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Structural phase transition and thermochromic behavior of synthesized W-substituted $CuMoO_4$

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Abstract

Tungsten (W)-substituted copper molybdenum oxide ($CuMoO_4$) compounds with different substitution ratios of W were synthesized, and the effects of the substitution ratio on the structural phase transition and thermochromic behavior were investigated. Precursor powders prepared by a liquid-phase method were heat-treated at 550–600 °C for 24 h to obtain $CuMo_{1-x}W_xO_4$ ($x=0.04$–0.12) powders. Differential scanning calorimetry (DSC) revealed that the temperature at which $CuMo_{1-x}W_xO_4$ ($x=0.04$–0.12) underwent a structural phase transition of the γ phase to the α phase increased with increasing x. $CuMo_{1-x}W_xO_4$ ($x=0.06$) underwent a structural phase transition in the range of RT to 100 °C and showed a significant change in the diffuse reflectance spectrum in the visible light range, suggesting that the color of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder changed visually in the range of RT to 100 °C. The thermal change in color of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder was recognized even after 10 times repetition of heating and cooling.

Keywords: D. Molybdate; D. Tungsten; E. Structural phase transition; E. Thermochromic

1. Introduction

Thermochromic materials are of much importance in various temperature indicators such as cooking tools, hotplates, and electrical furnaces. Especially, heat-resistant and chemically stable inorganic oxide pigments with thermosensitivity would be useful in many applications and in various environments [1]. Temperature indicators composed of inorganic materials that undergo a structural phase transition take an advantage of showing a drastic change in color at a desired temperature in comparison with oxides [2] such as Cr-doped Al_2O_3 ruby due to their thermal expansion, $BaMnO_3$ [3], MoO_3 [4], and VO_2 [5–7] due to a transition from insulator to metal. However, few inorganic oxides exhibiting a distinct color change in the range of RT to 100 °C have been reported.

Recently, there have been some reports on $CuMoO_4$ with the temperature and pressure dependence of the optical and magnetic properties [8–11]. There are two copper molybdenum oxide ($CuMoO_4$) phases under an atmospheric pressure [12,13]: one is a reddish brown γ-$CuMoO_4$ phase that is stable at low temperatures and the other is a green α-$CuMoO_4$ phase that is stable at high temperatures [1]. The α phase undergoes a structural phase transition to the γ phase at low temperatures, whereas the γ phase undergoes a transition to the α phase at high temperatures. Thus, the structural phase transition of $CuMoO_4$ is reversible with respect to temperature and brings about a distinct change in color with temperature [1,14]. The crystal structure of the γ phase consists of octahedral CuO_6 and MoO_6. In the structural phase transition to the α phase, one-third of the octahedral CuO_6 changes to square-pyramidal CuO_5, and all of the octahedral MoO_6 changes to tetrahedral MoO_4 [9,12,13,15].

$CuMoO_4$ compounds would be expected to be thermosensitive inorganic oxide pigments showing a distinct change in color with temperature by inducing a structural phase transition from the γ phase to the α phase in the range of RT to 100 °C. However, two problems were reported: the phase transition temperature of $CuMoO_4$ was approximately -75 °C and the hysteresis of the phase

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transition temperature was increased by repeating the reversible phase transition [1,14,16,17]. The hysteresis of $CuMoO_4$ indicates the difficulty in returning the α phase to the γ phase due to the shift of the phase transition temperature to a lower temperature [1,14]. However, an influence of the repetition of the reversible phase transition on color parameters of $CuMoO_4$ has not been reported so far.

In this study, we partially replaced Mo with W in $CuMoO_4$ and changed the production ratio of the γ and α phases in $CuMoO_4$ by using liquid nitrogen. Then thermochromic behaviors, calorimetric parameters, and reversible phase transition behaviors of the synthesized W-substituted $CuMoO_4$ compounds were examined by X-ray diffractometry (XRD), differential scanning calorimetry (DSC), and ultraviolet–visible–near-infrared spectrophotometry (UV–vis–NIR).

2. Experimental

Aqueous solutions of copper nitrate, ammonium molybdate, and ammonium metatungstate were mixed to obtain a molar ratio of Cu:Mo:W = 1:1 − x:x (x = 0.04–0.12). The mixed solution was stirred on a hot plate and then evaporated to obtain precursor powder. $CuMo_{1-x}W_xO_4$ (x = 0.04–0.12) powder was synthesized by heating the precursor powder at 550–600 °C for 24 h in air. The crystalline phase of the synthesized powder was identified by powder X-ray diffractometry (XRD; 40 kV, 30 mA, RINT2000, Rigaku, Japan). The synthesized powder was cooled in liquid nitrogen for 5 min. The structural phase transition behavior was examined by differential scanning calorimetry (DSC; Seiko Instruments, Japan) in the range of RT to 140 °C with a heating rate of 5 °C min^{-1}. The changes in the reflectance spectra and color of the powders in the range of RT to 100 °C upon heating were examined using a diffuse reflectance ultraviolet–visible–near infrared spectrophotometer in the wavelength range of 400–800 nm (UV–vis–NIR; V670, Jasco, Japan).

3. Results and discussion

Fig. 1(a) shows the XRD patterns at RT of the as-synthesized $CuMo_{1-x}W_xO_4$ (x=0.04–0.12) powders. All the synthesized powders were confirmed to be a single phase W-substituted $CuMoO_4$ compound [13] by referring to the ICDD card of No. 22-0242. The ratio of the γ phase increased with increasing x value in $CuMo_{1-x}W_xO_4$. Fig. 1(b) shows the XRD patterns at RT of the powders after cooling using liquid nitrogen. In the case of x=0.06, almost all of the α phase of $CuMo_{1-x}W_xO_4$ (x=0.06) underwent a structural phase transition to the γ phase, and in the case of x=0.04, approximately 50% of the α phase of $CuMo_{1-x}W_xO_4$ (x=0.04) underwent a structural phase transition to the γ phase. On the other hand, in the case of x=0.08 or higher, a single γ phase was obtained. Thus, among the synthesized powders, the cooling treatment was particularly effective for the $CuMo_{1-x}W_xO_4$ (x=0.06) powder in the viewpoint of increasing the ratio of γ phase.

Fig. 2 shows the relationship between x in $CuMo_{1-x}W_xO_4$ and the temperature at which $CuMo_{1-x}W_xO_4$ underwent a structural phase transition from the γ phase to the α phase. The structural phase transition temperature of $CuMo_{1-x}W_xO_4$ increased with increasing x, suggesting that the structural phase transition temperature was influenced by the W content. Fig. 3(a) and (b) shows the thermal changes in the diffuse reflectance spectra of the $CuMo_{1-x}W_xO_4$ (x=0.06) and (x=0.12) powders, respectively, before and after cooling using liquid nitrogen. There were two absorption bands in the spectra of the $CuMo_{1-x}W_xO_4$ powders.

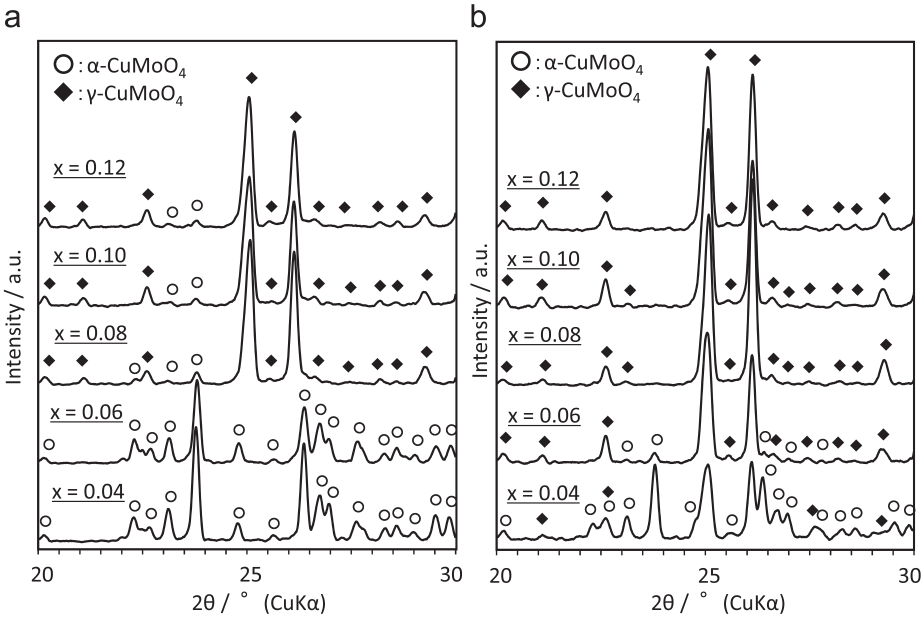

Fig. 1. XRD patterns of $CuMo_{1-x}W_xO_4$ (x=0.04–0.12) powders at RT (a) before and (b) after cooling.

The absorption band at a long wavelength above approximately 600 nm was mainly attributed to the d–d transition of Cu^{2+} [9,15], and that at a short wavelength below approximately 600 nm was mainly attributed to the charge transfer transitions of $O^{2-} \rightarrow Cu^{2+}$ and $O^{2-} \rightarrow Mo^{6+}$ [1,9,15]. Before cooling the powder, there was no significant difference between the diffuse reflectance spectra of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder at RT (solid line ①) and 100 °C (dotted line ②). In contrast, after cooling the powder, there was a significant difference between the diffuse reflectance spectra of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder at RT (dotted line ③) and 100 °C (dotted line ④). This is because the ratio of the γ phase in the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder at RT was increased by cooling using liquid nitrogen. The thermal change in diffuse reflectance spectra observed at approximately 500–600 nm for the $CuMo_{1-x}W_xO_4$ ($x=0.06$ and 0.12) powders was considered to correspond to the change in the coordination number associated with the phase transition from the γ phase (octahedral CuO_6) to the α phase (square-pyramidal CuO_5) [15]. On the other hand, the thermal change in the diffuse reflectance spectra was limited for the $CuMo_{1-x}W_xO_4$ ($x=0.12$) powder even though the ratio of the γ phase in the powder at RT was higher than in the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder. This is because the structural phase transition temperature of the $CuMo_{1-x}W_xO_4$ ($x=0.12$) powder was around 100 °C, as shown in Fig. 2.

As for the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder, which exhibited a significant change in the diffuse reflectance spectra in the range of RT to 100 °C, the effect of repeated heating and cooling on the behavior of the structural phase transition was examined by DSC. The result is shown in Fig. 4. As the repetition time increased (corresponding to

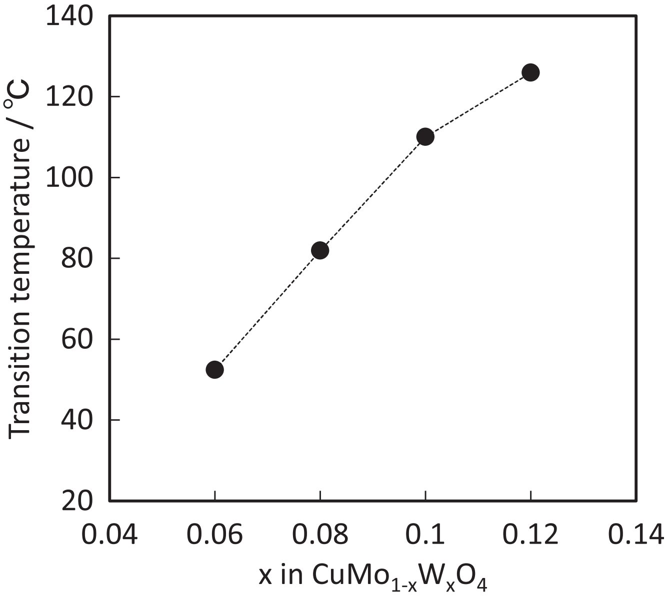

Fig. 2. Relationship between phase transition temperature and x of $CuMo_{1-x}W_xO_4$ ($x=0.06$–0.12) powders determined from endothermic peaks of DSC curves.

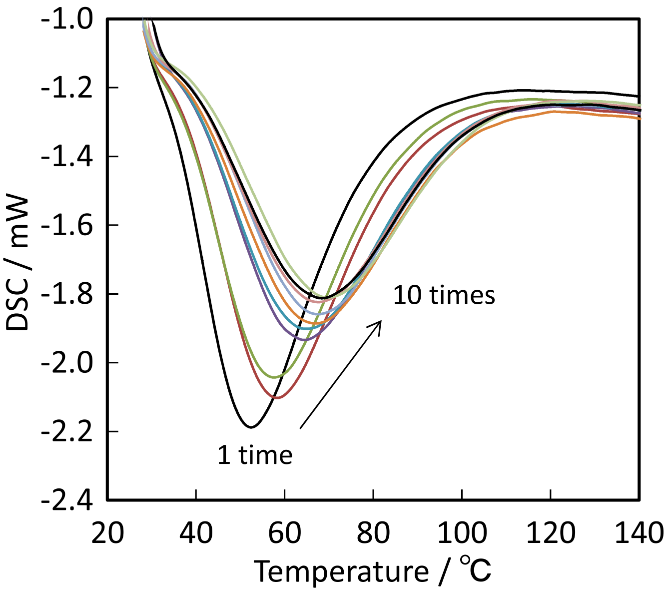

Fig. 4. DSC curves of $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder in the range of RT to 140 °C. The number of cooling times increases in the direction of the arrow (1–10).

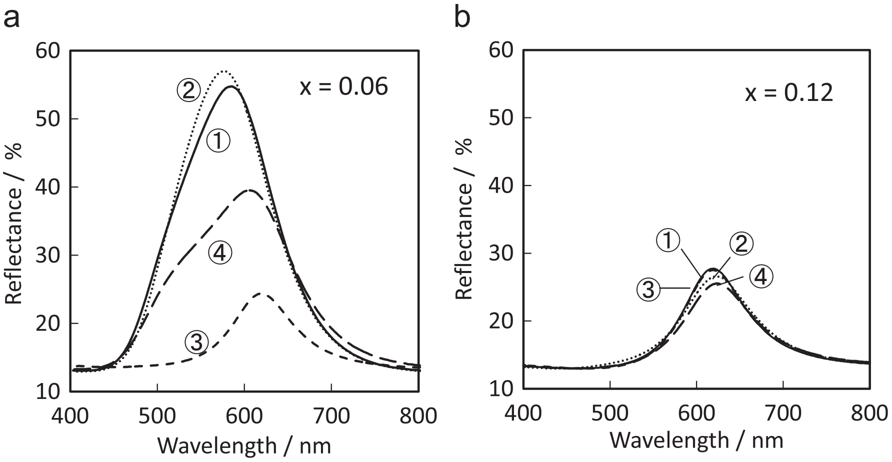

Fig. 3. Diffuse reflectance spectra of (a) $CuMo_{1-x}W_xO_4$ ($x=0.06$) and (b) $CuMo_{1-x}W_xO_4$ ($x=0.12$) powders at RT and 100 °C ① before cooling (RT), ② before cooling (100 °C), ③ after cooling (RT), and ④ after cooling (100 °C).

the direction of the arrow), the phase transition temperature increased. The endothermic peak area of the above DSC curve decreased and the phase transition temperature gradually decreased with increasing repetition time as shown in Fig. 5. After 10 times repetition, the endothermic peak area decreased by approximately 20%. However, the rate of decrease in the endothermic peak area gradually lowered with increasing repetition time, which indicates that the phase transition became saturated. This result indicates that a certain level of thermochromic behavior for the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder was retained even after the 10 times repetition. Fig. 6 shows the XRD patterns of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder at RT after cooling one, five, and ten times. With increasing number of cooling times, the ratio of the α phase in the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder increased and it reached approximately 26% after cooling 10 times. It was therefore found that the decrease in the endothermic peak area with increasing number of cooling times as shown in Fig. 4 was due to the increase in the ratio of the α phase in the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder.

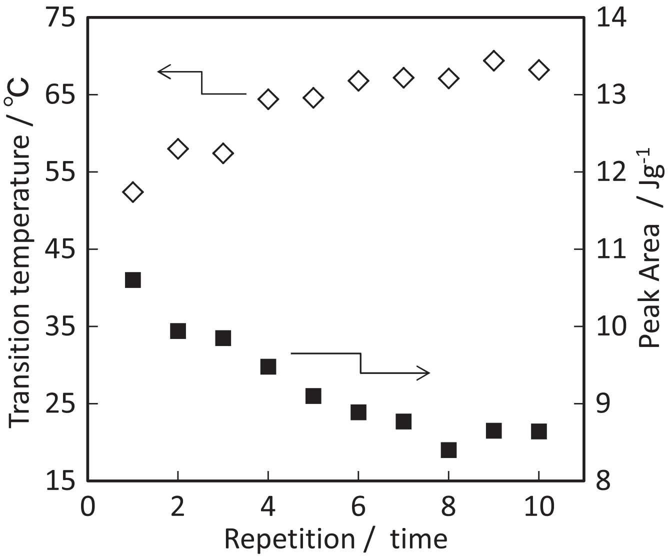

Fig. 5. Changes of phase transition temperature and endothermic peak area of DSC for $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder with increasing number of cooling times.

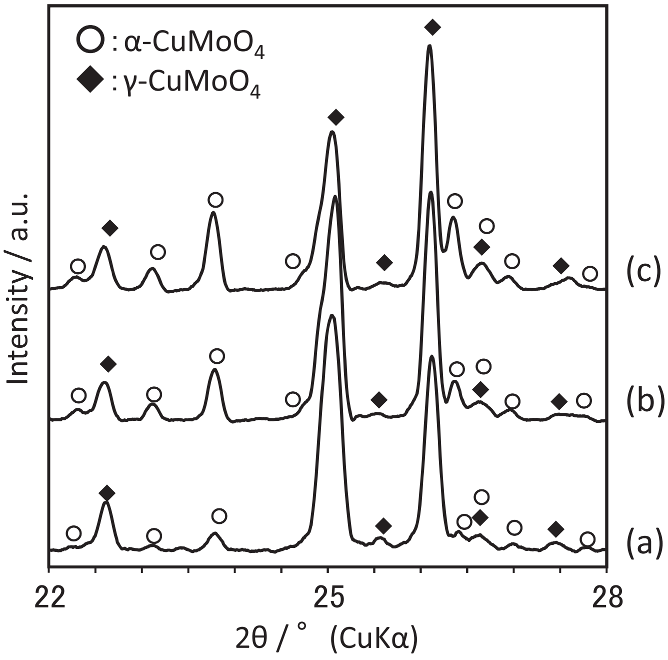

Fig. 6. XRD patterns of $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder after cooling (a) one, (b) five, and (c) ten times.

Fig. 7(a) and (b) shows the thermal changes in color parameters of a^* and b^* in the range of RT to 100 °C, on heating, of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) and $CuMo_{1-x}W_xO_4$ ($x=0.12$) powders, respectively. Fig. 7(a) shows that the thermal change in color of the non-cooled $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder (①) was limited because the ratio of the γ phase was small at RT. On the other hand, after cooling one time (②), the color parameters of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder significantly changed in the range of RT to 100 °C because the ratio of the γ phase at RT was increased. A thermal change in color parameters of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder cooled 10 times (③) was also clearly observed. In contrast, Fig. 7(b) shows that the thermal change in color parameters was limited for the $CuMo_{1-x}W_xO_4$ ($x=0.12$) powder even though the ratio of the γ phase at RT was higher than that of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder. This is because the $CuMo_{1-x}W_xO_4$ ($x=0.12$) powder underwent the structural phase transition at around 100 °C.

As shown in Fig. 7(a), there were two stages of thermal change in color parameters. In the case of the $CuMo_{1-x}W_xO_4$ ($x=0.12$) powder cooled one or 10 times, after both the color parameters of a^* and b^* slightly decreased due to the thermal expansion of the γ phase, a^* and b^* significantly decreased and increased, respectively, due to the phase transition from the γ phase to the α phase. This is because the ratio of the γ phase in the powder at RT was increased by the cooling treatment. In contrast, as shown in Fig. 7(b), in the case of the $CuMo_{1-x}W_xO_4$ ($x=0.12$) powder, the ratio of the γ phase that underwent the phase transition to the α phase was limited regardless of the number of cooling times. This is because the phase transition temperature was around 100 °C. As a result, the decrease in a^* and the increase in b^* due to the phase transition were limited. Fig. 8(a) and (b) shows the color photographs of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) and $CuMo_{1-x}W_xO_4$ ($x=0.12$) powders, respectively, obtained at RT and on heating to 50, 80, and 100 °C. As for the brown $CuMo_{1-x}W_xO_4$ ($x=0.12$) powder with the phase transition temperature around 100 °C, no significant change in color with temperature was observed. However, as for the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder with the phase transition temperature around 60 °C, a thermal change from brown to yellow was clearly observed in the range of RT to 100 °C even after the 10 times repetition.

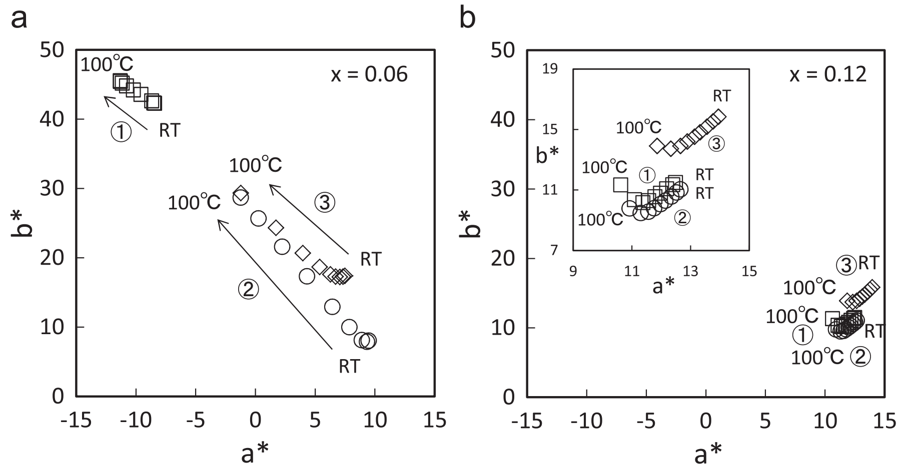

Fig. 7. Change in color parameters (a^* and b^*) of (a) $CuMo_{1-x}W_xO_4$ ($x=0.06$) and (b) $CuMo_{1-x}W_xO_4$ ($x=0.12$) powders in the range from RT to 100 °C after cooling ① zero, ② one, and ③ ten times.

Fig. 8. Change in color of (a) $CuMo_{1-x}W_xO_4$ ($x=0.06$) and (b) $CuMo_{1-x}W_xO_4$ ($x=0.12$) powders in the range from RT to 100 °C.

4. Conclusions

W-substituted $CuMoO_4$ compounds, $CuMo_{1-x}W_xO_4$ ($x=0.04$–0.12), were synthesized by a liquid-phase method. The ratio of the γ phase, that is stable at low temperatures, was increased by cooling the synthesized powder using liquid nitrogen. The ratio of the γ phase in the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder was most efficiently increased by the cooling treatment. The $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder showed the largest change in the diffuse reflectance spectra in the visible light region with increasing temperature ranging from RT to 100 °C because the temperature of the structural phase transition from the γ phase to the α phase was in the above temperature range. Consequently, it was found that the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder with large amount of the γ phase clearly exhibits the thermochromic behavior in the range of RT to 100 °C. Even after the 10 times repetition of heating and cooling, the thermal change in color of the $CuMo_{1-x}W_xO_4$ ($x=0.06$) powder was recognized.

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