

# Study of polycrystalline $Ba_{1-x}Ca_xMoO_4$ films prepared by electrochemical technique

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**Abstract** The polycrystalline  $Ba_{1-x}Ca_xMoO_4$  films were prepared directly on molybdenum substrates by electrochemical technique. The growing characteristics of the films were studied by scanning electron microscopy (SEM), x-ray diffraction (XRD), and energy dispersive x-ray analysis (EDRX) techniques, respectively. The SEM images show that the morphology of the  $Ba_{1-x}Ca_xMoO_4$  film is affected significantly by the composition of the films when the process parameters are preset. The XRD and EDRX analyses reveal that the compositions of the films are strongly controlled by the capability of bond between cation and anion, besides the cation concentration, temperature, and current density, in such situation.

**Keywords**  $Ba_{1-x}Ca_xMoO_4$  films · Prepared · Electrochemical technique

## 1 Introduction

The materials with scheelite structure exhibit attractive luminescence abilities when they are excited by definite

wavelength light at low temperature. Crystals of these materials have been studied as hosts for lasers. As we know, the scheelite-type alkaline-earth molybdate crystals and powders are important photo-electronic materials [1, 2]. Recent researches show that molybdate crystals can be used as cryogenic phonon-scintillation detectors [3, 4] in the search for rare events. However, the preparations of these kinds of films had been less investigated until electrochemical method deposition of  $CaMoO_4$  films reported by W-S Cho et al. [5]. Recently, a series of molybdate and tungstate films with scheelite type were prepared by electrochemical technique in our group and other groups [6–11]. The influences of processing parameters on the growth of these films by electrochemical technique were investigated. Yoshimura and Suchanek et al. [6] had confirmed that in the  $CaMoO_4$  or  $SrMoO_4$  film preparation by electrochemical process, a growth model had been proposed as follows:



Researches on crystals of scheelite-type molybdates show that scheelite-type molybdates of the same divalent metal are reciprocally soluble over the entire compositional range, which results in a rich family of solid-state solution compounds. According to Yoshimura and Suchanek [6] and Cho et al. [5], it seems that in alkaline solution containing both  $Ca^{2+}$  and  $Ba^{2+}$ , solid-solution films of  $Ba_{1-x}Ca_xMoO_4$

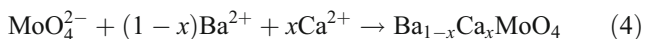
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could be prepared as follows:



Present work is devoted to the research on the growth of polycrystalline  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films by electrochemical technique. In our opinion, the growth of solid-solution films with multicomponent has significant meaning for the applicability of this technology. To our knowledge, this kind of research work is not reported previously.

## 2 Experimental

Molybdenum metal substrate with purity more than 99.9% and dimensions of 10 mm×10 mm×0.1 mm was used as the anode; platinum flake with the same purity and dimensions was used as the cathode. Before the electrochemical deposition, the molybdenum substrate and platinum flake were degreased in acetone with ultrasonic cleaner for 10 min, respectively, the molybdenum substrate was etched subsequently in mixture acid of hydrochloric acid and nitric acid for 5 min, and then, was washed in distilled water with ultrasonic cleaner two times.

All electrochemical depositions were performed under galvanostatic conditions by a PST050 analytical potentiostat (Radiometer analytical company, France) at near room temperature. The influences of process parameters, such as current density, reacting temperature, and the bivalent cation concentrations of electrolyte, on the growth of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films were considered. According to our previous work, the lower limit of  $\text{Ca}^{2+}$  concentration for electrochemical deposition  $\text{CaMoO}_4$  film is 0.011 M at 10°C, while the necessary current density is 0.5 mA/cm<sup>2</sup>. The lower limit of  $\text{Ba}^{2+}$  concentration for electrochemical deposition  $\text{BaMoO}_4$

film is 0.002 M at the same temperature, while the necessary current density is 0.3 mA/cm<sup>2</sup>. At the temperature range of from 10 to 25°C, the effects of the electrolyte temperature and current density on the growth of  $\text{CaMoO}_4$  film are stronger than that on the growth of  $\text{BaMoO}_4$  films. High temperature and large current density are helpful to the growth of  $\text{CaMoO}_4$  film. To investigate the growing characteristics of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films, the experiments were divided into two groups. For group 1, the  $\text{Ca}^{2+}$  content of initial electrolytes is preset as constant 0.055 M, and the values of  $\text{Ba}^{2+}/\text{Ca}^{2+}$  (mole ratio) are changed from 0.02/0.98 to 0.95/0.05. The electrochemical deposition current density is 0.8 mA/cm<sup>2</sup>. The electrolyte temperature is 10°C. For group 2, the Ba content of starting electrolytes is preset as 0.055 M, and the values of  $\text{Ca}^{2+}/\text{Ba}^{2+}$  (mole ratio) is changed from 0.02/0.98 to 0.95/0.05. The electrochemical reactions were carried out with the current density of 0.5 mA/cm<sup>2</sup> at 25°C.

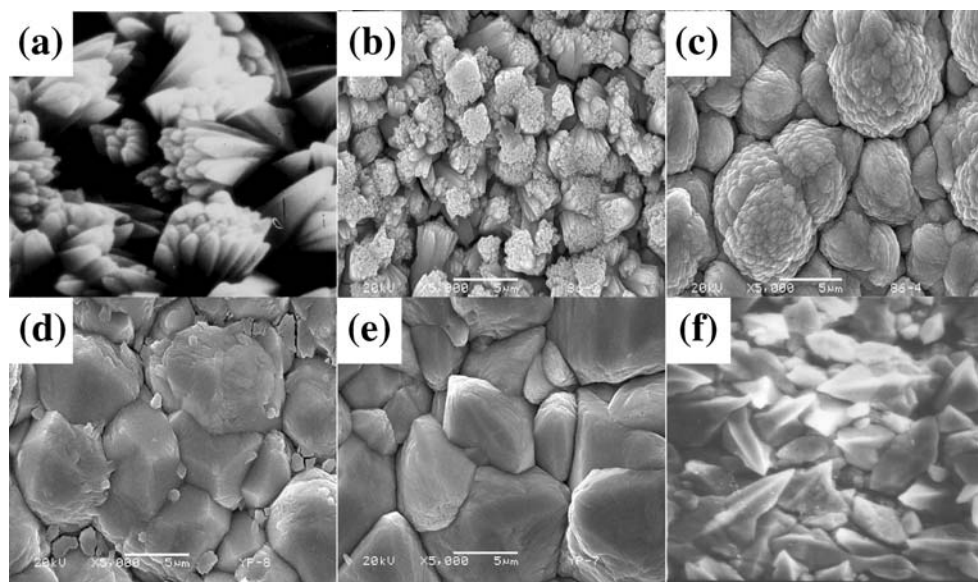
The resultant phase of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films was analyzed using x-ray diffraction (XRD) method, and the surfaces of the prepared films were observed by scanning electronic microscopy (SEM). The compositions of the film were examined by energy dispersive x-ray analysis (EDRX) method.

## 3 Results and discussions

### 3.1 SEM images

Figure 1 shows the SEM images of the surface of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films prepared by electrochemical technique in different starting Ba/Ca mole ratio electrolytes. Figure 1 indicates that the prepared  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films show

**Fig. 1** SEM images of the  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films prepared from different  $\text{Ca}^{2+}/\text{Ba}^{2+}$  mole ratio electrolytes. (a)  $\text{CaMoO}_4$ ; (b) Ba/Ca=0.02/0.98; (c) Ba/Ca=0.15/0.85; (d) Ba/Ca=0.2/0.8; (e) Ba/Ca=0.3/0.7; and (f)  $\text{BaMoO}_4$

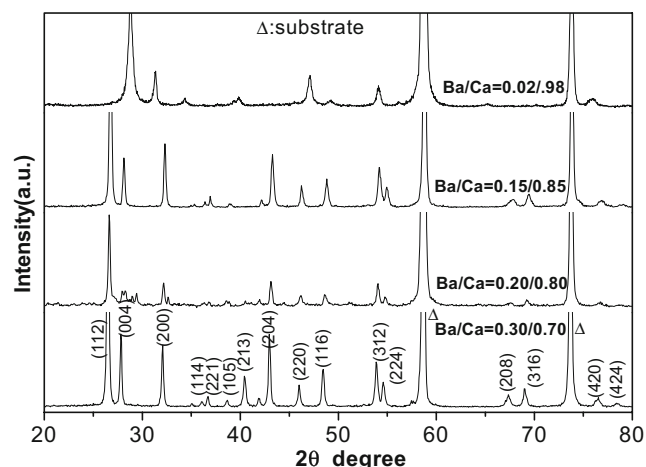


different surface morphology characteristics. According to our experiments [9] and Mikhailik et al. [4], the morphologies of the molybdate films can be affected by process parameters, and molybdates with different cations also have their own morphology characteristics. Intergrowth is the characteristic of  $\text{CaMoO}_4$  film prepared by electrochemical technique. The typical intergrowth is observed in Fig. 1(a) and (b). From Fig. 1(c) to (e), the intergrowth characteristic becomes weaker and weaker.

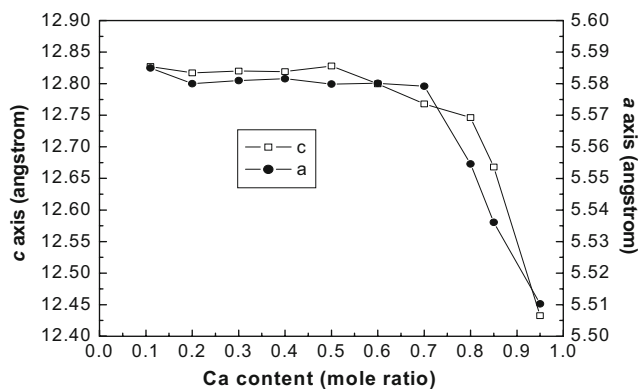
The surface morphology of the film [in Fig. 1(e)], which is prepared from the solution of 0.3 mole ratio  $\text{Ba}^{2+}$  contained, tend to be similar to that of  $\text{BaMoO}_4$  film. The grain of the  $\text{BaMoO}_4$  film is the typical tetragonal double tamper [Fig. 1(f)]. It is reasonable that the Ba content in the films should be increased with the increase of Ba content in the initial electrolyte. It seems that the morphologies of the  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films tend to be similar to that of the  $\text{BaMoO}_4$  film with the increase of Ba content in  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films. It is also understandable that the morphology characteristic of a solid solution compound should be determined by the main component of the compound when other process parameters are preset. So this can explain why the morphology characteristic of  $\text{CaMoO}_4$  film appears in the  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films with higher Ca contents [see Fig. 1(b) and (c)]. But it is perplexing and interesting why the morphology of the film in Fig. 1(e), which is prepared from the solution with only 0.3 mole ratio  $\text{Ba}^{2+}$  contained, tend to be similar to that of  $\text{BaMoO}_4$  film [Fig. 1(f)]. Then, XRD and EDRX techniques are employed to find the reason.

### 3.2 XRD analyses

Figure 2 gives the XRD patterns of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films prepared by electrochemical technique. The patterns indicate that all the films have single tetragonal feature of



**Fig. 2** XRD patterns of the  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films prepared from different Ca/Ba mole ratio electrolytes



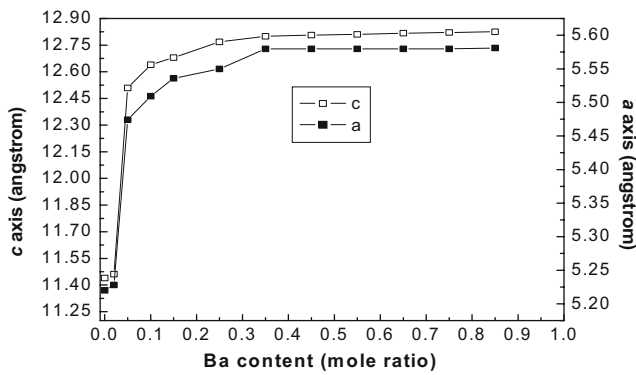
**Fig. 3** Values of  $a$  axis and  $c$  axis of the cell of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films vs Ca content in the solutions

scheelite type. Furthermore, when the mole ratio of  $\text{Ba}^{2+}/\text{Ca}^{2+}$  is 0.02/0.98 in the solution, the sites of diffraction peaks and the intensity characteristics of the film prepared are very close to that of the standard JCPDS data for  $\text{CaMoO}_4$  powder. From Fig. 2, it can be seen that with the increase of the Ba content in the initial electrolytes, the peaks of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films prepared shift to lower degree position incoordinately. In our experiment, when the  $\text{Ba}^{2+}/\text{Ca}^{2+}$  mole ratio exceeds 0.05/0.95 in the solution, the peak sites of the  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  films prepared are closer to that of  $\text{BaMoO}_4$  than to that of  $\text{CaMoO}_4$ . Moreover, when the Ba/Ca mole ratio exceeds 0.3/0.7 in the solution, all peaks are nearly consistent with that of  $\text{BaMoO}_4$  powder.

The diffraction peak left shift means that the cell of  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  becomes larger than before with the increase of Ba content in the film. Obviously, It results from the larger atom radius of Ba. As a closer inspection, the variations of the cell parameters with the change of  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$  content in the solution are also investigated experimentally.

Figure 3 shows the variations of the  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  cell parameters vs the  $\text{Ca}^{2+}$  content in the solution. Here, the amount of  $\text{Ba}^{2+}$  in the solution is 0.055 M, and the films were deposited in the solution at 25°C temperature. The current density used was 0.5  $\text{mA}/\text{cm}^2$ . From Fig. 3, one can see that the values of  $a$  axis and  $c$  axis are very close to that of  $\text{BaMoO}_4$  when the  $\text{Ca}^{2+}/\text{Ba}^{2+}$  mole ratio in the solution is less than 0.5/0.5. The values of  $a$  axis and  $c$  axis begin to decrease only when  $\text{Ca}^{2+}/\text{Ba}^{2+}$  mole ratios in the solution are more than 0.7/0.3 and 0.5/0.5, respectively. When  $\text{Ca}^{2+}/\text{Ba}^{2+}$  mole ratio in the solution reaches to 0.95/0.05, the values of  $a$  axis and  $c$  axis are still closer to that of  $\text{BaMoO}_4$  ( $a=5.58$  Å,  $c=12.81$  Å) than that of  $\text{CaMoO}_4$  ( $a=5.226$  Å,  $c=11.44$  Å). Such results suggest that only the  $\text{BaMoO}_4$  films are formed when  $\text{Ca}^{2+}/\text{Ba}^{2+}$  mole ratio in the solution is less than 0.5/0.5.

Figure 4 describes the dependence of the  $\text{Ba}_{1-x}\text{Ca}_x\text{MoO}_4$  cell parameters vs Ba content in the solution, while the

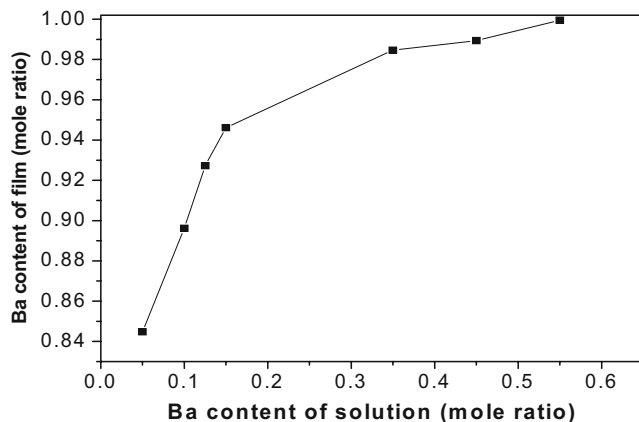


**Fig. 4** Values of *a* axis and *c* axis of the Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films made from different Ba content the solutions

initial Ca<sup>2+</sup> concentration in the solution is 0.055 M. The films were deposited in the solution at 10°C. The current density used was 0.8 mA/cm<sup>2</sup>. One can see that the values of *a* and *c* axes increase sharply with the increase of Ba<sup>2+</sup>/Ca<sup>2+</sup> value content from 0.02/0.98 to 0.05/0.95 mole ratio. The value of *a* axis is very close to that of BaMoO<sub>4</sub> when the Ba<sup>2+</sup>/Ca<sup>2+</sup> mole ratio value is only 0.25/0.75 in the solution. On the other hand, the value of *c* axis nearly reaches that of BaMoO<sub>4</sub> when the Ba<sup>2+</sup>/Ca<sup>2+</sup> mole ratio in the solution is 0.35/0.65. In our experiment, the values of *a* and *c* axes are consistent with that of BaMoO<sub>4</sub> when the Ba<sup>2+</sup>/Ca<sup>2+</sup> mole ratio is 0.45/0.55 in the solution.

**3.3 The compositions of as-prepared films**

Figure 5 gives the relationship of Ba content of as-prepared Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films vs that of initial solution (electrolytes). Ba contents of the Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films were measured by EDRX technique. Here, the amount of Ca<sup>2+</sup> is constant at 0.055 M in the solution, and Ba<sup>2+</sup> content in the solution is changeable. The films were



**Fig. 5** Relationship of Ba content of as-prepared Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films vs Ba content of the solution

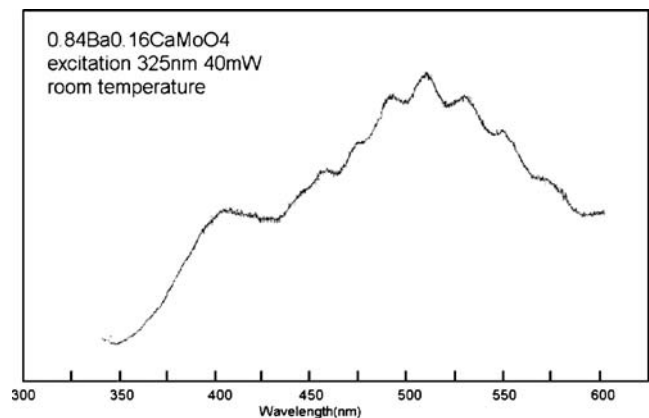
deposited in the solution of 10°C. The current density used was 0.8 mA/cm<sup>2</sup>. Apparently, when the Ba content of solution is very low (Ba<sup>2+</sup>/Ca<sup>2+</sup> is 0.05/0.95 mole ratio), the Ba content of as-prepared Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films is up to a very high value (Ba<sup>2+</sup>/Ca<sup>2+</sup> is about 0.84/0.16 mole ratio), and the Ba content in the Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films is always much higher than that of the solution preset. In other words, the as-prepared Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films are rich in Ba. As we know, Ba<sup>2+</sup> ion has larger radius than Ca<sup>2+</sup> ion. According to their electric structure, Ba<sup>2+</sup> ion should form a chemical bond easier with MoO<sub>4</sub><sup>2-</sup> than Ca<sup>2+</sup> ion. As a result, MoO<sub>4</sub><sup>2-</sup> will form a chemical bond with Ba<sup>2+</sup> preferentially in alkaline solution containing both Ca<sup>2+</sup> and Ba<sup>2+</sup>.

**3.4 Photo-luminescent (PL) property of Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> film**

Room temperature PL property of the Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> film was measured. Figure 6 shows PL feature of Ba<sub>0.84</sub>Ca<sub>0.16</sub>MoO<sub>4</sub> film. Here, emission peaks in about 395 and 510 nm are observed when the film is excited by light with 325 nm wavelength. The dependence of the PL properties on the morphology and composition of Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> film are being studied in detail.

**4 Conclusions**

Polycrystalline Ba<sub>1-x</sub>Ca<sub>x</sub>MoO<sub>4</sub> films were prepared by electrochemical technique at room temperature. The SEM images show that the composition of films has great influence on the growing characteristics of as-prepared films. The results of XRD and EDRX measurements reveal that the films are rich in Ba, whether the Ba ions are the predominant species in the solution or not. The compositions of the films are strongly controlled by the capability



**Fig. 6** Luminescence spectra of Ba<sub>0.84</sub>Ca<sub>0.16</sub>MoO<sub>4</sub> film under 325 nm excitation, RT

of bond between cation and anion, besides cation concentration, temperature, and current density, in such situation. This is very different from other technologies.

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