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Journal of the European Ceramic Society 27 (2007) 557–560

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Effect of Nb and K doping on the crack propagation behaviour of lead zirconate titanate ceramics

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Abstract

In the present study, we investigated the effect of doping on the crack propagation behaviour of lead zirconate titanate ceramics (PZT), particularly crack growth resistance and slow crack growth. Three PZT grades were processed: an undoped PZT, a soft PZT doped with niobium, PNZT, and a hard PZT doped with potassium, PKZT. The composition was chosen close to that of the morphotropic phase boundary (MPB), known to give excellent electromechanical properties. The soft material showed an important crack growth resistance and its slow crack growth curve V–K_I (crack velocity versus stress intensity factor, K_I) is shifted toward higher values of K_I. The results are discussed in terms of toughening due to ferroelastic domain switching under mechanical loading.

Keywords: PZT; Crack growth

1. Introduction

Lead zirconate titanate, $PbZr_{1-x}Ti_xO_3$, piezo-electric ceramics are widely used as sensors and actuators in several daily applications but seldom in simple chemical formulation. They are rather modified by the introduction of substitutionals in the A or B sites of their perovskite structure ABO_3. The role of the doping agents is to improve material properties for the adaptation to quite specific applications. However, because of the intrinsic brittleness of PZT materials, crack propagation occurs from pre-existing defects or singularities under electrical or mechanical loading, leading to a drastic decrease of electromechanical properties or device failure. Understanding of crack growth mechanisms is thus primordial for material reliability. Recent works have been focused on mechanical behaviour of PZT ceramics.[1–4] Their aptitude to reinforcement by ferroelastic domain switching[5] is of a great interest as it enhances their reliability by increasing flaw tolerance.

Addition of doping element to PZT ceramics lead to improve their properties for specific applications, via the substitution of cations within the A or B sites of their perovskite structure, ABO_3. In this study, the role of doping with Niobium and potassium on the crack growth behaviour is investigated.

2. Materials and procedure

2.1. Materials processing

Commercial powders of PbO, ZrO_2 and TiO_2 were used to prepare PZT specimens near MPB, with composition $Pb(Zr_{0.54}Ti_{0.46})O_3$. Nb_2O_5 and KCO_2 oxides were used as doping agents with respective amount of 0.2 and 0.1% to obtain a soft and a hard grade, respectively, designated by PNZT and PKZT (Fig. 1). The oxides were mixed and calcined at 900 °C then iso-statically compacted. Dense materials were obtained by sintering at 1250 °C for 4 h, using a powder bed of lead zirconate in order to keep a constant PbO vapor pressure.

X-ray diffraction analysis allowed verifying the development of perovskite structure and simultaneous morphotropic phase composition (Fig. 2). The microstructure of final materials, observed by scanning electron microscopy (SEM) is shown in Fig. 3. The measured theoretical density is, respectively, of 95, 99 and 93% for PZT, PNZT and PKZT materials and the mean grain size of 3.8, 2.4 and 13.7 μm, respectively.

2.2. Crack propagation tests

The crack growth resistance curves (*R*-curves) were determined using single edge-notched specimens of dimensions 4 mm × 6 mm × 40 mm, with a relative notch ratio of 0.55.

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doi:10.1016/j.jeurceramsoc.2006.04.073

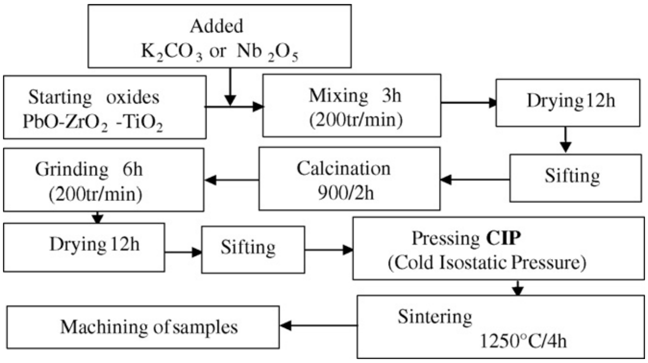

Fig. 1. Elaboration protocol of the PZT pure and doped.

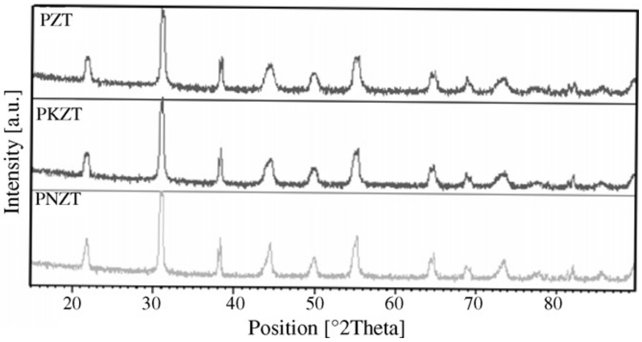

Fig. 2. X-ray diffraction of the studied materials.

Bending tests were conducted in a displacement-controlled mode with a constant speed of 3 μm/min. The crack growth resistance was determined in terms of stress intensity factor K_R, from the recorded load–displacement curve and plotted versus the crack extension Δa.

Slow crack growth tests were performed using the load relaxation method, with double torsion samples (40 mm × 20 mm × 3 mm). Details of samples preparation and the loading configuration are given in Ref.[6] The crack growth rate determined by a compliance method was plotted versus the stress intensity factor K_I, deduced from the relaxation curve to obtain slow crack growth curves (V–K_I).

3. Results and discussion

Table 1 shows the mechanical properties measured of the materials. Fig. 4 shows the *R*-curves determined for the studied PZT ceramics. No increase of the crack growth resistance was observed for the undoped PZT and the hard PKZT materials.

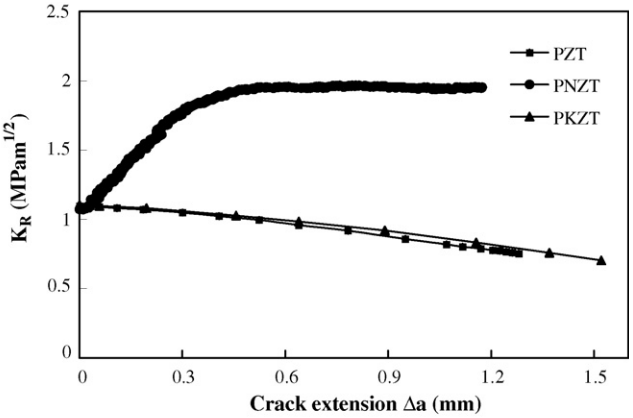

Fig. 4. Crack growth resistance curves (*R*-curves).

In contrast, the soft PNZT showed pronounced crack growth resistance traduced by a high amplitude of the *R*-curve: starting from an initial value of 1.1 $\mathrm{MPam}^{1/2}$, K_R increased steeply and reached a plateau value of 1.8 $\mathrm{MPam}^{1/2}$ after a crack extension of 500 μm. The high increase of the crack growth resistance, up to 65%, is rarely observed in monolithic ceramics and can be attributed to ferroelastic domain switching that shields the crack from the applied stress. The crack tip stress field leads to domain switching, resulting in compressive stresses (Fig. 5) in the crack wake that reduces the crack tip stress intensity factor, K_{tip}, which can be expressed as: $K_{\mathrm{tip}} = K_{\mathrm{app}} - K_{\mathrm{sh}}$, where K_{app} and K_{sh} represent, respectively, the applied stress intensity factor and the shielding contribution of domain switching. Due to crack shielding, larger applied stress intensity factor is required to induce crack growth (rising part of the *R*-curve) and the mechanism reaches a saturation corresponding to the plateau value.

Experimental evidence of the domain switching mechanisms in the PNZT material is shown in Fig. 6. The *R*-curve after annealing at 500 °C is identical to that of the initial behaviour. This heating procedure, above the Curie temperature, induces a reversible switching of ferroelastic domains within the crack wake, so that the shielding effect is completely destroyed.

The pronounced *R*-curve behaviour of PNZT is attributed to the nature of the doping agent. Niobium induces Pb vacancies,[7] leading to easier polarization by domain switching, that explains the high amount of reinforcement observed in this material. In the opposite, addition of potassium increases oxygen vacancies, which lead to restriction of domain motion.[7]

Fig. 7 shows the slow crack growth curves of the three studied materials. No plateau like regime corresponding to diffusion of

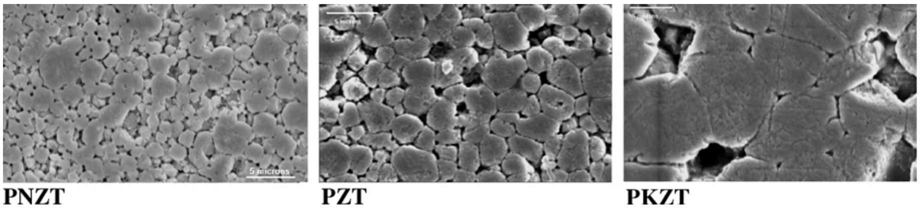
PNZT PZT PKZT

Fig. 3. SEM micrographs of the studied materials.

Table 1
Mechanical properties

Materials	Relative density (%)	[a]Youngs modulus E (GPa)	[b]Fracture strength σ_R (MPa)	[c]Hardness H_V (GPa)	[b]Toughness (SENB) K_{IC} (MPam$^{1/2}$)
PZT	95.2	74.8	92.5	2.26	1
PNZT	95.2	66.1	66.0	2.01	1.2
PKZT	93.9	74.9	58.6	1.97	0.9

[a] Measured by resonance method.
[b] Measured in four points bending.
[c] Measured Vikers hardness tester.

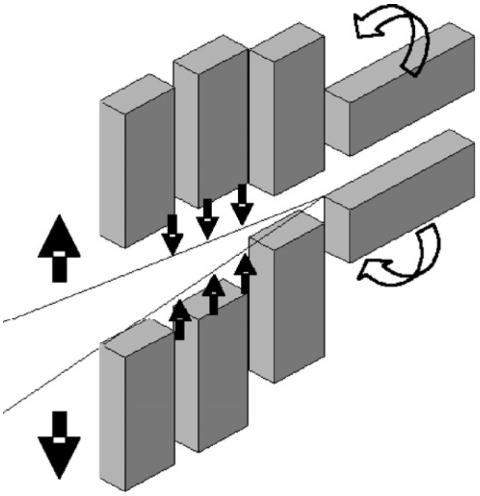

Fig. 5. Schematisation of the reinforcement by ferroelastic domains switching.

water molecules, generally occurring at crack growth rate about 10^{-4} m/s was observed. Only the first stage of stress induced corrosion mechanism[8] occurs and the curves are fitted to the Paris power law ($V = AK_I^n$). The values of the power exponent n, respectively, equal to 28, 25 and 62 for PZT, PKZT and PNZT are comparable to those observed for equivalent materials.[9] The shift of V–K_I curve of PNZT to higher values of K_I is due to the important reinforcement observed in this material: increasing the shielding effect of domain switching increases the applied stress intensity factor.

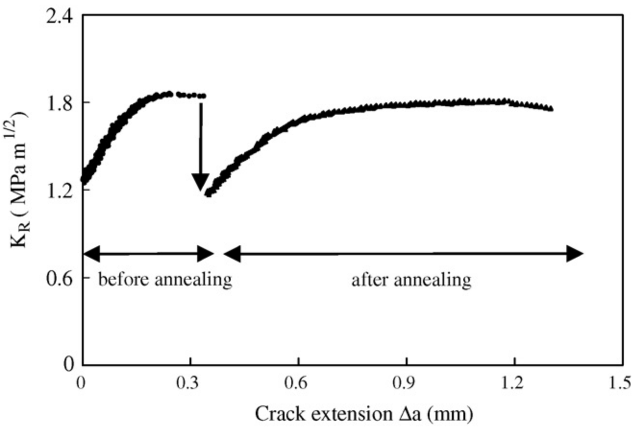

Fig. 6. *R*-curve of PNZT before and after annealing.

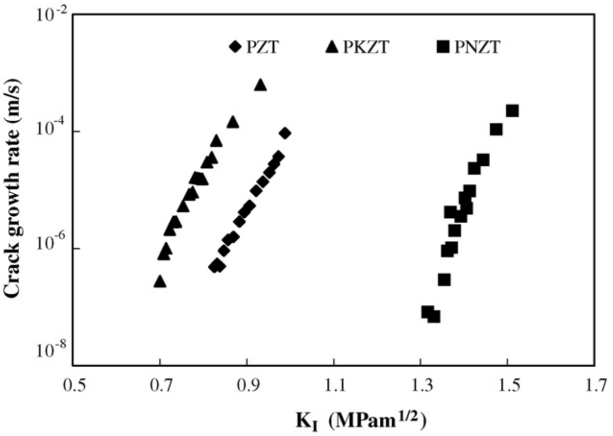

Fig. 7. Slow crack growth curves.

4. Conclusion

A pronounced crack growth resistance was observed in the soft PNZT ceramic. This is attributed to ferroelastic domain switching, becoming easier in this material due to Pb vacancies introduced by doping with niobium. In contrast, no domain switching was evidenced in the hard PKZT grade where the potassium leads to oxygen vacancies that restrict domain motion.

Only the first stage of slow crack growth was observed with a shift of the V–K_I curve towards higher stress intensity factor for PNZT due to the shielding effect of domain switching.

Acknowledgement

Région Rhône–Alpes is acknowledged for financial support (MIRA program).

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