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Transformation toughening in an antiferroelectric ceramic

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Abstract

Due to a larger specific volume of the ferroelectric phase, the antiferroelectric-to-ferroelectric transition is believed to have an enhanced toughening effect against fracture. The toughening requires a non-recoverable transformation in the crack process zone. Complementary measurement of the crystal symmetry, dielectric constant, field-induced polarization and Raman spectrum on ceramic $Pb_{0.99}Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{0.92}Ti_{0.08}]_{0.98}O_3$ indicates that the antiferroelectric and the ferroelectric states are equally stable at room temperature. Raman mapping further reveals the presence of the ferroelectric phase in a localized zone at the crack tip after unloading. A significant phase-transition-toughening effect is demonstrated in the antiferroelectric ceramic with both indentation fracture and *R*-curve experiments. The effect in this model composition leads to toughness values ~50% larger than other antiferroelectric ceramics with similar compositions and 60–130% higher than ferroelectric $Pb(Zr,Ti)O_3$ ceramics. A simple analysis confirms the toughening effect from both volumetric phase transition and deviatoric domain switching during the transformation. The results suggest that other materials near phase boundaries may have similar high fracture resistance.

Keywords: Antiferroelectric ceramics; Phase transition toughening; Raman mapping; *R*-curve

1. Introduction

Ceramics are intrinsically prone to fracture [1], and toughening is always desired for structural as well as functional applications [2–5]. Among the various toughening mechanisms reported in monolithic ceramics, phase-transition toughening demonstrated in ZrO_2-based ceramics is probably the most effective one [4]. Other extrinsic toughening mechanisms in polycrystalline ceramics, such as ferroelastic toughening [6] or frictional crack bridging [7], are difficult to control without altering the electrical, mechanical or electromechanical properties.

Antiferroelectric ceramics are promising candidates for dielectrics in high-energy-density electrical capacitors due to the electric-field-induced antiferroelectric-to-ferroelectric phase transition [8–11]. This first order transition is manifested by the abrupt development of large electrical polarization and dimension expansion in both longitudinal and transverse directions in $PbZrO_3$-based perovskite compositions [12–18]. The associated volume change makes the phase transition sensitive to mechanical stress and hydrostatic pressure [11,12,15,19] and also raises reliability issues of actuators and capacitors utilizing antiferroelectric ceramics [20]. On the other hand, following the same working mechanism in ZrO_2-based structural ceramics, the volumetric strain at the phase transition in antiferroelectric materials may be exploited to toughen these functional electroceramics [21,22]. The most studied and documented toughening mechanism in functional electroceramics so far is ferroelastic toughening through localized domain switching [6,23–29]. Since $PbZrO_3$-based ceramics contain non-180° antiferroelectric domains [30,31] and are ferroelastic prior to and after the phase transition [22,32], the ferroelastic toughening mechanism is still expected to contribute. In order for the volumetric phase-transition toughening to

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work in antiferroelectric ceramics, the induced ferroelectric phase must be stable at the crack tip after unloading [3]. Therefore, the composition of the ceramic needs to be fine-tuned to achieve an irreversible antiferroelectric-to-ferroelectric phase transition at room temperature. In such an antiferroelectric composition, the combined effect of both ferroelastic-toughening and phase-transition-toughening mechanisms is expected, and as a result, an enhanced toughness will be observed.

2. Experimental

Our previous studies indicate that the compositions $y = 0.07$–0.08 in the solid solution $Pb_{0.99}Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{1-y}Ti_y]_{0.98}O_3$ (PNZST 43/100y/2) display an irreversible antiferroelectric-to-ferroelectric phase transition at room temperature [17,33]. Therefore, PNZST 43/8.0/2 is selected to demonstrate the phase-transition toughening effect. To produce the ceramic, powders of PbO, ZrO_2, SnO_2, TiO_2 and Nb_2O_5 with purity levels >99.9% were batched with an additional 5 wt.% PbO to compensate for PbO evaporation during calcination and sintering. Calcination was repeated twice at 935 °C for 4 h for compositional homogeneity. Prior to each calcination, powder was vibratory-milled for 7 h in ethanol with zirconia media, dried and pressed. After a final milling of 15 h, 40 g of dried PNZST 43/8.0/2 powder was uniaxially pressed at ~75 MPa in a 43 mm diameter cylindrical die with acrylic binder. Cold isostatic pressing was then applied to the green compact at ~400 MPa. After the binder was burnt out at 450 °C, sintering was carried out at 1325 °C for 3 h. A double crucible method was used for sintering with plenty of protective powder. To further increase the density of the ceramic, hot isostatic pressing was carried out at 1150 °C and ~200 MPa for 2 h in a 20% O_2, 80% Ar atmosphere.

The density of the ceramic was measured with the Archimedes method, and the phase purity was analyzed with X-ray diffraction. Scanning electron microscopy was used to examine the fracture surface of the ceramic, and the linear intercept method was used to determine average grain size.

The dielectric constant and dielectric loss tangent of PNZST 43/8.0/2 were measured at 1 kHz, 10 kHz and 100 kHz with an LCZ meter (Model 3322, Keithley) during heating and cooling at a rate of 3 °C min^{-1}. The polarization vs. electric field hysteresis loop of the sample was recorded with a standardized ferroelectric test system (RT66A, Radiant Technologies) during the very first triangular wave cycle of a field at 4 Hz.

To reveal the ferroelectric phase induced by cooling, X-ray diffraction on the pseudocubic (200) peak with extended data collection time was conducted. The specimen was stored in a cooler with frozen carbon dioxide (−78 °C) for several hours just before the room temperature X-ray scan. To reveal the ferroelectric phase induced by the electric field, silver thin film electrodes were sputtered onto the specimen, and a DC field of 40 kV cm^{-1} was applied for 10 min. Then the silver films were dissolved with nitric acid, and the (200) peak was scanned on the broad face perpendicular to the poling direction.

For indentation fracture toughness assessment, Vickers indents were made by applying 0.5 kg of force for 13 s on the polished surface. The fracture toughness was estimated according to equations found in the literature [34].

Fracture resistance (R) curves were measured on a compact-tension (CT) specimen with dimensions of 24 mm × 25 mm × 3 mm. Experimental details can be found in our previous report [29]. For the purpose of comparison, R-curve tests were also carried out on an antiferroelectric ceramic PNZST 43/6.4/2, which is very similar chemically to PNZST 43/8.0/2 but with a reversible antiferroelectric-to-ferroelectric phase transition.

Raman spectroscopy experiments were performed with a Renishaw inVia Raman spectrometer using a 488 nm wavelength laser at 20 mW. A 20× objective lens was used to collect a single spectrum on as-processed, cooled and poled PNZST 43/8.0/2 specimens.

In addition, numerous spectra were collected to map the phase transition zone. For this purpose, a specimen with dimensions of 2 mm × 4 mm × 0.5 mm was polished and electroded. A Knoop indent was placed with 0.5 kgf for 13 s in the center of the polished surface with the longer diagonal perpendicular to the electric field direction. A 50× objective lens was used, which resulted in a laser spot size of ~3 μm. Raman mapping [35] was achieved by collecting spectra in the area around the indentation crack tip with step sizes of 2.5 μm (at virgin crack tip) and 3.0 μm (under electric field). A program in MATLAB® was created to compare the spectra and generate a contour map.

3. Results

Density measurements on PNZST 43/8.0/2 reveal that the ceramic prepared with hot isostatic pressing is 99% of theoretical density. X-ray diffraction indicates that the

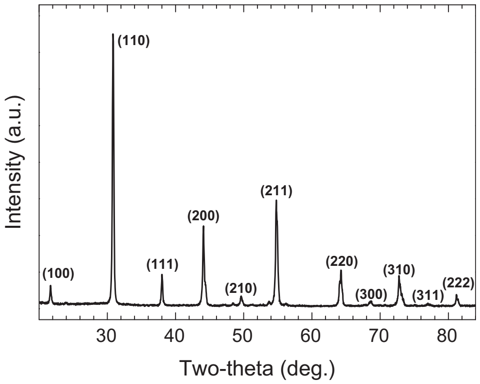

Fig. 1. X-ray diffraction spectrum of the antiferroelectric PNZST 43/8.0/2 ceramic prepared by hot isostatic pressing. The peaks are indexed according to a pseudocubic perovskite structure.