New considerations about the fracture mode of PZT ceramics

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Abstract

Sintered bulk ceramics such as PZT are brittle materials. This implies macroscopically 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 path the cracks propagate inside the material, along grain boundaries or through the grains themselves. An experimental study is carried out on hard and soft PZT by means of a 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 too as a stress concentrator. Its influence on the fracture mode and mechanical properties has been highlighted. For doped hard and soft PZT, a careful analysis of the microstructure is thus achieved through TEM micrographs. It reveals no second phase such as ZrO_2, which may enhance the fracture toughness, but different grain boundaries configurations according to the type of ceramic. Furthermore, domain structure is analysed for hard and soft PZT.

1. Introduction

If electric and piezoelectric properties of ferroelectrics ceramics have been thoroughly studied, their mechanical behaviour has retained much less attention. Sintered bulk ceramics such as PZT are brittle materials. This implies at the macroscopic scale 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 that a material puts up to 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 acceptor to harden the initial piezoceramics). It is however not very clear how these changes affect the fracture properties of the different types of ceramics.

This study begins with a statistical analysis of ultimate tensile strengths correlated with microscopic observations of the fractured areas of four type of soft and hard PZT. First results have been published in [5]. Another aspect of this brittle fracture phenomenon is the path the cracks follow 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 scanning electron microscopy (SEM) image quantitative analysis 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 too 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 [5]: Weibull's parameters (m describes the scattering of the data and T_0 is a scale factor), grain mean 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.

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

Table 1. Properties of PZT ceramics

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).

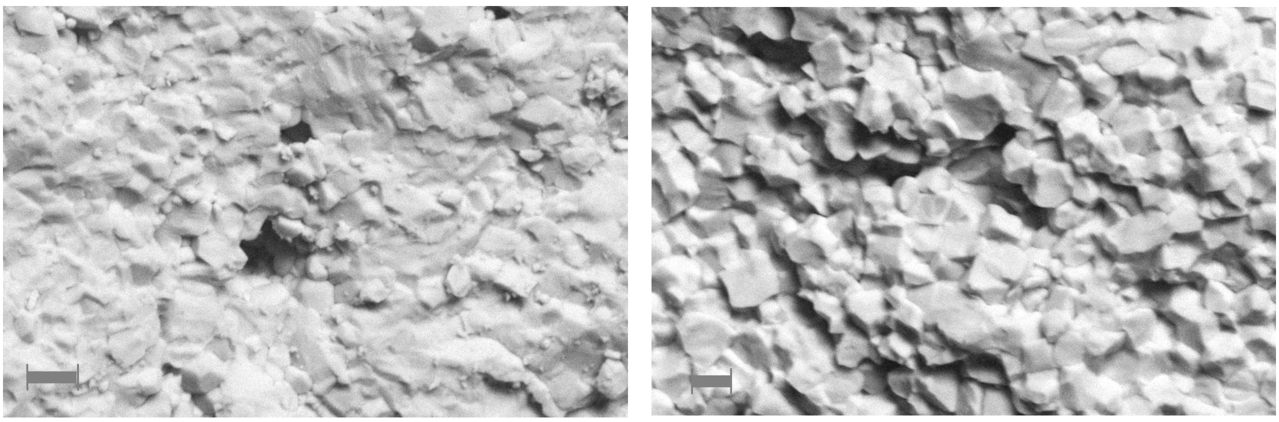


Figure 1. Fractured surfaces of a hard and soft PZT

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 micro cracks, segregation of impurities at the grain boundaries, presence of a second phase, grain size and poling-state. It is possible by observing TEM micrographs to determine if microstructure heterogeneities or presence of a liquid phase are present in the material.

3. Fracture toughness measurements

The measurement method is based on an indentation test with a Vickers micro-hardness device [6]. 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):

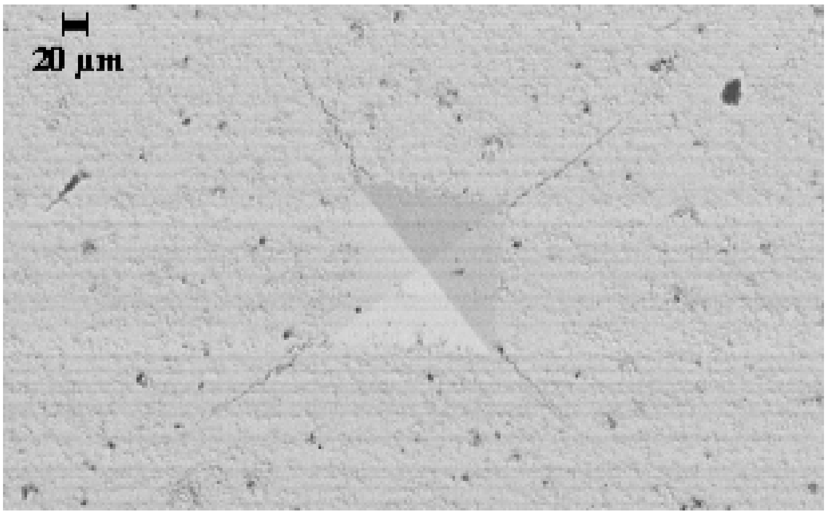


Figure 2. Vickers indentation to measure fracture toughness

Three indentations are made on the surface normal to the polarization, distant enough to avoid crack interactions. This plane is isotropic and the four cracks are taken to calculate the mean value of c. Ceramics are characterized by moderate hardness, below 3.5 GPa. It is however to difficult to differentiate hard from soft ones with this property. Table 2 shows that H1 and H2 present clearly a higher resistance to crack propagation compared to S1 and S2.

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

Table 3. Properties obtained by means of Vickers testing

It is known after Garg [2] 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. One can propose that not only lead oxide but also other chemical elements have an influence of the fine microstructure. This hypothesis developed in this paragraph may be confirmed by the study of the intergranular porosity.

4. Porosity measurements

Porosity in ferroelectrics ceramics is typically limited under 10 % and is not interconnected (closed porosity). Classical 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 [7]. The aim of this part is to separate the different populations of pores present in the ceramics and macro, meso and micro porosity can be highlighted according to the dimensions of their constitutive elements.

The apparent density of the materials tested is measured by means of a water pycnometer. Our values are relatively close to those given by the suppliers. To evaluate the density of the fully sintered product or theoretical density, it is necessary to carefully grind the ceramics in order to separate each single crystal grain. The size distribution of the powder obtained 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%). Total porosity is then computed from:

$$P_{total} = \frac{d_{theor} - d_{real}}{d_{theor}}$$

The mesoporosity is composed of spherical pores that size is bigger than the grains themselves. 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 [7].

The micro porosity (or intergranular porosity) that size is under the mean grain size and which is the focus of our study is not easy to measure. TEM photographs highlight this type of pores but a quantitative analysis seems rather difficult to carry out (Fig. 3).

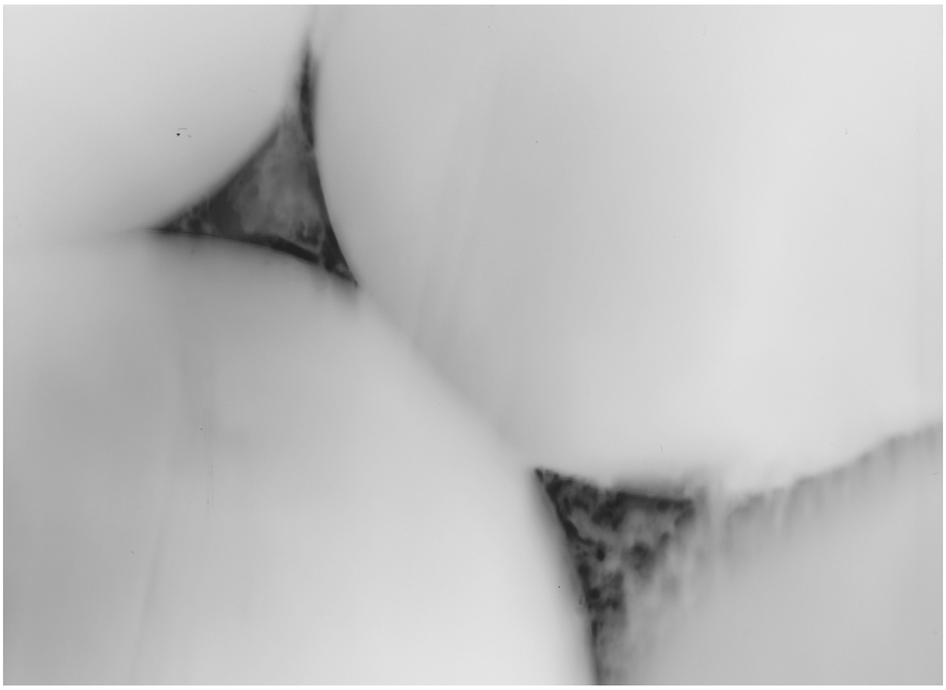


Figure 4. Transmission Electronic Micrograph of PZT H1 (× 30000)

Due to the previous difficulty, the micro porosity has been deduced from the other measurements with the formula:

$$P_{micro} = P_{total} - P_{meso} - P_{macro}$$

The macro porosity, responsible for crack initiation and fracture, is neglected. These macro pores although characterized by large dimensions (about 100 µm diameter) are excessively rare.
Experimental results are summarized in Table 2 for a hard and a soft ceramics:

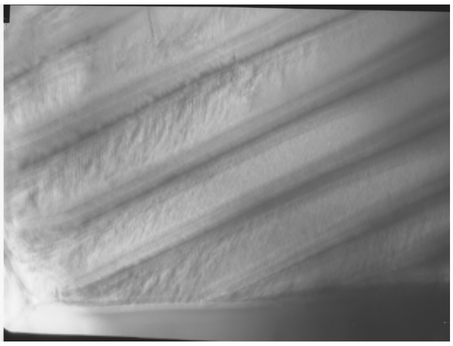
Type	$\mathbf{d_{theor}}$	$\mathbf{d_{real}}$	$\mathbf{P_{total}}$ **(%)**	$\mathbf{P_{meso}}$ **(%)**	$\mathbf{P_{micro}}$ **(%)**
H1	7.939	7.600	4.3	2.7	1.6
S2	8.484	7.559	10.9	2.1	8.8

Table 2. Porosity decomposition for hard and soft PZT ceramics

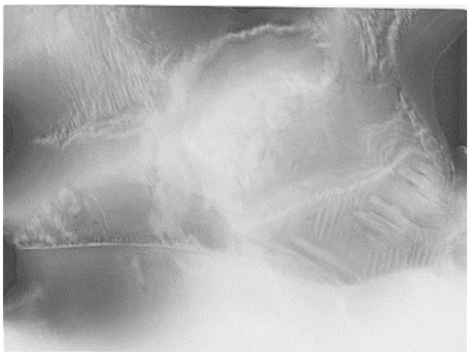
Real density of the soft PZT is equal to 89.1 % of the fully densified one (95.7% for the hard PZT). Therefore, since mesoporosity is quasi identical for both ceramics, micro porosity is much more important for S2 than for H1. This can easily explain why soft ceramics are characterized by so poor fracture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

5. Domain structure

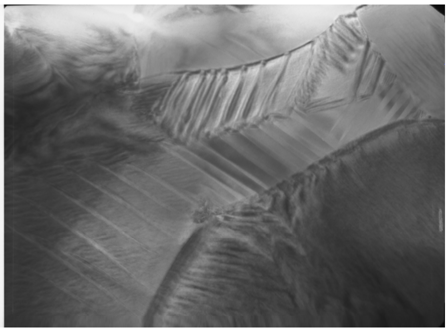
TEM images of PZT samples are shown in Fig. 5a-c. Distinct differences in domain size and morphology are evident between soft and hard PZT ceramics. For soft PZT, the domain structure has a lath like morphology with laths of the grain size in length and about 200 nm in width (Fig. 5a). For hard PZT samples, the width of the domains is smallest with significant wavy domains (Fig. 5b-c).



(a)



(b)



(c)

Fig. 5. Bright-field TEM images for soft and hard PZT samples: (a) S2, (b) H1, (c) H2.

It has been suggested in Cr-doped PZTMN and in K-modified PZT ceramics that, as a consequence of domain boundaries pinning by defect complexes of acceptor impurities, small wavy domains are developed [8]. Here, one could expect that the soft additives may migrate to the grain boundaries and modify consequently the rupture phenomenon. These segregated impurities may reduce the energy of the grain boundary strongly 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 role of the microstructure of PZT ceramics has been highlighted in the fracture mode. Indeed, hard PZT present better fracture properties and major intragranular mode of fracture. On the opposite, cracks propagate mainly through the grain boundaries in soft PZT. The observation and quantification of the intergranular micro porosity proves that it is responsible for these aspects of fracture behaviour. The fracture toughness is also higher for hard PZT than for soft ones. The size and morphology of the domains 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., White G. “Intelligent ceramic materials : issues of brittle fracture”. *Journal of intelligent materials and structures*, 6, 49-54, (1995).

[2] Garg A., Agrawal D.C. “Effect of net PbO content on mechanical and electromechanical properties of lead zirconate titanate ceramics”. *Materials science and Engineering B56*, 46-50, (1999).

[3] Kim S-B., Kim D-Y., Kim J-J., Cho S-H. “Effect of grain size and poling on the fracture mode of lead zirconate titanate ceramics”. *J. Amer. Ceram. Soc.*, 73,161-163, (1990).

[4] Watanabe T., Tsurekawa S. “The control of brittleness and development of desirable mechanical properties in polycrystalline systems by grain boudary engineering”. *Acta Materialia*, **47**, 15, 4171-4185, (1999).

[5] Guillon O., Thiebaud F., Perreux D. “Tensile fracture of hard and soft PZT”. *International Journal of Fracture*, 117(3), 235-246, (2002).

[6] 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. Amer. Ceram. Soc.,* 64, 533-539, (1981).

[7] DeHoff R.T., Rhines F.N. “Microscopie quantitative” Paris: Masson, 1972.

[8] 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.*, 21, 703-709, (2001).