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RAPID PUBLICATION

Preparation of Pyrochlore $Ca_2Ti_2O_6$ 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 $Ti(O\text{-}i\text{-}Pr)_2(dpm)_2$ 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 $Ca_2Ti_2O_6$ and perovskite $CaTiO_3$ phase were obtained at $T_{sub} = 1073$ K and $0.35 < R_{Ca/Ti} < 1$. The content of pyrochlore $Ca_2Ti_2O_6$ increased with decreasing $R_{Ca/Ti}$. Pyrochlore $Ca_2Ti_2O_6$ almost in a single phase was obtained at $R_{Ca/Ti} = 0.46$. The morphology of pyrochlore $Ca_2Ti_2O_6$ was agglomerated fine grains about 50 nm in diameter having a columnar texture.
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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.[1)] Perovskite, $CaTiO_3$, and several compounds such as $Ca_4Ti_3O_{10}$ and $Ca_3Ti_2O_7$ have been known as stable phases in the Ca-Ti-O system. Savenko and Sakharov reported a cubic phase of $Ca_2Ti_5O_{12}$ having a lattice parameter of 0.862 nm.[2)] 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 $Ca_2Ti_2O_6$ having a lattice parameter of 0.995 nm.[3)] Since then, no paper on the preparation of pyrochlore $Ca_2Ti_2O_6$ has been published.

Pyrochlore has a general composition formula of $A_2B_2X_6Y$, 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 $Tl_2Mn_2O_7$,[4)] metal-insulator transition of $Tl_2Ru_2O_{7-\delta}$[5)] and anomalous Hall effect of Mo system pyrochlore,[6)] pyrochlore $Ca_2Ti_2O_6$ would also have interesting properties. However, the thermal decomposition process can prepare only a powder form of pyrochlore $Ca_2Ti_2O_6$, and pyrochlore $Ca_2Ti_2O_6$ 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 $Ca_2Ti_2O_6$. In this paper, the effects of substrate temperature (T_{sub}) and Ca/Ti ratio ($R_{Ca/Ti}$) on the formation of pyrochlore $Ca_2Ti_2O_6$ 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 $Ti(O\text{-}i\text{-}Pr)_2(dpm)_2$ (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 ($FR_{tot} = FR_{Ar} + FR_{O2} + FR_{source\ vapor}$) was fixed at 3.33×10^{-6} m^3 s^{-1}. 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.[7)] The deposition conditions are summarized in Table 1. Fused quartz glass plates ($10 \times 15 \times 0.5$ 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).

Table 1 Deposition condition of Ca-Ti-O film.

Precursor Temperature, T_{prec}	
$Ca(dpm)_2$	: 323–573 K
$Ti(OiPr)_2(dpm)_2$	: 193–453 K
Total gas flow rate, FR_{tot}	: 3.33×10^{-6} m^3 s^{-1}
Carrier Gas	: Ar
$Ca(dpm)_2$	: 0.83×10^{-6} m^3 s^{-1}
$Ti(OiPr)_2(dpm)_2$	: 0.83×10^{-6} m^3 s^{-1}
O_2 gas glow rate, FR_{O_2}	: 1.2×10^{-6} m^3 s^{-1}
Total pressure, P_{tot}	: 0.8 kPa
Deposition temperature, T_{dep}	: 873–1073 K
Deposition time	: 0.3–0.9 ks
Substrate	: fused quartz glass

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 $Ca_2Ti_2O_6$ and anatase TiO_2. A small amount of $Ca_2Ti_2O_6$ phase was detected at $R_{Ca/Ti} = 0.95$ (Fig. 1(c)), and the intensity of $Ca_2Ti_2O_6$ increased with decreasing $R_{Ca/Ti}$, and the $Ca_2Ti_2O_6$ phase became as a main phase at $R_{Ca/Ti} = 0.34$ (Fig. 1(a)). Pyrochlore $Ca_2Ti_2O_6$ is a face-centered cubic structure whose lattice parameter could be 0.9953 nm.[3] The Ca-Ti-O film showed in Fig. 1(a) was identified as a mixture of $CaTiO_3$, $Ca_2Ti_2O_6$ and a small amount of anatase TiO_2. The lattice parameter of $Ca_2Ti_2O_6$ was calculated as $a = 0.999$ nm that was close to that of JCPDS data of pyrochlore $Ca_2Ti_2O_6$.[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 $Ca_2Ti_2O_6$ phase was identified at $T_{sub} = 873$ and 973 K.

Figure 2 shows the electron diffraction pattern of the Ca-Ti-O film prepared at $T_{sub} = 1073$ K, $P_{tot} = 0.8$ kPa and $R_{Ca/Ti} = 0.34$. The film was mainly $Ca_2Ti_2O_6$ where the incident zone axis was [001] and every electron diffraction spots were indexed as pyrochlore $Ca_2Ti_2O_6$.

Figure 3 shows the surface and cross-sectional morphology of the Ca-Ti-O film prepared at $T_{sub} = 1073$ K, $P_{tot} = 0.8$ kPa and $R_{Ca/Ti} = 0.34$. 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 $R_{Ca/Ti}$ and the fraction of $Ca_2Ti_2O_6$ phase (F) in the Ca-Ti-O films prepared at $T_{sub} = 1073$ K and $P_{tot} = 0.8$ kPa. The fraction of pyrochlore $Ca_2Ti_2O_6$ phase can be calculated from eq. (1).

$$F = \frac{I_{Ca_2Ti_2O_6}}{I_{Ca_2Ti_2O_6} + I_{CaTiO_3} + I_{TiO_2}} \quad (1)$$

where, I is the sum of all peaks for each phase in the Ca-Ti-O films. The $Ca_2Ti_2O_6$ phase formed in a Ti-rich region of $0.3 < R_{Ca/Ti} < 1$. The fraction of $Ca_2Ti_2O_6$ phase increased with decreasing $R_{Ca/Ti}$, and the content of $Ca_2Ti_2O_6$ phase reached 82% at $R_{Ca/Ti} = 0.46$. Savenko and Sakharov reported that the metastable $Ca_2Ti_5O_{12}$ phase formed in a Ti-rich region of $R_{Ca/Ti} = 0.2$–0.4. An excess TiO_2 may be necessary to stabilize the pyrochlore $Ca_2Ti_2O_6$ phase.

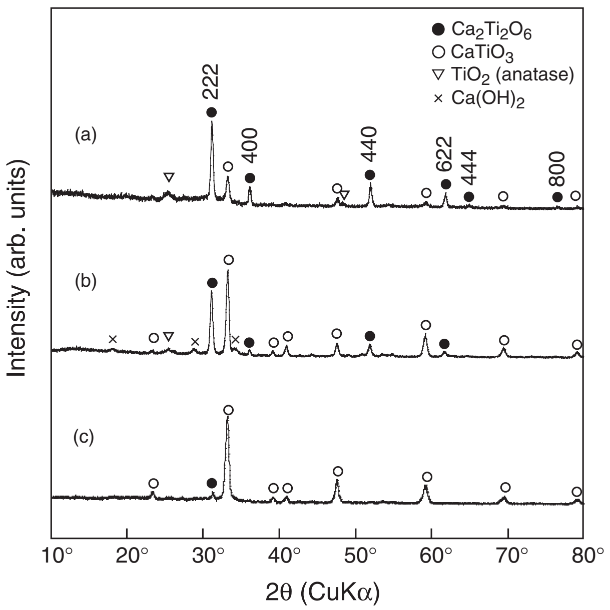

Fig. 1 XRD patterns of Ca-Ti-O films prepared at $T_{sub} = 1073$ K and $P_{tot} = 0.8$ kPa. (a) $R_{Ca/Ti} = 0.34$, (b) $R_{Ca/Ti} = 0.66$ and (c) $R_{Ca/Ti} = 0.95$.

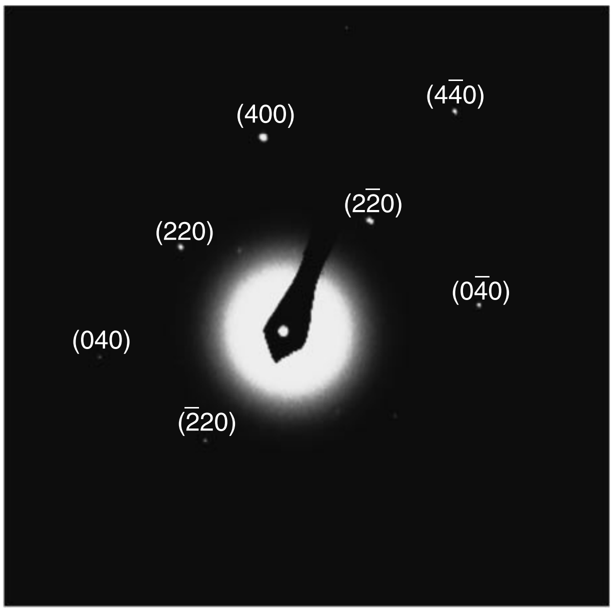

Fig. 2 Electron diffraction pattern of mainly pyrochlore $Ca_2Ti_2O_6$ phase prepared at $T_{sub} = 1073$ K, $P_{tot} = 0.8$ kPa and $R_{Ca/Ti} = 0.34$.

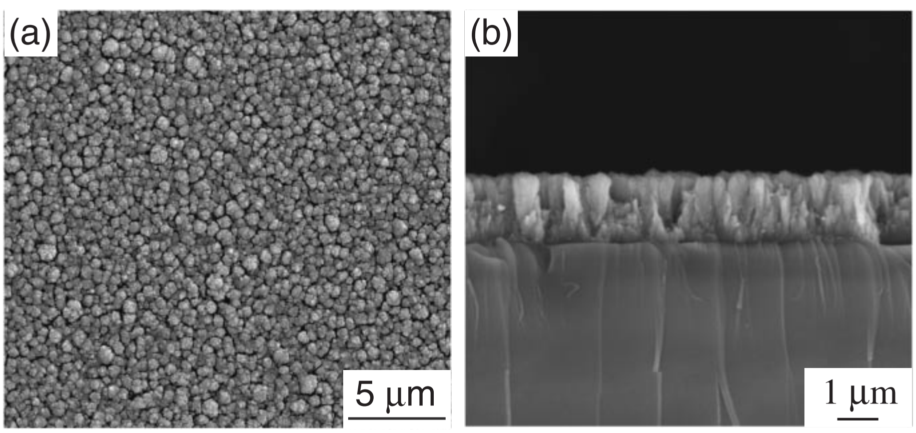

Fig. 3 Surface and cross-sectional morphologies of mainly pyrochlore $Ca_2Ti_2O_6$ phase prepared at $T_{sub} = 1073$ K, $P_{tot} = 0.8$ kPa and $R_{Ca/Ti} = 0.34$.

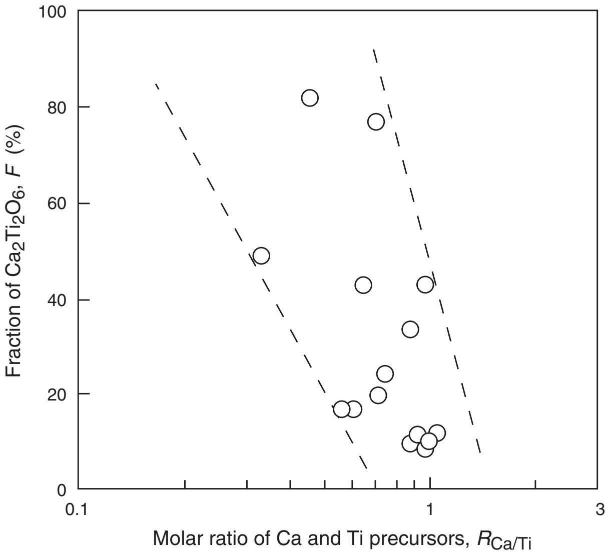

Fig. 4 Effect of $R_{Ca/Ti}$ on the peak intensity ratio of $Ca_2Ti_2O_6$ in the films prepared at $T_{sub} = 1073$ K and $P_{tot} = 0.8$ kPa.

4. Conclusions

Pyrochlore $Ca_2Ti_2O_6$ almost in a single phase was firstly prepared by MOCVD using $Ca(dpm)_2$ and $Ti(O\text{-}i\text{-}Pr)_2(dpm)_2$ precursors at $T_{sub} = 1073$ K, $P_{tot} = 0.8$ kPa and $0.3 < R_{Ca/Ti} < 1$. The content of $Ca_2Ti_2O_6$ phase increased with decreasing $R_{Ca/Ti}$, and reached 82% at $R_{Ca/Ti} = 0.46$. The pyrochlore $Ca_2Ti_2O_6$ showed a columnar texture consisting of agglomerated grains of 50 nm in diameter.

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