

Synthesis of Tungstate Thin Films and Their Optical Properties

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A simple and new synthetic method of tungstate thin films (CaWO_4 , MgWO_4 , PbWO_4 , ZnWO_4) was developed. The absorption and luminescence spectra of tungstate thin films synthesized on quartz substrates were measured; the optical properties were also studied. It was found that CaWO_4 has $E_g = 5.4$ eV of a direct transition nature. Tungstate thin films were strongly luminescent when irradiated with UV-light. Excitation at around 290 nm was interpreted as a singlet-triplet transition.

Tungstates represented by CaWO_4 have been widely used as typical fluorescents^{1,2)} for a long time. Various techniques to synthesize tungstates, such as a solid-state reaction for powders,³⁾ a flux method for whiskers,⁴⁾ the Czochralski method for single crystals,^{5,6)} and an electrochemical method for a highly crystallized luminescent CaWO_4 film at room temperature⁷⁾ have been used.

In spite of many studies of the luminescence properties of tungstates,^{1–9)} there are only few reports on the absorption properties of tungstates.^{8,10)} In a measurement of the transmittance absorption spectra of CaWO_4 single crystals^{8,10)} the absorption at wavelengths shorter than 270 nm (4.6 eV) becomes saturated because of the thickness (e.g. 2.7 mm). To our knowledge, there is no absorption data presently available at shorter wavelengths for the tungstates.

It is important to measure these transmittance absorption spectra in order to clarify the mechanism of the luminescence of tungstates. To measure these shorter wavelength transmittance-absorption spectra, transparent samples with little light scattering are desirable. Since the light scattering of a single crystal is small, it is desirable to synthesize thin single crystals for an absorption measurement. However, the synthesis of thin single crystals is difficult. Highly crystallized CaWO_4 films were prepared on a W electrode, which is not transparent at room temperature by the electrochemical method.⁷⁾ Tungstate thin films on a transparent substrate would be desirable to measure the transmittance-absorption spectra. However, no simple synthetic method of tungstate thin films is yet known.

In this study, tungstate thin films were prepared by reacting various metal oxide thin films with WO_3 vapor. A synthetic method to produce these films was studied. The absorption characteristic and the luminescence characteristic were studied by measuring the opto-physical properties of these films.

Experimental

Non-fluorescent quartz plates (10 mm×20 mm×3 mm) were

washed with hot aqua regia and rinsed with distilled water. After they were immersed in a 20% HF aqueous solution for 10 min they were rinsed with distilled water and ethanol. These quartz plates were used as substrates. Metal films (Ca, Mg, Pb, Zn; 0.1–1 μm) deposited on these substrates by vacuum evaporation ($< 5 \times 10^{-3}$ Pa, evaporation rate; 0.5–5 nm s^{-1}) were oxidized in the air at 1000 °C for 10 h. These oxide films were exposed to WO_3 vapor in a reaction cell (Fig. 1) at 1000 °C for 10 h.

The crystal structures of these films were analyzed by X-ray diffraction (XRD) (JEOL, JDX-85). The surface conditions were observed on a scanning electron micrograph (SEM) (JEOL, JSM-T220). The compositions of these films were analyzed on an energy-dispersive X-ray spectrometer (EDX) (Philips, PV9900). The thicknesses of the films were measured on a surface profiler (Sloan, Dektak³⁾). The transmittance absorption spectra were measured using a UV-vis scanning spectrophotometer (Shimadzu, UV-2100PC) in the air at room-temperature. The absorption coefficient of synthesized tungstate thin films was determined from these thicknesses and the absorbance. Photoluminescence spectra were measured by a spectrofluorometer (SPEX, Fluoromax[®]) in the air at room-temperature. The excitation light power was corrected by using a radiometer (The Eppley Laboratory, 21666). The photomultiplier tube sensitivity was not corrected.

Results and Discussion

The adhesion of metal thin films on a quartz plate has been improved by a treatment in a HF solution. XRD patterns of

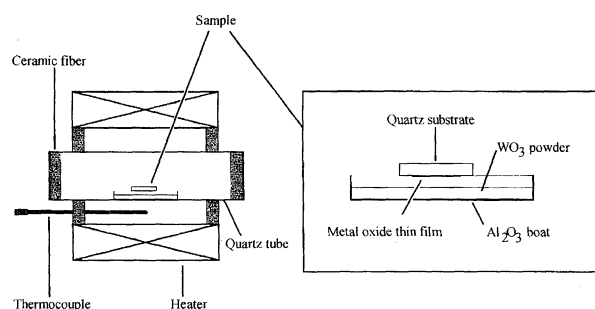


Fig. 1. Schematic illustration of the apparatus for preparing various tungstate films.

oxidized-metal thin films agreed well with the XRD patterns of these metal oxide powders. Figure 2 shows an SEM photograph of a thin film prepared by the reaction of an oxidized Zn thin film with WO_3 vapor at 1000 °C. This Fig. 2 indicates that the film comprises tiny crystals of ca. $2 \times 5 \mu\text{m}$. Figure 3 shows XRD patterns of the oxidized Mg thin film after a reaction with WO_3 vapor and those of MgWO_4 powder. These XRD patterns agree well with each other. The XRD patterns of thin films prepared by this method agree well with those of corresponding tungstates. Table 1 summarizes the results of an EDX analysis. It shows that (Ca, Mg, Pb, Zn) and W are included in a ratio of

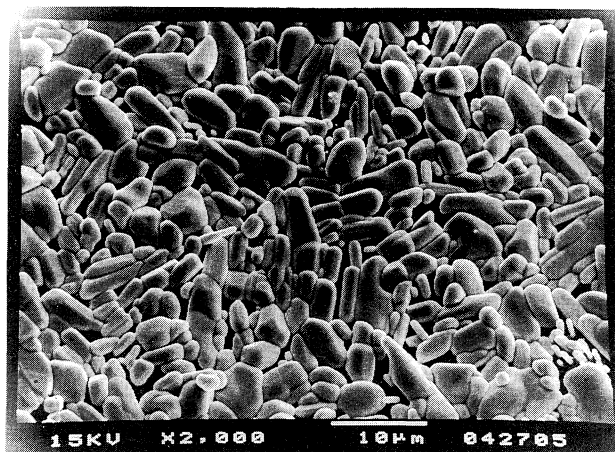


Fig. 2. Scanning electron micrograph of the thin film prepared from ZnO and WO_3 at 1000 °C.

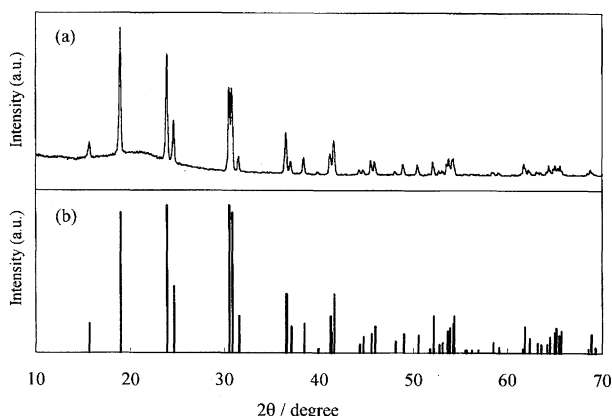


Fig. 3. XRD patterns of (a) the oxidized Mg thin film after the reaction with WO_3 vapor and (b) MgWO_4 powder determined from "data of joint committee on powder diffraction standards" (JCPDS; 27—789).

Table 1. Energy-Dispersive X-Ray Spectrometry Results of Various Tungstate Films

Films	Ratio (Ca, Mg, Pb, Zn) : W
CaWO_4	1.00 : 0.91
MgWO_4	1.00 : 0.79
PbWO_4	1.00 : 0.92
ZnWO_4	1.00 : 1.07

1 : 1 in these films. These results have clarified that various tungstate films can be synthesized by this method. However, when these reactions were carried out at a temperature lower than 700 °C, tungstate thin films were not synthesized. The above-mentioned results suggest that this reaction proceeds according to the thermal reactions shown in the following Eqs. 1 and 2:

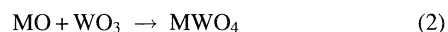
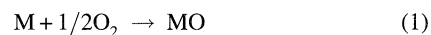


Figure 4 shows the absorption spectra of synthesized tungstate thin films. Figures 5 and 6 show the absorption spectra of Na_2WO_4 aqueous solutions in the low- and high-energy regions, respectively. As shown in Fig. 4, the absorption of these synthesized tungstate thin films starts from about 4—5 eV (250—310 nm). Their absorption coefficients at 6.2 eV (200 nm) are $2.9 \times 10^5 \text{ cm}^{-1}$; CaWO_4 , $2.5 \times 10^5 \text{ cm}^{-1}$; MgWO_4 , $2.4 \times 10^5 \text{ cm}^{-1}$; PbWO_4 , $2.5 \times 10^5 \text{ cm}^{-1}$; ZnWO_4 respectively. As shown in Fig. 5, the absorption of Na_2WO_4 in an aqueous solution has only weak absorption at around 4—5 eV (300—250 nm). As shown in Fig. 6,

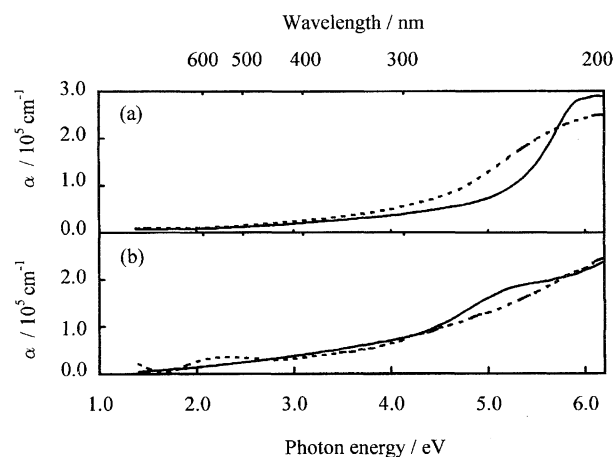


Fig. 4. Absorption spectra of CaWO_4 (a, —), MgWO_4 (a, ···), PbWO_4 (b, —), and ZnWO_4 (b, ···) thin films.

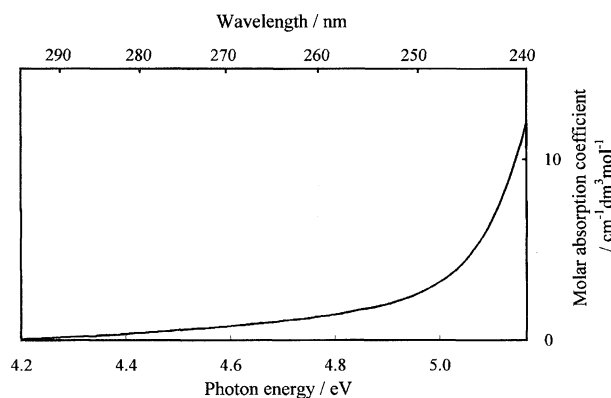


Fig. 5. Absorption spectrum of Na_2WO_4 aqueous solution in a low energy region.

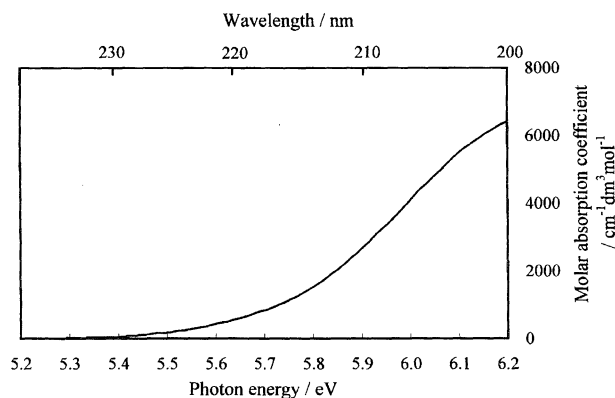


Fig. 6. Absorption spectrum of Na_2WO_4 aqueous solution in a high energy region.

peak near 6.2 eV (200 nm). The molar absorption coefficient of the Na_2WO_4 aqueous solution at 6.2 eV (200 nm) is $6400 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$. The absorption observed both in synthesized tungstate thin films and in Na_2WO_4 aqueous solution is assigned to the absorption based on the charge transfer (CT absorption) between the oxygen ions and the tungsten ion in a tungstate ion.²⁾ From the formula weight and density of CaWO_4 , the concentration of CaWO_4 in this thin film is estimated to be 21 mol dm^{-3} . The molar absorption coefficient of CaWO_4 thin film is estimated to be $12000 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$. This value is twice as large as that of the Na_2WO_4 aqueous solution. Although the concentration of the tungstate ions in the solid film is much larger than that in aqueous solution, these absorption spectra and those absorption coefficients are essentially the same as those of the tungstate ion in aqueous solution. This suggests that the interaction between tungstate ions at the excited state in the solid state is not large. Therefore, the electronic structure of these solid tungstates is essentially the same as that of WO_4^{2-} in the solution. Figure 7 indicates the excitation and emission spectra of the synthesized tungstate thin films. When synthesized tungstate thin films are irradiated with 4.0–5.0 eV (250–310 nm) UV-light, they showed luminescence with a

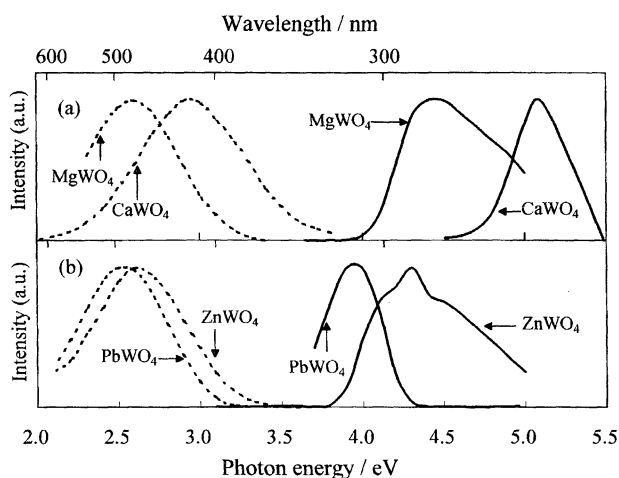


Fig. 7. Excitation (—) and emission (....) spectra of CaWO_4 , MgWO_4 , PbWO_4 , and ZnWO_4 thin films.

peak near 2.5–2.8 eV (440–500 nm). These luminescence properties of tungstate thin films agreed well with those of tungstate powders synthesized from metal oxide and WO_3 powder by heating in air.^{2,11)} This luminescence has been ascribed to the triplet–singlet transition ($^3\text{T}_1 \rightarrow ^1\text{A}_1$).²⁾ These results have clarified that luminescent tungstate thin films can be synthesized by the present method.

As shown in Fig. 7, peaks of the excitation spectra are observed at about 4–5 eV (300–250 nm). Interestingly, absorption peaks corresponding to the peak in the excitation spectra are not observed in the absorption spectra of Fig. 4, though such absorption was suggested to exist.¹¹⁾ Moreover, as shown in Fig. 5, the molar-absorption coefficient in 5.0 eV (250 nm) of Na_2WO_4 aqueous solution is extremely small, $2.59 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$. So far, these films of the tungstate ion have shown only weak absorption at around 4–5 eV (300–250 nm), the peaks of the excitation spectra, though it has been expected that there is a singlet–singlet transition ($^1\text{A}_1 \rightarrow ^1\text{T}_1$) in the vicinity of 4–5 eV (300–250 nm) corresponding to the peak of the excitation spectra.¹¹⁾ The fact that tungstate thin films show luminescence under irradiation with 4–5 eV (300–250 nm) where the tungstate ion has weak absorption can not be explained by the idea that there exists a singlet–singlet transition corresponding to the excitation spectra at around 4–5 eV (300–250 nm).¹¹⁾ This excitation is reasonably explained by assuming that the excitation at around 4–5 eV (300–250 nm) is based on a singlet–triplet transition ($^1\text{A}_1 \rightarrow ^3\text{T}_1$). The singlet–triplet transition is spin forbidden, and the transition probability is small. However, the prohibition loosens for the tungstate ion by a heavy atom effect of tungsten, and the transition probability increases. Actually, the luminescence of tungstates has been ascribed to the triplet–singlet transition ($^3\text{T}_1 \rightarrow ^1\text{A}_1$).²⁾ The luminescence lifetime of CaWO_4 is about 10 μs with a high quantum yield.⁸⁾ It is generally agreed that the top-most filled molecular orbitals of T_d entity are $1e$, $2t_2$, $2a_1$, $3t_2$, and $1t_1$.⁹⁾ The lowest-energy transition is usually of the $t_1 \rightarrow 2e$ type.⁹⁾ This orbital excitation gives rise to four excited states: $^1\text{T}_2$, $^3\text{T}_2$, $^1\text{T}_1$, and $^3\text{T}_1$.⁹⁾ It is conceded that the allowed electric-dipole transition is $^1\text{A}_1 \rightarrow ^1\text{T}_2$.^{9,12,13)} Consequently, it seems reasonable to ascribe the strong absorption band at 6.2 eV (200 nm) to the $^1\text{A}_1 \rightarrow ^1\text{T}_2$ transition.

We now consider that energy levels and transitions shown in Fig. 8, where 1 represents the ground state ($^1\text{A}_1$), 2 is

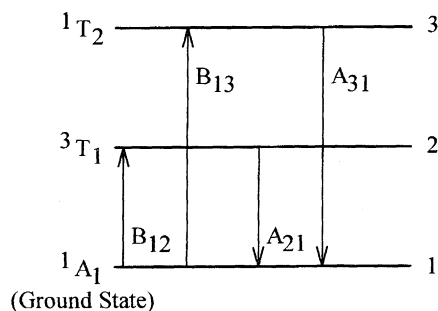


Fig. 8. Schematic illustration of energy levels and transitions in tungstate.

3T_1 and 3 is 1T_2 . The transition probabilities of spontaneous emission from excited states 3 and 2 to the ground state 1 are A_{31} and A_{21} , respectively. The transition probabilities of absorption from the ground state to excited states 2 and 3 are expressed as B_{12} and B_{13} , respectively.

From the Einstein's theory of radiation^{14,15)}

$$A_{21} = \frac{\hbar\omega_{12}^3}{\pi^2 c^3} \cdot \frac{g_1}{g_2} \cdot B_{12} \quad (3)$$

and

$$A_{31} = \frac{\hbar\omega_{13}^3}{\pi^2 c^3} \cdot \frac{g_1}{g_3} \cdot B_{13} \quad (4)$$

are obtained. Here, g_1 , g_2 , and g_3 are the degeneracies at the 1, 2, and 3 states, respectively. In the present system, $g_1=1$, $g_2=3$, and $g_3=1$. $\hbar\omega_{12}$ and $\hbar\omega_{13}$ indicate the energies of transitions 1→2 and 1→3, respectively. From Eqs. 3 and 4

$$\frac{B_{12}}{B_{13}} = 3 \left(\frac{\omega_{13}}{\omega_{12}} \right)^3 \cdot \frac{A_{21}}{A_{31}} \quad (5)$$

is obtained. When the experimental values of $\hbar\omega_{12}=5.0$ eV (250 nm) and $\hbar\omega_{13}=6.2$ eV (200 nm) are used,

$$\left(\frac{\omega_{13}}{\omega_{12}} \right)^3 = \left(\frac{\hbar\omega_{13}}{\hbar\omega_{12}} \right)^3 = 1.91 \quad (6)$$

is obtained. Since B_{12}/B_{13} is considered to be equal to the ratio of the absorption coefficients at 5.0 eV (250 nm) and 6.20 eV (200 nm) for a Na_2WO_4 aqueous solution,

$$\frac{B_{12}}{B_{13}} = \frac{2.59}{6400} = 4.05 \times 10^{-4} \quad (7)$$

is obtained. On the other hand, the luminescence lifetime of CaWO_4 (10 μs) is equal to A_{21}^{-1} ,

$$A_{21} = \frac{1}{10 \times 10^{-6} \text{ s}} \quad (8)$$

By using these values for Eq. 5,

$$A_{31}^{-1} = \frac{1}{1.42 \times 10^9 \text{ s}^{-1}} = 7.0 \times 10^{-10} \text{ s} = 700 \text{ ps} \quad (9)$$

is obtained. This value seems to be reasonable as the lifetime of a singlet–singlet allowed transition. This result is consistent with the present assumption that this long-wavelength excitation at around 4–5 eV (300–250 nm) is the singlet–triplet transition ($^1A_1 \rightarrow ^3T_1$).

As shown in Fig. 4, the absorption coefficients at 4.3 eV (290 nm) of these films are about 1/10 of the absorption coefficient at 6.2 eV (200 nm); they are stronger than the absorption coefficient at 4.3 eV (290 nm) of the tungstate ion in the aqueous solution. This would be caused by light scattering by microcrystals in these thin films. Although we tried to decrease the light scattering by immersing the tungstate films in transparent solvents, it was impossible to completely remove the effect of light scattering on the absorption at around 4.3 eV (290 nm). Therefore, at the present stage of research, we can not neglect the possibility that this absorption comprises forbidden singlet–singlet transitions, as discussed by McGlynn et al. in the case of molybdates.⁹⁾

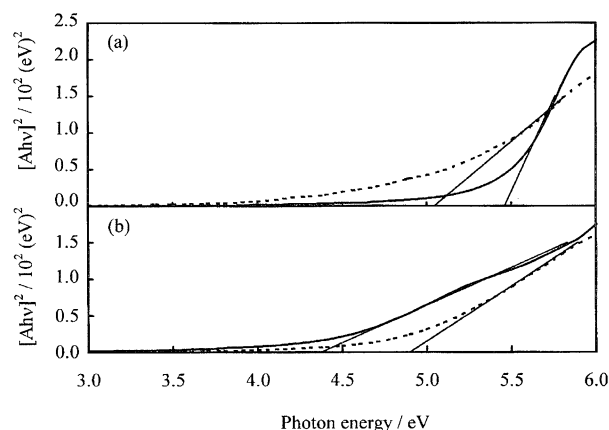


Fig. 9. $(Ah\nu)^2$ vs. $h\nu$ plots for CaWO_4 (a, —), MgWO_4 (a,), PbWO_4 (b, —), and ZnWO_4 (b,) thin films.

A further study using thin single crystals would be important to solve this problem.

Generally speaking Eq. 10 holds between the absorption (A) of a material with a band gap (E_g) and a photon energy of $h\nu$,¹⁶⁾

$$A = k(h\nu - E_g)^{n/2} / h\nu, \quad (10)$$

where k and n are constants. For a material of direct transition, n is equal to 1. For a material of indirect transition n is 4. Thus, when $(Ah\nu)^2$ is proportional to $(h\nu)$ it can be considered that the absorption is of direct transition type. In order to determine the band gaps (E_g) of these films, $(Ah\nu)^2$ was calculated from the absorbance of tungstate thin films (A) and the photon energy. Figure 9 shows $(Ah\nu)^2$ plotted against $h\nu$. A part of $(Ah\nu)^2$ of the synthesized tungstate thin films increased straight with an increase in $h\nu$. On the other hand, such a straight relation was not observed between $(Ah\nu)^{1/2}$ and $h\nu$. This demonstrates that the strong absorption band at 6.2 eV (200 nm) of these synthesized tungstate thin films is of the direct transition type. The band gaps (E_g) of tungstates ($E_g=5.4$ eV; CaWO_4 , $E_g=5.0$ eV; MgWO_4 , $E_g=4.4$ eV; PbWO_4 , $E_g=4.9$ eV; ZnWO_4) were estimated for the first time from the intercept of the x axis by this method.

Conclusion

A simple and new synthetic method of tungstate thin films was developed in order to measure the transmittance absorption spectra of these tungstates. Strong visible luminescence was observed when synthesized tungstate thin films were irradiated with UV-light. Tungstates excitation in the small absorption coefficient range could be reasonably explained based on the singlet–triplet transition. The band gaps of the tungstates were found to be much larger than the onsets of excitation.

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