Preparation of Pyrochlore Ca$_2$Ti$_2$O$_6$ by Metal-Organic Chemical Vapor Deposition

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Preparation of Pyrochlore Ca$_2$Ti$_2$O$_6$ by Metal-Organic Chemical Vapor Deposition

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Ca-Ti-O films were prepared by metal-organic chemical vapor deposition (MOCVD) using Ca(dpm)$_2$ and Ti(O-i-Pr)$_2$(dpm)$_2$ precursors, and the effects of substrate temperature ($T_{sub}$) and Ca/Ti ratio ($R_{Ca/Ti}$) on the crystal structure and morphology were studied. Ca-Ti-O films consisting of pyrochlore Ca$_2$Ti$_2$O$_6$ and perovskite CaTiO$_3$ phase were obtained at $T_{sub} = 1073$ K and $0.35 < R_{Ca/Ti} < 1$. The content of pyrochlore Ca$_2$Ti$_2$O$_6$ increased with decreasing $R_{Ca/Ti}$. Pyrochlore Ca$_2$Ti$_2$O$_6$ almost in single phase was obtained at $R_{Ca/Ti} = 0.46$. The morphology of pyrochlore Ca$_2$Ti$_2$O$_6$ was agglomerated fine grains about 50 nm in diameter having a columnar texture.

1. Introduction

Since a Ca-Ti-O system contains many useful materials, so many studies on the phase diagram and crystal structure of calcium titanates have been reported.$^{11}$ Perovskite, CaTiO$_3$, and several compounds such as Ca$_3$Ti$_2$O$_{10}$ and Ca$_3$Ti$_2$O$_7$ have been reported. Savenko and Sakharov reported a cubic phase of Ca$_3$Ti$_2$O$_7$ having a lattice parameter of 0.862 nm.$^{22}$ They prepared this compound by thermal decomposition of mixed hydroxides of Ti and Ca at 1023 K. This compound partially transformed to perovskite CaTiO$_3$ and rutile TiO$_2$ at 1273 K, and completely transformed at 1373 K. Ball and White re-indexed the XRD data by Savenko and Sakharov, and concluded that the metastable phase should be pyrochlore Ca$_2$Ti$_2$O$_6$ having a lattice parameter of 0.995 nm.$^{33}$ Since then, no paper on the preparation of pyrochlore Ca$_2$Ti$_2$O$_6$ has been published.

Pyrochlore has a general composition formula of A$_2$B$_2$X$_6$Y, where A and B are metals, and X and Y are O, OH or F. Since pyrochlore oxides have unique properties such as giant magnetoresistance (GMR) of Ti$_2$Mn$_2$O$_7$,$^{44}$ metal-insulator transition of Ti$_2$Ru$_2$O$_7$,$^{45}$ and anomalous Hall effect of Mo$_2$Ti$_2$O$_7$,$^{46}$ pyrochlore Ca$_2$Ti$_2$O$_6$ would also have interesting properties. However, the thermal decomposition process can prepare only a powder form of pyrochlore Ca$_2$Ti$_2$O$_6$, and pyrochlore Ca$_2$Ti$_2$O$_6$ bodies can not be obtained by sintering due to the transformation to perovskite.

We have been studying metal-organic chemical vapor deposition (MOCVD) of Ca-Ti-O system, and firstly prepared pyrochlore Ca$_2$Ti$_2$O$_6$. In this paper, the effects of substrate temperature ($T_{sub}$) and Ca/Ti ratio ($R_{Ca/Ti}$) on the formation of pyrochlore Ca$_2$Ti$_2$O$_6$ were reported.

2. Experimental Procedures

A vertical cold-wall type CVD apparatus was used to prepare Ca-Ti-O films. Source precursors of Ca(dpm)$_2$ (bis-dipivaloylmethanato-calcium) and Ti(O-i-Pr)$_2$(dpm)$_2$ (bis-isopropoxy-bis-dipivaloylmethanato-titanium) powders were heated at 523 to 573 and 393 to 453 K, respectively. The source vapors were carried into the CVD reactor with Ar gas. O$_2$ gas was separately introduced by using a double tube nozzle, and mixed with the precursor vapors above a substrate holder. The total gas flow rate ($F_R_{tot} = F_R_{Ar} + F_R_{O_2} + F_R_{source}$ vapor) was fixed at $3.33 \times 10^{-6} \text{ m}^3 \text{s}^{-1}$.$^{4}$ The total pressure ($P_{tot}$) in the CVD reactor was kept at 0.8 kPa, and the substrate temperature ($T_{sub}$) was changed from 873 to 1073 K. Detailed experimental set up and the experimental procedure were reported elsewhere. The deposition conditions are summarized in Table 1. Fused quartz glass plates ($10 \times 15 \times 0.5 \text{ mm}$) were used as substrates. The crystal structure was identified by X-ray diffraction (XRD). The microstructure was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and Discussion

Figure 1 shows that the XRD patterns of the Ca-Ti-O films prepared at $T_{sub} = 1073$ K and $P_{tot} = 0.8$ kPa. The Ca-Ti-O films consisted of perovskite CaTiO$_3$, pyrochlore Ca$_2$Ti$_2$O$_6$ and anatase TiO$_2$. A small amount of Ca$_2$Ti$_2$O$_6$ phase was detected at $R_{Ca/Ti} = 0.95$ (Fig. 1(c)), and the intensity of Ca$_2$Ti$_2$O$_6$ increased with decreasing $R_{Ca/Ti}$, and the Ca$_2$Ti$_2$O$_6$ phase became as a main phase at $R_{Ca/Ti} = 0.34$ (Fig. 1(a)). Pyrochlore Ca$_2$Ti$_2$O$_6$ is a face-centered cubic

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<th>Table 1 Deposition condition of Ca-Ti-O film.</th>
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<td>Precursor Temperature, $T_{prec}$</td>
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<tr>
<td>Ca(dpm)$_2$</td>
</tr>
<tr>
<td>Ti(OiPr)$_2$(dpm)$_2$</td>
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<tr>
<td>Total gas flow rate, $F_R_{tot}$</td>
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<tr>
<td>Carrier Gas</td>
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<td>Ca(dpm)$_2$</td>
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<tr>
<td>Ti(OiPr)$_2$(dpm)$_2$</td>
</tr>
<tr>
<td>O$<em>2$ gas flow rate, $F_R</em>{O_2}$</td>
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<tr>
<td>Total pressure, $P_{tot}$</td>
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<tr>
<td>Deposition temperature, $T_{dep}$</td>
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<tr>
<td>Deposition time</td>
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<td>Substrate</td>
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Keywords: metal-organic chemical vapor deposition, calcium titanate, pyrochlore, microstructure
structure whose lattice parameter could be 0.9953 nm. The Ca-Ti-O film showed in Fig. 1(a) was identified as a mixture of CaTiO$_3$, Ca$_2$Ti$_2$O$_6$ and a small amount of anatase TiO$_2$. The lattice parameter of Ca$_2$Ti$_2$O$_6$ was calculated as $a = 0.999$ nm that was close to that of JCPDS data of pyrochlore Ca$_2$Ti$_2$O$_6$. $^{3}$ Ca(OH)$_2$ peaks in Fig. 1(b) must be formed by the reaction of CaO and moisture in air after deposition. Mixed phases of CaTiO$_3$, anatase TiO$_2$ and/or CaO were obtained but no Ca$_2$Ti$_2$O$_6$ phase was identified at $T_{\text{sub}} = 873$ and 973 K.

Figure 2 shows the electron diffraction pattern of the Ca-Ti-O film prepared at $T_{\text{sub}} = 1073$ K, $P_{\text{tot}} = 0.8$ kPa and $R_{\text{Ca/Ti}} = 0.34$. The film was mainly Ca$_2$Ti$_2$O$_6$ where the incident zone axis was [001] and every electron diffraction spots were indexed as pyrochlore Ca$_2$Ti$_2$O$_6$.

Figure 3 shows the surface and cross-sectional morphology of the Ca-Ti-O film prepared at $T_{\text{sub}} = 1073$ K, $P_{\text{tot}} = 0.8$ kPa and $R_{\text{Ca/Ti}} = 0.34$. The film had a columnar texture as shown in Fig. 3(b). The surface had a granular microstructure with 300 nm in diameter, and the agglomerated grains consisted of smaller grains about 50 nm in diameter (Fig. 3(a)).

Figure 4 shows the relationship between $R_{\text{Ca/Ti}}$ and the fraction of Ca$_2$Ti$_2$O$_6$ phase (F) in the Ca-Ti-O films prepared at $T_{\text{sub}} = 1073$ K and $P_{\text{tot}} = 0.8$ kPa. The fraction of pyrochlore Ca$_2$Ti$_2$O$_6$ phase can be calculated from eq. (1).

$$ F = \frac{I_{\text{Ca}_2\text{Ti}_2\text{O}_6}}{I_{\text{Ca}_2\text{Ti}_2\text{O}_6} + I_{\text{CaTiO}_3} + I_{\text{TiO}_2}} $$

where, $I$ is the sum of all peaks for each phase in the Ca-Ti-O films. The Ca$_2$Ti$_2$O$_6$ phase formed in a Ti-rich region of $0.3 < R_{\text{Ca/Ti}} < 1$. The fraction of Ca$_2$Ti$_2$O$_6$ phase increased with decreasing $R_{\text{Ca/Ti}}$, and the content of Ca$_2$Ti$_2$O$_6$ phase reached 82% at $R_{\text{Ca/Ti}} = 0.46$. Savenko and Sakharov reported that the metastable Ca$_2$Ti$_2$O$_{12}$ phase formed in a Ti-rich region of $R_{\text{Ca/Ti}} = 0.2$–0.4. An excess TiO$_2$ may be necessary to stabilize the pyrochlore Ca$_2$Ti$_2$O$_6$ phase.
4. Conclusions

Pyrochlore Ca$_2$Ti$_2$O$_6$ almost in a single phase was firstly prepared by MOCVD using Ca(dpm)$_2$ and Ti(O-i-Pr)$_2$(dpm)$_2$ precursors at $T_{sub} = 1073$ K, $P_{tot} = 0.8$ kPa and $0.3 < R_{Ca/Ti} < 1$. The content of Ca$_2$Ti$_2$O$_6$ phase increased with decreasing $R_{Ca/Ti}$ and reached 82% at $R_{Ca/Ti} = 0.46$. The pyrochlore Ca$_2$Ti$_2$O$_6$ showed a columnar texture consisting of agglomerated grains of 50 nm in diameter.

Acknowledgements

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REFERENCES