

## Fabrication and Characterization of ZrB<sub>2</sub>-Based Ceramic Using Synthesized ZrB<sub>2</sub>-LaB<sub>6</sub> Powder

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ZrB<sub>2</sub>-LaB<sub>6</sub> powder was obtained by reactive synthesis using ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, and carbon powders. Then ZrB<sub>2</sub>-20 vol% SiC-10 vol% LaB<sub>6</sub> (ZSL) ceramics were prepared from commercially available SiC and the synthesized ZrB<sub>2</sub>-LaB<sub>6</sub> powder via hot pressing at 2000°C. The phase composition, microstructure, and mechanical properties were characterized. Results showed that both LaB<sub>6</sub> and SiC were uniformly distributed in the ZrB<sub>2</sub> matrix. The hardness and bending strength of ZSL were 17.06 ± 0.52 GPa and 505.8 ± 17.9 MPa, respectively. Fracture toughness was 5.7 ± 0.39 MPa · m<sup>1/2</sup>, which is significantly higher than that reported for ZrB<sub>2</sub>-20 vol% SiC ceramics, due to enhanced crack deflection and crack bridging near SiC particles.

### I. Introduction

KNOWN as ultra-high-temperature ceramics, transition metal diborides and carbides show a number of excellent properties such as high melting temperature, high strength, high thermal and electrical conductivity, and chemical stability.<sup>1</sup> Therefore, these ceramics are potential candidates for a variety of high-temperature structural applications such as thermal protection systems for leading edges.<sup>2</sup> Zirconium diboride is especially promising,<sup>3–7</sup> as it has a relatively low density compared with the other candidates for ultra-high-temperature applications, a desired property in the aerospace industry.

Although ZrB<sub>2</sub> has many excellent properties, one of the hurdles to overcome is its poor oxidation resistance at high temperatures.<sup>8–11</sup> The addition of SiC to ZrB<sub>2</sub> has led to improvements in oxidation resistance because of the formation of a protective SiO<sub>2</sub> layer at temperatures above roughly 1200°C.<sup>12–14</sup> However, oxidation resistance of ZrB<sub>2</sub>-SiC composites markedly degrades beyond 1800°C, as the SiC actively oxidizes or the SiO<sub>2</sub> layer volatilizes.<sup>15–16</sup> Zhang *et al.*<sup>17</sup> improved the oxidation resistance of ZrB<sub>2</sub>-SiC ceramics to temperatures up to 2400°C by the addition of LaB<sub>6</sub>.

The higher oxidation resistance of ZrB<sub>2</sub>-SiC-LaB<sub>6</sub> was mainly attributed to the formation of La<sub>2</sub>Zr<sub>3</sub>O<sub>7</sub>, which effectively limited the inward transport of oxygen.<sup>17</sup> Further, a homogeneous dispersion of LaB<sub>6</sub> in the ZrB<sub>2</sub> matrix was considered to be the key to providing improved oxidation resistance. Reactive synthesis of ZrB<sub>2</sub>-LaB<sub>6</sub> powder can be used

as an alternative route to providing similar oxidation resistance results. The advantage of this approach is that it offers the possibility to obtain ZrB<sub>2</sub>-based ceramics with an improved dispersion of LaB<sub>6</sub> and the use of less expensive raw materials.

To supplement and complete the previous research on the addition of LaB<sub>6</sub> to the ZrB<sub>2</sub>-SiC composite, the current study focuses on fabrication and characterization of ZrB<sub>2</sub>-based ceramics using synthesized ZrB<sub>2</sub>-LaB<sub>6</sub> powder and commercially available SiC. ZrB<sub>2</sub>-SiC-LaB<sub>6</sub> (ZSL) samples were prepared by hot pressing. Microstructure and mechanical properties were characterized on dense ZSL ceramics.

### II. Experimental Procedure

The raw materials used in this study were ZrO<sub>2</sub> (Tosoh, Toyama, Japan), La<sub>2</sub>O<sub>3</sub> (SCRC, Shanghai, China), B<sub>4</sub>C (Jingangzuan Boron Carbide Co. Ltd., Mudanjiang, China), and carbon and α-SiC (*D*<sub>50</sub> = 0.45 μm, Changle Xinyuan Carborundum Micro-powder Co. Ltd., Changle, China), with purities of 99%, 99.95%, 96%, 99%, and 98.5%, respectively.

With La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, B<sub>4</sub>C, and carbon in the desired molar ratio as starting powders, ZrB<sub>2</sub>-LaB<sub>6</sub> powder with a volume ratio of 7:1 was obtained by reactive synthesis at temperatures ranging from 1300° to 1600°C. SiC powder was then added to the synthesized ZrB<sub>2</sub>-LaB<sub>6</sub> powder to fabricate ZrB<sub>2</sub>-20 vol% SiC-10 vol% LaB<sub>6</sub> (ZSL) ceramics.

The starting mixture was mixed for 24 h in a polyethylene jar using ethyl alcohol and zirconia balls, and then dried by rotary evaporation. After being dried, the mixed powder was ground to -200 mesh and then placed in a graphite die with a BN coating. Powder compacts were heated to 2000°C and held for 1 h under a pressure of 30 MPa in an argon atmosphere.

Archimedes' method and the rule of mixtures were used to determine the actual and theoretical densities, respectively. Phase composition and microstructure of the composite were determined by X-ray diffraction (XRD, D/max 2550 V, Tokyo, Japan) and an electron probe microanalyzer (JEOL JXA-8100F, Tokyo, Japan) along with energy-dispersive spectroscopy (EDS, Oxford INCA energy, Oxon, UK), respectively. The hardness was measured by the indentation method, using a load of 1 kg for 10 s on a polished surface (Wilson-Wolpert Tukon 2100B, Instron, Norwood, MA). For the fracture toughness, a load of 10 kg was used. Without Young's modulus, the fracture toughness can be calculated by the following equations:<sup>18,19</sup>

$$K_{IC} = P \left( \pi \left( \frac{C_1 + C_2}{4} \right) \right)^{3/2} (tg\beta)^{-1} \quad (1)$$

where *P* is the indentation load (N), *C*<sub>1</sub> and *C*<sub>2</sub> is the measured diagonal crack length (*m*), and β is an angle constant (68°).

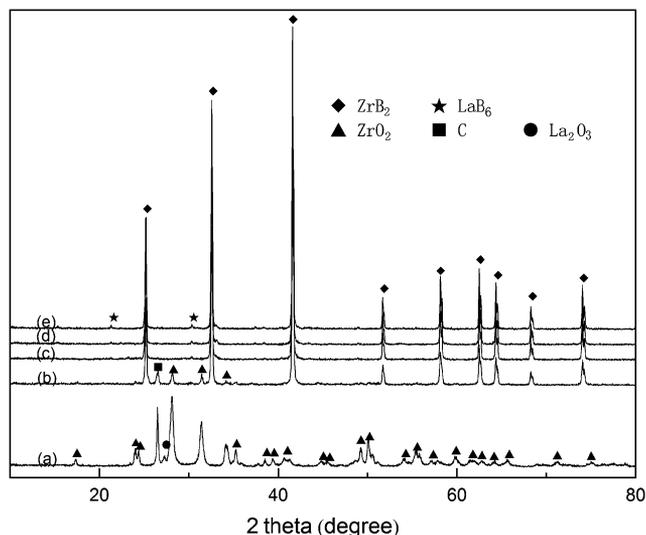
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**Fig. 1.** X-ray diffraction patterns of the synthesized  $\text{ZrB}_2\text{-LaB}_6$  powder at (a) raw powder, (b)  $1300^\circ\text{C}$ , (c)  $1400^\circ\text{C}$ , (d)  $1500^\circ\text{C}$ , and (e)  $1600^\circ\text{C}$ .

Flexural strength was determined via a four-point bending with sample dimensions of  $2\text{ mm} \times 1.5\text{ mm} \times 25\text{ mm}$ . The outer span was 20 mm and inner span was 10 mm.

### III. Results and Discussion

#### (1) $\text{ZrB}_2\text{-LaB}_6$ Powder Synthesis

XRD analysis of synthesized  $\text{ZrB}_2\text{-LaB}_6$  powder, with a hold time of 1 h at temperatures of  $1300^\circ$  to  $1600^\circ\text{C}$ , included as Fig. 1. By  $1400^\circ\text{C}$ , the initial compounds had almost fully reacted, with only small amounts of C and  $\text{ZrO}_2$  remaining. Above  $1500^\circ\text{C}$ , only peaks for  $\text{ZrB}_2$  and  $\text{LaB}_6$  were present, indicating that by this temperature, the reaction appears to have proceeded to completion. It should be noted that because of the relatively strong intensity of the  $\text{ZrB}_2$  peaks, the  $\text{LaB}_6$  peaks are difficult to observe. Figure 2 contains scanning electron microscopic (SEM) images of the  $\text{ZrB}_2\text{-LaB}_6$  powder synthesized at  $1500^\circ$  and  $1600^\circ\text{C}$ . From Fig. 2, the powder produced at  $1500^\circ\text{C}$  appears to contain a more uniform distribution of  $\text{ZrB}_2$  and  $\text{LaB}_6$  particles compared with the powder synthesized at  $1600^\circ\text{C}$ . The uniform distribution of  $\text{ZrB}_2$  and  $\text{LaB}_6$  particles would help in forming a more uniform microstructure during sintering. Hence, the  $\text{ZrB}_2\text{-LaB}_6$  powder synthesized at  $1500^\circ\text{C}$  was chosen to complete this study.

#### (2) Hot-Pressed ZSL Ceramics

The bulk density of the ZSL ceramics was  $5.32\text{ g/cm}^3$ , which corresponds to 99% of the theoretical density, in accordance with the rule of mixtures. A backscattered electron (BSE) image

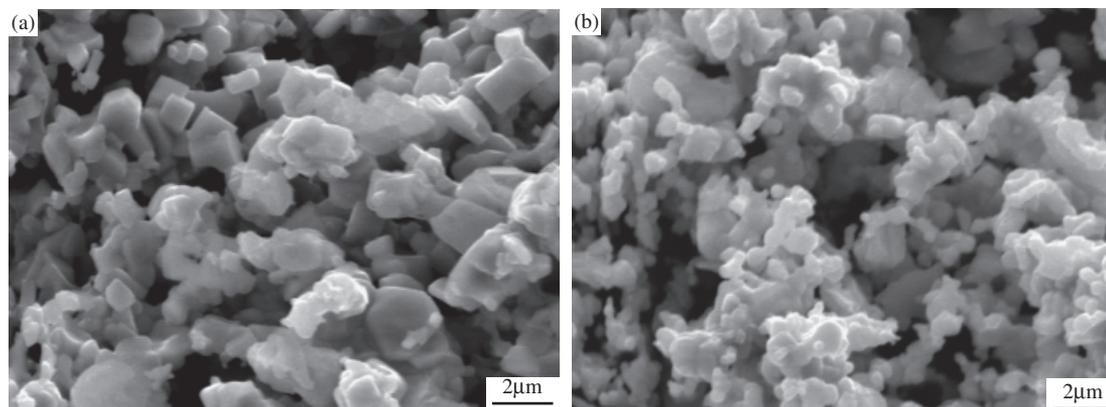
and EDS analysis of the ZSL ceramics are shown in Fig. 3. The dark, SiC phase was easily identified. From the EDS included in Fig. 3, zones labeled as 1 are the  $\text{LaB}_6$  phase and zones labeled as 2 are the  $\text{ZrB}_2$  phase. The microstructure consisted of three distinct phases, well distributed throughout the sample. The size of the  $\text{ZrB}_2$  grains is largest in the microstructure (about  $4\text{--}6\text{ }\mu\text{m}$ ), while the  $\text{LaB}_6$  grains are smaller (about  $1\text{--}3\text{ }\mu\text{m}$ ). The SiC particles had become elongated, having an aspect ratio of roughly 2:1 (approximately  $1\text{--}2\text{ }\mu\text{m}$  wide by  $2\text{--}4\text{ }\mu\text{m}$  long) after densification. Zhang *et al.*<sup>20</sup> indicated that the morphology of SiC grains in  $\text{ZrB}_2\text{-SiC}$  ceramics varied from equiaxed to whisker-like, depending on the initial size of raw SiC particles, even if all SiC particles with different sizes were  $\alpha$ -polymorphic. The aspect ratios of SiC grains were about 1.05, 1.75, and 3.05, with the starting particle sizes of 1.45, 1.05, and  $0.45\text{ }\mu\text{m}$ , respectively.<sup>20</sup> They thought that the finer SiC particles more readily formed an interconnected network, which provided a higher driving force for sintering.<sup>20</sup> As a result, the finer SiC particles coarsened and elongated during sintering. Based on the above study of Zhang *et al.*, elongation of the SiC grains should be mainly due to the small size of the raw SiC particles ( $D_{50} = 0.45\text{ }\mu\text{m}$ ) in our work.

The hardness of ZSL was  $17.06 \pm 0.52\text{ GPa}$ , which was slightly higher than the value of  $\text{ZrB}_2\text{-}20\text{ vol}\%$  SiC reported by our previous research ( $15.8\text{ GPa}$ )<sup>18</sup> and the work of Zhang *et al.*<sup>21</sup> ( $15.0\text{ GPa}$ ), but lower than the value of  $\text{ZrB}_2\text{-}20\text{ vol}\%$  SiC reported by Chamberlain *et al.*<sup>6</sup> ( $24\text{ GPa}$ ). The bending strength of ZSL was  $505.8 \pm 17.9\text{ MPa}$ , which was lower than the value of  $\text{ZrB}_2\text{-}20\text{ vol}\%$  SiC reported by our research ( $582\text{ MPa}$ )<sup>18</sup> and Zhang *et al.* ( $523\text{ MPa}$ )<sup>21</sup> as well as Chamberlain *et al.*<sup>6</sup> ( $1003\text{ MPa}$ ). Zhu *et al.*<sup>22</sup> reported that the fracture strength of  $\text{ZrB}_2\text{-SiC}$  was a strong function of SiC grain size, increasing from  $400\text{ MPa}$  with a SiC grain size of  $6\text{ }\mu\text{m}$  to over  $900\text{ MPa}$  with a SiC grain size of  $1\text{ }\mu\text{m}$  or less. So the relative lower strength of ZSL may be due to the larger grain size, especially due to the growth of SiC grains.

The fracture toughness for ZSL ceramics is  $5.7 \pm 0.39\text{ MPa}\cdot\text{m}^{1/2}$ , which is significantly higher than those reported in the literature for  $\text{ZrB}_2\text{-}20\text{ vol}\%$  SiC materials ( $4.0\text{--}4.8\text{ MPa}\cdot\text{m}^{1/2}$ ).<sup>6,18,21</sup> To better elucidate the toughening mechanisms, the paths of some Vickers-indentation-induced cracks were examined on polished sections via SEM. Figure 4 is an SEM image of a crack path on the polished surface of ZSL. The crack in the ZSL ceramics, containing slightly elongated SiC grains was tortuous. SEM inspection of the crack propagation demonstrated crack deflection and perhaps crack bridging near the SiC particles. These toughening mechanisms cause energy dissipation during crack propagation, resulting in higher measured-toughness values.

### IV. Summary

In this study,  $\text{ZrB}_2\text{-}20\text{ vol}\%$  SiC- $10\text{ vol}\%$   $\text{LaB}_6$  (ZSL) ceramics were prepared by hot pressing using synthesized  $\text{ZrB}_2\text{-LaB}_6$



**Fig. 2.** SEM images of the  $\text{ZrB}_2\text{-LaB}_6$  powder synthesized at (a)  $1500^\circ\text{C}$  and (b)  $1600^\circ\text{C}$ .

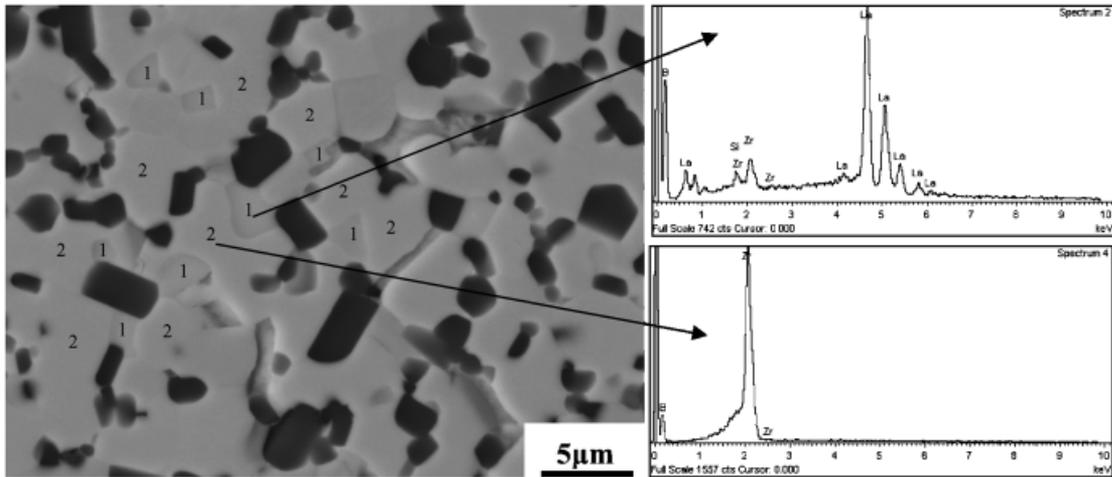


Fig. 3. Backscattered electron image and energy-dispersive spectroscopy analysis of the  $\text{ZrB}_2$ -20 vol% SiC-10 vol%  $\text{LaB}_6$  ceramics.

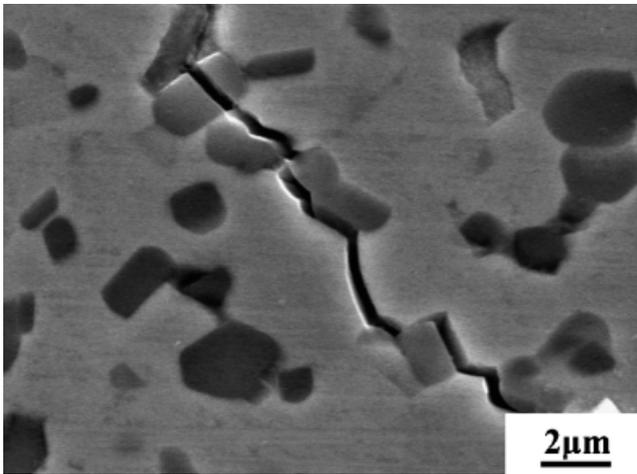


Fig. 4. Scanning electron microscopic image of indentation crack propagation of  $\text{ZrB}_2$ -20 vol% SiC-10 vol%  $\text{LaB}_6$ .

powder and commercial SiC. The optimal synthesis temperature for the  $\text{ZrB}_2$ - $\text{LaB}_6$  powder was determined to be  $1500^\circ\text{C}$ . BSE analysis showed  $\text{LaB}_6$  uniformly distributed in a  $\text{ZrB}_2$  matrix. Hardness and four-point bending strength of the sintered ceramics were  $17.06 \pm 0.52$  GPa and  $505.8 \pm 17.9$  MPa, respectively. The ZSL ceramics had a higher fracture toughness ( $5.7 \pm 0.39$   $\text{MPa} \cdot \text{m}^{1/2}$ ) compared with other  $\text{ZrB}_2$ -based ceramics, which may be due to crack deflection and crack bridging near SiC particles.

## References

- <sup>1</sup>W. G. Fahrenholtz, G. E. Hilmas, A. L. Chamberlain, and J. W. Zimmermann, "Processing and Characterization of  $\text{ZrB}_2$ -Based Ultra-High Temperature Monolithic and Fibrous Monolithic Ceramics," *J. Mater. Sci.*, **39** [19] 5951-7 (2004).
- <sup>2</sup>S. R. Levine, E. J. Opila, M. C. Halbig, J. D. Kiser, M. Singh, and J. A. Salem, "Evaluation of Ultra-High Temperature Ceramics For Aeropropulsion Use," *J. Eur. Ceram. Soc.*, **22** [14-15] 2757-67 (2002).

- <sup>3</sup>C. Mroz, "Zirconium Diboride," *Am. Ceram. Soc. Bull.*, **74** [6] 164-5 (1995).
- <sup>4</sup>G. J. Zhang, Z. Y. Deng, N. Kondo, J. F. Yang, and T. Ohji, "Reactive Hot Pressing of  $\text{ZrB}_2$ -SiC Composites," *J. Am. Ceram. Soc.*, **83** [9] 2330-2 (2000).
- <sup>5</sup>F. Monteverde, A. Bellosi, and S. Guicciardi, "Processing and Properties of Zirconium Diboride-Based Composites," *J. Eur. Ceram. Soc.*, **22** [3] 279-88 (2002).
- <sup>6</sup>A. L. Chamberlain, W. G. Fahrenholtz, and G. E. Hilmas, "High-Strength Zirconium Diboride-Based Ceramics," *J. Am. Ceram. Soc.*, **87** [6] 1170-2 (2004).
- <sup>7</sup>Y. J. Yan, Z. R. Huang, S. M. Dong, and D. L. Jiang, "Pressureless Sintering of High-Density  $\text{ZrB}_2$ -SiC Ceramic Composites," *J. Am. Ceram. Soc.*, **89** [11] 3589-92 (2006).
- <sup>8</sup>R. J. Irving and I. G. Worsley, "Oxidation of Titanium Diboride and Zirconium Diboride at High Temperatures," *J. Less-Common Metals*, **16** [2] 102-12 (1968).
- <sup>9</sup>A. K. Kuriakose and J. L. Margrave, "The Oxidation Kinetics of Zirconium Diboride and Zirconium Carbide at High Temperatures," *J. Electrochem. Soc.*, **111** [7] 827-31 (1964).
- <sup>10</sup>J. B. Berkowitz-Mattuck, "High-Temperature Oxidation III. Zirconium and Hafnium Diborides," *J. Electrochem. Soc.*, **113** [9] 908-14 (1966).
- <sup>11</sup>W. C. Tripp and H. C. Graham, "Thermogravimetric Study of the Oxidation of  $\text{ZrB}_2$  in the Temperature Range of  $800^\circ\text{C}$  to  $1500^\circ\text{C}$ ," *J. Electrochem. Soc.*, **118** [7] 1195-9 (1971).
- <sup>12</sup>W. C. Tripp, H. H. Davis, and H. C. Graham, "Effect of an SiC Addition on the Oxidation of  $\text{ZrB}_2$ ," *Am. Ceram. Soc. Bull.*, **52** [8] 612-6 (1973).
- <sup>13</sup>F. Monteverde and A. Bellosi, "Oxidation of  $\text{ZrB}_2$ -Based Ceramics in Dry Air," *J. Electrochem. Soc.*, **150** [11] B552-9 (2003).
- <sup>14</sup>A. Rezaie, W. G. Fahrenholtz, and G. E. Hilmas, "Evolution of Structure During the Oxidation of Zirconium Diboride-Silicon Carbide in Air up to  $1500^\circ\text{C}$ ," *J. Eur. Ceram. Soc.*, **27** [6] 2495-501 (2007).
- <sup>15</sup>E. Opila, S. Levine, and J. Lorincz, "Oxidation of  $\text{ZrB}_2$ - and  $\text{HfB}_2$ -Based Ultra-High Temperature Ceramics: Effect of Ta Additions," *J. Mater. Sci.*, **39** [19] 5969-77 (2004).
- <sup>16</sup>W. G. Fahrenholtz, "Thermodynamic Analysis of  $\text{ZrB}_2$ -SiC Oxidation: Formation of a SiC-Depleted Region," *J. Am. Ceram. Soc.*, **90** [1] 143-8 (2007).
- <sup>17</sup>X. H. Zhang, P. Hu, J. C. Han, L. Xu, and S. H. Meng, "The Addition of Lanthanum Hexaboride to Zirconium Diboride for Improved Oxidation Resistance," *Scripta Mater.*, **57** [11] 1036-9 (2007).
- <sup>18</sup>W. B. Tian, Y. M. Kan, G. J. Zhang, and P. L. Wang, "Effect of Carbon Nanotubes on the Properties of  $\text{ZrB}_2$ -SiC Ceramics," *Mater. Sci. Eng. A*, **487** [1-2] 568-73 (2008).
- <sup>19</sup>A. G. Evans and E. A. Charles, "Fracture Toughness Determinations by Indentation," *J. Am. Ceram. Soc.*, **59** [7-8] 371-2 (1976).
- <sup>20</sup>S. C. Zhang, G. E. Hilmas, and W. G. Fahrenholtz, "Pressureless Sintering of  $\text{ZrB}_2$ -SiC Ceramics," *J. Am. Ceram. Soc.*, **91** [1] 26-32 (2008).
- <sup>21</sup>X. H. Zhang, X. Y. Li, J. C. Han, W. B. Han, and C. Q. Hong, "Effects of  $\text{Y}_2\text{O}_3$  on Microstructure and Mechanical Properties of  $\text{ZrB}_2$ -SiC Ceramics," *J. Alloys Compd.*, (2007), in press.
- <sup>22</sup>S. M. Zhu, W. G. Fahrenholtz, and G. E. Hilmas, "Influence of Silicon Carbide Particle Size on the Microstructure and Mechanical Properties of Zirconium Diboride-Silicon Carbide Ceramics," *J. Eur. Ceram. Soc.*, **27**, 2077-83 (2007). □