

## Formation of New Compound $13\text{CaO}\cdot 6\text{Al}_2\text{O}_3\cdot 2\text{HfO}_2$ by Melt Processing

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Ternary compound in the  $\text{CaO-Al}_2\text{O}_3\text{-HfO}_2$  system,  $13\text{CaO}\cdot 6\text{Al}_2\text{O}_3\cdot 2\text{HfO}_2$  (stated by  $\text{C}_{13}\text{A}_6\text{Hf}_2$  hereafter), was fabricated by melt process using an arc-imaging furnace. This compound has not been reported ever, based on our knowledge. The new phase has similar XRD patterns to the  $13\text{CaO}\cdot 6\text{Al}_2\text{O}_3\cdot 2\text{ZrO}_2$  ( $\text{C}_{13}\text{A}_6\text{Z}_2$ ) phase in the ternary phase diagram  $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ . Though Zirconium and Hafnium generally shows similar properties, the reactivity of these two compounds in the solid phase was totally different. The Zirconium compound ( $\text{C}_{13}\text{A}_6\text{Z}_2$ ) was fabricated by both solid state reaction (1200°C, 6h) and the melt process, starting from powder mixture of  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{ZrO}_2$ . On the other hand, the Hafnium compound ( $\text{C}_{13}\text{A}_6\text{Hf}_2$ ) was fabricated only by the melt process from powder mixture of  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{HfO}_2$ . The zirconium pure phase was not fabricated by the solid state reaction; it gave three isolated phases,  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  ( $\text{C}_{12}\text{A}_7$ ),  $\text{CaHfO}_3$ , and  $\text{C}_{13}\text{A}_6\text{Hf}_2$ . This difference might be caused by a low diffusion rate of Hf ions in the  $\text{C}_{12}\text{A}_7$  structure.

Key words: Melt Processing, Solid State, Diffusion, Hafnium, New Compound

### 1. INTRODUCTION

Recently melt process for the fabrication of ceramics has attracted increasing attention due to the easy shaping of work pieces and other advantages compared to traditional powder sintering methods.<sup>1</sup> Generally in the powder methods based on the solid state reaction, diffusion of the ions determine the reaction rate because the diffusivities of the ions are quite low compared to the liquid state of the ceramics. Due to the slow ion diffusion rate in the solids, intermediate phases which differ from a given stoichiometry frequently appears; even though you select a stoichiometric composition precisely, you may obtain the other phases by solid state reaction. In some systems, it gets in the way to find a stable phase which can not be easily obtained by the solid state reaction. For such case, melt process has high potentials to solve the problem. Melt state of the ceramics allows ions to modify the bonding length and surrounding atoms each other due to high thermal vibration at high temperatures, and therefore, ions are able to diffuse more rapidly than in the solid. We have studied by melting method on binary or ternary oxides systems<sup>2-4</sup> e.g. the titania-rich side of the  $\text{Al}_2\text{O}_3\text{-TiO}_2$  system (up to 50 mol% titania) under rapid cooling conditions with respect to the phase

formation etc.<sup>5</sup>

In this study, we report an unknown compound  $\text{Ca}_{13}\text{Al}_{12}\text{Hf}_2\text{O}_{35}$  fabricated by a melt / solidification method.  $\text{Ca}_{13}\text{Al}_{12}\text{Hf}_2\text{O}_{35}$  has a quite similar compositions and crystal structure to the  $\text{Ca}_{13}\text{Al}_{12}\text{Zr}_2\text{O}_{35}$ . The zirconium compound and  $\text{ZrO}_2\text{-CaO-Al}_2\text{O}_3$  ternary phase were studied by some research groups but the hafnium compound has not, even though it has a high potential for many application e.g. transparent material with a high refractive index<sup>6</sup>. In the present study, we report the ternary phase diagram with tie lines near the new compound as well as fabrication techniques.

### 2. EXPERIMENTAL

Commercially available  $\text{HfO}_2$  (99.9%, Daiichi Kigenso Kagaku Kogyo Co., Ltd.),  $\text{CaCO}_3$  (99.5 %, Cica-Reagent, Kanto Chemical Co. Inc.),  $\text{Al}_2\text{O}_3$  (99.99 %, AKP-30, Sumitomo Chemical Co., Ltd.), and  $\text{ZrO}_2$  (99.8%, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) powders were used as starting materials. The powders weighed with cation molar ratios shown in Table I and Table II were wet blended for 20 minutes using an alumina mortar with ethanol added and dried in an oven at 80 °C for 1 day to remove the ethanol. The mixed powder was subsequently reacted by melting using an arc imaging furnace or by annealing at 1200 °C. In the

Table I. Sample composition prepared in the present study and corresponding crystal phases.  $\text{C}_{13}\text{A}_6\text{Hf}_2$  and  $\text{C}_3\text{A}$  indicate  $\text{Ca}_{13}\text{Al}_{12}\text{Hf}_2\text{O}_{35}$  and  $\text{Ca}_3\text{Al}_2\text{O}_6$ , respectively.

Sample	Composition (mol %)			Phase
	HfO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	
1	30.0	10.0	60.0	CaHf <sub>4</sub> O <sub>9</sub> , CaHfO <sub>3</sub>
2	30.0	25.0	45.0	CaHf <sub>4</sub> O <sub>9</sub>
3	30.0	40.0	30.0	CaHf <sub>4</sub> O <sub>9</sub> , CA <sub>2</sub>
4	45.0	10.0	45.0	CaHfO <sub>3</sub> , CaHf <sub>4</sub> O <sub>9</sub>
5	45.0	25.0	30.0	CaHfO <sub>3</sub>
6	45.0	40.0	15.0	CaHfO <sub>3</sub>
7	60.0	10.0	30.0	CaHfO <sub>3</sub> , C <sub>3</sub> A
8	60.0	25.0	15.0	CaHfO <sub>3</sub>
9	61.9	28.6	9.5	C <sub>13</sub> A <sub>6</sub> Hf <sub>2</sub>

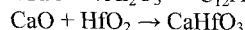
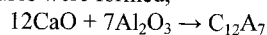
arc imaging furnace for the melt process, sample powders were placed on a water-cooled copper plate and melted by focused irradiating light of a 10-kW Xe-lamp (UF-10001, Ushio Inc., Japan) for several molten sample formed a spherical shape with 3-4mm in size due to the surface tension. By a sudden cutoff of the irradiating light, the sample sphere was solidified on the water-cooled copper plate. The solidified sample was re-melted on another copper plate to complete melting. The total melting time was from 5 to 10 seconds. The cooling rate was estimated to be approximately 200-500 °C/sec. Negligible contamination could be observed during melting because the spherical sample was almost point-contacted to the copper plate. The detailed procedure and equipment were reported in previous reports<sup>6,7</sup>. Samples 6, a, and c-i generated transparent glass phase by the arc-imaging furnace. In order to crystallize them, the samples were subsequently annealed at 1200 °C for 6h in air using an electric furnace.

In the annealing process for the solid state reaction, the sample 9 was put into a platinum crucible and heated at 1200 °C in air using electric furnace. In order to compare two neighboring phases composed of hafnium and zirconium, the sample 10, which had the same molar ratio as the sample 9, but hafnium was substituted by zirconium, was prepared by the same matters as the sample 9. The sample 10 was subjected to the arc-imaging furnace as well as the annealing process. For all of the samples prepared, crystallographic analysis was performed by the XRD (CuK $\alpha$ , MXP3VA, MAC Science Co. Ltd., Tokyo, Japan).

### 3. RESULT AND DISCUSSION

#### 3.1 New compound $\text{C}_{13}\text{A}_6\text{Hf}_2$

As shown in Fig. 1, the new phase  $\text{C}_{13}\text{A}_6\text{Hf}_2$  was prepared by the arc-imaging melt. The compound showed similar XRD patterns as the  $\text{C}_{13}\text{A}_6\text{Zr}_2$ , which was reported by Berezhnoi et al.<sup>8</sup> and Espinosa et al.<sup>9</sup> As easily understood, pure  $\text{C}_{13}\text{A}_6\text{Hf}_2$  obtained by the melting was not obtained by annealing; three phases  $\text{C}_{13}\text{A}_6\text{Hf}_2$ ,  $\text{C}_{12}\text{A}_7$ , and  $\text{CaHfO}_3$  appeared. From this result, we can assume the solid state reaction mechanisms; first two binary phases were formed,



These two phases reacted each other and the  $\text{C}_{13}\text{A}_6\text{Hf}_2$  were formed finally. Interestingly, even though the annealing time at 1200 °C was increased, to 12h and 24h,

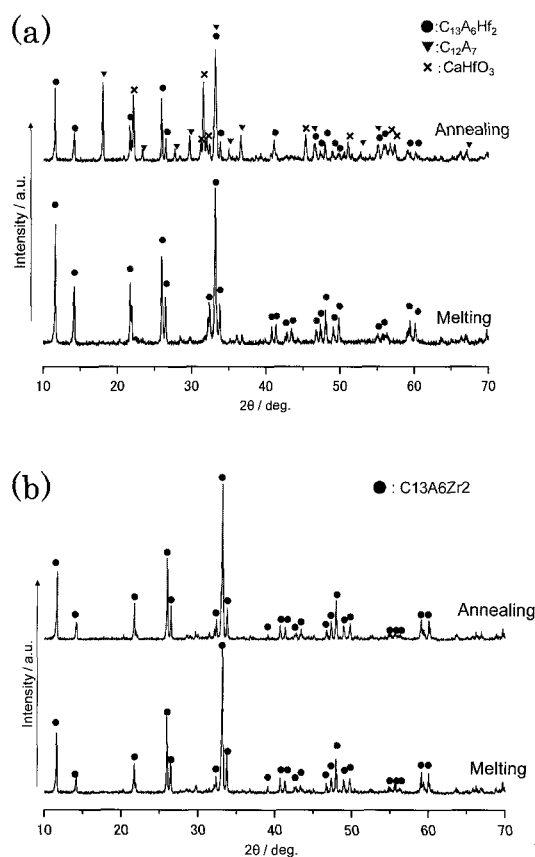


Fig. 1. (a) XRD patterns of the sample 9 prepared by annealing at 1200 C (upper) and by the arc-imaging melt (lower). (b) XRD patterns obtained for the sample 10 by annealing at 1200 C (upper) and by the arc-imaging melt (lower).

the XRD patterns showed almost no decreasing of the impurity phases.

On the other hand for the zirconium compound, pure  $\text{C}_{13}\text{A}_6\text{Zr}_2$  was obtained both by melting and annealing. These differences imply that a diffusion rate of Hf ion in the  $\text{C}_{12}\text{A}_7$  is considerably lower than Zr ion.

#### 3.2 HfO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> phase diagram

HfO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> ternary phase diagram was obtained as shown in Fig. 2. Due to rapid cooling by the

Table II. Sample composition prepared in the present study and corresponding crystal phases. Sample names with asterisk indicate sample obtained as glass phases by the arc imaging melt, which was subsequently crystallized by annealing.  $C_{13}A_6Hf_2$ ,  $C_3A$ ,  $CA_2$ , and  $CA$  indicate  $Ca_{13}Al_{12}Hf_2O_{35}$ ,  $Ca_3Al_2O_6$ ,  $CaAl_4O_7$ , and  $CaAl_2O_4$ , respectively.

Sample	Composition (mol %)			Phase
	HfO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	
a*	50.0	35.0	15.0	$C_{13}A_6Hf_2$ , $CaHfO_3$ , $CA_2$
b	60.0	30.0	10.0	$C_{13}A_6Hf_2$
c*	55.0	35.0	10.0	$C_{13}A_6Hf_2$ , $CA_2$ , $CaHfO_3$
d*	50.0	40.0	10.0	$C_{13}A_6Hf_2$ , $CA_2$
e*	45.0	45.0	10.0	$C_{13}A_6Hf_2$ , $CaHfO_3$ , $CA_2$
f*	65.0	35.0	5.0	$C_{13}A_6Hf_2$ , $C_{12}A_7$ , $C_3A$
g*	60.0	35.0	5.0	$C_{13}A_6Hf_2$ , $C_{12}A_7$ , $CA$
h*	55.0	40.0	5.0	$C_{13}A_6Hf_2$ , $CA$
i	50.0	45.0	5.0	$CA$ , $CaHfO_3$

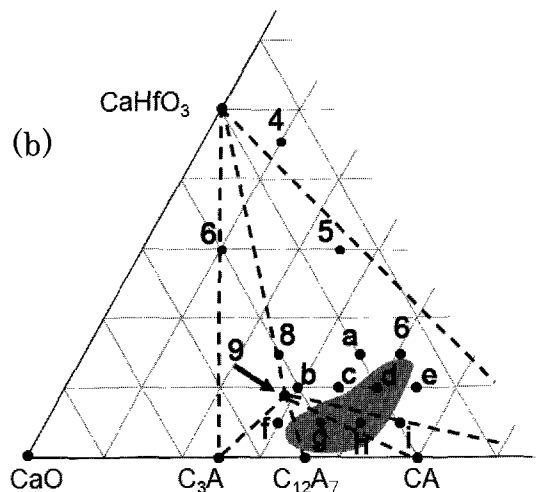
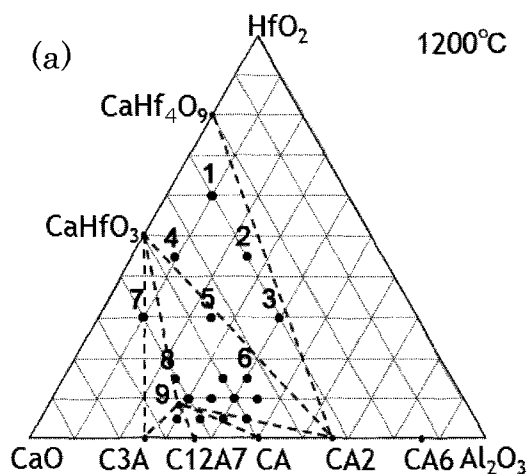


Fig. 2. (a) Phase diagram and tie lines in the HfO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> system and (b) enlarged phase diagram near the sample 9 ( $C_{13}A_6Hf_2$ ). Amorphous phase region by the arc-imaging melt was indicated by dark area.

arc-imaging furnace, some of the samples, near the compositions d, g, and h, were obtained as glass phases as marked out in the figure. From the crystal phases obtained (shown in Table I and II), tie lines can be drawn between  $C_{13}A_6Hf_2$  and the binary phases,  $CaHfO_3$ ,  $C_3A$ ,  $C_{12}A_7$ ,  $CA$ , and  $CA_2$ , respectively. It is not confirmed in this study whether the new compound melts congruently or in-congruently as seen in the  $C_{13}A_6Zr_2$  compound.<sup>10</sup>

#### CONCLUSION

HfO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> ternary phase diagram was studied by the melt process. New compound,  $C_{13}A_6Hf_2$ , was found in the ternary system. The compound had similar structure to the  $C_{13}A_6Zr_2$  phase. The compound was fabricated by melt process, but was not fabricated by annealing process at 1200 °C. Phase diagram near the new compound was suggested.

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