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Effect of $BaTiO_3$ addition on structures and mechanical properties of 3Y-TZP ceramics

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Abstract

Effect of $BaTiO_3$ addition on grain size, phase constitution and mechanical properties of 3Y-TZP ceramics was investigated for discussing the possible application of piezoelectric secondary phase toughening process. Under certain conditions, high content of tetragonal zirconia could be obtained with modest amount of $BaTiO_3$ addition, and the hardness of the composite ceramics could be increased with the addition of $BaTiO_3$. However, the increased stability of t-ZrO_2 appears as a new problem which obstructs the stress-induced t–m transformation and subsequently suppresses the effect of transformation toughening.

Keywords: $BaTiO_3$; Mechanical properties; Microstructure-final; Toughening; ZrO_2

1. Introduction

Within the last 20 years, numerous approaches to improve the fracture toughness of ceramics have been developed, and the individual mechanisms include transformations, microcracking, twinning, ductile reinforcements, fiber/whisker reinforcements, and grain bridging.[1–13] The authors[14] also proposed a novel approach for toughening of ceramics, where some piezoelectric secondary phase was introduced into the matrix and the energy dissipation due to the piezoelectric effect and domain wall's motion was suggested as the main toughening mechanism. Based on this concept, the systems of $BaTiO_3/Al_2O_3$[14] and $Nd_2Ti_2O_7/Al_2O_3$[15] were investigated and the fracture toughness, K_{IC} reached 5.1 and 6.7 MPa. $m^{1/2}$, respectively, which were much higher than that of single phase Al_2O_3.

Among the preceding toughening mechanisms, transformation toughening of tetragonal zirconia has been paid much attention due to the remarkable toughening effect and the interesting effect of the microstructures on the mechanical properties of ceramics. The contribution of the stress-induced transformation to the fracture toughness is directly related to the volume-fraction of the retained transformable tetragonal phase. In fact, a critical grain size exists below which the high-temperature tetragonal phase can be retained and above which retention is not observed. Early studies[2,16] show that the critical grain size of t-ZrO_2 is associated with the sort and amount of stabilizer such as Y_2O_3 and CeO_2, with which high-temperature tetragonal phase can be retained to lower temperature.

Studies[2] also show that the fracture toughness of ceramics can be improved by combining the transformation toughening with other toughening mechanism. The toughness of these types of composites is determined by the alloy content, volume content and size of transformable zirconia particles. The latter factors also indicate that processing of such composites requires careful selection of compositions and advanced processing technology to achieve the desired microstructures.

What effect will be obtained if the piezoelectric secondary phase, $BaTiO_3$, is introduced into TZP ceramics? Can a synergistic toughening effect of transformation toughening and piezoelectric energy dissipation mechanism be achieved? In the present work, these questions were answered by investigating the effect of $BaTiO_3$ addition on structures and mechanical properties of 3Y-TZP ceramics.

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2. Experimental procedure

Reagent grade (99.9% purity) TiO_2 and $BaCO_3$ in 1:1 mol ratio were mixed for 24 h by milling in distilled water using zirconia media. The slurry was dried and then calcined at 1300°C for 3 h to create $BaTiO_3$. The xBaTiO$_3$/(1-x)3Y-TZP composite powders ($x=0.02$, 0.03, 0.05, 0.1, 0.15) were mixed by ball milling with zirconia media in distilled water for 24 h. Such mixed powders were pressed into disc compacts of 12 mm in diameter and 2 to 5 mm in height. Sintering experiments were performed at 1400 to 1500°C in air for 3 h.

Scanning electron microscopy (SEM) was used to observe the microstructures, and the grain size was estimated from the SEM micrographs by the intercept method. X-ray diffraction analysis was used for phase identification. The tetragonal fraction of ZrO_2 in the composites were calculated with the relation of Garvie and Nicholson,[17] using the (111) tetragonal and the (111)+(111) monoclinic peak intensities.

The hardness and fracture toughness were evaluated by the indention method at room temperature using a diamond Vickers indenter with a loading time of 15 s at a constant load of 100 N. The results were averaged over six indentations per specimen and the following formula was used in the calculations.[18, 19]

$$(K_{IC}\phi/Ha^{1/2})(H/E\phi)^{2/5} = 0.035(1/a)^{-1/2} \quad (1)$$

where K_{IC} is the toughness of the composite ceramic, H is the Vickers hardness, E is the elastic modulus, ϕ is the constraint factor (≈ 3), l is the length of the crack, and a is the half diagonal length of an indentation.

3. Results and discussion

Densification of $BaTiO_3$ added 3Y-TZP ceramics can be achieved by pressureless sintering at 1400 to 1500°C in air for 3 h, and higher $BaTiO_3$ content leads to lower densification temperature. The fine microstructures for such dense ceramics are shown in Fig. 1. The co-presence of $BaTiO_3$ secondary phase with the 3Y-TZP matrix is confirmed by the results of XRD analysis (Fig. 2). Based on Figs. 1 and 2, Table 1 gives the effects of the content of $BaTiO_3$ addition upon the phase constitution and average grain size of 3Y-TZP ceramics sintered at 1400°C. The phase content of each specimen was compared to

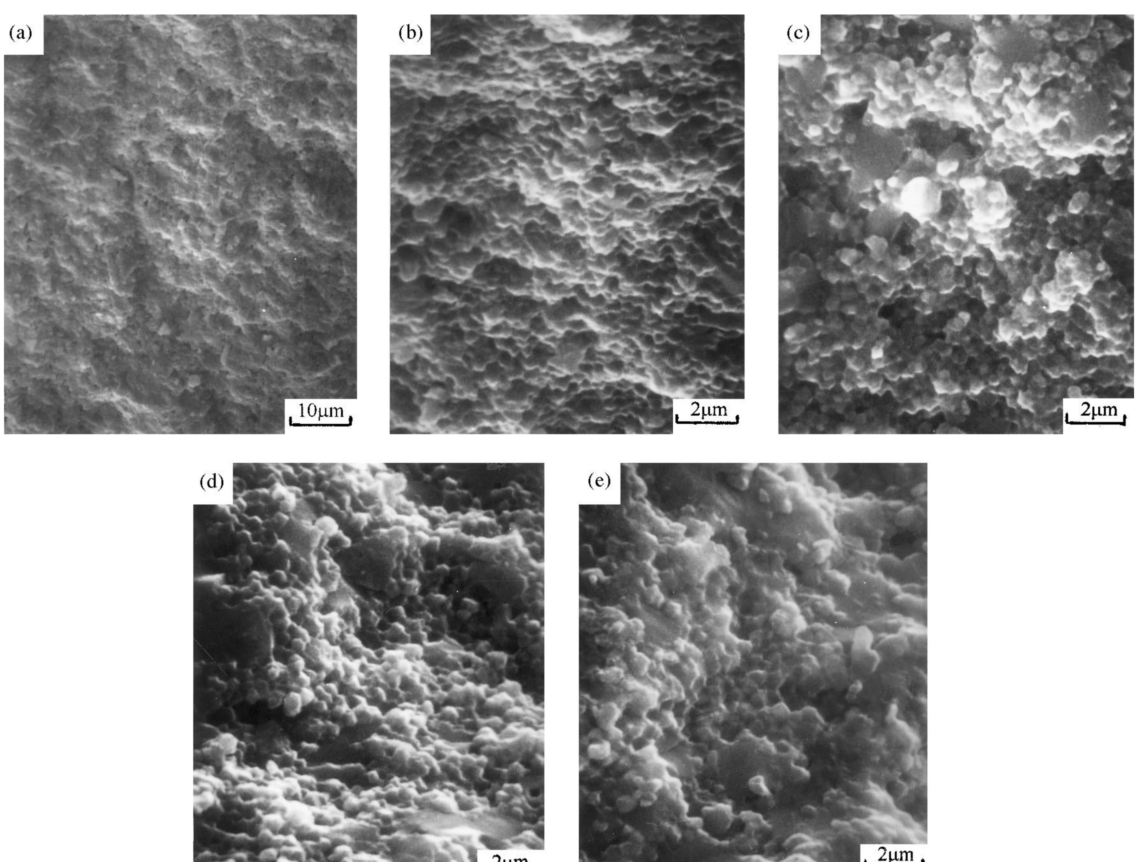

Fig. 1. SEM micrographs of fracture surface of xBaTiO$_3$/(1-x)3Y-TZP ceramics sintered at 1400°C. (a) $x=0$, (b) $x=0.03$, (c) $x=005$, (d) $x=0.1$, (e) $x=0.15$.

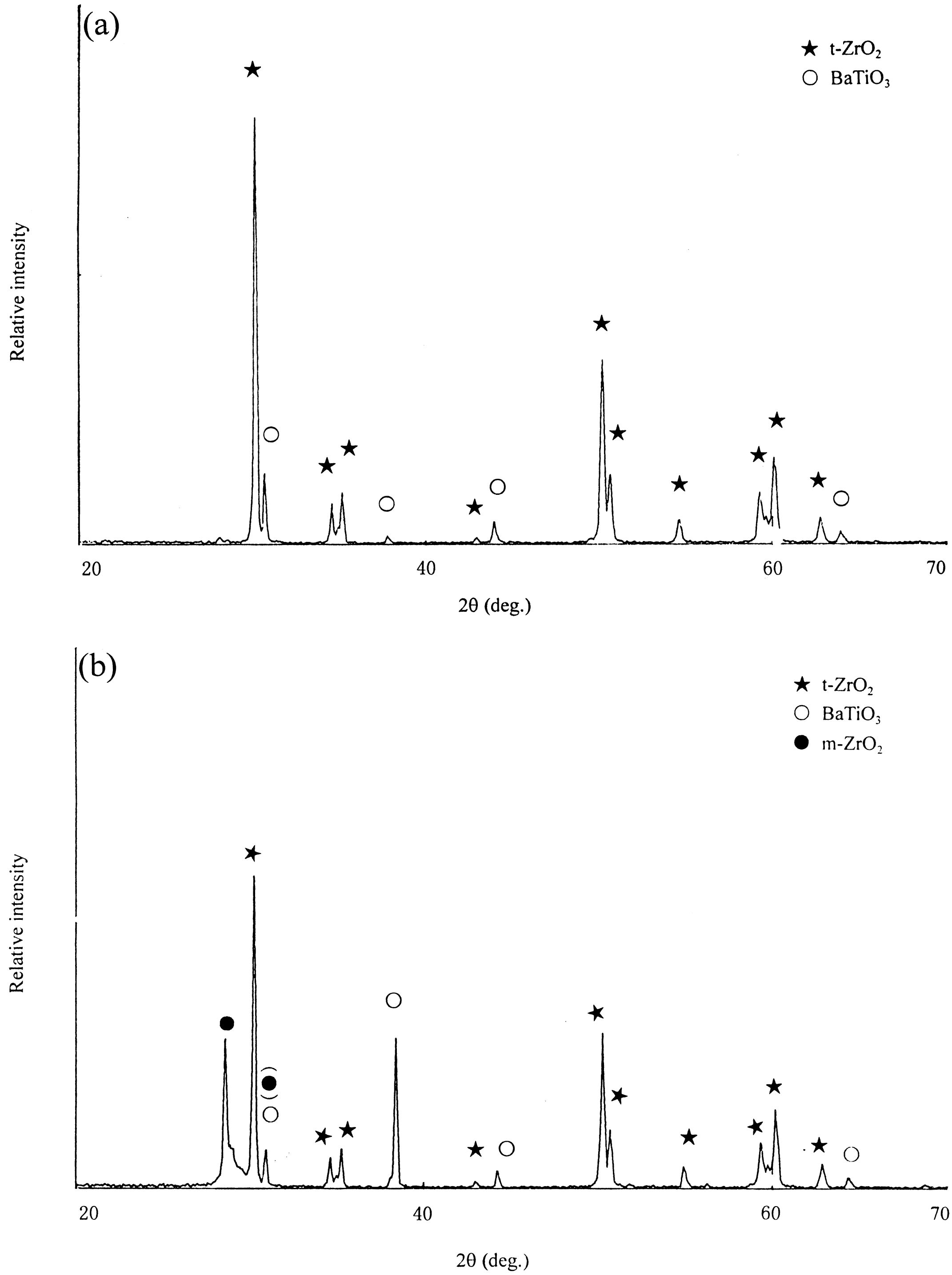

Fig. 2. XRD patterns of xBaTiO$_3$/(1−x)3Y-TZP ceramics (a) $x=0.05$, 1400°C/3 h; (b)$x=0.1$, 1400°C/3 h.

the grain size measurement in order to determine the critical grain size required to retain ⩾90% of the tetragonal phase. As shown in Table 1, high tetragonal phase content could be achieved for the composition with modest amount of $BaTiO_3$. And it is observed that complete tetragonal phase content could be achieved with 3 and 5 mol% $BaTiO_3$ addition, and the corresponding average grain size is 0.33–0.4 μm. For situation of high concentration of $BaTiO_3$ ($x>5$ mol%), the volume fraction of tetragonal phase of zirconia decreases. This is because more t-ZrO_2 transforms to m-ZrO_2 due to the larger grain size. These results indicate that the critical grain size for the retention of high-temperature tetragonal in the system of xBaTiO$_3$/(1-x)3Y-TZP exists, and this value is about 0.35 μm for the composite ceramics sintered at 1400°C.

Table 1
Phase compositions and average grain size xBaTiO$_3$/(1−x)3Y-TZP ceramics sintered at 1400C in air for 3 h

$BaTiO_3$ content (mol%)	Phase compositions	Average grain size (μm)	T-phase fraction (vol%)
0	T + M	< 0.2	85
3	T + $BaTiO_3$	≈0.33	100
5	T + $BaTiO_3$	≈0.4	100
10	T + $BaTiO_3$ + M	≈0.5	63
15	T + $BaTiO_3$ + M	≈0.6	76

Table 2
Phase compositions and average grain size of 0.03BaTiO$_3$/0.97 (3Y-TZP) ceramics sintered at different temperatures in air for 3 h

Temperature (°C)	Phase compositions	Average grain size (μm)	T-phase fraction (vol%)
1400	T + $BaTiO_3$	≈0.33	100
1425	T + M + $BaTiO_3$	≈0.45	90
1450	T + M + $BaTiO_3$	≈0.5	77
1500	M + T + $BaTiO_3$	≈1.0	22

Based on the micrographs (Fig. 3) and XRD analysis results, the estimated grain size and tetragonal phase content for 0.03BaTiO$_3$/0.97(3Y-TZP) ceramics are given in Table 2 as the functions of sintering temperature. Generally, the fraction of t-ZrO_2 phase will decrease with increasing the sintering temperature while the grain size increases. With incorporating small amount of $BaTiO_3$, the hardness of 3Y-TZP ceramics will be significantly enhanced (Fig. 4). However, the fracture toughness monotonously decreases with $BaTiO_3$ addition (Fig. 5).

The above effects of $BaTiO_3$ addition upon 3Y-TZP is interpreted as following. Because of the same valence and close ion radii, Ti^{4+} may partially substitute for Zr^{4+} in ZrO_2. That is, some of TiO_2 in $BaTiO_3$ may dissolve into ZrO_2 to form a solid solution of Y_2O_3-stabilized tetragonal (Zr,Ti)O_2, and the decreased densification temperature due to liquid phase sintering can support this conclusion. The larger grain size for higher $BaTiO_3$ content is also a result of the grain growth promoted by this process. In such a solid solution, the c/a ratio will be smaller than that of 3Y-TZP because of the small c/a ratio of tetragonal TiO_2 (∼0.644, after JCPDS

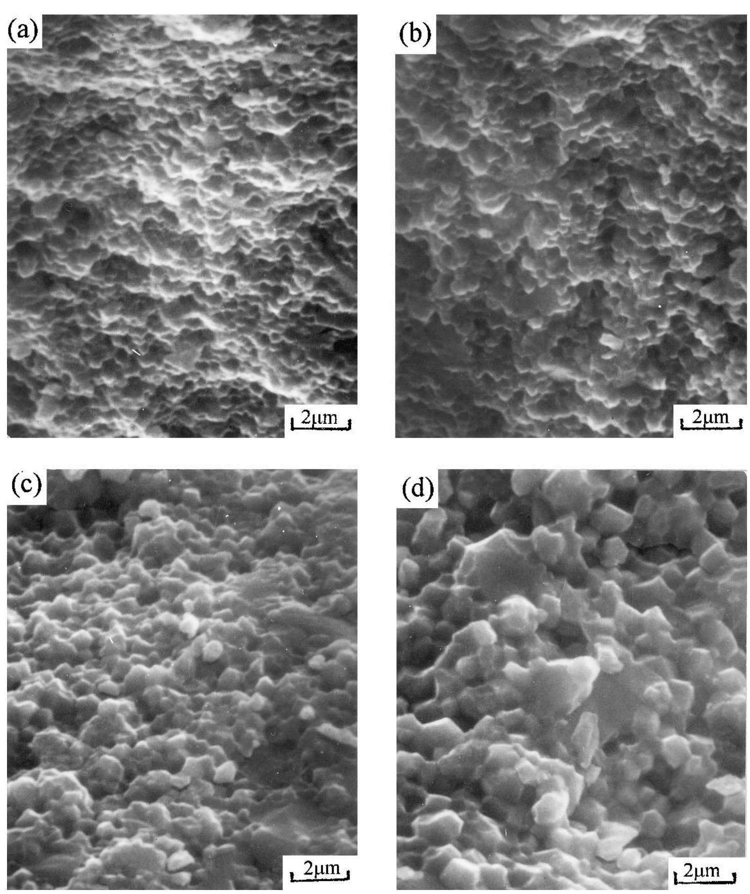

Fig. 3. SEM micrographs of fracture surface of 0.03BaTiO$_3$/0.97(3Y-TZP) composite ceramics 1400°C/3h , (b) 1425°C/3 h, (c) 1450°C/3 h, (d) 1500°C/3 h.

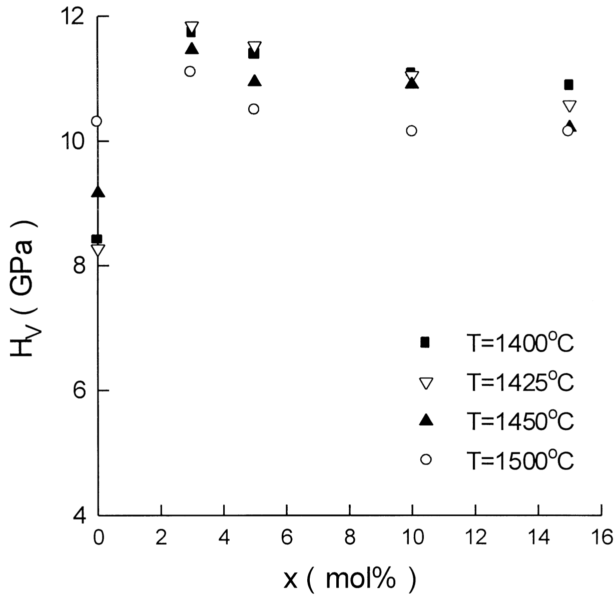

Fig. 4. Hardness of xBaTiO$_3$/(1$-x$)3Y-TZP ceramics vs. x and sintering temperature.

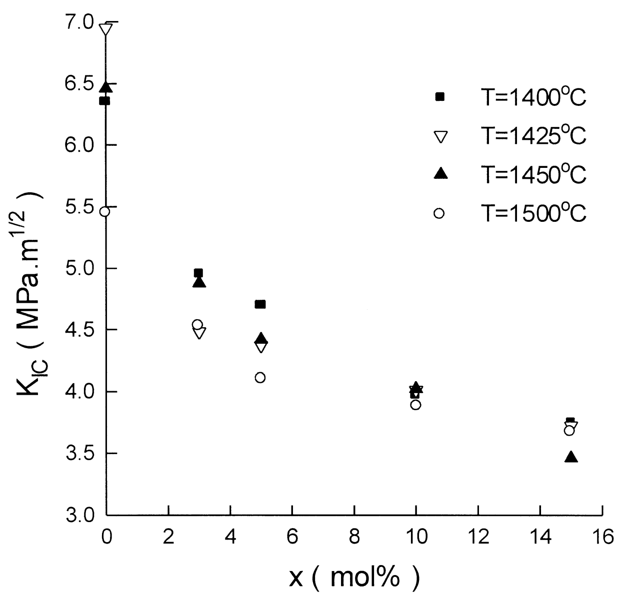

Fig. 5. Fracture toughness of xBaTiO3/$(1-x)$3Y $-$ TZP ceramics vs. x and sintering temperature.

Card No. 21-1276). On the other hand, based on the previous work of Kim, [20] the decreased c/a ratio of TZP will increase the stability of t-ZrO_2. Therefore, although the t-ZrO_2 fraction for some composition increases, the $BaTiO_3$ addition increases the stability of t-ZrO_2 phase simultaneously, and subsequently obstructs the stress-induced t–m transformation and finally suppresses the phase transformation toughening. Therefore, the coupling toughening effect of piezoelectric energy dissipation mechanism and transformation toughening mechanism can not be expected, and the primary issue for the further work in the present system is to adjust the stability of t-ZrO2 and to promote the stress-induced t–m transformation.

4. Conclusion

$BaTiO_3$ secondary phase can co-exist with 3Y-TZP ceramics, and increase the hardness of such ceramics, but the increased stability of t-ZrO_2 appears as a new problem which obstructs the stress-induced t→m transformation and subsequently suppress the effect of transformation toughening. Therefore in order to get a synergistic toughening effect of piezoelectric energy dissipation and transformation toughening, the primary issue in this system is to promote the stress-induced t→m transformation in BaTiO3/3Y-TZP ceramics by controlling the microstructures.

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