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Journal of the European Ceramic Society 25 (2005) 2421–2424

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New considerations about the fracture mode of PZT ceramics

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Abstract

Sintered bulk ceramics, such as PZT are brittle materials. This macroscopically implies a statistical distribution of the ultimate strengths, because defects, such as pores or cracks are responsible for the initiation of the specimen failure. Another aspect of this fracture phenomenon is the crack propagation inside the material, along grain boundaries or through the grains themselves. An experimental study was carried out on hard and soft PZT by means of a scanning electron microscopy (SEM) quantitative analysis of tensile fractured areas. This reveals that the fracture mode is mixed, although it seems to be rather intragranular for hard ceramics and more intergranular for soft ones. Further investigations deal with the characterization of the residual porosity, which has to be distinguished from the population of critical defects. This porosity is located at grain boundaries and likely acts also as a stress concentrator and has an effect on the fracture mode and mechanical properties. For doped hard and soft PZT, a careful analysis of the microstructure is thus achieved through transmission electron microscopy (TEM) micrographs. Furthermore, domain structure is analysed for hard and soft PZT.

Keywords: PZT; Fracture; Electron microscopy; Porosity; Grain boundaries

1. Introduction

If electric and piezoelectric properties of ferroelectric ceramics have been thoroughly studied, their mechanical behaviour has retained much less attention. Sintered bulk ceramics, such as lead zirconate titanate ($PbZr_xTi_{1-x}O_3$) are brittle materials. This implies at a macroscopic level a statistical distribution of the ultimate strengths, because defects, such as pores or cracks are responsible for the initiation of the specimen failure.[1]

Once induced, cracks propagate quasi-instantaneously. The fracture toughness K_{IC} quantifies the resistance of a material against crack propagation. For PZT ceramics, it may be affected by chemical and physical properties: composition, existence of a second phase, grain size and porosity.[2,3] It is also known that the application of an electric field modifies the fracture phenomenon.[4] The addition of doping ions highly changes the whole properties of the material (donor additives are used to soften and acceptors to harden the initial piezoceramics).[5,6] However, it is not very clear how these changes affect the fracture properties of the different types of ceramics.

The first part of our study deals with the statistical analysis of ultimate tensile strengths correlated with microscopic observations of the fractured areas of four types of soft and hard PZT. First results have been published in.[7] Another aspect of this brittle fracture phenomenon is the crack propagation inside the material. The fracture mode can be either intragranular (through the grains themselves) or intergranular (along grain boundaries) or a mixture of both types. A quantitative analysis of scanning electron microscopy (SEM)

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doi:10.1016/j.jeurceramsoc.2005.03.074

images reveals that the fracture mode is mixed, although it seems to be rather intragranular for hard ceramics and more intergranular for soft ones.

Further investigations concern the characterization of the residual porosity, which has to be distinguished from the population of critical defects. This porosity is located at grain boundaries and likely acts also as a stress concentrator.

For doped hard and soft PZT, a careful analysis of the microstructure is thus achieved through transmission electron microscopy (TEM). It reveals no second phase, such as ZrO_2, which may enhance the fracture toughness.

2. Material properties

All the poled ceramics used here are commercially available and conventionally processed. In a general manner, hard PZT are characterized by better mechanical coefficients. Table 1 recapitulates the experimental data obtained for the previous study in short-circuit conditions:[7] Weibull's parameters (m describes the data scattering and T_0 is a scale factor) and mean grain size. Grain size was measured by classical linear intercept method performed with SEM photographs of polished specimens, without the use of correction factors. The microstructure is fine and roughly similar: all mean grain sizes are under 5 μm.

In order to study the fracture mode of these ceramics, SEM micrographs of the fractured surfaces were taken. Quantitative measurements were carried out by point counting method on several random areas and at least 250 points were taken into account for each ceramic type (Fig. 1). For both hard PZT H1 and H2 fracture mode is mainly intragranular (about 75%). Fracture mode is rather intergranular for soft piezoceramics S1 and S2 (in the same order of magnitude). As for the fracture toughness K_{IC}, the fracture mode may depend on pores and microcracks, segregation of impurities at the grain boundaries, presence of a second phase, grain size and poling state. TEM observations will allow to determine if microstructure heterogeneities or a liquid phase are present in the materials.

3. Fracture toughness measurements

The measurement method is based on the penetration of a brittle specimen by a Vickers indenter.[8] Fracture toughness is then related to the applied load P generating cracks of length c at the angles of the print (Fig. 2), the Young's modulus of the material Y and its hardness H_v (measured from print dimensions):

$$K_{IC} = \alpha \left(\frac{Y}{H_v} \right)^{1/2} \frac{F}{c^{3/2}} \quad (1)$$

Coefficient α is 0.016 for PZT ceramics. Three indentations are made on the surface normal to the polarization direction. This plane is isotropic and all four cracks are taken into account to calculate the mean value of c. Tested ceramics are characterized by a moderate hardness, below 3.5 GPa. It is, however, impossible to differentiate hard from soft ones with this property. Table 2 shows that H1 and H2 present clearly

Table 1
Properties of PZT ceramics

Type	Weibull's modulus, m	Weibull's scale factor, T_0 (MPa)	Mean grain size (μm)
H1	17.0	57	4.8
H2	14.3	78	2.5
S1	9.7	55	2.8
S2	7.9	54	4.3

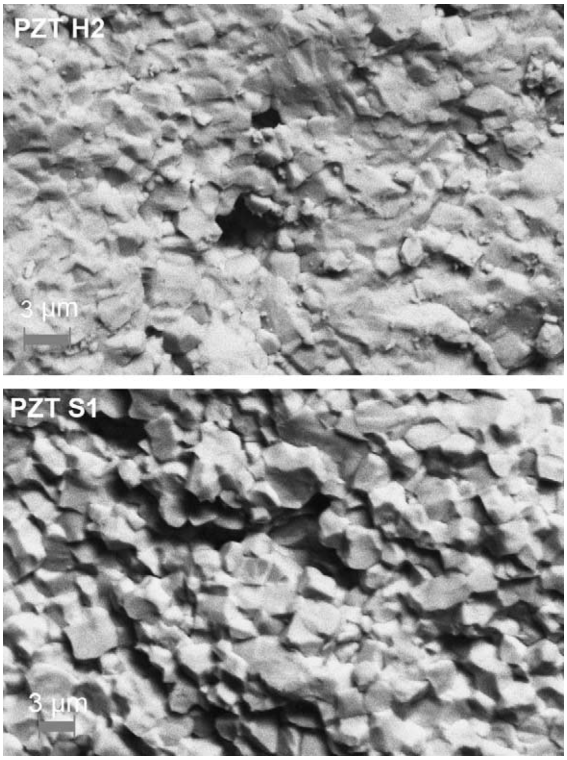

Fig. 1. Fractured surfaces of a hard and soft PZT.

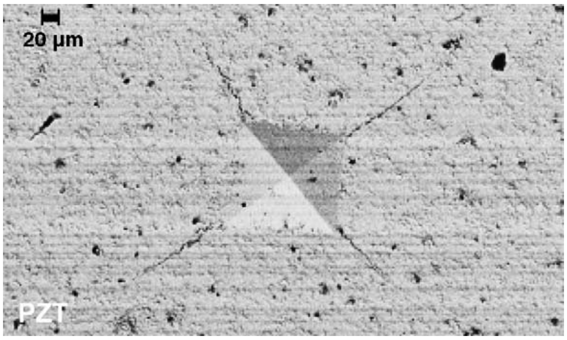

Fig. 2. Vickers indentation to measure fracture toughness.

Table 2
Properties obtained by means of Vickers testing

Type	Young's modulus, Y_{33}^{E} (GPa)	Hardness, H_v (GPa)	Fracture toughness, K_{IC} (MPa m$^{1/2}$)
H1	60	2.69	1.92
H2	69	3.38	1.59
S1	43	3.15	0.93
S2	43	3.07	0.86

a higher resistance to crack propagation compared to S1 and S2.

Garg and Agrawal[2] showed that there is not much variation in grain size with increasing PbO content but the fracture mode changes from intergranular to intragranular as the PbO ratio increases. This can be attributed to the improvement of the sintered density and reduction of intergranular porosity by adding a higher amount of lead oxide in excess. It can be suggested that not only lead oxide but also other chemical elements (namely dopants) have an influence of the fine microstructure. This hypothesis developed here may be confirmed by the study of the intergranular porosity.

4. Porosity measurements

Porosity in ferroelectric ceramics is typically below 10% and is not interconnected (closed porosity). Classical measuring techniques using fluid intrusion (air or mercury) under pressure are thus not adapted in this case. The stereological analysis of polished surfaces is the only way to observe the pore distribution and evaluate their 3D size distribution.[9] Our goal is to separate the different pore populations present in the ceramics. Macro, meso and micro porosities can be distinguished according to the dimensions of their constitutive elements.

First the apparent density of the materials tested is measured by means of a water pycnometer. Our values are relatively close to those given by suppliers. To evaluate the density of the fully sintered product (theoretical density), it is necessary to grind carefully the ceramics in order to separate each single crystal grain. The size distribution of the powder is assessed by means of a Coulter laser granulometer. The mean grain size is under 2 μm. Volume measurements are achieved through a helium pycnometer (Micromeritics Accupyc 1330 type, precision: 0.01%). The total porosity is then computed from:

$$P_{\mathrm{total}} = \frac{d_{\mathrm{theor}} - d_{\mathrm{real}}}{d_{\mathrm{theor}}} \qquad (2)$$

The mesoporosity is composed of spherical pores which size is bigger than the grains. SEM photographs of polished sections perpendicular to the tensile direction were taken in order to count the intersected pores and measure their size. More than 300 pores are analysed for each ceramic. Snapshots are digitally processed with filter tools and then binarized. Spherical pore size 3D distribution is then computed through Schwartz–Saltikov algorithm applied to the maximal Feret diameter distribution.[9]

Fig. 3. Transmission electronic micrograph of PZT H1 (×30,000).

The microporosity (also called intergranular porosity), which size is typically below mean grain diameter, is really difficult to measure. TEM photographs highlight this type of pores but a quantitative analysis seems rather difficult to carry out (Fig. 3). The microporosity has then been deduced from the other measurements by means of the following formula:

$$P_{\mathrm{micro}} = P_{\mathrm{total}} - P_{\mathrm{meso}} - P_{\mathrm{macro}} \qquad (3)$$

The macroporosity, responsible for crack initiation and fracture, is neglected. These macro pores of large dimensions (about 100 μm diameter) are excessively rare.

Experimental data are summarized in Table 3 for a hard and a soft ceramics. Real density of the soft PZT is equal to 89.1% of the fully densified one (95.7% for the hard PZT). Therefore, since mesoporosity is quasi identical for both ceramics, micro porosity is much more important for S2 than for H1. This result could easily explain why soft ceramics are characterized by so poor fracture properties. Further investigations about the aspect and morphology of grain boundaries are carried out by means of TEM observations.

5. Domain structure

TEM images of PZT samples are shown in Fig. 4a–c. Distinct differences in domain size and morphology are obvious between soft and hard PZT ceramics. For soft PZT (Fig. 4a), the domain structure has a lath-like morphology (grain size length and about 200 nm width). For hard PZT samples, domain width is smallest with significant wavy domains (Fig. 4b–c).

Table 3
Porosity decomposition for hard and soft PZT ceramics

Type	d_{theor}	d_{real}	P_{total} (%)	P_{meso} (%)	P_{micro} (%)
H1	7.939	7.600	4.3	2.7	1.6
S2	8.484	7.559	10.9	2.1	8.8

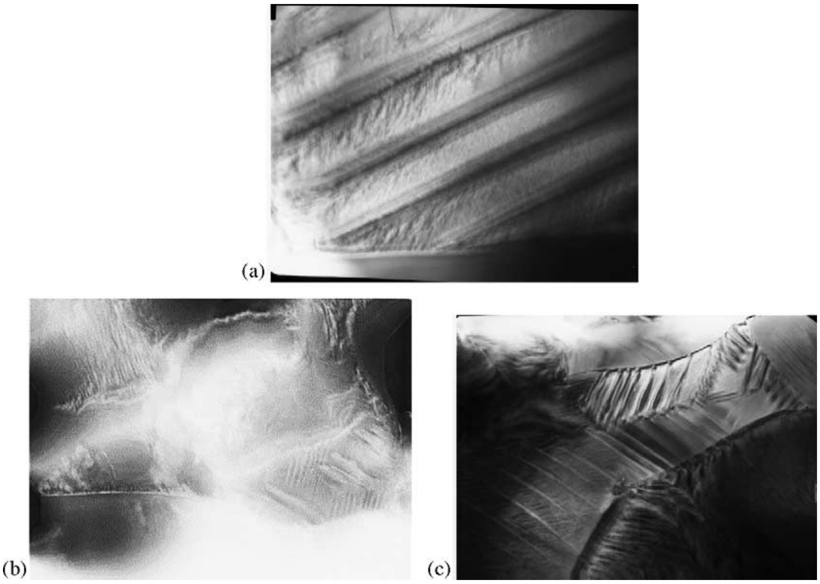

Fig. 4. Bright-field TEM images for soft and hard PZT samples: (a) S2; (b) H1; (c) H2.

It has been suggested that small wavy domains develop in Cr-doped $PbZr_xTi_y(Mg_{1/3}Nb_{2/3})_{1-x-y}O_3$ and in *K*-modified PZT ceramics as a consequence of domain boundaries pinning by defect complexes of acceptor impurities.[10] Here, one could expect that the soft additives may migrate to the grain boundaries and modify consequently the fracture phenomenon. These segregated impurities may strongly reduce the grain boundary energy in soft PZT samples. A reduction of the grain boundary energy by impurities generally means a reduction of the cohesive strength of the boundary.

6. Conclusion

In this work, the microstructure of PZT ceramics has a clear effect on the fracture properties. Indeed, hard PZT present better fracture properties and major intragranular fracture mode. On the opposite, cracks propagate mainly through the grain boundaries in soft PZT. The observation and quantification of the intergranular microporosity demonstrate that it is responsible for these aspects of fracture behaviour. The fracture toughness is also higher for hard PZT than for soft ones. The domain size and morphology are different for the two types of PZT. The lath-like form indicates a possible boundary segregation of the soft additives, changing the grain boundary energy and weakening the grain boundaries in the soft PZT ceramics. An interesting extension of this work is the local study of chemical composition by means of STEM analysis. These measurements would also allow the determination of chemical heterogeneities.

References

1. Freimann, S. and White, G., Intelligent ceramic materials: issues of brittle fracture. *J. Int. Mater. Struct.*, 1995, **6**, 49–54.
2. Garg, A. and Agrawal, D. C., Effect of net PbO content on mechanical and electromechanical properties of lead zirconate titanate ceramics. *Mater. Sci. Eng. B*, 1999, **56**, 46–50.
3. Kim, S.-B., Kim, D.-Y., Kim, J.-J. and Cho, S.-H., Effect of grain size and poling on the fracture mode of lead zirconate titanate ceramics. *J. Am. Ceram. Soc.*, 1990, **73**, 161–163.
4. Watanabe, T. and Tsurekawa, S., The control of brittleness and development of desirable mechanical properties in polycrystalline systems by grain boundary engineering. *Acta Mater.*, 1999, **47**(15), 4171–4185.
5. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London, 1971.
6. Xu, Y., *Ferroelectric Materials and Their Applications*. North-Holland Press, Amsterdam, 1991.
7. Guillon, O., Thiebaud, F. and Perreux, D., Tensile fracture of hard and soft PZT. *Int. J. Fract.*, 2002, **117**(3), 235–246.
8. Anstis, G. R., Chantikul, P., Marshall, D. B. and Lawn, B. R., A critical evaluation of indentation techniques for measuring fracture toughness. I. Direct crack measurements. *J. Am. Ceram. Soc.*, 1981, **64**, 533–539.
9. DeHoff, R. T. and Rhines, F. N., *Microscopie Quantitative*. Masson, Paris, 1972.
10. He, L.-X., Gao, M., Li, C.-E., Zhu, W.-M. and Yan, H.-X., Effects of Cr_2O_3 addition on the piezoelectric properties and microstructure of $PbZr_xTi_y(Mg1/3Nb2/3)_{1-x-y}O_3$ ceramics. *J. Eur. Ceram. Soc.*, 2001, **21**, 703–709.