution process to achieve the smart window.

In the present study, we studied the reflectance spectra change of $V_{1-x}Ti_xO_2$ system as well as their structures and morphologies. The samples of $V_{1-x}Ti_xO_2$ were prepared through a new solution process from peroxovanadate and peroxotitanate aqueous solutions. The spectra changes in the near-infrared region above 45 °C were presented.

Experimental

Preparation of materials

Peroxotitanate solution (ammonium citratoperoxotitanate aqueous solution) was prepared by mixing metallic titanium powder (0.25 g) with the mixture of hydrogen peroxide solution (30 wt% aq, 20 g), ammonia solution

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(28 wt% aq, 5 g), and citric acid (0.25 g), according to the literature [12]. A vigorous reaction took place mainly between the metallic titanium and the hydrogen peroxide with emission of oxygen gas to yield a transparent light yellow peroxotitanate solution. Although it has been generally recognized that to prepare titanium aqueous solution is technically difficult, titanium aqueous solution containing about 0.20 mol/kg of titanium was successfully prepared through the present procedure.

Similarly, peroxovanadate solution was prepared by mixing metallic vanadium powder (0.25 g) with the mixture of hydrogen peroxide solution (30 wt% aq, 20 g), ammonia solution (28 wt% aq, 5 g), and citric acid (0.25 g). This reaction yielded a transparent orange solution containing the complex ion of vanadium.

These two solutions were mixed and dried at room temperature. We obtained a yellow residue and used this as a precursor of vanadium–titanium complex oxide. The residue was pressed into pellet and heated at 400 °C for 2 h in hydrogen atmosphere. The pellet transformed from yellow to black by reduction. The composition of the reduced sample was estimated as $V_{0.48}Ti_{0.52}O_2$. The two types of pellet after and before reduction were used for optical thermochromic measurement.

Optical measurement

Temperature dependence of the reflectance spectra in the wavelength range 750–2,500 nm was measured using a spectrophotometer (Ubest V-570DS, JASCO corporation). The incident angle was 5°.

Structural aspects

Powder XRD (X-ray diffraction) patterns were taken to check crystal structures of the powder samples before and after the reduction in hydrogen atmosphere. SEM and EDX observations (SEMEDX Type N, Hitachi) were performed on the reduced powder sample at the acceleration voltage of 25 kV.

Results and discussion

Reflectance spectra of the reduced black sample pellet $V_{0.48}Ti_{0.52}O_2$ in 750–2,500 nm at 40–90 °C are shown in Fig. 1. The reflectivity in 700–1,000 nm is gradually increased with increasing the temperature. The increase starts at 45 °C and saturates at 80 °C. We also confirmed that this reflectivity change was reversible. In addition to this gradual change in 700–1,000 nm, the reflectivity in

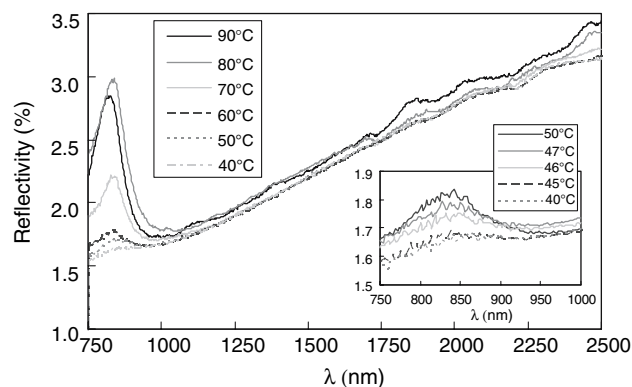


Fig. 1 Reflectance spectra for $V_{0.48}Ti_{0.52}O_2$ pellet after reduction in H_2 at 400 °C. Reflectivity in the range 750–1,000 nm was increased with increasing temperature from 40 to 90 °C. Inset is reflectance spectra from 40 to 50 °C. The reflectivity begins to increase at 45 °C and continues increasing gradually over 45 °C. These changes were reversible

1,000–2,500 nm is slightly changed above 80 °C as reported for the conventional vanadium oxides in the earlier researches. Our critical temperature T_c is 45 °C, much lower than that of the reported vanadium oxide VO_2 , 67 °C. It should be noted that our reflectivity change occurs gradually over T_c , while the reflectivity change of the reported VO_2 takes place abruptly at T_c .

Reflectance spectra of the yellow sample pellet before reduction were also measured for comparison (Fig. 2). The baseline was changed with increasing temperature due to desorption of hydrated water and thus relative comparison among these curves is impractical. However, it is important to note that the gradual reflectivity change in 700–1,000 nm was also observed for the sample pellet before

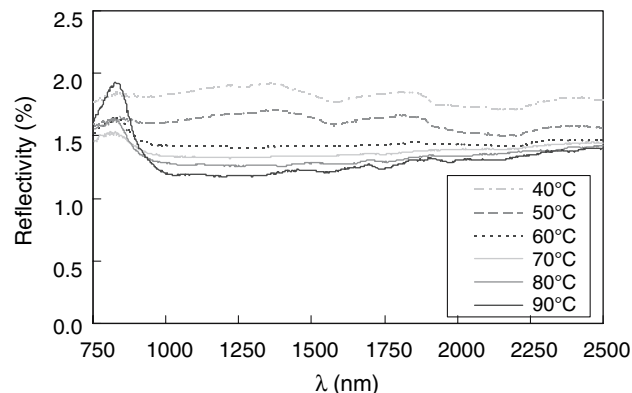


Fig. 2 Reflectance spectra for the precursor of $V_{0.48}Ti_{0.52}O_2$ before reduction. Reflectivity increase peaking around 820 nm was also observed for the pellet before reduction. The baseline was changed due to desorption of hydrated water, and thus relative comparison among these curves is inappropriate

reduction. Reduction from pentavalent vanadium to tetravalent was found to be unnecessary for the present samples.

Figure 3a and b shows powder XRD patterns of the reduced and unreduced samples, respectively. The reduced sample contained V_2O_3 [13] and amorphous phase. The V_2O_3 has been reported to show thermochromism around 150 K, much lower than the present measurement. The yellow powder before reduction contained ammonium vanadium oxide ($(NH_4)_4V_2O_{11}$) [14] along with amorphous phase.

SEM and EDX analysis were performed to provide details on the amorphous phase. Figure 4a shows the SEM image of the reduced sample, and Fig. 4b and c show the element distribution map of the same sample for titanium and vanadium. Figure 5a–c shows more magnified images. The distributions of the two elements were heterogeneous, and the compounds consisted of multi-phase with various vanadium/titanium ratios. The regions

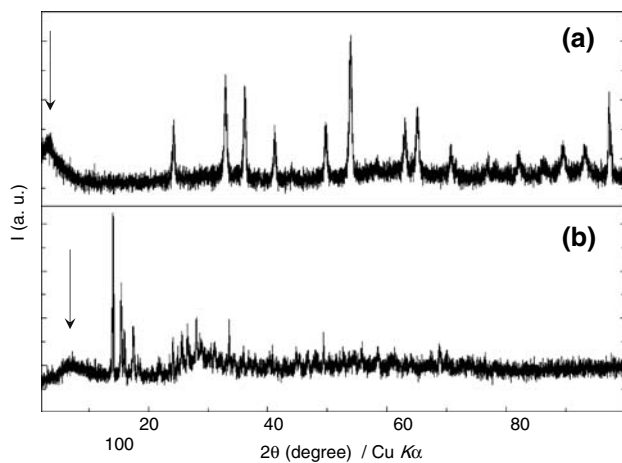
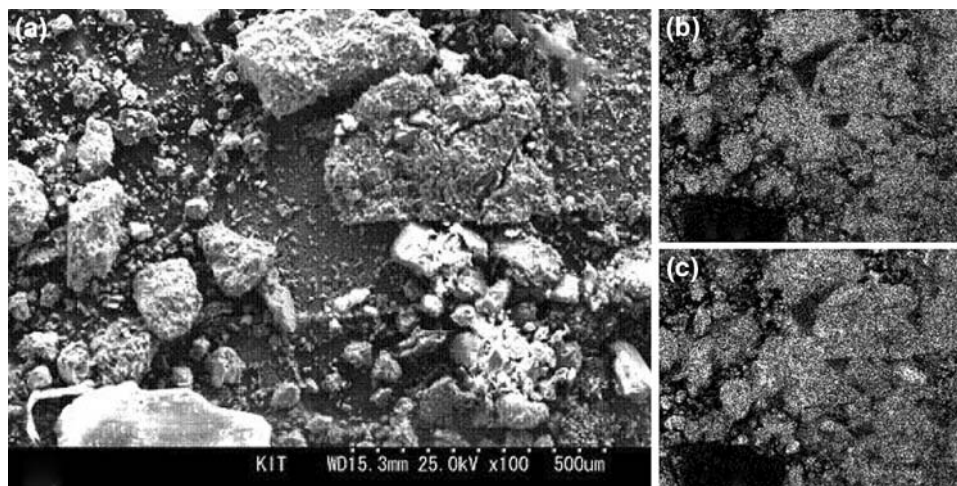


Fig. 3 Powder XRD patterns for (a) $V_{0.48}Ti_{0.52}O_2$ and (b) the precursor before reduction. Sharp peaks are due to (a) V_2O_3 and (b) $(NH_4)_4V_2O_{11}$. Long-range periodicities were observed for both samples (indicated by arrows)

Fig. 4 (a) SEM image for $V_{0.48}Ti_{0.52}O_2$ and its element distribution maps of (b) Ti and (c) V



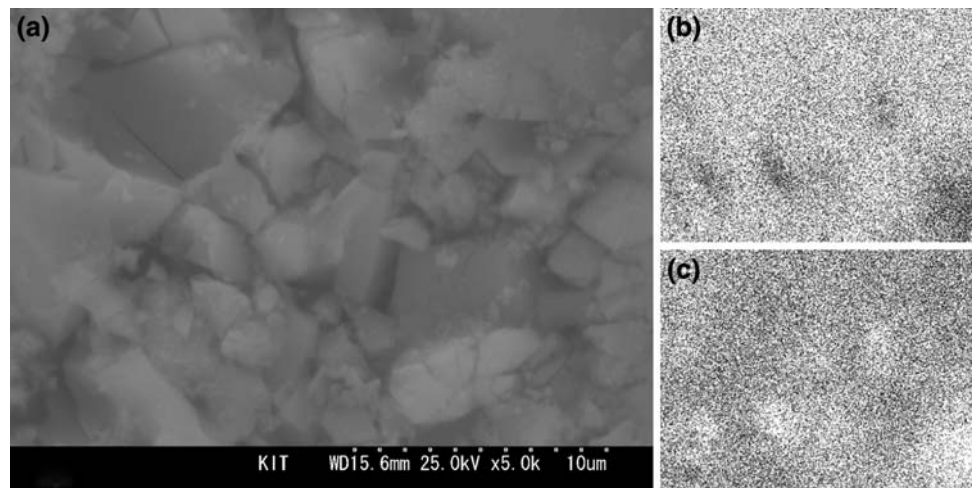
with high vanadium content contained lower titanium, and vice versa.

Our experimental results suggested that the amorphous phase was the thermochromic phase, and that the gradual increase was due to the variety of the vanadium/titanium ratios. More studies are needed for details. For example, analysis of radial distribution functions (RDFs) of the amorphous phases will provide insight into the thermochromism of the present samples, because long-range periodicity was observed in the XRD patterns for the two samples around $2\theta = 3$ or 7° ($Cu K\alpha$) corresponding to d values of 2.9 or 1.3 nm. In practical point of view, it will be possible to prepare the smart window which shades sunlight at $45^\circ C$ by purifying an amorphous phase with a certain vanadium/titanium ratio. In the design of the smart window, high reflectivity in near-infrared region and high transmittance in far-infrared region are simultaneously essential for preventing temperature rise, because heat ray from the sunlight consists of near-infrared rays and visible light, and substance cools by emitting far-infrared rays. The reflectivity change in 700–1,000 nm observed for the present material is highly appropriate for the smart window. It is expected that the smart window will be developed by fabricating thin films of this material on glass windows. Taking advantage of the solution process, fabrication of large area thin film will be possible by the spin coating method.

Conclusions

$V_{0.48}Ti_{0.52}O_2$ was prepared through a new synthetic route from peroxovanadate and peroxotitanate solutions. The reflectance spectra of $V_{0.48}Ti_{0.52}O_2$ pellet showed a gradual reflectivity increase in the wavelength region of 700–1,000 nm above $45^\circ C$, along with a slight reflectivity increase in 1,000–2,500 nm above $80^\circ C$. The gradual

Fig. 5 (a) SEM image for $V_{0.48}Ti_{0.52}O_2$ and its element distribution maps of (b) Ti and (c) V with higher magnification than Fig. 4



reflectivity increase in 700–1,000 nm was also observed for the sample pellet before reduction as prepared from the mixed solution of peroxovanadate and peroxotitanate. Powder XRD patterns, SEM images and element distribution maps suggested that an amorphous phase containing vanadium and titanium played an important role in the thermochromism. Analysis of the amorphous phase is highly desirable to elucidate the reflectivity change mechanism. Purification of the amorphous phase will be useful in practical use as well as in the analysis.

References

1. Goodenough JB (1971) In: Reiss H (ed) Progress in solid state chemistry, 5. Pergamon, New York, pp 145–399
2. Goodenough JB (1971) J Solid State Chem 3:490
3. Lu S, Hou L, Gan F (1993) J Mater Sci 28:2169, doi: 10.1007/BF00367579
4. Tsuyumoto I, Uchikawa H, (2000) J Mater Sci Lett 19(23):2075
5. Tsuyumoto I, Uchikawa H, (2004) Mater Res Bull 39(11):1737
6. Takahashi I, Hibino M, Kudo T (1996) Jpn J Appl Phys 35(4A):L438
7. Lawton SA, Theby EA (1995) J Am Ceram Soc 78(1):238
8. Takahashi I, Hibino M, Kudo T (2001) Jpn J Appl Phys 40(3A):1391
9. Rao CNR, Natarajan M, Subba Rao GV, Loehman RE (1971) J Phys Chem Solids 32:1147
10. Balberg I, Abeles B, Arie Y (1974) Thin Solid Films 24:307
11. Beteille F, Morineau R, Livage J (1997) Mater Res Bull 32(8):1109
12. Tada M, Yamashita Y, Petrykin V, Osada M, Yoshida K, Kakihana M (2002) Chem Mater 14(7):2845
13. Hanawalt JD (1938) Anal Chem 10:475, JCPDS 01–1293
14. Svensson IB, Stomberg R (1971) Acta Chem Scand 25:898, JCPDS 26–0026