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# Fabrication of luminescent SrWO<sub>4</sub> thin films by a novel electrochemical method

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#### Abstract

Highly crystallized  $SrWO_4$  thin films with single scheelite structure were prepared within 60 min by a cell electrochemical method. X-ray diffraction analysis shows that  $SrWO_4$  thin films have a tetragonal structure. Scanning electron microscopy examinations reveal that  $SrWO_4$  grains grow well in tetragonal tapers and grains like flowers or bunches, which can usually form by using the electrolysis electrochemical method, have disappeared under cell electrochemical conditions. X-ray photoelectron spectra and energy dispersive X-ray microanalysis examinations demonstrate that the composition of the film is consistent with its stoichiometry. These  $SrWO_4$  films show a single blue emission peak (located at 460 nm) using an excitation wave of 230 nm. The speed of cell electrochemical method can be controlled by changing temperature. The optimum treatment temperature is about 50–60 °C.

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# 1. Introduction

Scheelite-structured tungstates and molybdates are good laser host materials [1–4], particularly for pulsed lasers [5]. They are also important materials in electrooptics due to their blue or green luminescence [6,7]. They remain a tetragonal structure over wide range of temperatures [3] and pressures [8]. For this reason, they may become the first-chosen materials under some extreme environments.

It is generally agreed that a thin film phosphor has superior resolution compared to powders because of their inherently smaller grain size and less lateral scattering. Various film preparation methods, such as sputtering [9], vacuum evaporation [10], pulsed-laser deposition [11] and spray pyrolysis [12], have been adopted to prepare AMO<sub>4</sub> (A = Ca, Sr, Ba; M = Mo, W) thin films. But such films as-prepared show no luminescence [9,12] because of poor crystallization. In order to obtain good quality films, heat treatments (500–1100 °C) are necessary. This not only consumes a huge amount of energy but also is apt to produce impurity phases [9]; at the same time, this leads to Schottky defects and poor adhesion. These problems make it important to develop new ways to prepare thin films without or with lower temperature annealing treatment.

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Ever since the end of last century, electrochemical methods, such as galvanostatic or potentiostatic methods, have been widely used to prepare AMO<sub>4</sub> (A = Ca, Sr, Ba; M = Mo, W) films [13–18]. Advantages of electrochemical coating techniques over conventional techniques have been summarized by Switzer [19]. During the course of reactions, energy in form of currents or potentials should be supplied by electrochemical apparatuses.

But the following investigations reveal that such energy is unnecessary for preparations of AMO<sub>4</sub> (A = Ca, Sr, Ba; M = Mo, W) films. According to the Pourbiax Diagram [20], in alkaline solutions tungsten exists  $WO_4^{2^-}$  ions:

$$W + 8OH^{-} \rightarrow WO_{4}^{2-} + 4H_{2}O + 6e$$
 (1)

Handbook on Standard Potential of Electrode Reaction [21] shows that the standard potential of  $WO_4^{2-}/W$  is -1.05 V versus normal hydrogen electrode.

The following equation [22] shows the relation between the loss of Gibbs energy and standard potential.

$$\Delta G^0 = nFE^0 \tag{2}$$

where  $\Delta G^0$  stands for the loss of Gibbs energy (J), *n* refers to the number of electron transferred in reaction [1], *n* equals 6 and  $E^0$  is the standard electrode potential of WO<sub>4</sub><sup>2-</sup>/W.

From formula (2), it can be concluded that reaction (1) (i.e., metal corrosion) occurs spontaneously with an accompanying negative loss of Gibbs energy.

Since tungsten metal becomes solvated ions in alkaline solutions spontaneously, it is unnecessary to supply energy to make reaction (1) work. Our attention will be rather concentrated on applications of the spontaneous dissolution phenomenon (i.e., corrosion) to synthesize crystalline AMO<sub>4</sub> (A = Ca, Sr, Ba; M = Mo, W) thin films directly.

In general, it is unpractical to prepare functional ceramic thin films using pure corrosion because of its low rate. To overcome the slow rate of natural corrosion, we have proposed cell electrochemical techniques [23]. It is well-known that two different metals generally have different potentials when dipped in an electrolyte. While connected by wires or conductors, they constitute a cell so that electrons can transfer from one metal to the other efficiently. The method based on cell and metal's spontaneous corrosion phenomenon is called cell electrochemical technique. It has its own characteristics:

(1) it has two different electrodes which can constitute a cell;

- (2) one electrode acts as reducer;
- (3) electrode reactions happen spontaneously.

It is interesting that scheelite-typed crystalline  $AMO_4$  (A = Ca, Sr, Ba; M = Mo, W) thin films have been successfully prepared by cell electrochemical methods in our research group. As far as we know, this is the first time that cell electrochemical methods have been used to prepare functional ceramic thin films directly. This paper is devoted to the fabrication of luminescent SrWO<sub>4</sub> thin films by this novel method.

## 2. Experimental procedure

Tungsten (20 mm  $\times$  10 mm  $\times$  0.1 mm, with purity of 99.5%) and platinum plates were used as the anode and cathode, respectively. An Ag/AgCl (saturated KCl) standard electrode was used as reference electrode.

After being polished mechanically, the tungsten plates were pretreated with degreasing and ultrasonic cleaning. The electrolyte was prepared from  $SrCl_2 \cdot 6H_2O$  (with purity of 99.5%) and NaOH (with purity of 96%). The concentration of  $Sr^{2+}$  ions was 0.4 mol/l. Before experiments, solutions were purged with N<sub>2</sub> gas for 10 min. During electrochemical treatments, solution temperature was controlled by a constant temperature regulator. After treatments, samples were washed with deionized water and dried.

The films were characterized by X-ray diffraction (X'Pert PRO MPD, made in Netherlands) using Cu K $\alpha$  radiation at the conditions of 40 kV and 40 mA with a graphite monochrometer. The scanning rate of 2 $\theta$  was 0.06°/s. Morphologies and microstructures of films were investigated by scanning electron microscopy (JSM-5000, JEOL, Tokyo, Japan). Compositions of the thin films were measured by X-ray photoelectron spectrometry (XSAM-800, made in U.K.) using Al K $\alpha$  radiation and under FRR mode. EDXA measurement was tested by scanning electron microscopy, too. Luminescence was examined by spectrofluorometry (M-850, Hitachi, Japan).

#### 3. Results and discussions

### 3.1. XRD analysis

Fig. 1 gives the XRD patterns of a SrWO<sub>4</sub> thin film prepared by a cell electrochemical method for 60 min at 60 °C in alkaline solutions containing Sr<sup>2+</sup> ions. It can be seen from Fig. 1 that the SrWO<sub>4</sub> film is well-crystallized and has the scheelite-typed structure. The peak intensities, the peak positions and the lattice parameters (a = 5.4119 Å and c = 12.0103 Å) agree well with the standard JCPDS data [24].

#### 3.2. Scanning electron micrographs examinations

Fig. 2(a and b) present the comparison of scanning electron micrographs of  $SrWO_4$  thin films prepared by constant current and cell electrochemical method, respectively.

Fig. 2(a) shows that under the condition of constant current,  $SrWO_4$  polycrystals are inclined to growing in clusters like bunches or flowers. Such a phenomenon is often observed in surfaces of  $SrWO_4$  thin films prepared by constant current method. In addition, grain sizes are not homogeneous and the surfaces of thin films are very rough.

Fig. 2(b) reveals that SrWO<sub>4</sub> polycrystals fabricated by the cell electrochemical technique grow in tetragonal tapers. Though intergrowth is easily seen, the clusters like bunches or flowers are not observed yet. The average grain size is about 2  $\mu$ m in width and 6  $\mu$ m in length.

From Fig. 2, it can be deduced that the film surface has been markedly improved by using cell electrochemical technique instead of the constant current method. Since currents in cell electrochemical methods are correspondingly low, the driving force of nucleation of  $SrWO_4$  is accordingly weak. Thus, growth units could freely transfer to sites with lower energy. Clusters are not apt to form.

## 3.3. XPS and EDXA measurements

Fig. 3(a-c) shows the narrow-scan XPS spectra for W, Sr and O elements of SrWO<sub>4</sub> films prepared by cell electrochemical method, respectively.

To investigate the multi-spitting effect caused by the coupling of spinning momentum and orbiting momentum, Gaussian–Lorentzian fitting was employed (Fig. 3) according to the program provided by the XPS operator.

It can be seen from Fig. 3 that the XPS peak of W 4f7/2 is at 35.470 eV, the peak of Sr 3d5/2 is at 133.410 eV and the peak of O 1s is at 529.850 eV. The results are consistent with those reported in literature [25]. Therefore, the



Fig. 1. XRD patterns of SrWO<sub>4</sub> thin films prepared by a cell electrochemical method at 60 °C for 60 min.



Fig. 2. SEM images of SrWO<sub>4</sub> thin films prepared by electrochemical methods at 60 °C. (a) Constant current method, I = 0.4 mA/cm<sup>2</sup>, t = 230 min; (b) cell electrochemical technique, 60 min.

measurement results reveal the presence of Sr, W and O elements in the films and confirm that the valence of Sr, W and O elements are +2, +6 and -2, respectively.

EDXA measurements show that the atomic ratio of Sr:W in the film is 46.499:53.501. Considering that the detective depth of electron beam might exceed the thickness of SrWO<sub>4</sub> film, electron beam can reach tungsten substrate. So the amount of tungsten might appear to be a little larger than that of strontium. The results of XPS and EDXA measurements agree well with the XRD analysis, which firmly demonstrate that the composition of the film accords with its stoichiometry.

## 3.4. Luminescence

Fig. 4 presents the luminescent property of SrWO<sub>4</sub> thin films prepared by a cell electrochemical method. These SrWO<sub>4</sub> thin films show single emission peak around 460 nm at the excitation of 230 nm at room temperature, which is in agreement with literature results [14–16]. Other researchers [7,26] obtained green emission from their SrWO<sub>4</sub> powders or CaWO<sub>4</sub> crystals in addition to the blue emission at liquid-nitrogen temperature. This green emission was ascribed to the transition on WO<sub>3</sub> group [7,26]. Such defect is usually produced due to the volatilization of oxygen on WO<sub>4</sub><sup>2–</sup> group during the high temperature treatment. However, the present sample was prepared directly via solution routines and without any annealing treatment. In the present study, such green emission is not observed, but there exists only single blue emission, which suggests that the SrWO<sub>4</sub> film should be free of Schottky defect WO<sub>3</sub>.

#### 3.5. A solution to control the rate of cell electrochemical methods

For a long time, cell electrochemical method was considered to be an uncontrollable and taking-time method to deposit functional thin films. Because of these problems, almost no researchers thought cell electrochemical methods seriously. While in our research group, much consideration has been paid on how to improve cell electrochemical techniques. It is found that assisted by hydrothermal treatments the time span of deposition can be reduced from several days into several tens of minutes. Obviously, experiment efficiency has been greatly improved.

Here, we define average current density in the starting 5 min as the parameter indicating the speed of cell electrochemical method.

Table 1 gives the effects of temperature on average current density. It shows that average current density increases with the increase of temperature at first and then decreases with the increase of temperature. The increase trend is ascribed to the following reasons.

On one hand, increasing the temperature can speed up the rate of cell reactions. According to the Arrhenius equation [22],

$$k = k_0 \mathrm{e}^{-E_\mathrm{a}/RT} \tag{3}$$



Fig. 3. XPS spectra of SrWO<sub>4</sub> film prepared by a cell electrochemical method: (a) W 4f; (b) Sr 3d; (c) O 1s.

where  $k_0$  stands for frequency coefficient,  $E_a$  stands for active energy, k stands for reaction rate, T means temperature and  $R = 8.314 \text{ J} \cdot \text{K}^{-1}$ . From the equation, it can be seen that reaction rate increases with increasing the temperature.

Secondly, increasing temperature can accelerate hydrogen desorption. In the tungsten-platinum cell system, the reduction of hydrogen is the cathodic reaction. Hydrogen often adsorbs on cathode. The higher the temperature is, the



Fig. 4. Excitation (a) and emission (b) spectra of SrWO<sub>4</sub> thin films prepared by a cell electrochemical method at room temperature.

more tempestuously hydrogen molecules move, which makes hydrogen be desorbed easier. According to the laws of reaction equilibriums, the loss of hydrogen helps the generation of hydrogen, which makes anodic oxidation reaction go efficiently.

Thirdly, temperature will affect the diffusion of  $\mathrm{Sr}^{2+}$  and  $\mathrm{WO_4}^{2-}$  ions. The diffusion driving force of these two ions lies in their concentration gradients. Their movements can be treated as Brownian movement among the medium with viscosity coefficient of  $\alpha$ . The temperature dependence of the diffusion coefficients [27] is

$$D = \frac{kT}{\alpha} \tag{4}$$

where *D* is the diffusion coefficient (m<sup>2</sup>·s<sup>-1</sup>), *k* the Boltzman constant,  $1.38 \times 10^{-23}$  J·K<sup>-1</sup>, *T* the absolute temperature (K) and  $\alpha$  is the viscosity coefficient (kg·s<sup>-1</sup>).

 Table 1

 Effects of temperature on average current density

Number	Temperature	Average current density (mA/cm <sup>2</sup> )
1	25	0.045
2	40	0.2818
3	50	0.4787
4	60	0.4402
5	70	0.2481
6	80	-0.2393

It shows that the diffusion will be accelerated by increasing temperature.

The decrease of average current density may arise from counter-polarization. Once counter-polarization happens, tungsten will serve as cathode and tungsten's oxidation will be stopped. This counter-polarization phenomenon was observed when the temperature came up to 80  $^{\circ}$ C.

Table 1 reveals that the speed of cell electrochemical method can be altered by changing the temperature. To deposit thin films quickly, the optimum temperature is about 50–60  $^{\circ}$ C.

## 4. Conclusions

Highly crystallized  $SrWO_4$  thin films have been prepared on tungsten foils by a cell electrochemical method. The XRD result shows that the film is well-crystallized and has single scheelite structure. SEM examinations reveal that  $SrWO_4$  polycrystalline grains grow well with di-pyramid growth habits and clusters like flowers or bunches, which can usually form by using the electrolysis electrochemical method, have disappeared under cell electrochemical conditions. XPS and EDXA measurements demonstrate that the composition of the film consists with its stoichiometry. The as-grown films show single blue emission at 460 nm with the excitation light of 230 nm at room temperature.

The cell electrochemical technique is a novel electrodeposition method. Its reaction speed can be controlled by changing treatment temperature. The optimum temperature is about 50-60 °C.

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