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Solution synthesis of crystallized AMO_4 (A=Ba, Sr, Ca; M=W, Mo) film at room temperature

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A well-crystallized AMO_4 (A=Ba, Ca, Sr; M=W, Mo) films have been prepared at room temperature through a simple solution reaction in respective alkaline solution at higher pH ranging from 12–14. Adopting the corrosion principle for oxidation of metal substrate, these double oxide films were carried out in presence of chemical driving force without any special apparatus or devices. Hydrogen peroxide was used to enhance the dissolution rate of metal substrates. The driving force for the film formation and growth were high concentration of A^{2+}, $MO_4{}^{2-}$ ions with high pH conditions. Average grain sizes of 8–10 μm with bipyramidal shaped particle were grown to the thickness of about 10–14 μm after 3–6 hours treatment. The crystallization of AMO_4 was characterized by three-dimensional nucleation. This work demonstrates the possibility of fabrication of functional ceramic films directly from the aqueous solution in a single step by solution reactions. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Preparation of alkaline earth molybdate and tungstate materials have been received much attention because of their significance in electro-optics and microwave ceramics [1, 2]. Different techniques including solid-state reaction [3], the flux method [4], Czochralski method [5, 6], hydrothermal method [7] and the co-precipitation route [8] was used for the preparation of single crystals, whiskers and particles. It is generally agreed that the thin film phosphor has superior resolution when compared with powder because of its inherently smaller grain size and less lateral scattering. Nevertheless, less extensive investigations have been made on preparation of these films. A variety of physical and chemical deposition methods including chemical vapor deposition [9, 10], evaporation method [11], sputtering evaporation [12], sol-gel processes [13, 14] and electrochemical method have been reported for the preparation of those films. They have still problems to get high quality films, i.e. compositional fractuations due to the difference of vaporization between A and MO_4 species and peeling off films by mismatching the thermal expansion between AMO_4 and the substrate in those deposition methods. In addition, these chemical vapour deposition and physical vapour deposition methods have essential problems to consume lots of energy and materials, which can hardly be recovered or recycled, thus they are regarded as environmental unfriendly. In these regards our group has proposed and developed Soft Solution Processing (SSP), where crystallized inorganic materials could be fabricated directly on appropriate substrates in the solution [15–24]. Cho *et al.* reported the formation of AMO_4 films on the M metal substrate by electrochemical or hydrothermal/ electrochemical methods [20–23, 24]. It requires anodic dissolution of M metal by electric current supply. Moreover, hydrothermal conditions above 100°C were often used to proceed the reactions.

Hydrogen peroxide has often been used in solution processing as an oxidizer. Xiao and co-worker deposited thin titania film consisting of anatase and rutile on Ti metal substrate when soaked in a $TiOSO_4$/ H_2O_2 and aged in hot water [25]. Ohtsuki *et al.* indicated that the treatment of Ti with a $TaCl_5$ containing

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hydrogen peroxide solution was effective in providing *in vitro* bioactivity or the ability of materials to be covered with apatite in simulated body fluid [26]. Cheng *et al.* have developed novel aqueous chemical solution as a precursor both for $LiNbO_3$ powder and thin film [27]. In this method the hydrogen peroxide aqueous solution reacts with niobium and lithium alkoxide ethanol solution to form metal peroxide aqueous solution. Kudo *et al.* reported that H_2O_2 aqueous solution can react with metal alkoxides and form M-O-O-M′ (M and M′ metals) [28]. Lee *et al.* synthesized well crystallized nano ceria powders by hydrothermal synthesis using a mixture of H_2O_2 as the oxidizer and NH_4OH as mineralizer [29]. Woodhead reported novel approach for Ce (IV) oxide which is precipitated from Ce(III) nitrate solution using mixture of NH_4OH and H_2O_2 [30]. The role of H_2O_2 was to make it much easier to change the valence state of Ce ion from Ce (III) to Ce (IV).

However, in the present study we have demonstrated our first success in preparing crystallized AMO_4 (A= Ba, Sr, Ca, M = W, Mo) films at room temperature by using hydrogen peroxide with alkaline earth solution neither electric current supply nor special apparatus or devices were used. Here, oxidation and dissolution of the metal substrate was achieved by using hydrogen peroxide with alkaline earth solution.

2. Experimental procedure

A 99.9 wt%-pure tungsten or molybdenum metal substrate with dimension of $10 \times 10 \times 0.1\ mm^3$ and $10 \times 10 \times 0.2\ mm^3$ respectively (Niraco, Japan) were mechanically polished and degreased in acetone with an ultrasonic cleaner. Solutions of $Ba(OH)_2$, $Sr(OH)_2$ and $Ca(OH)_2$ were made from redistilled water and $Ba(OH)_2{\cdot}8H_2O$, $Sr(OH)_2{\cdot}8H_2O$, $Ca(OH)_2{\cdot}8H_2O$ of minimum 98% assay (Kanto Kagaku, Japan) respectively. Distilled water was purged free of O_2 and CO_2 with N_2 gas for 30 min before using in experiments.

In a typical experiment, 50 ml of $Ba(OH)_2$ solution containing 0.0008 moles of Ba^{2+} was added with 20 volume percent of hydrogen peroxide. The W or Mo metal substrate was placed in the solution as shown in schematic representation, Fig. 1. The pH of the solution was adjusted to 12. AMO_4 (A = Ba, Ca, Sr; M = W, Mo) films were fabricated through this simple solution reaction at room temperature for 6–12 h using respective substrate and alkaline earth solutions.

The products were characterized by X-ray diffraction (XRD) and Raman scattering techniques. A standard X-ray diffractometer (MAC Science, Model MXP^{3VA}) with CuKα radiation was operated at 40 kV and 40 mA with the scan rate of 2°/min for a 2θ range from 10 to 55°. Raman spectra were measured at the 514.5 nm line of an Ar laser at room temperature in a backscattering geometry using microprobe optics (designed by Atago Bussan). The laser beam was focused on to the sample surface with a spot size of 1 μm. The scattered light was analyzed with Jobin Yvon/Atoago Bussan T64000 Triple spectrometer and collected with a liquid-nitrogen-cooled charge coupled device detector. The microstructures of these films were investigated by SEM (Hitachi, S-4000) and Environmental SEM (Nikon, ESEM-2700).

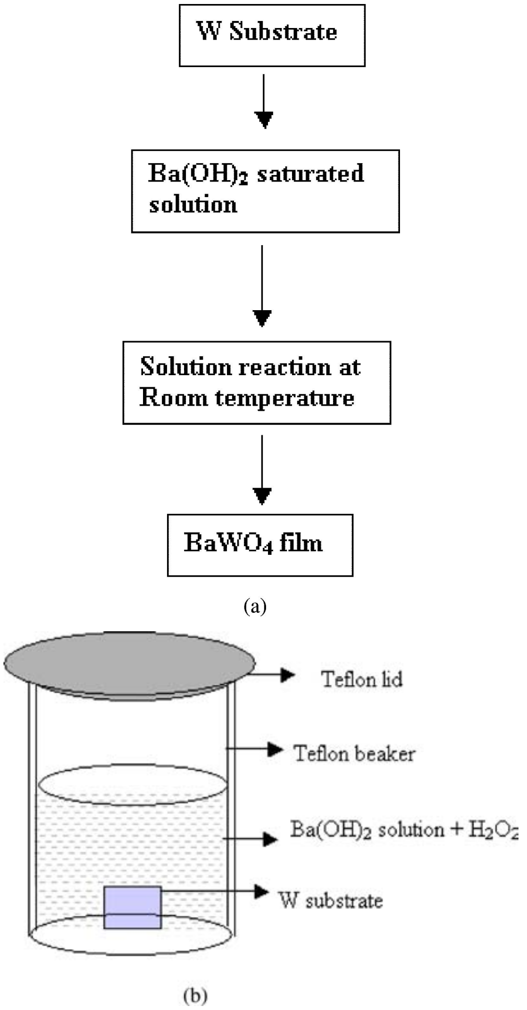

Figure 1 (a) Flow chart of the $BaWO_4$ fabrication, (b) schematic illustration of the experimental set up.

3. Results and discussion

3.1. Formation of AMO_4 films

In general, the corrosion process like dissolution of a metal is normally electrochemical in nature, where electron transfer occurs from metal to solution. Adopting the dissolution by the oxidation of metal substrate, we could fabricate a well crystallized AMO_4 films on the respective substrate with addition of suitable concentration of hydrogen peroxide. H_2O_2 acted as the oxidation and the dissolution agent of M metals even at room temperature. The

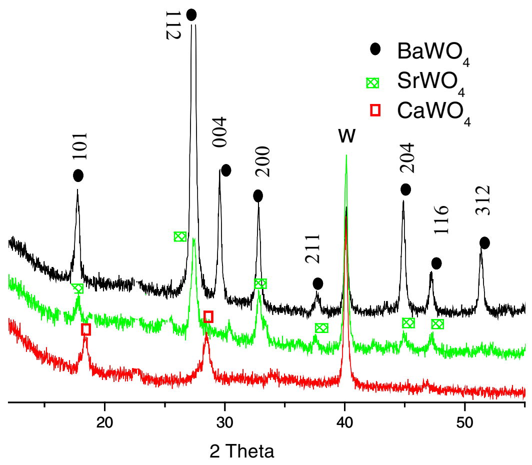

Figure 2 X-ray diffraction patterns of AWO_4 films formed in the solution containing 0.0008 M A^{2+} ions at room temperature.

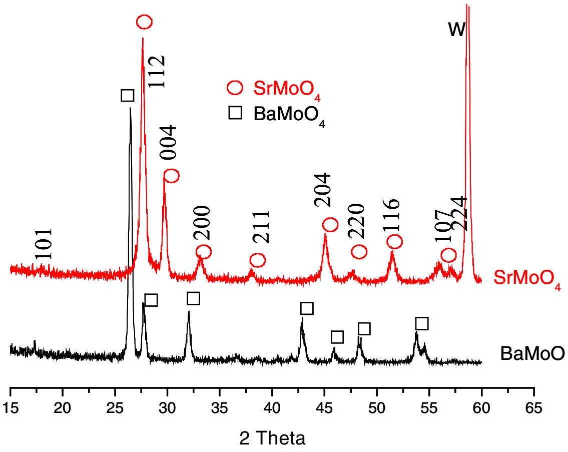

Figure 3 X-ray diffraction patterns of $AMoO_4$ films formed in the solution containing 0.0008 M A^{2+} ions at a room temperature.

AMO_4 films were not formed in the absence of H_2O_2. The supply of 20-40 volume percent of H_2O_2 was crucially important. So, it was the first success that AMO_4 films were formed at room temperature without any electrochemical treatment. In our previous works, either an electrical current [23] or hydrothermal [17] treatment was essential to deposit film. The XRD patterns of films formed after the treatment of 3–6 h in Figs. 2 and 3 showed a single phase of crystalline tetragonal AMO_4 films without any impurity phases. The lattice parameters calculated by Cellcalc software version 1.51 developed by. Miura using observed *d*-value and hkl values.

Calculated lattice parameters (Table I) agreed rather well with the JCPDS data [22] and other literature data [23, 24]. The homogeneity of films was confirmed by Raman studies. Fig. 4, the Raman spectra of the $BaWO_4$ film revealed that the same spectra of tetragonal $BaWO_4$ for a large crystal grain and for relatively flat part with small crystals, showing the homogeneity in composition.

TABLE I Comparison of the lattice parameters calculated from XRD data and data published in literature

Compound	Lattice parameter	Present work (nm)	Ref. work (nm)	Ref.
$BaWO_4$	a	0.565	0.561	
	c	1.238	1.270	[19]
$SrWO_4$	a	0.544	0.542	
	c	1.203	1.195	[20]
$CaWO_4$	a	0.514	0.524	
	c	1.150	1.137	[21]
$BaMoO_4$	a	0.558	0.580	
	c	1.282	1.282	
$SrMoO_4$	a	0.532	0.539	
	c	1.211	1.202	

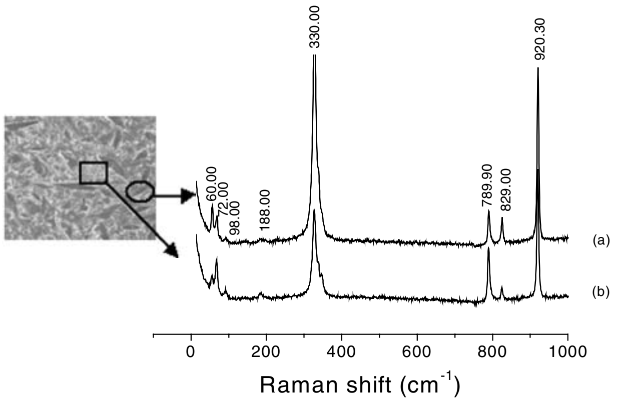

Figure 4 Micro Raman spectra for $BaWO_4$ crystals of (a) Large grains (b) Flat part of the film covered by small crystals both were formed at 3 h solution reaction at room temperature.

The difference in relative peak intensity seems to be caused from the orientation-dependence of peak intensity [31].

3.2. Growth mechanism of $BaWO_4$ film

According to Pourbaix [32], tungsten metal has tendency to dissolve and form $WO_4{}^{2-}$ ions in an alkaline solution, particularly at high pH ranging from 12–14, even at zero or in negative electrode potential range at room temperatures. This oxidation reaction however, proceeds very slowly at low temperatures in the absence of some externally applied driving forces like supplied current. In the present case the oxidation and dissolution of W substrate was accelerated by the use of H_2O_2. M metal was attacked by the H_2O_2 to form $MO_4{}^{2-}$ ions as shown in equation 1, which reacts with A^{2+} ions in the solution and precipitates as AMO_4 on the respective metal substrate (equation 2).

$$M + 2OH^- + 3H_2O_2 \rightarrow MO_4{}^{2-} + 4H_2O \qquad (1)$$

$$MO_4{}^{2-} + A^{2+} \rightarrow AMO_4 \qquad (2)$$

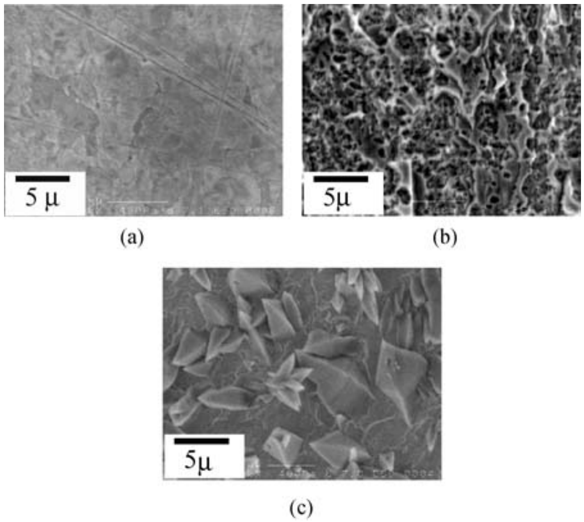

Figure 5 Dissolution of the substrate under different conditions; (a) oxidized W substrate immersed in pure water for 3 h, (b) oxidized W substrate immersed in solution containing 20 volume % H_2O_2 and water for 3 h, (c) formation of $BaWO_4$ films in 20 volume% H_2O_2 and Ba^{2+}-containing solution.

Fig. 5 demonstrates those phenomena where W metal substrate was immersed in pure H_2O, the oxidation proceeded negligible as seen in the Fig. 5a. But when 20 volume percent of H_2O_2 was added, the surface of W substrate was corroded drastically yielding porous surface as shown in Fig. 5b, indicating the formation of WO_4^{2-} as indicated in equation 1. This WO_4^{2-} encountered with Ba^{2+} ions to precipitate as $BaWO_4$ films when Ba^{2+} ions were added to the solution as shown in the Fig. 5c. Since formed MO_4^{2-} ions can be entrapped by A^{2+} ions in the solution, the AMO_4 formation was increased with the concentration of A^{2+} ions as seen in Fig. 6.

The formation of $BaWO_4$ was smaller when Ba^{2+} concentration was lower as < 0.0004 mole/50 g solution. With solutions having lower pH < 9, WO_4^{2-} formation was very slow, thus the formation of $BaWO_4$ was also slow. Fig. 7 illustrates schematically the formation and growth mechanism of AMO_4 film as $BaMoO_4$. The H_2O_2 addition had important roles to oxidize and dissolve W surface, however, excess addition of H_2O_2 above 40 volume% hindered the formation of $BaWO_4$ as seen in Fig. 8. Probably this was due to the rapid precipitation of Ba^{2+} as barium hydroxide powder in solution. The precipitated alkaline earth hydroxide in solution was confirmed by X-ray diffraction.

Above discussion indicates that the optimum deposition of AMO_4 crystals might be occurred when concentrations of WO_4^{2-} and Ba^{2+} would become optimum that is, the solubility product $[WO_4^{2-}]$ $[Ba^{2+}]$ would become maximum in the solution, as seen in Fig. 7.

The feature of AMO_4 formation seems to be similar to that of reported by Slamovich *et al.* for the $BaTiO_3$ film growth [33]. They indicated that the structural evolution of films was consistent with the Avrami-type nucleation and growth, i.e. particles continuously nucleated throughout the film formation with the termination caused by the impingement of adjacent particles growing at a constant rate. The AWO_4 films showed different grain size with average size of 10 μm as shown in Fig. 9.

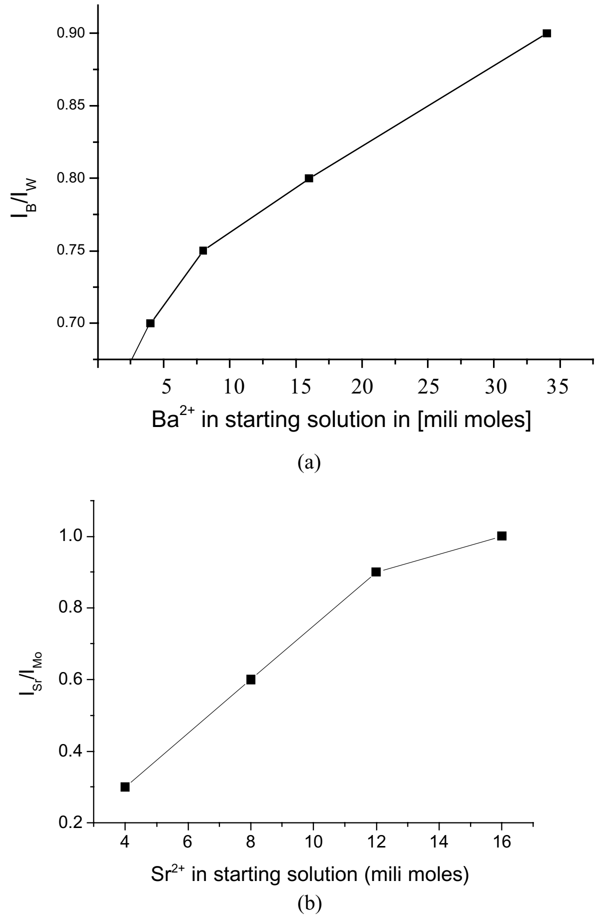

Figure 6 Plot of XRD intensity ratio (IB/IW) in (a) $BaWO_4$ films against mole concentration of Ba^{2+} ions in starting solution, I_B and I_W are peak intensity of $BaWO_4$ and W, respectively, (b) $SrMoO_4$ film against mole concentration of Sr^{2+} ions in the starting solution.

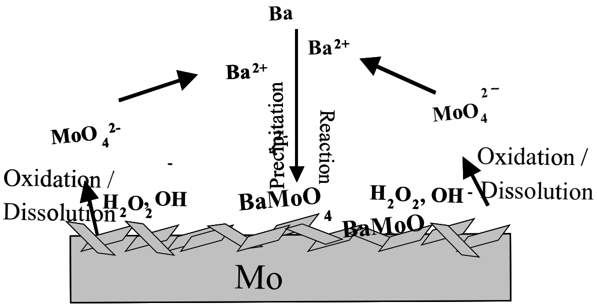

Figure 7 A model for $BaWO_4$ film formation on the W substrate in a solution containing 8 mili mole $Ba(OH)_2$ and 20 weight percent of H_2O_2 in solution at room temperature.

The average thickness measured from the cross section of SEM photographs was about 10–15 μm after 2–3 h treatment. The $AMoO_4$ film was consisted with grains of about 6–8 μm in size but some crystals have grown larger than the film thickness, Fig. 10. This means that the initially formed crystallites grow preferentially in the horizontal direction of the substrate, which provides a greater supply of the tungstate species from the substrate [24]. Thickness of the film increased as the reaction time increased.

4. Conclusions

Crystalline AMO_4 films were fabricated through a simple and low cost solution process at room temperature. Growth of AMO_4 films started with the dissolution of the M-metal substrate, which was accelerated by 20–40 volume percent of oxidizing agent H_2O_2. The present study demonstrates that high temperature or current supply is not needed to prepare a crystallized ceramic material if an appropriate process and starting materials are chosen. The present novel method should contribute to the development of highly desired low energy-cost processes.

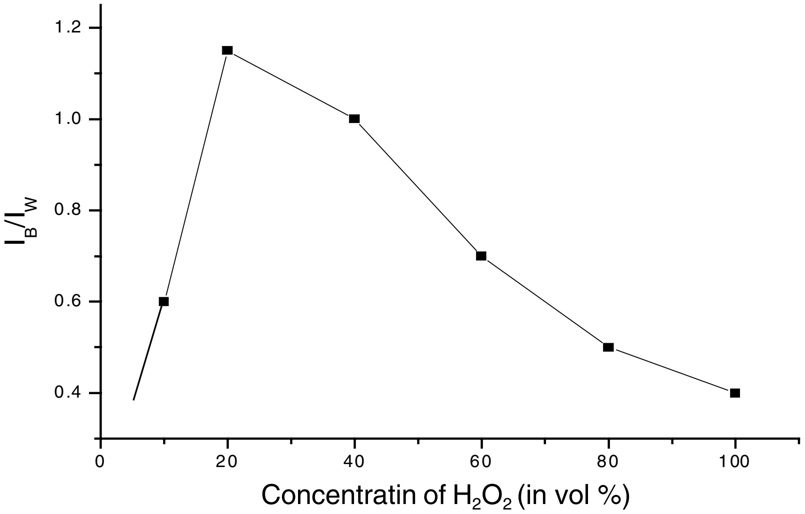

Figure 8 Plot of XRD intensity ratio $BaWO_4$/W, against different concentration of H_2O_2 solution in the starting solution.

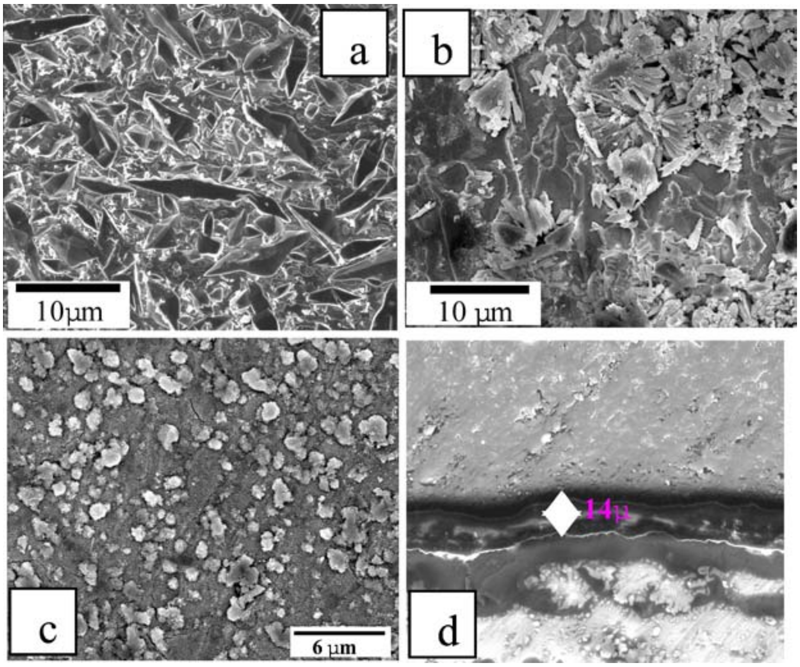

Figure 9 SEM photographs of (a) $BaWO_4$, (b) $SrWO_4$, (c) $CaWO_4$ and (d) cross section of $BaWO_4$ film obtained from 3 h in solution at room temperature.

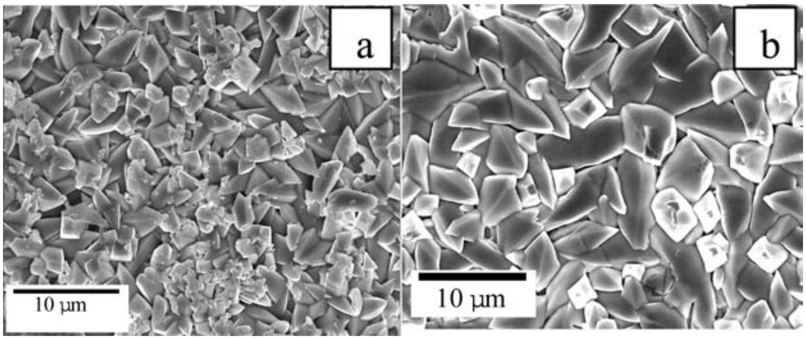

Figure 10 SEM photographs of (a) $SrMoO_4$, (b) $BaMoO_4$ films fabricated on M substrate in solution at a room temperature for 6 h.

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