



## Thermal Oxidation Curing of Polycarbosilane for SiOC Fiber Process†

DONG-GEUN SHIN

Energy Efficient Materials Team, Korea Institute of Ceramic Engineering and Technology, 233-5 Gasan-dong, Geumcheon-gu, Seoul 153-801, Republic of Korea

Corresponding author: E-mail: dgshin73@kicet.re.kr

Published online: 23 June 2014;

AJC-15424

Two types of polycarbosilane having a different molecular weight were prepared from polydimethylsilane in the presence of zeolite as a catalyst and additional heating at 400 °C for 5-15 h. They were compared the thermal oxidation behaviour to optimize the curing condition for SiC fiber fabrication process. From the thermogravimetry analysis, the weight of low  $M_w$  polycarbosilane (PCS\_1) was rapidly increased and decreased than that of high  $M_w$  polycarbosilane (PCS\_2) which represents that oxygen act as a cross-linking among react with methyl in the polycarbosilane molecule caused to rapid increase whereas they are also decomposed in the form of alkane ( $C_2H_6$ ) or methane ( $CH_4$ ) at the temperature up to 350 °C, which leads the total weight decrease in PCS\_1. For the isothermal oxidation of PCS\_1, weight gain at 200 °C was consistently increased with isothermal time and reached to 13 wt % after 5 h. From SEM and XRD results, SiOC fibers obtained by pyrolysis at 1200 °C in Ar showed clean surface and a typical fracture behaviour of glassy phase which represent an excellent mechanical strength.

**Keywords:** Polycarbosilane, SiC fiber, Ceramic matrix composites, Curing, Thermal oxidation.

### INTRODUCTION

Silicon carbide (SiC) fibers have developed by Yajima group exhibit an excellent mechanical strength, creep and oxidation resistance at high temperatures which make it possible to use as a reinforcements for ceramic matrix composites (CMCs) for the harsh environmental application<sup>1-5</sup>. It is usually produced from a preceramic polymer known as polycarbosilane (PCS) through the following steps: (1) synthesis and rheology control of PCS, (2) the fiber spinning of PCS in a molten state for the preparation of continuous PCS green fibers, (3) a curing treatment to make the PCS fibers infusible (thermal oxidation is one of the common methods) and (4) the pyrolysis up to 1200 °C for making a SiC fiber in the form of silicon-oxycarbide (SiOC) through the organic to inorganic conversion mechanism<sup>6,7</sup>. The melt spinning step is one of important steps to determine the mechanical properties of the SiC fiber because fiber diameters and macro-defects such as void, artifact are controlled during this step. In case of thermal oxidation curing, oxygen acts as a cross-linker among carbosilane molecules (Fig. 1) and it remains in the fiber until the amorphous SiOC matrix decomposes into SiO(g) and CO(g) at higher temperature up to 1400 °C<sup>3,4</sup>. At this time, the decomposition of the matrix induces the inhomogeneous SiC crystal growth with a lot of

pore formation and lowers the mechanical strength if the oxygen content is high enough.

Above mentioned three steps [from step (2) to step (4)] strongly depend on the first step because the rheological properties of the PCS have a critical effect to the fiber spinning and curing condition and the defect formation in the fiber.

In this study, it has been considered to carry out a comparative study on the thermal oxidation behaviour for two types of PCS having a different molecular weight to identify suitable precursor properties for SiC fiber fabrication process.

### EXPERIMENTAL

Polycarbosilane was synthesized from polydimethylsilane (PDMS) under mild pressure (below 10 atm) in the presence of zeolite as a catalyst. Polydimethylsilane and 10 wt % of ZSM-5 were uniformly mixed and loaded into an autoclave vessel<sup>9,10</sup>. Then it was heated to 350 °C for 10-20 h and the temperature was further heated to 400 °C for 10 h. After filtering the insoluble portion and vacuum distillation of low molecular portion in the as-synthesized product, the molecular weight was adjusted through additional heating at 400 °C for 5-15 h. Table-1 shows the properties of the synthesized products with different additional heating condition.

†Presented at 5<sup>th</sup> International Symposium on Application of Chemical and Analytical Technologies in Nuclear Industries (Nu-ACT 2013), Daejeon, Korea

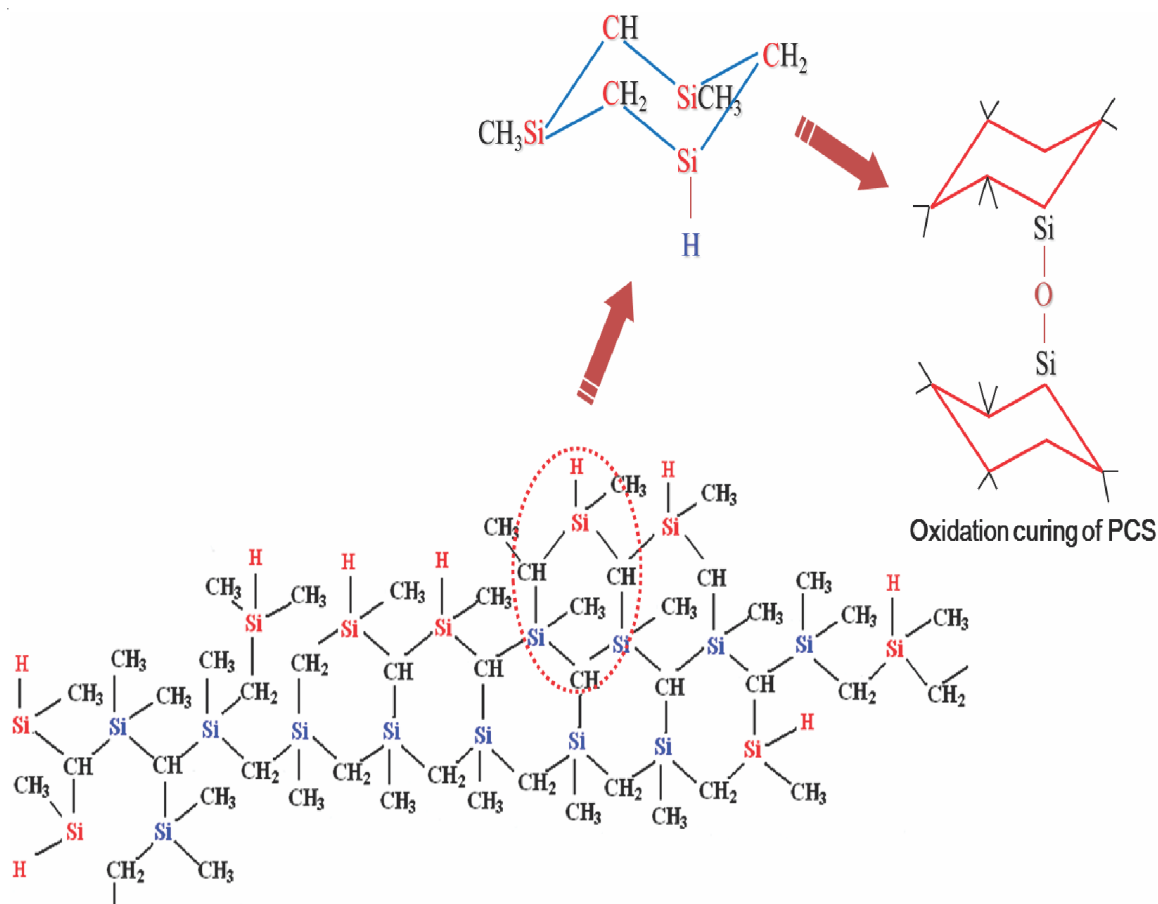


Fig. 1. Molecular structure of polycarbosilane and cross-linking mechanism by oxidation

TABLE-1  
SOME PROPERTIES OF POLYCARBOSILANE  
SYNTHESIZED IN THIS STUDY

Sample	$M_n$	$T_m$ (°C)	$T_s$ (°C)	$T_c$ (°C)	$T_{py}$ (°C)
PCS_1	2350	210	250	180-220	1200
PCS_2	2979	250	280	—	—

$T_m$ : Melting temperature,  $T_s$ : spinning temperature,  $T_c$ : curing temperature,  $T_{py}$ : pyrolysis temperature.

The whole experimental process for fabrication of SiOC fibers was described in Fig. 2. Polycarbosilane was melt spun between 230-250 °C using a lab-scale spinning apparatus with a spinneret having 500 mm single nozzle under argon gas pressure in order to get a continuous green PCS fiber. The spinning conditions were optimized with respect to melting temperature of PCS since the viscosity critically affected to the spinn-

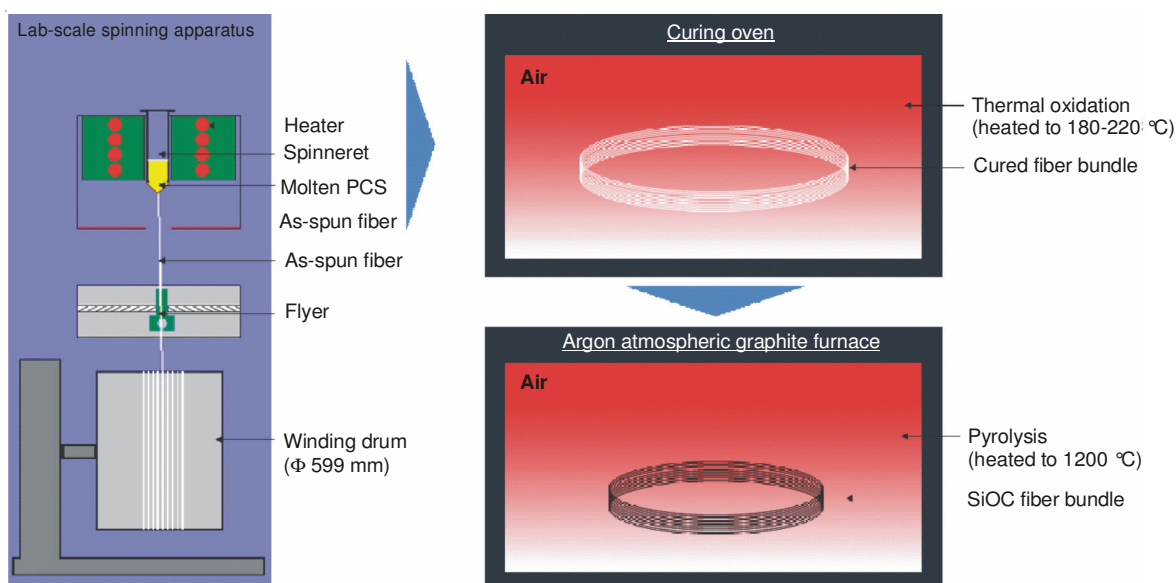


Fig. 2. Whole experimental processes for preparing the SiOC fiber from molten polycarbosilane

ability<sup>6,9,10</sup>. The diameter of the as-spun PCS fibers were 20–30  $\mu\text{m}$  as determined by optical microscopy.

The as-spun PCS fiber bundles were cured through the thermal oxidation in the oven to introduce oxygen into the fibers. The amount and distribution of the oxygen was controlled by curing time (between 1 and 10 h) and temperature (between 180 and 220  $^{\circ}\text{C}$ ). Then, the cured fibers were pyrolyzed at 1200  $^{\circ}\text{C}$  for 1 h in an argon atmospheric graphite furnace to obtain a SiOC fiber.

Thermogravimetric analysis (TGA/SDTA 851, Mettler Toledo, USA) was used to analyze the thermal oxidation behaviour of the green fiber. Microstructure and morphology of the SiC fibers with experimental conditions were observed using scanning electron microscopy (SEM, S-2700, Hitachi, Japan) and the structural change during pyrolysis was characterized by X-ray diffraction (XRD, FR-150, Enraf-Nonius Co., Netherlands).

## RESULTS AND DISCUSSION

The as-spun PCS fibers have a smooth surface and were easily broken under weak stress. Fig. 3 shows the thermogravimetry analysis (TGA and DTG) results for two types of PCS fiber prepared from PCS\_1 (red line) and PCS\_2 (blue line) under (a) nitrogen and (b) air conditions. The weight of PCS fibers was gradually decreased with increasing temperature under  $\text{N}_2$  and there were three major reductions at around 400, 530 and 650  $^{\circ}\text{C}$  (DTG curve in Fig. 3). During the thermal decomposition, pendant group of PCS molecular structure such as methyl, methylene, hydrogen and carbon monoxide are removed away in the form of ethane ( $\text{C}_2\text{H}_6$ ), methane ( $\text{CH}_4$ ), hydrogen ( $\text{H}_2$ ) and other minor gases with remaining inorganic Si-C-O residue<sup>11–13</sup>. In contrast, the weight was increased and decreased again with increasing temperature when PCS fibers were heated under air atmosphere. Weight gain was closely related to the introduction of oxygen as a cross-linker among polymer chains<sup>12,13</sup>. The slope of the curve was gradually increased which means that the oxidation was initially started with slow and then accelerated. However, the weight gain became slow down at the temperature up to 350  $^{\circ}\text{C}$  because PCS started to decompose. This thermal behaviour of PCS fibers is strongly dependent on the properties of PCS itself. In Fig. 3, both of PCS fibers were started to increase their weight at the same temperature when heated under air atmosphere. However, the weight gain of PCS\_1 rapidly increased and decreased again than that of PCS\_2. It is closely related to molecular structure of PCS. Model of the molecular structure of PCS which was reported by Hasegawa *et al.*<sup>2</sup> and Kim *et al.*<sup>14</sup> indicates that molecular PCS composes  $\text{SiC}_4$  bond structure in the backbone and methyl and hydrogen bond in the pendent which act as a cross-linking site with oxygen during thermal oxidation curing<sup>3,14</sup>. Low  $M_w$  PCS (PCS\_1) has high  $\text{SiC}_3\text{H}$  bond whereas high  $M_w$  PCS (PCS\_2) has high  $\text{SiC}_4$  bond portion. It represents that PCS\_1 have much methyl ( $\text{CH}_3$ -) and they react with oxygen for cross-linking among PCS molecule caused to rapid increase of the weight in PCS\_1. At the temperature up to 350  $^{\circ}\text{C}$ , they are also decomposed in the form of alkane ( $\text{C}_2\text{H}_6$ ) or methane ( $\text{CH}_4$ ) which leads the total weight decrease in PCS\_1, while decomposed gas species mainly composed  $\text{CH}_4$  and  $\text{H}_2$  in PCS\_2.

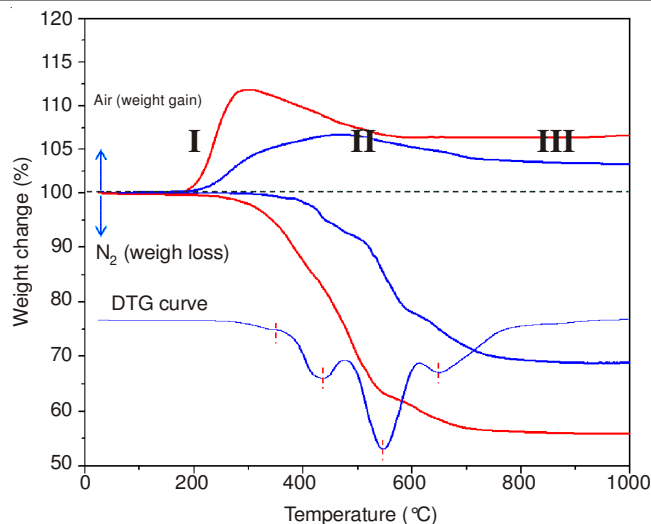


Fig. 3. Thermogravimetry analyses for polycarbosilane fiber under  $\text{N}_2$  and air atmosphere

This result indicates that it can be easily controlled for thermal oxidation curing at the initial stage of weight gain and the curing condition was set at the initial stage between 180 and 200  $^{\circ}\text{C}$ . Fig. 4 shows the isothermal oxidation of PCS\_1 at the temperature between 180 and 200  $^{\circ}\text{C}$  for finding optimum curing condition of as-spun PCS fibers. When cured at 180  $^{\circ}\text{C}$ , weight gain have become slow down and reached a plateau just after 2 h and the total weight gain was about 5.5 wt %. In case of 190  $^{\circ}\text{C}$ , it showed a similar behaviour except a steady increase even after 2 h and the total weight gain was 7.3 wt % after 5 h. On the other hand, the weight gain of as spun PCS fiber cured at 200  $^{\circ}\text{C}$  was consistently increased with isothermal time and reached to 13 wt % after 5 h.

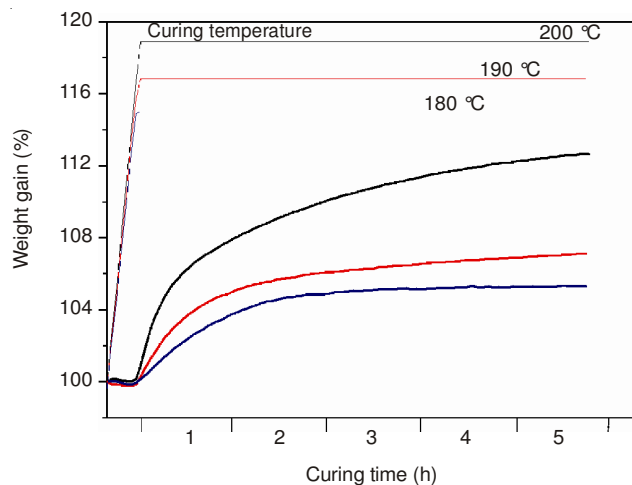


Fig. 4. Thermogravimetry analysis for PCS\_1 under isothermic condition of (a) 180, (b) 190 and (c) 200  $^{\circ}\text{C}$

Fig. 5 shows the photograph of SiOC fibers after pyrolysis at 1200  $^{\circ}\text{C}$  in Ar atmosphere with different isothermal curing condition of (a) 180, (b) 190 and (c) 200  $^{\circ}\text{C}$ . Fibers were nearly melted and difficult to collect the sample when cured at 180  $^{\circ}\text{C}$  (Fig. 5(a,d)). In case of (b) and (e), fibers were maintained its shape after pyrolysis even if stuck together. When cured at 200  $^{\circ}\text{C}$ , all the fibers were smooth and clean and there were no damage or detriment in the fibers as shown in the Fig. 5(c,f).

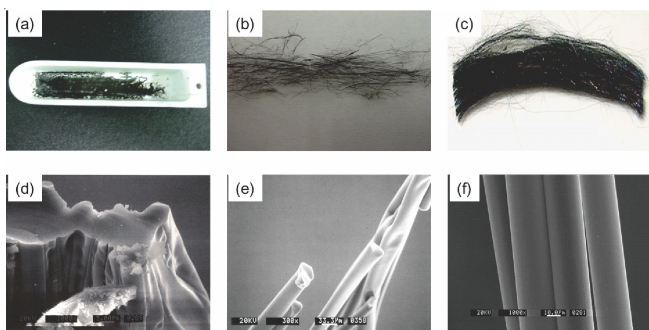


Fig. 5. Photograph of SiOC fibers after pyrolysis at 1200 °C in Ar atmosphere with different isothermal curing condition of (a) 180, (b) 190 and (c) 200 °C

It would undergo further decomposition during pyrolysis at a temperature up to 1200 °C. There was no weight change after thermal decomposition completed and amorphous SiOC structures having nanometer size of SiC crystallites were formed in the fiber. Fig. 6 shows SEM images of (a) SiOC fibers and (b) fracture surface of single filament which was cured at 200 °C for 6 h and pyrolyzed at 1200 °C for 1 h under Ar atmosphere.

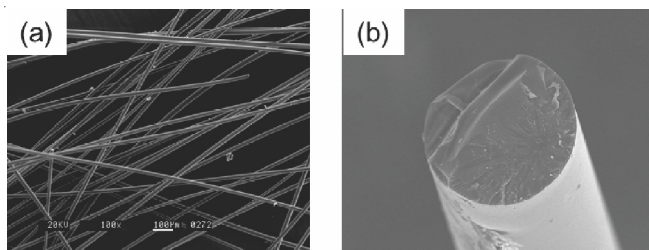


Fig. 6. SEM images of SiOC fiber pyrolyzed at 1200 °C for 1 h under Ar: (a) overall image, (b) fracture surface

Surface of the SiOC fibers were very smooth and clean with a uniform longitudinal fiber size distribution as shown in the Fig. 6(a). Fracture surface just after tensile test showed a glassy appearance. A mirror zone was observed around the internal flaw which was surrounded by a region of multiple fracture planes called as hackle region<sup>5,15</sup>.

Fig. 7 shows the X-ray diffraction pattern of pyrolyzed fiber cured at 200 °C for 6 h and pyrolyzed at 1200 °C for 1 h under Ar atmosphere. The diffraction peaks around 36°, 60° and 73° corresponded to the  $\beta$ -SiC and they were quite broad. It indicated that nanometer size of SiC phase was formed in the pyrolysis stage which signified that it was early stage of crystallization<sup>9,10</sup>.

### Conclusion

We have prepared two types of polycarbosilane having different molecular weight to identify the optimum spinning and curing condition from precursor to pyrolysis. From the TGA studies under argon and air atmosphere, the thermal behaviour of PCS fibers is strongly dependent on the properties of PCS itself and curing can be controlled at the initial stage

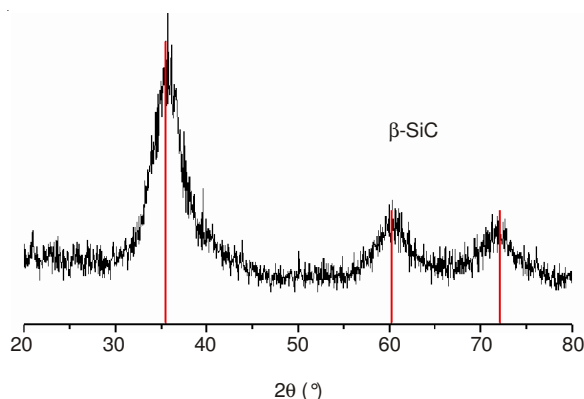


Fig. 7. X-Ray diffraction pattern of SiOC fiber pyrolyzed at 1200 °C for 1 h under argon atmosphere

of weight gain between 180 and 230 °C. SiOC fibers obtained by pyrolysis at 1200 °C in Ar showed clean surface and a typical fracture behaviour of glassy phase which represent an excellent mechanical strength.

### ACKNOWLEDGEMENTS

This research was supported by the Pioneer Research Center Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT & Future Planning (NRF-2010-0019468) and the R&D program (KPP 14008-1) by Korea Institute of Ceramic Engineering and Technology.

### REFERENCES

1. S. Yajima, J. Hayashi, M. Omori and K. Okamura, *Nature*, **261**, 683 (1976).
2. S. Yajima, Y. Hasegawa, K. Okamura and T. Matsuzawa, *Nature*, **273**, 525 (1978).
3. T. Ishikawa, Y. Kohtoku, K. Kumagawa, T. Yamamura and T. Nagasawa, *Nature*, **391**, 773 (1998).
4. T. Ishikawa, S. Kajii, K. Matsunaga, T. Hogami, Y. Kohtoku and T. Nagasawa, *Science*, **282**, 1295 (1998).
5. A. Holscher and K. Schulte, in ed.: A.R. Bunsell, *Fiber Reinforcements for Composite Materials*, Elsevier (1988).
6. A. Idesaki, M. Narisawa, K. Okamura, M. Sugimoto, S. Tanaka, Y. Morita, T. Seguchi and M. Itoh, *J. Mater. Sci.*, **36**, 5565 (2001).
7. M. Tang, Z. Yu, Y. Yu, L. Zhang and L. Chen, *J. Mater. Sci.*, **44**, 1633 (2009).
8. Z. Su, M. Tang, Z. Wang, L. Zhang and L. Chen, *J. Am. Ceram. Soc.*, **93**, 679 (2010).
9. D.H. Riu, S.J. Kim, D.G. Shin, H.R. Kim and Y.H. Kim, *J. Ceram. Soc. Jpn.*, **112**, 432 (2003).
10. D.G. Shin, D.H. Riu, Y. Kim, H.R. Kim, H.S. Park, H.E. Kim and J. Kor, *Ceram. Soc.*, **42**, 593 (2005).
11. H. Ichikawa, H. Teranishi and T. Ishikawa, *J. Mater. Sci. Lett.*, **6**, 420 (1987).
12. M. Sugimoto, T. Shimoo, K. Okamura and T. Seguchi, *J. Am. Ceram. Soc.*, **78**, 1013 (1995).
13. M. Sugimoto, T. Shimoo, K. Okamura and T. Seguchi, *J. Am. Ceram. Soc.*, **78**, 1849 (1995).
14. Y. Kim, D. Shin, H.R. Kim, D.Y. Han, Y.U. Kang and D.H. Riu, *Key Eng. Mater.*, **317-318**, 85 (2006).
15. K. Itatani, T. Tanaka, H. Suemasu, A. Nozue and I.J. Davies, *J. Australasian Ceram. Soc.*, **41**, 1 (2005).