

## Densification and mechanical properties of multiphase ceramic composites fabricated by a polymer complexation route

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Multi-component ceramic composites consisting of two, three and four phases, based on duplex microstructures of zirconia and alumina, were fabricated by a polymer complexation route employing polyethylene glycol (PEG) as a polymeric carrier. The polymer complexation route showed an unique exothermic reaction involving expansion of the powder structure and it provided highly sinterable powder by a simple ball milling process. In this study, the microstructures and flexural strengths of the multi-component ( $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$ ) ceramic composites were examined on the processing variations of the forming and sintering for close to nano-structures. A composite having four phases showed grain growth retardation and the microstructure and final phases were largely dependant on the sintering conditions. Needle-like grains from the addition of SrO improved the flexural strength of the multiphase composites.

**Key words:** Multiphase ceramic composites, Sintering, Flexural strength, Polyethylene glycol, Porous powders, Polymer complexation route.

### Introduction

Zirconia-toughened alumina (ZTA) ceramics have been studied because of their excellent mechanical properties and easy control of microstructure. By mixing  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  phases which have limited solid solubility, the growth of each phase is inhibited. In particular, a dual interpenetrating microstructure can be expected in pure zirconia-alumina composites that have the same volume percentage [1]. Furthermore, it is anticipated that multi-component ceramic composites, which have a small grain size, can be formed due to grain growth retardation by second and third phases [2]. The new multi-compositions lead to the formation of multiphase composite systems, where some phases have faceted shapes [3, 4].

Chemical processing routes based on organic-inorganic solution techniques have recently been used to produce pure and homogeneous ceramic powders [5-8]. In these processes, polymeric long chains in the mixture ensure a homogeneous distribution of the metal ions in the polymeric network structure and inhibit their segregation and/or precipitation from the solution. Duplex microstructures of zirconia and alumina have been achieved by a polymer complexation technique [9, 10]. In this process, zirconium 2,4-pentanedionate, aluminum nitrate and polyethylene glycol (PEG), as a long chain polym-

eric carrier, were dissolved in ethyl alcohol without any precipitation. The organic-inorganic precursor gels were turned to porous powders having a volume expansion through an explosive, exothermic reaction during the drying process. The volume expansion was caused by the abrupt decomposition of the organic groups in the gels during the vigorous exothermic reaction. With the optimum amount of the PEG polymer, the metal cations were well dispersed in the solution and a homogeneous polymeric network was formed. The polymer content also affected the specific surface area of the synthesized powder and the powder microstructure.

In this study, based on the duplex microstructure of zirconia and alumina, three- and four-component composites ( $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2$  and  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$ ) were made by a polymer complexation route involving polyethylene glycol as an organic carrier. In particular, the sintering and mechanical behavior of the composites were examined using the synthesized, ball-milled porous powders. On the basis of dual phase composites, which have  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  in 1:1 mole ratio, novel microstructures of multiphase composites, which involve  $\text{CeO}_2$  and SrO, were examined with different forming and sintering conditions.

### Experimental Procedure

#### Powder Preparation and Sintering Process

Transparent precursor sols were prepared from zirconium 2,4-pentanedionate ( $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ ), which is a source of zirconium, and metal nitrate salts (aluminum nitrate, cerium nitrate, and strontium nitrate) for other

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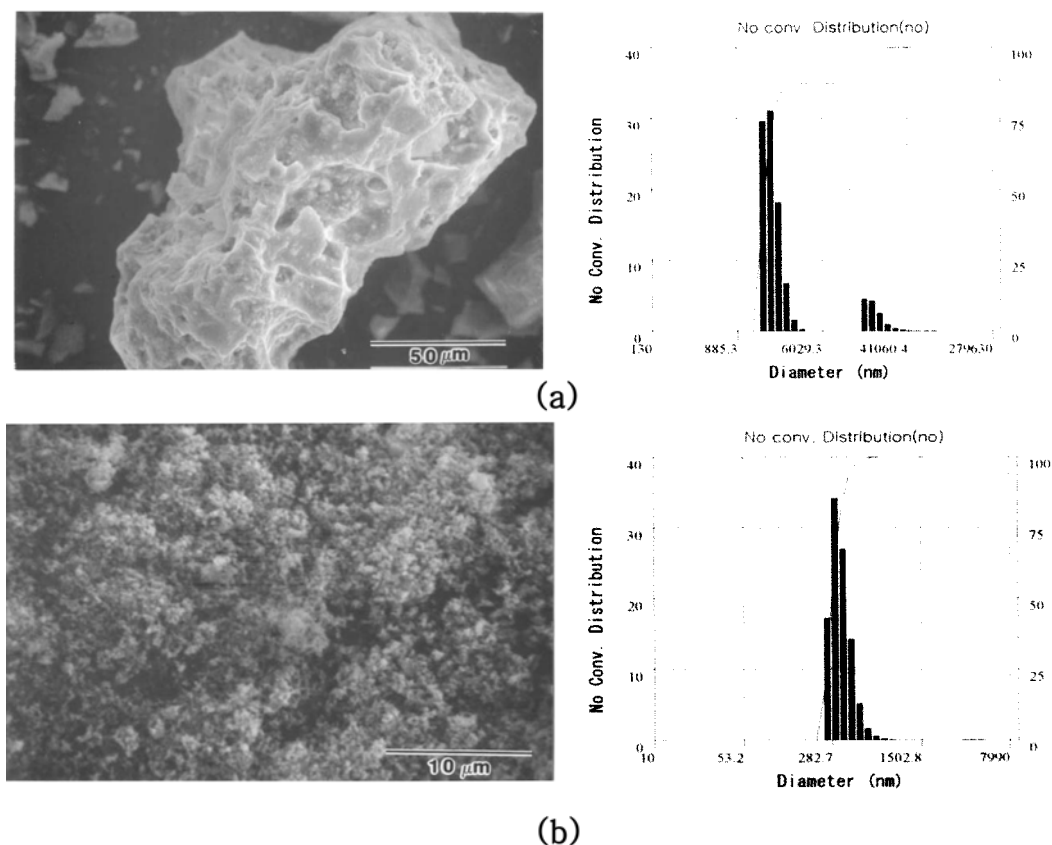
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metal sources in proportions of several mole ratios. After dissolving these reagents in ethyl alcohol, the organic carrier, PEG (of M.W.: 2000) was added, and the mixtures were stirred and heated up to 100 °C. The amount of PEG was calculated using a ratio of total weight of metal ions from cation sources to weight of PEG. In this study, a 3:1 ratio was used [10]. As the viscosity increased by evaporation of ethyl alcohol, the sols turned to a syrup-like gels. Subsequently, a vigorous exothermic reaction occurred which, with continuous heating, converted the gel into an expanded, porous solid. Finally, the precursors were calcined at 900 °C for 1 h and then subjected to ball milling for 12 h with zirconia (3Y-TZP) balls as the milling media. Isopropyl alcohol was used as a solvent for wet milling. The calcined and ball-milled powders were densified in three different ways. As the first method, the ball-milled powder was uniaxially pressed at 10 MPa, and the pellet-shaped green compacts were pressureless sintered in an air atmosphere at 1500 °C for 1 h with a heating rate of 4 K·minute<sup>-1</sup>. As the second method, the uniaxially pressed sample was cold iso-statically pressed at 300 MPa for 10 minute. Then it was pressureless sintered in an air atmosphere at 1450 °C for 3 h with a heating rate of 4 K·minute<sup>-1</sup>. As the third method, the uniaxially pressed sample was hot pressed at 1500 °C for 30 minute. The hot pressing conditions

were at 30 MPa, a nitrogen atmosphere with a heating rate of 20 K·minute<sup>-1</sup>.

### Characterization

The crystallization of the four-component precursor was observed by Raman spectroscopy (single monochromatic Renishaw 1000) with an attached CDD detector and holographic notch filter, with 514 nm Argon. The final phases present in the sintered composites were determined with an X-ray diffractometer (Dmax automated powder diffractometer, Rigaku/USA, Danvers, MA) using CuK<sub>α</sub> radiation (40 kV, 40 mA). The measurements were made with a scanning speed of 10°/minute and a sampling interval of 0.02° at room temperature. The powder morphologies and surface microstructures of sintered pellets were examined by scanning electron microscopy (SEM, Hitachi S530, Hitachi, Japan). The specimens were mounted on an aluminum stub and Au-Pd sputtered at 15 mA for 40 s. The average grain sizes of sintered microstructures were analyzed according to the Jeffries-Saltykov method [11]. The average particle sizes of the ball-milled powders were monitored by an electrophoretic light scattering spectrophotometer (ELS-8000, Photol, Tokyo, Japan). The sample cells were prepared by an ultrasonicator for 20 minute with a mixture of de-ionized water and powder. The flexural strength was measured



**Fig. 1.** SEM micrographs and particle size distributions of Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub>-SrO powders (a) as calcined and (b) ball milled, prepared by the PEG complexation route.

by a three point bending test using a  $20.0 \pm 0.1$  mm support span, at a crosshead speed of 0.1 mm/minute, using an universal testing machine (model 4502, Instron Corp., Canton, MA). Flexural bars of dimensions  $30 \text{ mm} \times 4 \text{ mm} \times 3 \text{ mm}$  were surface polished finally using #1200 SiC paper. Five samples were tested for each case and an average value was used for representative data. The density of a sintered sample was calculated from a density measuring instrument (Mirage. MD-200S, Japan).

## Results and Discussion

The syrup-like, precursor gels were quite flammable and had a vigorous explosive reaction on continuous heating. After the reaction, the gels changed to a sooty, porous powders with a large volume expansion. By a Fourier Transform Infrared study with the expanded precursor powder, it was speculated that the reason for the explosive reaction is the residual, flammable alcohol solvent in the precursor gel. The alcohol ignited at about  $150^\circ\text{C}$ , and the abrupt decomposition of the organic groups during the vigorous exothermic reaction resulted in the volume expansion of the precursor powder which formed extensive voids in the powder structure [9, 10].

The powder morphologies and particle size distributions of the calcined, porous powder and the ball milled powder are shown in Fig. 1. The calcined powder revealed a soft and porous powder structure with a bimodal particle size distribution. The average particle size was about  $10 \mu\text{m}$  and the SEM micrograph of the one large particle is shown in Fig. 1(a). The powder ball milled for 12 h showed submicrometre particles with some agglomeration (Fig. 1(b)). In the milling process, the efficiency was improved by the soft and porous powder structure in comparison with non-porous powders. After the simple milling process, the particle size distribution was notably narrowed with an average particle size of  $0.4 \mu\text{m}$ . Two and three component powders showed almost similar powder structures and milling behavior.

The Raman spectra of the powder precursor and calcined powder are shown in Fig. 2. In the gel sample, some peaks come from the organic compounds. At  $800^\circ\text{C}$ , some notable peaks were observed. In general, metal oxide spectra peaks are shown in the range of  $200\text{--}900 \text{ cm}^{-1}$  in the Raman observations. The peaks at

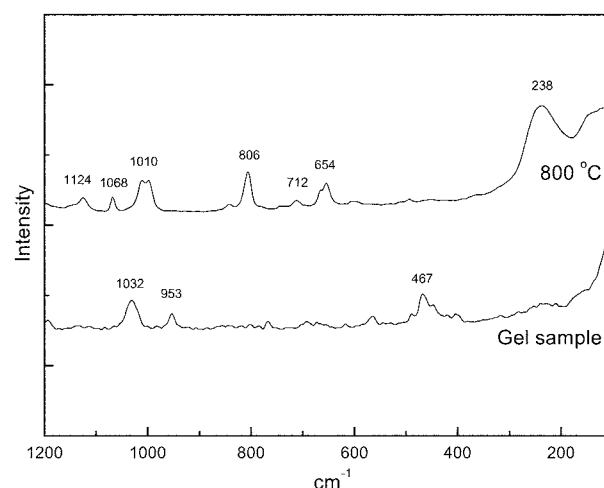


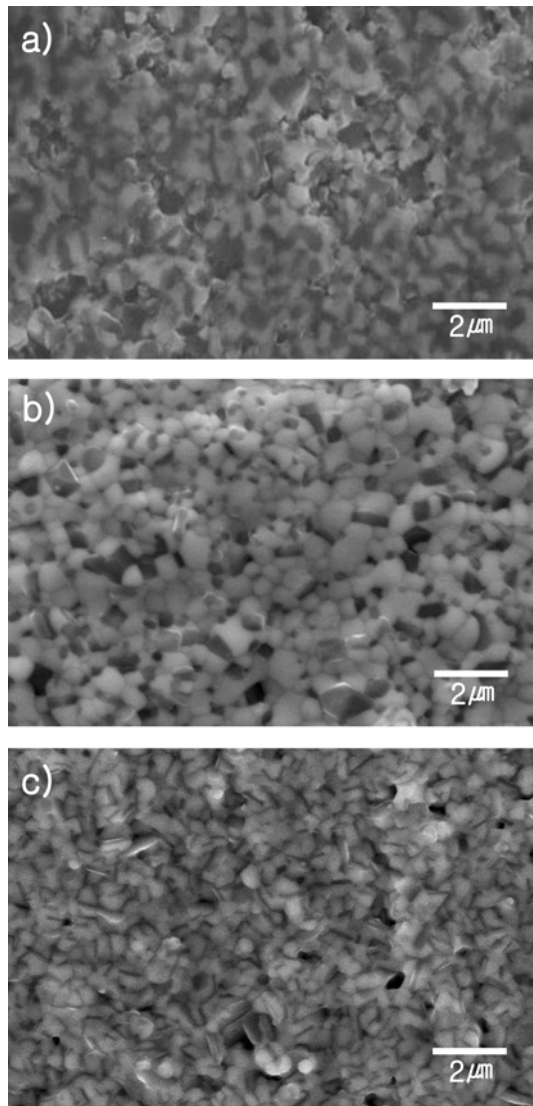
Fig. 2. Raman spectra of the four-component powder precursor and calcined powders.

$806$ ,  $712$ ,  $654$  and  $238 \text{ cm}^{-1}$  mean the crystallization of metal ions for forming composites occurs at  $800^\circ\text{C}$ . In addition, new peaks at  $1010$  and  $1068 \text{ cm}^{-1}$  indicate symmetry stretching modes of  $\text{CO}_3^{2-}$  according to reference [12]. From this result, it is speculated that some residual carbon compounds exist in the powder structure calcined at  $800^\circ\text{C}$ .

Table 1 presents the observed final phases and average grain sizes of two, three and four-component systems. All samples were uniaxially pressed at 10 MPa and densified at  $1500^\circ\text{C}$  for 1 h in an air atmosphere. In the  $\text{ZrO}_2\text{--Al}_2\text{O}_3$  composite,  $m\text{-ZrO}_2$  and  $t\text{-ZrO}_2$  coexisted with the  $\alpha\text{-Al}_2\text{O}_3$  phase showing an average grain size of  $0.8 \mu\text{m}$ . In the  $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--CeO}_2$  system, three obvious phases of  $t\text{-ZrO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$  were observed in 1:1:0.5 mole ratio. In the composite, the microstructure showed an average grain size of  $0.7 \mu\text{m}$ . In the  $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--CeO}_2\text{--SrO}$  system, four obvious phases were observed in 1:1:0.5:0.2 mole ratio. In particular,  $\text{SrO}$  and  $\text{SrAl}_{12}\text{O}_{19}$  phases were observed with needle-like particles. Figure 3 shows the SEM micrographs of the sintered  $\text{Al}_2\text{O}_3\text{--ZrO}_2$ ,  $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--CeO}_2$  and  $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--CeO}_2\text{--SrO}$  composites. The smallest grain size was observed in the four-phase composite in comparison with the three-component composite as listed in Table 1. This means that the effect of grain growth retardation worked in the multiphase system consisting of  $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--CeO}_2\text{--SrO}$ . In addition, it may be speculated that the needle-like phases were  $\text{SrO}$  and  $\text{SrAl}_{12}\text{O}_{19}$ .

Table 1. Observed phases and average grain sizes of two, three and four-component composites, pressureless sintered at  $1500^\circ\text{C}$  for 1 h at each mole ratio

| Component                                                          | Mole ratio        | Observed phases                                                                    | Avg. grain size ( $\mu\text{m}$ ) |
|--------------------------------------------------------------------|-------------------|------------------------------------------------------------------------------------|-----------------------------------|
| $\text{Al}_2\text{O}_3 : \text{ZrO}_2$                             | 1 : 1             | $\text{Al}_2\text{O}_3$ , $t\text{-ZrO}_2$ , $m\text{-ZrO}_2$                      | 0.8                               |
| $\text{Al}_2\text{O}_3 : \text{ZrO}_2 : \text{CeO}_2$              | 1 : 1 : 0.5       | $t\text{-ZrO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{CeO}_2$                        | 0.7                               |
| $\text{Al}_2\text{O}_3 : \text{ZrO}_2 : \text{CeO}_2 : \text{SrO}$ | 1 : 1 : 0.5 : 0.2 | $t\text{-ZrO}_2$ , $\text{CeO}_2$ , $\text{SrO}$ , $\text{SrAl}_{12}\text{O}_{19}$ | 0.4                               |



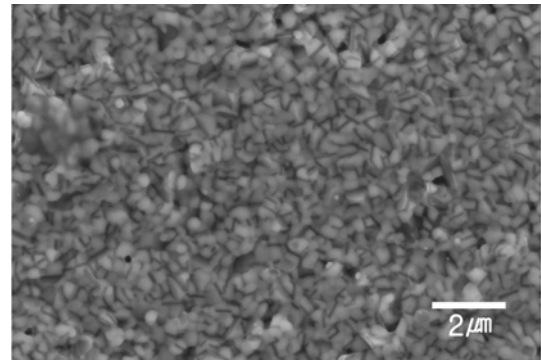
**Fig. 3.** SEM micrographs of the surface microstructures of densified composites consisting of (a)  $\text{Al}_2\text{O}_3\text{-ZrO}_2$ , (b)  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2$  and (c)  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$ .

[13].

The results of mechanical tests for the two, three and four-component systems are listed in Table 2. The highest flexural strength was observed in the 1:1:0.5:0.2 ratio sample. It can be speculated that the smaller grain size and needle-shape phases, SrO and  $\text{SrAl}_{12}\text{O}_{19}$ , had an influence on the increase of strength. The four-component composites showed almost two times higher strength in comparison with the three-component composite. It is certain that the improved strength is due to the decreased grain size by grain growth retardation in the multiphase composite. The two and three phase composites had almost the same grain size, however, the  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composite showed a much lower flexural strength than the  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2$  composite. This is caused by the larger grain size of  $m\text{-ZrO}_2$  than the critical grain size for transformation [2] existed which induced microcracks in the matrix.

**Table 2.** Mechanical behavior of two, three and four-component composites, pressureless sintered at 1500 °C for 1 h at each mole ratio

| Component                                                          | Mole ratio        | Flexural strength (MPa) |
|--------------------------------------------------------------------|-------------------|-------------------------|
| $\text{Al}_2\text{O}_3 : \text{ZrO}_2$                             | 1 : 1             | 190                     |
| $\text{Al}_2\text{O}_3 : \text{ZrO}_2 : \text{CeO}_2$              | 1 : 1 : 0.5       | 270                     |
| $\text{Al}_2\text{O}_3 : \text{ZrO}_2 : \text{CeO}_2 : \text{SrO}$ | 1 : 1 : 0.5 : 0.2 | 490                     |



**Fig. 4.** SEM micrograph of the surface microstructure of the densified, iso-statically pressed sample consisting of  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$ .

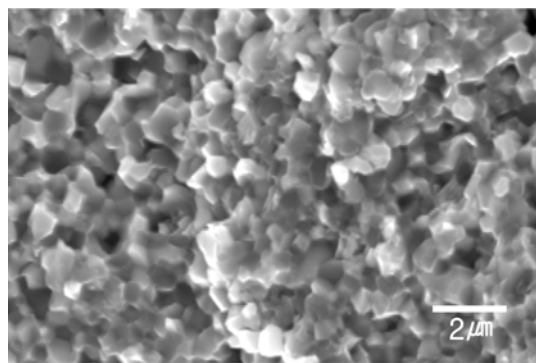
Iso-statically pressed and hot pressed  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$  composites showed different microstructures in comparison with the composites pressureless sintered after uniaxially pressing. The iso-statically pressed sample was densified at 1450 °C for 3h and had four final phases of  $t\text{-ZrO}_2$ ,  $\text{CeO}_2$ , SrO,  $\text{SrAl}_{12}\text{O}_{19}$ . In this sintering process, the iso-statically pressed sample was not fully densified below 1450 °C even with long time holding. An SEM micrograph of the iso-statically pressed sample is presented in Fig. 4. The average grain size was about 0.3  $\mu\text{m}$ , and the decrease in grain size could be caused by the lower sintering temperature used with the compacted powder packing caused by high iso-statically pressing.

The hot-pressed sample showed a special densification behavior. With the fast heating schedule of 20  $\text{K}\cdot\text{minute}^{-1}$ , the density change is listed in Table 3. The sample hot pressed at 1400 °C was not densified at all. At a 50 °C higher temperature, however, significant densification occurred and it was fully densified at

**Table 3.** Densification behavior of  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$  (1 : 1 : 0.5 : 0.2 mole ratio) composites in the hot pressed sintering condition

| Temperature (°C) | Density ( $\text{g}/\text{cm}^3$ ) |
|------------------|------------------------------------|
| 1400             | 1.65                               |
| 1450             | 4.99                               |
| 1500             | 5.27*                              |

\*Density of  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$  pressureless sintered sample = 5.29  $\text{g}/\text{cm}^3$



**Fig. 5.** SEM micrograph of the fracture surface microstructure of the densified, hot-pressed sample consisting of  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$ .

**Table 4.** Mechanical behavior of  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$  (1 : 1 : 0.5 : 0.2 mole ratio) composites, according to sintering method

| Sintering method                                         | Flexural strength (MPa) |
|----------------------------------------------------------|-------------------------|
| Pressureless sintering without cold iso-statically press | 490                     |
| Pressureless sintering with cold iso-statically press    | 540                     |
| Hot pressing                                             | 390                     |

1500 °C with a density of 5.27 g/cm<sup>3</sup>. In particular, the hot-pressed sample showed  $t\text{-ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SrO}$  phases. An SEM micrograph of the fracture surface of a hot-pressed sample is presented in Fig. 5. The average grain size of about 0.8 μm was larger than the size of the sample which was pressureless sintered, and needle-like grains were not observed. From the hot-pressing behavior, it can be speculated that fast mass transformation for densification occurred mainly at temperatures higher than 1400 °C for a short time, and that grain growth by fast mass transformation under a high pressure and nitrogen atmosphere works more actively than grain growth retardation by the fast sintering effect. In addition, needle-like grains were not observed in spite of the existence of the  $\text{SrO}$  phase. This means that the grain morphology is also significantly dependent on sintering conditions.

Table 4 lists the flexural strengths of the four-component composites according to the sintering method. The iso-statically pressed samples showed highest flexural strength of 540 MPa and this must be caused by the finer grain size involving needle-like grains. By contrast, the hot-pressed sample, which has a larger grain size without needle-like grains, showed a lower flexural strength of 390 MPa.

## Conclusions

Multi-component ceramic composites retaining fine grains by grain growth retardation were successfully fabricated by a polyethylene glycol complexation process. Volume expanded, porous precursor powders were ground easily by ball milling and turned to highly sinterable powders.  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-CeO}_2\text{-SrO}$  compositions made multiphase composites, in which grain growth was inhibited by a constraint effect. Some phases had faceted shapes and needle-like grains were observed. The newly textured microstructures showed improved flexural strength. In particular, sintering conditions greatly affected the microstructure and strength of the densified samples. The finest microstructure by the grain growth retardation effect was observed with the sintering conditions of a lower temperature for a long time holding with highly compacted powders.

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