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SHOCK-RECOVERY EXPERIMENTS ON PZT 95/5*

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ABSTRACT

Recovery experiments on porous PZT 95/5 ferroelectric have been performed on a single-stage compressed gas gun over the stress range of 0.3 to 4.6 GPa. Density measurements on the recovered specimens suggest permanent pore compaction. X-ray diffraction analysis indicates that the shock-induced FE-to-AFE phase transformation is reversible, with a reduction in the residual lattice strain, as compared with the unshocked material. SEM and TEM microscopy show evidence of ferroelectric domains with fewer numbers at the higher stress. The microstructure of the 3.0 GPa sample is significantly affected, as evidenced by dislocation slip bands and oval-shaped voids.

INTRODUCTION

PZT 95/5 is a ferroelectric ceramic material which has a stress-induced ferroelectric-to-antiferroelectric (FE-to-AFE) phase transformation. Recently, shock and pressure-shear loading experiments performed on the porous ceramic (9% porous)[1] over the stress range of 0.8 GPa to 4.6 GPa, have indicated complex material behavior during shock compression. Under a hydrostatic pressure environment, the material shows a complex pressure-temperature phase field with considerable hysteresis[2] (Figure 1). It is expected that the behavior under shock compression will be more complex, and stress, strain and pore dynamics will play important intermingled roles. Transformation of the ceramic from the FE phase to the AFE phase commences near 0.5 GPa with a mixture of phases indicated over the stress range of 0.9 GPa to 2.6 GPa. Above 2.6 GPa, the kinetics of pore compaction dominate the dynamic response. Upon release, a remnant strain is measured which may be due to irreversible phase transformation and/or permanent densification. Pressure-shear experiments suggest a constant shear stress being sustained over the mixed-phase region of 0.9 to 2.6 GPa.

These hypotheses were pursued with experiments on shock-recovered material. The samples were embedded in an OFHC copper capsule, chosen because its shock impedance is similar to the PZT sample. Impact of copper flyer plates accelerated, on the single-stage compressed gas gun, yielded stress levels of 0.3, 0.8, 1.7, 3.0, and 4.6 GPa, respectively, in the PZT sample. The dimensions of the sample and the copper assembly were chosen to prevent spallation, either in the capsule, or in the PZT sample. Numerical simulations of

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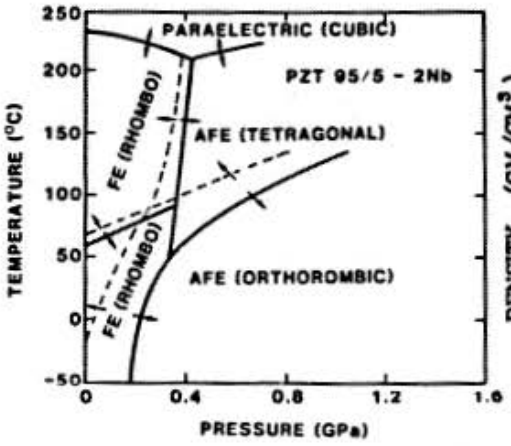

Figure 1: Phase Diagram for 95/5 PZT Ceramic.

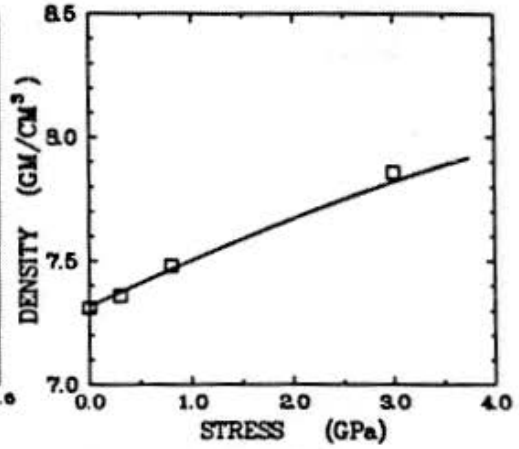

Figure 2: Measured density of shock recovered specimens.

the recovery fixture, using the two dimensional code CSQ,[3] suggest similar loading histories at the center of the sample for early shock loading times, based on either one-dimensional or two-dimensional loading assumptions. Density measurements, x-ray diffraction techniques, scanning and transmission electron microscopy techniques were used to determine the nature of the recovered phase and the deformation features induced in the ceramic due to shock loading. The results are summarized in this paper.

RESULTS AND DISCUSSION

Density Measurements and X-ray Analysis

Density measurements on the recovered specimens are shown in Figure 2, which indicate permanent shock-induced compaction. The material investigated has ~9% porosity, arising from incomplete volume filling during sintering and from 0.8 weight percent of 100 μm lucite spheres added to the ceramic powder to control the final density. (Since the recovered samples were cracked after shock loading, the density measurements obtained by immersion techniques are of limited accuracy.) The increase in density is thought to result primarily from the shock-induced compaction process. X-ray diffraction analysis was also performed to determine if part of the densification resulted from irreversible phase transformation. The density of the 4.6 GPa sample was not measured since the recovered sample was pulverized. The recovered 3.0 GPa sample suggests the presence of ~3% porosity when compared to its theoretical density of 8.028 gm/cm^3 calculated on the basis of its chemical composition $Pb_{.9897}Nb_{.0206}(Zr_{.96}Ti_{.04})_{.9794}O_3$ and the x-ray lattice constants determined in this investigation.

X-ray diffraction generally allows detection of different structural phases of material. When the differences between the crystal structures are small, x-ray lines of a higher symmetry phase are split for the phases of lower symmetry. Should the splitting be sufficiently large (greater than the line width), a precise determination can be made. One may then predict how the cubic line would split under tetragonal, rhombohedral, and orthorhombic symmetry, both with respect to line position and relative intensity. Using several selected lines and avoiding cubic degenerate lines (*e.g.* 300 and 221), an unambiguous choice can be made. In the case of perovskites, and in particular for this composition of PZT 95/5, some of this splitting is small. It should be noted that the actual cell dimensions may be more

complex than the simple cell deduced because of weak lines. Furthermore, in shock-loaded materials, the x-ray line profiles may be broadened by two effects: reduction of crystallite domain size and retained residual lattice strain. Generally, these two effects are not very severe in inorganic materials at modest pressures of 5 GPa[4].

X-ray diffraction studies employed Cu Kα and Cr Kα radiation, the latter to take advantage of obtaining non-degenerate cubic lines at large scattering angles. A standard 114.5 nm Norelco powder camera was used in order to obtain data at large angles. No line broadening studies for size and strain were carried out since these lines were expected to be split from structure considerations; however, an estimate can be made from the present data using an approximate method developed in previous studies. The x-ray specimens were generally taken from edges of the fractured specimen. In samples purposely broken, no differences were seen in the x-ray diffraction characteristics as to their origin, *i.e.*, either near the center of the disk or the edge. The most striking observation was that the unshocked PZT showed broader x-ray line profiles at higher scattering angles than the shocked material. This is consistent with a marked residual lattice strain (near 10^{-3}) in the as-received unshocked material. Upon recovery from shock loading the lines are much sharper and allowed the determination of the lattice parameter for this material.

The lattice parameters determined using the 3 GPa recovered sample and Cr Kα radiation are a = 4.138(2) A°, and α = 89.83(4)°. This rhombohedral distortion corresponds to a 10-minute angular departure from cubic symmetry, a value sufficiently small that distinct separation of certain x-ray lines, which in the cubic form appear as single lines, is not achieved. Nevertheless, the appropriate lines which are split or broadened allow verification of the lattice symmetry of the material.

Optical Microscopy

Disc-shaped test specimens of unshocked and shock-recovered material were encapsulated under vacuum in a room temperature cured epoxy resin. The mounted specimens were cut diametrically, through the disc thickness and were polished through a 1-μm diamond slurry on a vibratory polisher. A Leitz metallograph was used to examine the specimens for pore compaction and to compare the microstructures after recovery from shock loading to various stresses.

Except for the unshocked material, all of the specimens had cracks across the width and thickness which typically, but not necessarily, interconnected the pores. The degree of cracking increased markedly with shock level. The pores in the unshocked, 0.3 GPa and 0.8 GPa shocked specimens were uniformly circular and approximately 100 μm in diameter. In the material shocked to 1.6 GPa and higher, many of the pores were flattened to an oval shape in the plane parallel to the shocked surface. The number of oval-shaped pores increased with increasing shock level such that the majority of the pores in the 4.6 GPa shocked material were deformed. This compaction by permanent pore deformation substantiates the measured increase in density with shock level.

Scanning Electron Microscopy

The unshocked and shocked materials were examined using a Hitachi S-500 scanning electron microscope (SEM) at 25 KeV in two conditions *i.e.*, as-polished, and as-etched. In the first, a thin conductive carbon coating was evaporated onto the freshly polished surface, and a backscattered electron imaging mode was used to view the topography of the polished surface. In the second, an etchant[5] (0.5% to 1% by volume of a $HF - HNO_3$ mixture in water) was used to reveal the domain structure. The etched specimens were also carbon coated for SEM examinations. The as-polished surfaces of both unshocked and shocked materials revealed no topographical feature such as grain boundaries or domain walls in

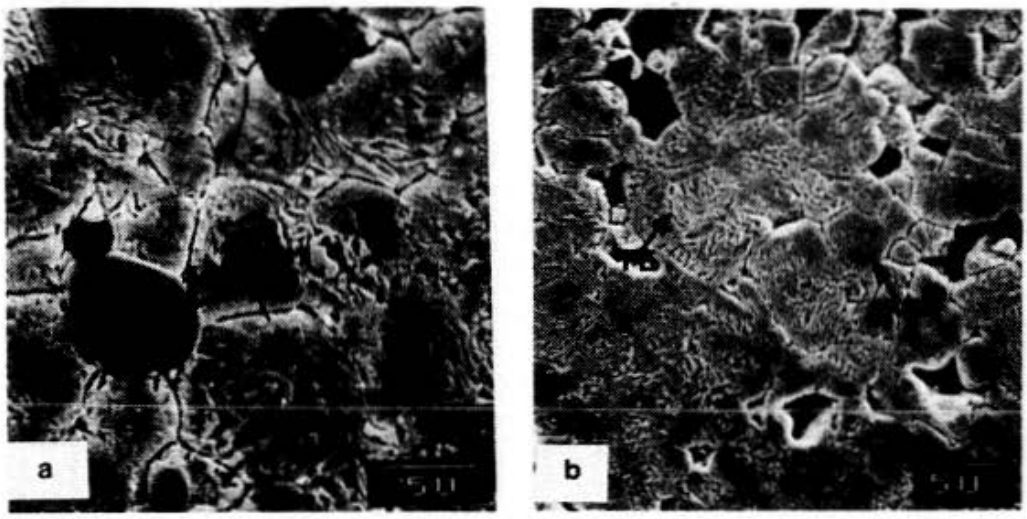

Figure 3: Scanning electron micrographs of the 3.0 GPa shock-recovered PZT 95/5.

either a secondary electron or a topographical backscattered imaging mode. This is consistent with other attempts at microstructural examination of unetched barium titanate and lead zirconate titanate[6].

In contrast, etching of the unshocked, as well as the shocked specimens, clearly delineates 5 - 10 μm diameter grains and reveals FE domain walls within the grains. Figure 3(a) shows typical etched microstructure. The porosity observed at the crystallite triple junctions is inherent to the material as a result of the sintering process. A classical "herringbone" domain pattern is clearly visible in which the narrow light and dark stripes are alternating pairs of 90 degree domains[6]. The thickness, t, of the domains (Figure 3(a)) is of the order of 1.0 μm which agrees with that reported for the finely textured domains seen in other niobium-modified PZT. The width of the domains varies from tenths of microns to tens of microns, although, the domains typically do not extend across the entire grain diameter.

A comparison of SEM micrographs of unshocked and shocked specimens indicates the absence of a clearly defined domain structure in some grains of the material shocked to high stress levels. The 3-GPa sample in Figure 3(b) exhibited the most "blank" grains, whereas virtually all grains in the unshocked and the low level shocked material showed evidence of FE domains. The absence of visible FE domains in some grains subjected to high shock levels suggests the presence instead of an AFE phase. This suggests, in turn, that the degree of reversibility of the shock-induced FE to AFE phase transformation depends on the shock level.

Transmission Electron Microscopy

The microstructure of unshocked starting material and recovered material shock loaded to 0.3 GPa, 0.8 GPa and 3.0 GPa was examined. Specimens were prepared by ion milling in a cold stage to avoid heating the specimens above the AFE transition. All specimens were examined at 200 Kev with a JEOL 200CX.

The structure of the unshocked material consisted of well-annealed grains exhibiting very low dislocation density (10^6 per cm^2), as shown in Figure 4. Substructural features of the ferroelectric domains, typically <100 nm wide, were present in all grains. These fine structures are not resolved in SEM micrographs of etched surfaces. An intergranular phase filled some smaller grain boundary triple points. This phase was observed to be crystalline, but was not identified. The 0.3 and 0.8 GPa material also indicated features similar to the unshocked material, indicating that loading to that point was elastic.

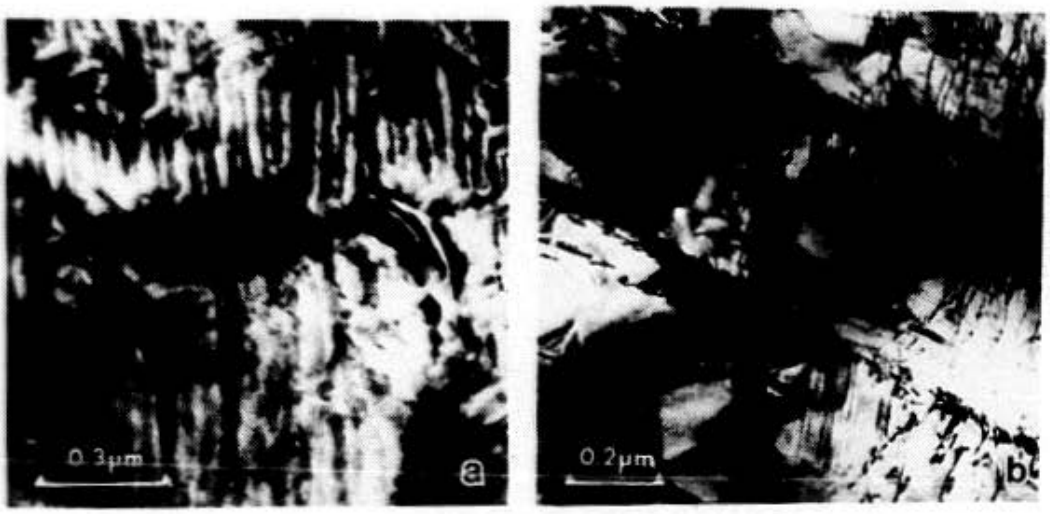

Figure 4: Transmission electron micrographs of unshocked and 3.0 GPa shock-recovered PZT 95/5.

The microstructure of the 3.0-GPa material was substantially affected by the shock loading process; the deformation was inhomogeneous. Optical micrographs showed a network of lighter bands crisscrossing the thickness of the specimen. Deformation was found to be concentrated in these bands. Grains outside these bands showed the same low dislocation density as the starting material. The bands were found to consist of fractured and deformed grains. Deformed material exhibited dislocations, often lying along well defined slip planes (Figure 4). Some slip bands terminated at fractures suggesting that slip may precede cleavage or fracture in some grains. Dislocation density varied from grain to grain; typical dislocation densities in deformed grains were about 10^9 per cm^2. In all grains, deformed and undeformed, no ferroelectric domains like those in the unshocked material were found. Initially, it appeared that there were no ferroelectric domains at all, but more detailed work showed what appeared to be widely spaced domain boundaries pinned to substructural features. The domain size in these materials ranged from 500 to 1000 nm, which agrees with that observed in SEM. The microstructural changes which occur in the 3.0-GPa shock-loaded material are consistent with plastic flow by dislocation motion and fracture.

SUMMARY

Density measurement, x-ray diffraction, scanning and transmission electron microscopy have been used to characterize the microstructure and the phase morphology of shock-recovered 95/5 PZT ceramic. Density increases suggest pore-compaction as a densification mechanism, which is also substantiated by observations of permanently deformed oval-shaped pores.

X-ray diffraction analysis suggests that the shock-induced FE-to-AFE phase is reversible, and also that the rhombohedral crystal structure of the FE phase is only a slight distortion from the cubic structure.

Ferroelectric domains observed by electron microscopy on shock-recovered specimens complement the results of the x-ray analysis which suggest that the shock-induced FE-to-AFE phase is reversible. The degree of reversibility, however, appears to depend on stress, since a decreasing number of FE domains are observed in material recovered from high stresses.

Inhomogeneous deformation of the material at higher stresses is indicated by a higher density of dislocations concentrated in a network of criss-crossing slip bands.

Shock-recovery experiments on PZT 95/5 complement the instrumented (time-resolved wave profile) studies[1] performed on the material. The results deduced from the analysis of the recovered material in general agrees with the observations inferred from the instrumented studies. Considering that the time scales of these two types of experiments are vastly different, this apparent agreement is indeed gratifying. It lends credence to the assumption that the microstructure of shock-recovered specimens reflects complex deformation mechanisms that occur at the shock front. This seems to be particularly true for shock-recovered 95/5 PZT.

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