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Microstructures and mechanical properties of $Sr_2Nb_2O_7$-toughened 3Y-TZP ceramics

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Abstract

The effects of sintering time upon microstructures and the mechanical properties were investigated for $Sr_2Nb_2O_7$-toughened 3Y-TZP ceramics. The incorporation of $Sr_2Nb_2O_7$ secondary phase significantly enhanced the fracture toughness of 3Y-TZP ceramics, and the toughening effect was noticeably influenced by sintering conditions through microstructural changes: the fracture toughness increased with increasing soaking time for compositions of $x \leqslant 0.01$, but a slight decrease of fracture toughness with soaking time was observed for $x = 0.015$, where x is the mole fraction of $Sr_2Nb_2O_7$. The high fracture toughness, K_{1C}, of 13.7 MPa $m^{1/2}$, was achieved in the ceramic with $x = 0.005$ sintered at 1500 °C for 6 h. This is almost a doubling of fracture toughness, compared to the specimens without $Sr_2Nb_2O_7$. It should be emphasized that the high fracture toughness, K_{1C} of 10 MPa $m^{1/2}$(1.4 times that of the matrix) could be obtained even for the situation without transformable tetragonal phase where the phase transition toughening was not active and the piezoelectric/ferroelectric secondary phase played an important role.

Keywords: A. Sintering; B. Microstructure; C. Mechanical properties; 3Y-TZP

1. Introduction

During the past two decades much attention had been focused on the tetragonal to monoclinic phase transition of zirconia ceramics [1–3], which can remarkably enhance the fracture toughness of ZrO_2-based ceramics. According to previous work [1,2,4,5], the contribution to fracture toughness of the stress-induced transformation of ZrO_2-based ceramics is related to transformable tetragonal phase fraction at room temperature, and which is affected by a number of factors, such as alloy type [6,7], alloy content [6], cooling rate [8] and the grain size of tetragonal ZrO_2 phase in TZP (Tetragonal Zirconia Polycrystal) ceramics [6,7,9]. In TZP, for a specific composition, the grain size plays an important role. The tetragonal phase can only exist steadily below a critical grain size.

Recently, a novel ceramic toughening process has been proposed by the authors, in which some dispersed ferroelectric or piezoelectric secondary phase is the toughening agent [10–12]. In the previous work [13], the fracture toughness of 3Y-TZP ceramics was improved significantly by incorporating $Sr_2Nb_2O_7$ ferroelectric secondary phase. On the other hand, the stability of tetragonal phase of 3Y-TZP was directly related to grain size, and therefore the sintering conditions should have significant effects upon the fracture toughness. In the present work, the effects of sintering conditions on microstructures and mechanical properties of $Sr_2Nb_2O_7$-toughened 3Y-TZP ceramics were investigated.

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 ($x = 0.0$, 0.005, 0.01, 0.015, 0.02) were mixed by ball milling with zirconia media in ethanol for 24 h. After drying, the mixed powders were pressed into disc compacts of 12 mm in diameter and 1–4 mm in height, and these compacts were sintered at 1500 °C in air for different soaking time (1–6 h).

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The microstructures were evaluated by scanning electron microscopy (SEM, HITACHI S-570), and the phase content of the composite ceramics was characterized by X-ray diffraction (XRD) analysis using CuKα radiation. The tetragonal fraction of ZrO_2 in the composites were calculated with the relation of Garvie and Nicholson [14], using the following formula:

$$t(\%) = \frac{I_t(111)}{I_t(111) + I_m(111) + I_m(\bar{1}11)} \times 100\% \quad (1)$$

where, $I_t(111)$, $I_m(111)$ and $I_m(\bar{1}11)$ denote the intensity of corresponding peaks, and subscripts t and m indicate tetragonal and monoclinic phase, respectively, while the transformable tetragonal phase fraction is the difference

Table 1
Average grain size, phase constitutions and transformable tetragonal fractions of $x\mathrm{Sr_2Nb_2O_7}/(1-x)$3Y-TZP ceramics sintered at 1500 °C for different soaking times

Sintering condition	x	Average grain size (μm)	Volume fraction of tetragonal phase	Transformable tetragonal phase
1500 °C/1 h	0.000	–	100%	23.1%
	0.005	≈0.33	100%	36.7%
	0.015	–	100%	57.6%
1500 °C/3 h	0.000	≈0.50	100%	25.4%
	0.005	≈0.56	100%	44.4%
	0.015	≈0.63	89.2%	58.1%
1500 °C/6 h	0.000	≈0.70	100%	28.6%
	0.005	≈0.85	92.6%	43.1%
	0.015	≈1.00	17.2%	0.00%

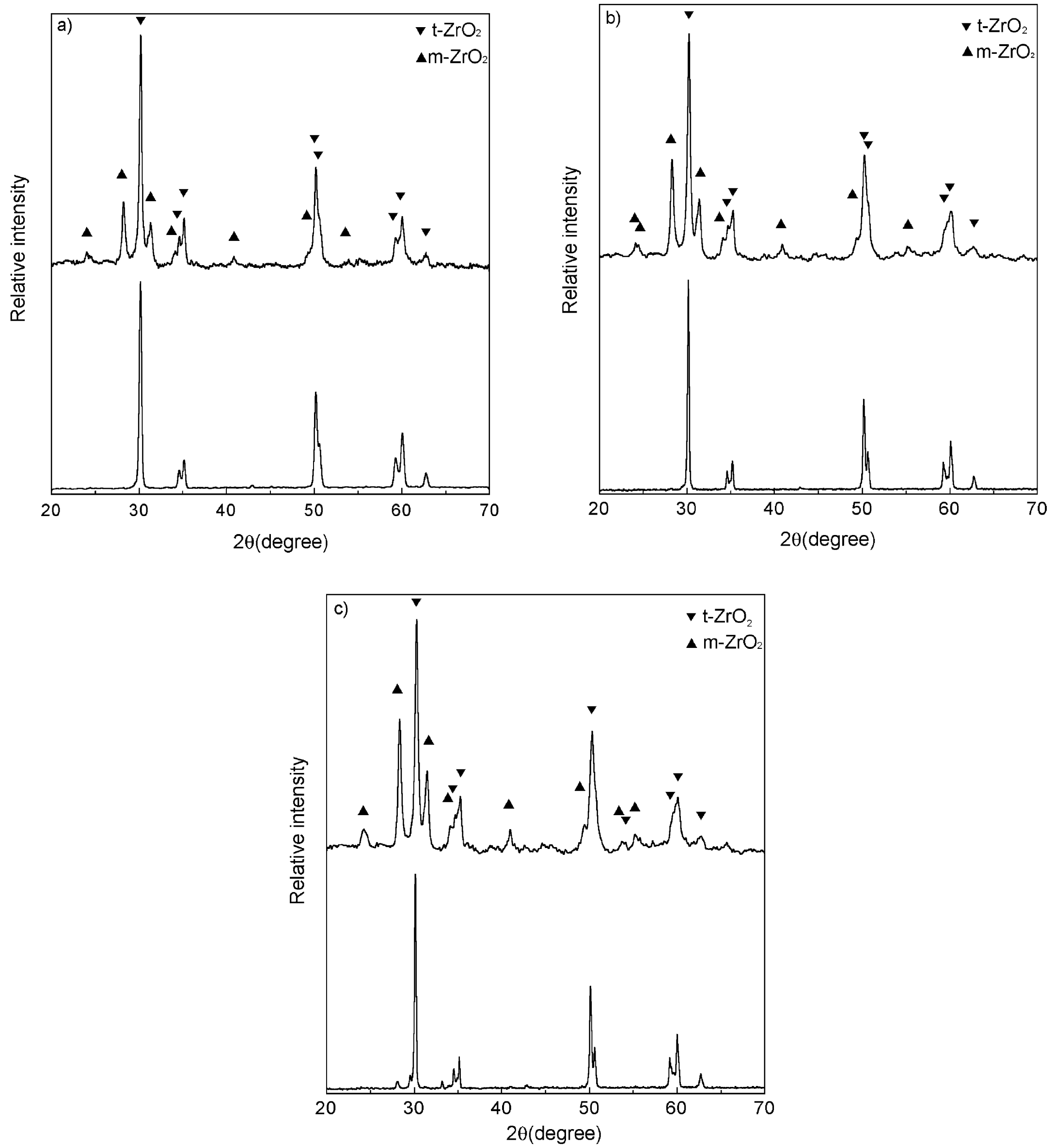

Fig. 1. XRD patterns of as-sintered surface (lower) and crushed powders (upper) for $0.005\mathrm{Sr_2Nb_2O_7}/0.995$(3Y-TZP) ceramics sintered at 1500 °C for different soaking time: (a) 1 h; (b) 3 h; (c) 6 h.

of the tetragonal ziroconia fraction of as-sintered surface and crushed powder.

The effective elastic modulus was evaluated using the method proposed by Marshall et al. [15] where a diamond Knoop indenter was used combined with a diamond Vickers indenter. The results were averaged over six indentations per specimen and the following formula was used in the calculations [15]:

$$b'/a' = b/a - \alpha H/E, \tag{2}$$

where b'/a' and b/a are the ratio of diagonal dimensions of Knoop indentation and that of Knoop indenter, respectively, α is a constant, H is Vickers hardness and E was effective elastic modulus. Here, $b/a = 1/7.11$ and $\alpha = 0.45$ were used during calculations.

The fracture toughness was evaluated by the modified indention method [16,17] at room temperature using a diamond Vickers indenter with a loading time of 15s at a constant load of 100 N on a polished surface. The results were averaged over six indentations per specimen and the following formula was used in the calculations [16,17]:

$$(K_{1C}\phi/Ha^{1/2})(H/E\phi)^{2/5} = 0.035(l/a)^{-1/2} \tag{3}$$

where K_{1C} was the toughness of the composite ceramic, H was the Vickers hardness, E was the effective elastic modulus, ϕ was the constraint factor($\approx$3), l was the length of the crack, and a was the half diagonal length of an indentation.

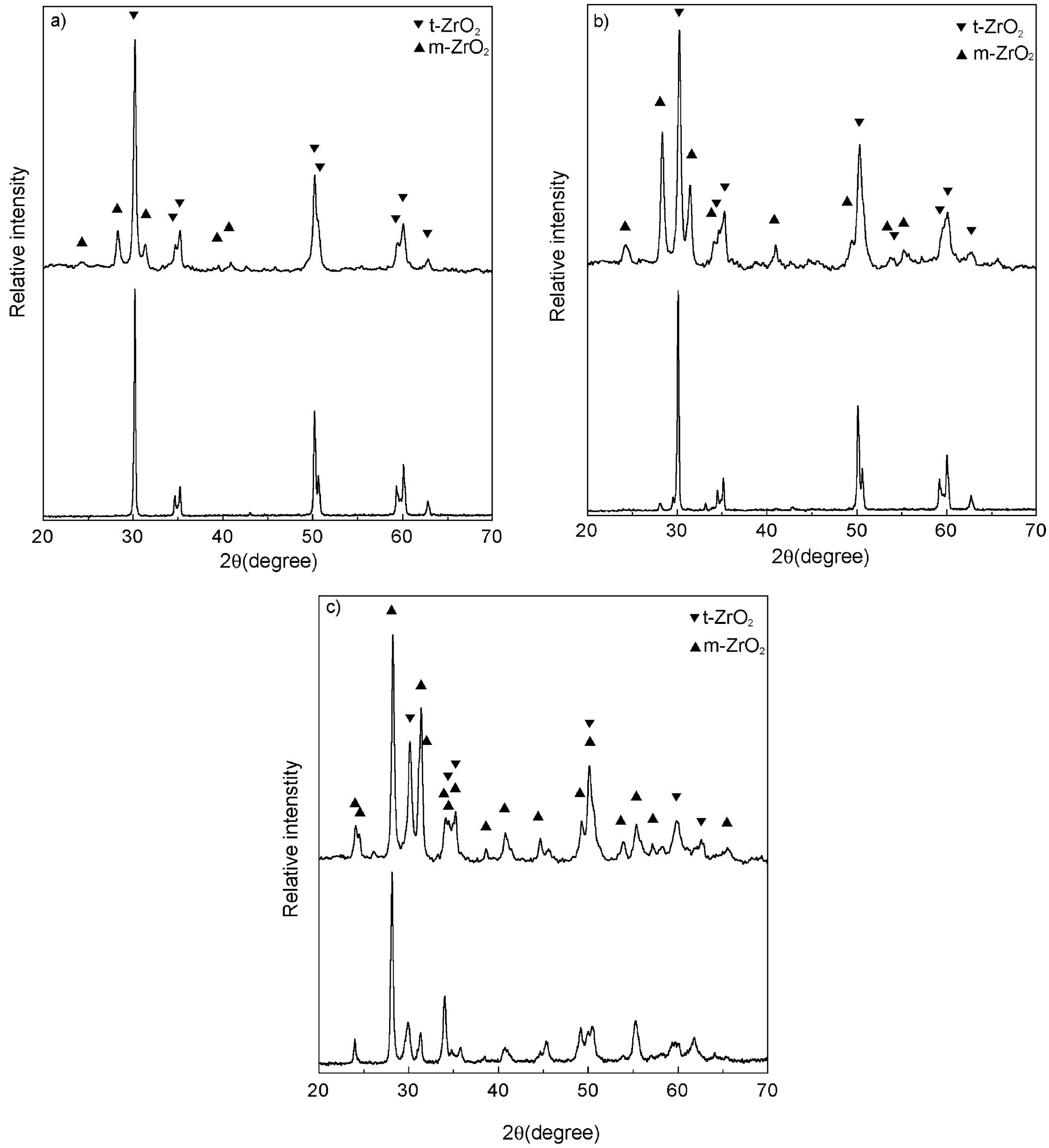

Fig. 2. XRD patterns of as-sintered (lower) and crushed powders (upper) for xSr$_2$Nb$_2$O$_7$/(1−x)3Y-TZP ceramics sintered at 1500 °C for 6 h: (a) $x = 0.000$; (b) $x = 0.005$; (c) $x = 0.015$.

3. Results and discussion

The densification of $x\mathrm{Sr_2Nb_2O_7}/(1-x)$3Y-TZP ceramics with $x \leqslant 0.015$ can be performed well at 1500 °C in air for 3 and 6 h, but no dense ceramics can be obtained for $x > 0.02$. Table 1 shows the grain size, the phase constitution and the fraction of transformable tetragonal phase as a function of the sintering condition and the additive content. The grain size increases with increasing the soaking time and the additive content, and the fraction of tetragonal phase at room temperature remains at almost 100% except for ceramics with $x = 1.5$mol% and sintered for 6 h, where the grain size becomes larger than the critical value [9] (see Figs. 1 and 2). The fraction of transformable tetragonal zirconia increases to a maximal value and then decreases with increasing $Sr_2Nb_2O_7$ content in the ceramics sintered for 6 h, while that increases all along in the ceramics sintered for 1 and 3 h (see Fig. 3). $Sr_2Nb_2O_7$ secondary phase is difficult to be detected by XRD because the content is too small, but presence of $Sr_2Nb_2O_7$ piezoelectric secondary phase can be confirmed by TEM [13].

The effective elastic modulus, Vickers hardness and fracture toughness of ceramics are shown in Table 2. The Vickers hardness decreases with the content of $Sr_2Nb_2O_7$, while the tendency of elastic modulus is not clear and further investigation is needed.

Generally, the incorporation of $Sr_2Nb_2O_7$ secondary phase leads to the significant enhancement of fracture toughness (see Fig. 4). However, the fracture toughness will reach the maximum value at a critical content of $Sr_2Nb_2O_7$ and beyond which the toughening effects will be limited, and no dense ceramics can be obtained if the content of $Sr_2Nb_2O_7$ is too large. Moreover, the critical content of $Sr_2Nb_2O_7$ varies with soaking time. This is because the larger content of $Sr_2Nb_2O_7$ may lead to the decrease of stability of tetragonal phase, which will have two different effects: (1) increase of the fraction of transformable tetragonal phase when x is modest; (2) decrease of the fraction of the stabilized tetragonal phase and even causes the macrocracks in ceramics during the cooling process after sintering when x is too large.

For the compositions of $x = 0.005$ and $x = 0.01$, the fracture toughness increases with increasing the soaking time, while a slight decrease of the fracture toughness

Table 2
Effective elastic modulus, Vickers hardness and fracture toughness of $x\mathrm{Sr_2Nb_2O_7}/(1-x)$3Y-TZP ceramics sintered at 1500 °C for different soaking times

Sintering condition	x	E (GPa)	Hv (GPa)	K_{1C} (MPa m$^{1/2}$)
1500 °C/1 h	0.000	210±29	13.0±0.2	5.4±0.1
	0.005	191±19	12.2±0.1	5.2±0.6
	0.010	177±14	10.9±0.2	7.0±0.8
	0.015	184±14	10.4±0.2	11.3±1.0
	0.020	156±11	9.7±0.1	9.0±0.8
1500 °C/3 h	0.000	177±12	12.4±0.5	5.3±0.2
	0.005	197±18	11.7±0.1	9.6±0.9
	0.010	175±11	10.6±0.1	10.2±0.8
	0.015	181±13	10.2±0.1	10.2±0.8
	0.020	153±11	9.2±0.1	9.8±0.5
1500 °C/6 h	0.000	182±18	13.2±0.2	7.2±0.8
	0.005	182±11	11.5±0.2	13.7±1.9
	0.010	181±12	10.6±0.1	11.2±0.6
	0.015	163±19	9.9±0.04	10.0±0.6

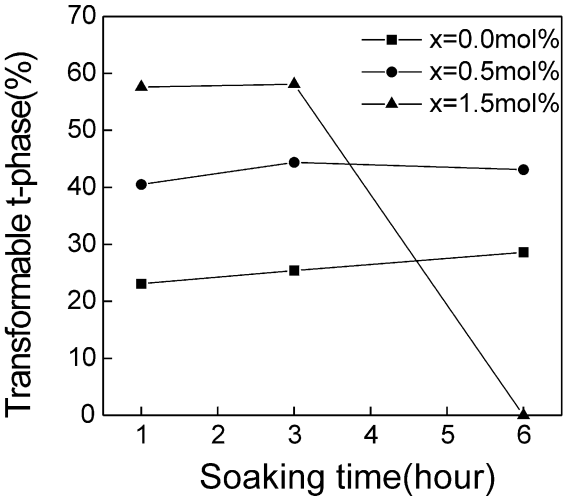

Fig. 3. Effect of soaking time on fraction of transformable tetragonal phase in $x\mathrm{Sr_2Nb_2O_7}/(1-x)$3Y-TZP ceramics.

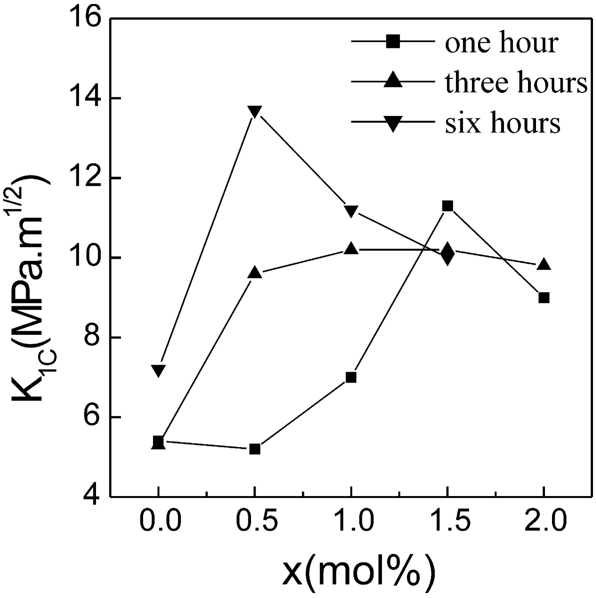

Fig. 4. Effect of $Sr_2Nb_2O_7$ content on fracture toughness of $x\mathrm{Sr_2Nb_2O_7}/(1-x)$3Y-TZP ceramics sintered at 1500 °C for different soaking times.

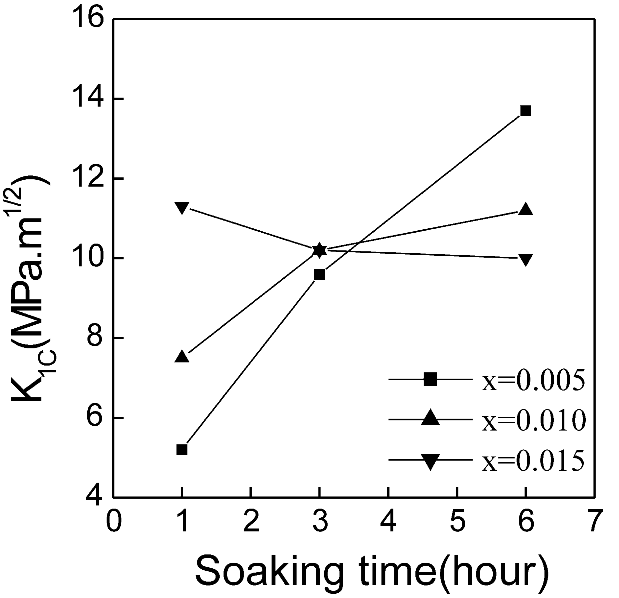

Fig. 5. Effect of soaking time on fracture toughness of $x\mathrm{Sr_2Nb_2O_7}$/(1−x)3Y-TZP ceramics sintered at 1500 °C.

with the soaking time is observed in the situation of $x = 0.015$ (see Fig. 5). These tendencies are concerned with the content of the piezoelectric secondary phase and the microstructures. That is, the longer soaking time is of benefit to the ceramics with a smaller content of piezoelectric secondary phase where the fraction of transformable t-phase increases with increasing soaking time. However, for the situation of $x = 0.015$, the fraction of transformable t-phase decreases with increasing soaking time and becomes zero for the soaking time of 6 h, and subsequently the longer soaking time leads to the decrease of fracture toughness. Special attention should be paid to the ceramics with $x = 0.015$ sintered for 6 h, although the transformable tetragonal phase decreases to zero, its fracture toughness value still reaches 10 MPa m$^{1/2}$. In this case, the stress-induced transformation toughening is absent since there is no transformable tetragonal zirconia and ferroelastic toughening of $Sr_2Nb_2O_7$ is also absent because it is not ferroelastic at all [18], therefore an alternative toughening mechanism should be considered. Although ferroelstatic domain switching of tetragonal phase in TZP ceramics may contribute to the toughening in this system [3,19], the effect will not be so large for the poor content of t-phase in the present composites. Also the micro-cracking toughening may be active, but the effect should not so notable and the piezoelectric secondary phase toughening should be the primary mechanism. In this mechanism, the extension of cracks is suppressed due to the energy dissipation and the conversion of mechanical energy into electric energy caused by the domain wall motion and piezoelectric effects of the piezoelectric and/or ferroelectric secondary phase.

4. Conclusions

The grain size increased with increasing the additive content and soaking time in $Sr_2Nb_2O_7$-toughened 3Y-TZP ceramics. However, the fraction of transformable tetragonal zirconia increased to a maximal value and then decreased to zero with increasing $Sr_2Nb_2O_7$ content in the ceramics sintered for 6 h, while that increased all along in the ceramics sintered for 1 and 3 h. The incorporation of $Sr_2Nb_2O_7$ secondary phase significantly enhanced the fracture toughness of 3Y-TZP ceramics, and the toughening effect was notably affected by the composition and the sintering conditions through the microstructures change: the fracture toughness increased with increasing the soaking time for compositions of $x \leqslant 0.01$, but a slight decrease of fracture toughness with soaking time was observed for $x = 0.015$. The highest fracture toughness K_{1C} of 13.7 MPa m$^{1/2}$ was achieved in the ceramics with $x = 0.005$ sintered at 1500 °C for 6 h. It should be emphasized that the high fracture toughness K_{1C} of 10 MPa m$^{1/2}$ could be obtained even for the situation without transformable tetragonal phase where the t-phase transition toughening was not active and the piezoelectric secondary phase was thought to play an important role.

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