3Y-TZP ceramics toughened by $Sr_2Nb_2O_7$ secondary phase

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Abstract

3 mol% yttria stabilized tetragonal zirconia ceramics (3Y-TZP) were significantly toughened by a $Sr_2Nb_2O_7$ ferroelectric secondary phase incorporated into the matrix to serve as toughening agent. A high K_{IC} value, 13.0 MPa.m$^{1/2}$ was achieved in 1 mol% $Sr_2Nb_2O_7$ composite ceramics, while that of the 3Y-TZP matrix was 6.0 MPa.m$^{1/2}$. Energy transformation and consumption due to piezoelectric effects and domain wall motion was suggested as an important toughening mechanism along with that of phase transformation toughening. Moreover, it should be emphasized that a high K_{IC} value of 12.0 MPa.m$^{1/2}$ was achieved in the present composite ceramics even where the transformation toughening mechanism was inactive. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ferroelectric properties; $Sr_2Nb_2O_7$; Toughening; ZrO_2

1. Introduction

Ceramic toughening has attracted much interest in the past two decades, and a range of toughening approaches have been proposed and developed.[1,2] Recently, the present authors proposed and investigated the use of a piezoelectric or ferroelectric secondary phase incorporated into the matrix ceramic; toughening is achieved through energy dissipation due to the piezoelectric effect or/and domain wall motion.[3,4] In the previous work, alumina ceramics were pronouncedly toughened by this approach.[3,4]

Zirconia ceramics have been widely investigated as toughened ceramics, and transformation toughening has been recognised as an important toughening mechanism in which the stress-induced phase transformation from t-ZrO_2 to m-ZrO_2 plays the primary role.[1,2,5–8] In order to determine the combined effect of transformation toughening and piezoelectric secondary phase toughening, the authors introduced $BaTiO_3$ secondary phase into 3Y-TZP ceramics in the initial work.[9] However, improvements were not obtained because the increased stability of the t-ZrO_2 phase suppressed the stress-induced t/m transformation.[9]

In the present work, $Sr_2Nb_2O_7$ with a high Curie point (1615 K)[10] is adopted as the ferroelectric secondary phase, for which the crystallographic and dielectric properties[11] are shown in Table 1, and the toughening effects of $Sr_2Nb_2O_7$ ferroelectric secondary phase on 3Y-TZP ceramics are investigated together with the microstructural characterization.

2. Experimental procedure

Reagent-grade (99.5% purity) $SrCO_3$ and Nb_2O_5 in 2:1 mole ratio were mixed for 24 h by ball milling in ethanol using zirconia media. The slurry was dried and then calcined at 1200°C for 3 h to prepare $Sr_2Nb_2O_7$. Then, $xSr_2Nb_2O_7/(1-x)(3Y\text{-}TZP)$ composite powders ($x = 0.0$, 0.01, 0.02, 0.03, 0.04) were mixed by ball milling with zirconia media in ethanol for 24 h. Such mixed powders were pressed into disc compacts of 12 mm in diameter and 2–5 mm in height, and dense composite ceramics were created by sintering these compacts at 1450 to 1500°C in air for 3 h.

The microstructures were evaluated by scanning electron microscopy (SEM, HITACH S-570) and transmission electron microscopy (TEM, PHILIPS CM200)

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Table 1
Crystallographic and dielectric properties of $Sr_2Nb_2O_7$ single crystal[11]

Property	Value
Melting point (°C)	~1700
Crystal system	Orthorhombic
Space group	$Cmc2_1$
Lattice constant (Å)	$a = 3.97 \pm 0.01$
	$b = 26.86 \pm 0.05$
	$c = 5.72 \pm 0.02$
Cell content	$Z = 4$
X-ray density (g/cm^3)	5.15 ± 0.04
Curie point (°C)	1342 ± 2
Dielectric constant at room	$\varepsilon_a^T = 75$
temperature and at 1 kHz	$\varepsilon_b^{\ T} = 46$
	$\varepsilon_c^{\ T} = 43$
[a]Spontaneous polarization	9 μC/cm^2
[a]Remnant polarization	7 μC/cm^2
[a]Coercive field	6 kV/cm
Coupling factor (k^{33})	0.26

[a] Along the c-axis at room temperature and at $E_0 = 25$ kV/cm.

equipped with energy dispersive X-ray spectrometry (EDS), and the phase constitution of the composite ceramics was characterized by X-ray powder diffraction (XRD) analysis using CuK_α radiation.

The fracture toughness was evaluated by the modified indention method[12,13] at room temperature using a diamond Vikers indenter with a loading time of 15 s at a constant load of 60 N. The results were averaged over six indentations per specimen, and the following formula was used in the calculations:

$$\left(3K_{IC}/Ha^{1/2}\right)(H/3E)^{2/5} = 0.129(c/a)^{-3/2} \qquad (1)$$

where K_{IC} is the toughness of the composite ceramic, H is the Vickers hardness, E is the elastic modulus, c is the radius of the crack, and a is the half diagonal length of an indentation.

3. Results and discussions

For $x = 0$, 1 and 2 mol%, dense composite ceramics were obtained by sintering the samples at 1500°C in air for 3 h (see Fig. 1), but it was difficult to prepare dense

composite ceramics with $x \geqslant 3$ mol% where macro-cracks generally formed in the samples during cooling after sintering. The relative densities were shown in Table 2, in which room temperature lattice parameters after Porter[14] and $\rho(\text{t-ZrO}_2) = 6.16$ g cm^{-3}, $\rho(\text{m-ZrO}_2) = 5.83$ g cm^{-3}, $\rho(Sr_2Nb_2O_7) = 5.15$ g cm^{-3} were used to calculate the theoretic densities. In 3Y-TZP ceramics, the tetragonal phase would remain as the major phase after cooling where the t–m transformation was suppressed. In the present composite ceramics, the introduction of $Sr_2Nb_2O_7$ secondary phase might affect the phase constitution. As shown in Fig. 2 and Table 3, the addition of $Sr_2Nb_2O_7$ secondary phase led to a decrease of tetragonal phase fraction in the as-sintered state; however, the fraction of transformable tetragonal phase reached a maximum at $x = 1$ mol% and became zero at $x = 2$ mol%. Because of the small content, the $Sr_2Nb_2O_7$ secondary phase was difficult to detect by XRD, but there was still some evidence of a secondary phase in Fig. 2(c) (a weak peak at 26.6°, which was assigned to the strongest peak for $Sr_2Nb_2O_7$). The presence of $Sr_2Nb_2O_7$ secondary phase is confirmed by TEM micrographs and the EDS results for different grains (Fig. 3), where grain A contains Zr, O and Y, and grain B contains Sr, Nb, Zr and O elements. The presence of Zr in grain B suggests that Zr is dissolved into the $Sr_2Nb_2O_7$. The details for the structure need further investigation.

The fracture toughness was evaluated by the indentation method, and the results are given in Fig. 4 for $xSr_2Nb_2O_7/(1-x)(3Y\text{-TZP})$ ceramics sintered at 1500°C in air for 3 h. The fracture toughness, K_{IC} of the 3Y-TZP ceramics was significantly improved by incorporating small amounts of $Sr_2Nb_2O_7$ secondary phase, and the maximum fracture toughness of 13.0 MPa·m$^{1/2}$ was achieved for the composition of $0.01Sr_2Nb_2O_7/0.99(3Y\text{-TZP})$, while the K_{IC} of the 3Y-TZP end-member was about 6.0 MPa·m$^{1/2}$. For $x = 2$ mol%, the high K_{IC} value (12.0 MPa·m$^{1/2}$) was also obtained even though the fraction of transformable tetragonal phase approached zero. This meant that the transformation toughening mechanism was inactive in this situation, and alternative mechanisms must be considered. The micro-cracking toughening mechanism might be active here, but the effect should not be so significant. The most possible mechanism was so-called ferroelectric or

Table 2
Relative densities of $xSr_2Nb_2O_7/(1-x)3Y\text{-TZP}$ ceramics sintered at 450°C and 1500°C for 3 h

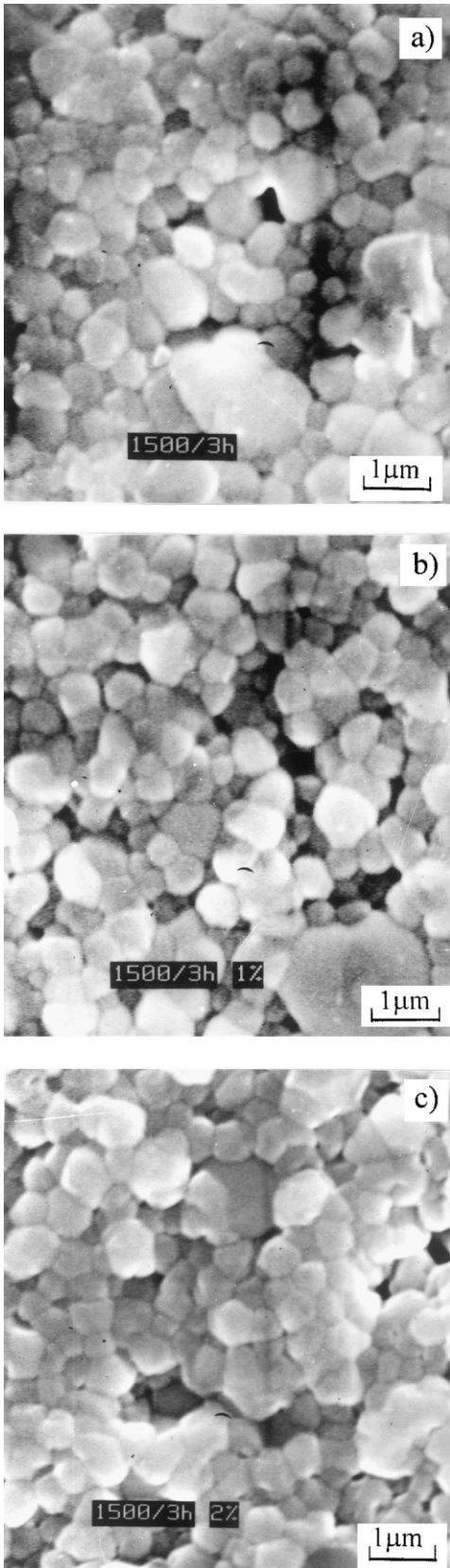| Sintering condition	x	t-Phase portion (%)	Measured density (g.cm^{-3})	Theoretic density (g.cm^{-3})	Relative density (%)
1450°C/3 h	0.02	29	5.8622	5.9102	99.2
1500°C/3 h	0.00	95	6.0753	6.1435	98.8
	0.01	66	5.9704	6.8038	98.9
	0.02	26	5.8918	5.9005	99.9

Fig. 1. Scanning electron microscopy images of as-sintered surfaces of (a) 3Y-TZP, (b) $0.01Sr_2Nb_2O_7/0.99(3Y\text{-}TZP)$ and (c) $0.02Sr_2Nb_2O_7/0.98(3Y\text{-}TZP)$ ceramics sintered at 1500°C in air for 3 h.
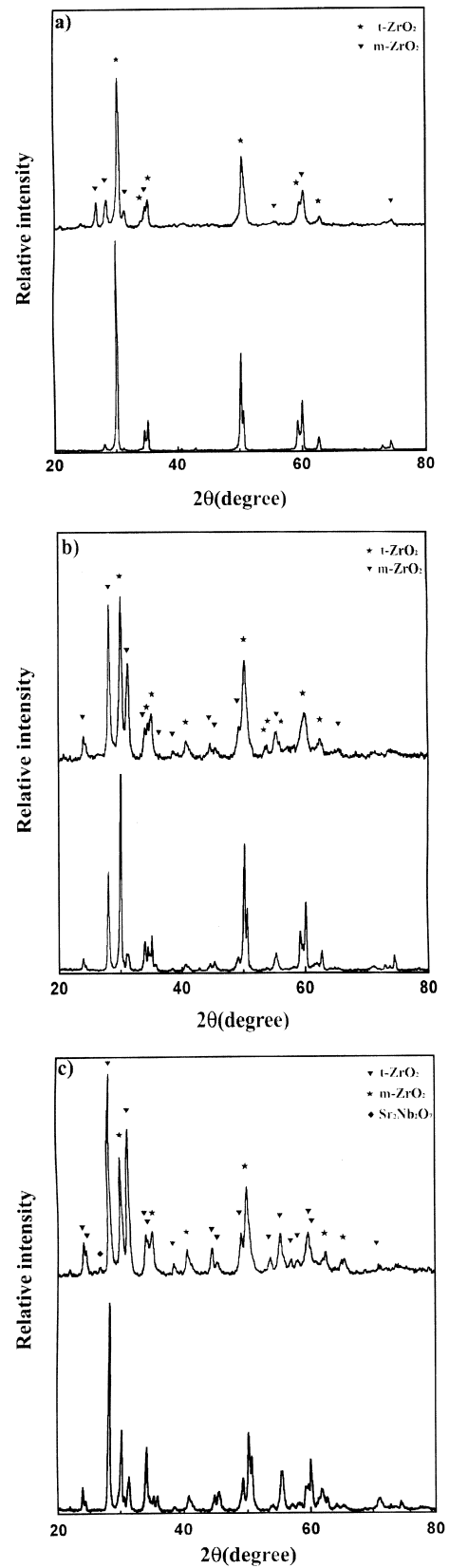
Fig. 2. XRD patterns of as-sintered surface (lower) and crashed powders (upper) for (a) 3Y-TZP. (b) $0.01Sr_2Nb_2O_7/0.99(3Y\text{-}TZP)$ and (c) $0.02Sr_2Nb_2O_7/0.98(3Y\text{-}TZP)$ ceramics sintered at 1500°C in air for 3 h.

Table 3
Influence of $Sr_2Nb_2O_7$ content on fraction of tetragonal phase in $xSr_2Nb_2O_7/(1-x)(3Y\text{-}TZP)$ ceramics sintered at 1500°C in air for 3 h

	$x = 0$	$x = 0.01$	$x = 0.02$
%Tetragonal (as-sintered)	95	66	26
%Tetragonal (crushed)	71	39	26
%Tetragonal (transformable)	24	27	0
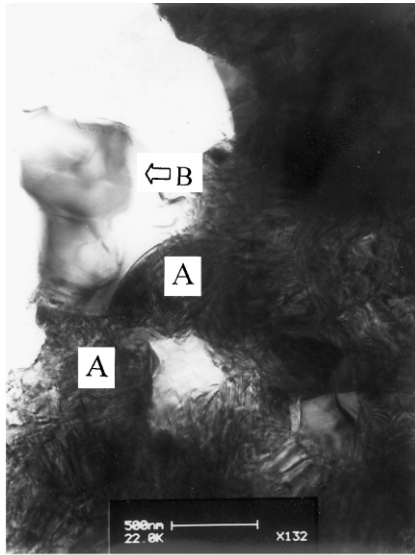
a)
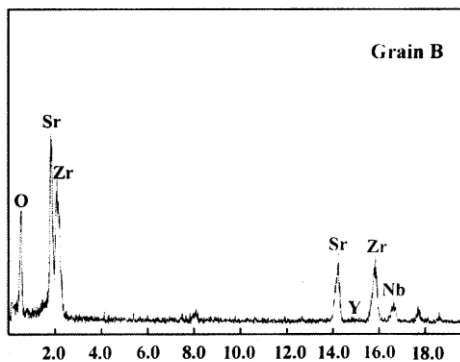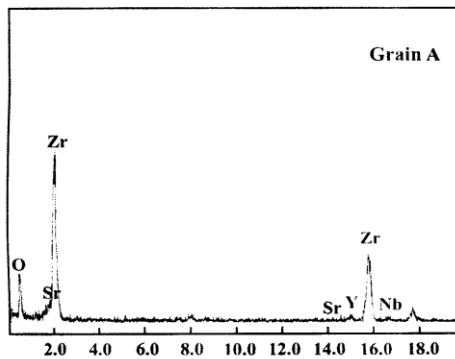
b)

Fig. 3. (a)TEM micrograph and (b) EDS analysis results for different grains of $0.02Sr_2Nb_2O_7/0.98(3Y\text{-}TZP)$ ceramics sintered at 1500°C in air for 3 h.
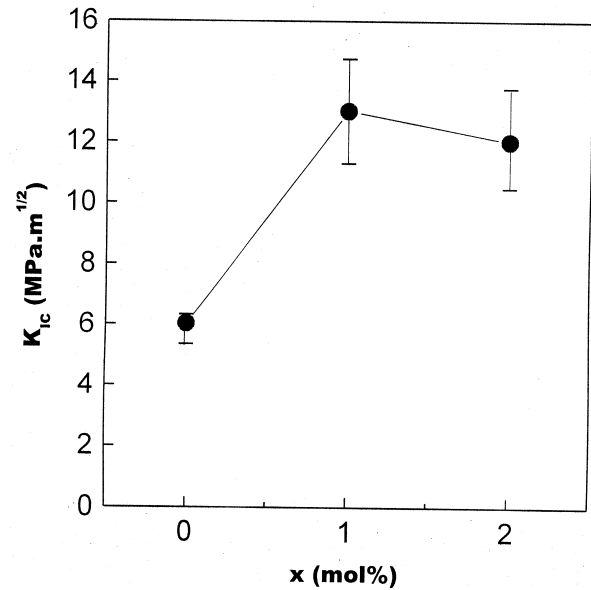

Fig. 4. Influence of $Sr_2Nb_2O_7$ ferroelectric secondary phase on fracture toughness of 3Y-TZP ceramics sintered at 1500°C in air for 3 h.

piezoelectric secondary phase toughening, where the toughening process was based on the elastic energy dispersion due to mechanical/electrical energy convention and domain wall motion in the ferroelectric particles in the crack-tip stress field.

4. Conclusions

3Y-TZP ceramics were significantly toughened by the present novel approach, in which a $Sr_2Nb_2O_7$ ferroelectric secondary phase was incorporated into the matrix to serve as toughening agent. The fracture toughness of 3Y-TZP ceramics could be more than doubled with a 1 mol% $Sr_2Nb_2O_7$ addition. It should be emphasized that a high K_{IC} value of 12.0 MPa.m$^{1/2}$ was achieved in the present composite ceramics even in the situation where the transformation toughening mechanism was inactive. Although further investigation is needed for details, so-called ferroelectric or piezoelectric secondary phase toughening is an effective approach for ceramic toughening. Moreover, because of the high Curie point of $Sr_2Nb_2O_7$ (1342°C), the ferroelectric secondary phase toughening effect in the present ceramics may be active up to a high temperature. Therefore, the present approach may have the great potential in enhancing fracture toughness of ceramics at both elevated and room temperatures.

Acknowledgements

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