Bull. Mater. Sci., Vol. 28, No. 5, August 2005, pp. 453–455. © Indian Academy of Sciences.

Characterization and microstructure of porous lead zirconate titanate ceramics

B PRAVEENKUMAR, H H KUMAR and D K KHARAT*
PZT Centre, Armament Research and Development Establishment, Pune 411 021, India

MS received 9 December 2004; revised 10 March 2005

Abstract. Porous lead zirconate titanate (PZT) ceramics are widely used because of their low acoustic impedance, high figure of merit and high hydrostatic sensitivity. In the present work, porous PZT ceramics were fabricated by incorporating polyethylene oxide (PEO) as pore-forming agent. Both PZT powder and PEO were mixed with a binder at different ratios and compaction was carried out. The samples were slowly heated to remove the pore-forming agent and binder without cracks, followed by controlled sintering and electrode forming. Samples were poled using corona poling technique. The ferroelectric properties and microstructure of the prepared ceramics were characterized. The correlation of porosity with microstructure and ferroelectric properties were discussed.

Keywords. Porous PZT; corona poling; ferroelectric properties.

1. Introduction

Lead zirconate titanate (PZT) plays a prominent role in modern electroceramic industry. Its applications cover ultrasonic and underwater transducers, nonvolatile memory elements, pyroelectric detectors and photoelectric devices (Newnham and Ruschau 1991; Haertling 1999; Ramesh *et al* 2004). For underwater transducer applications we need to have porous piezoelectric materials. These can be made by combining a PZT ceramic with a passive polymer or air phase. These materials greatly extend the range of properties offered by conventional PZT ceramics. Moreover, porosity in the materials could reduce the effective acoustical impedance leading to an improved acoustic matching between the component and the media through which signals are transmitted or received (Roncari *et al* 2001; Li *et al* 2003; Praveenkumar *et al* 2004).

Piezoelectric sensitivity, charge generated per unit force or electric field generated per unit stress, is an important parameter for heterogeneous ferroelectric materials. The need for increased piezoelectric sensitivity has led to the study of optimization of processing parameters and novel porous ceramics structures (Newnham 1997). Depending on the transducer applications, piezoelectric sensitivity is characterized by a set of parameters or figures of merit, such as hydrostatic voltage coefficient (g_h), hydrostatic charge coefficient (d_h) and hydrostatic figure of merit ($d_h \times g_h$). Composites with large figures of merit offer considerable advantages over single crystal or monolithic polycrystalline ceramics in hydrophone and related underwater applications (Bowen and Topolov 2003).

*Author for correspondence (tircarde@vsnl.com)

In the present study, porous PZT materials were characterized for hydrostatic and piezoelectric charge coefficients. The correlation of porosity with the properties and microstructure are discussed.

2. Experimental

PZT powders were synthesized from commercially available PbO, ZrO_2, TiO_2, La_2O_3 and Nb_2O_5 powders. The weighed powders were calcined in a high temperature furnace at 950°C for 30 min. After drying and granulating, the calcined powder was mixed with PEO and polyvinyl alcohol at different volume ratios of PZT/PEO as 50/50, 60/40, 80/20 in agate pestal mortar. The mixed powder was compacted to 22 mm disks by uniaxial pressing machine and fired at 550°C for 9 h to burn out the binder. The specimens were stacked in a hermetically sealed alumina crucible and sintering was carried out at 1250°C for 30 min. The specimens were poled by using corona poling technique (Waller and Safari 1988).

The density of the sintered components was measured from its mass and dimensions. The microstructure of sintered component was examined by a FEI, Quanta 200 Scanning Electron Microscope. The ferroelectric properties were measured using copper adhesive foils. The dielectric, piezoelectric and hydrostatic properties were measured using LF impedance analyser (HP 4192A) and dual range piezometer system (Take Control PM 35).

3. Results and discussion

Figure 1 shows the density of specimens in relation to amount of PEO added. The density of the specimen decreases with increase in the amount of PEO, which subsequently decreases the acoustic impedance of material to be matched with water. Consequently as the density of the material decreases its porosity increases followed by subsequent increase in the hydrostatic coefficients.

Figure 2 indicates the effect of hydrostatic charge coefficient (d_h) and hydrostatic voltage coefficient (g_h) with increase in the amount of PEO. It is observed that d_h increases with increase in the amount of PEO. The peak value of d_h was observed at (50/50) PZT/PEO. The improved d_h with this composition of porous PZT ceramics is due to the effective anisotropy in the microstructure which also decreases the dielectric constant of the specimens. Similarly g_h also increases with increase in the amount of PEO. The g_h increases in porous PZT ceramics because of its higher d_h values. This is because, air replaces high value dielectric PZT phase at low permittivity, and increases the g_h value as per (1)

$$g_h = d_h/k_{33}e_\circ, \quad (1)$$

where k_{33} is the dielectric constant in the poling direction and $e_\circ$ the permittivity of free space. The highest hydrostatic voltage coefficient measured for PZT porous ceramics using PEO as pore forming agent is 48×10^{-3} Vm^{-1}. This value is considerably higher than that of dense PZT ceramic made of the same powder. In reality, continuously increasing the g_h without decreasing ceramic volume, is not practically possible as permittivity decreases, the capacitance declines to a level where its use as an active element for a hydrophone becomes unacceptable.

Figure 3 shows the variation of figure of merit (FoM) and piezoelectric charge coefficient (d_{33}) with different amounts of PEO and the FoM increases with an increase in the amount of PEO. Because d_h and g_h values increase with increase in the amount of porosity which subsequently increases the FoM values since it is a product of d_h and g_h. The reason for high FoM in case of porous PZT ceramics was discussed earlier (Chen and Wu 2004). The d_{33} values of porous PZT ceramics are considerably lower than that of the conventional PZT ceramics, and also it decreases with increase in the amount of PEO. The d_{33} value of porous PZT ceramics is lower than that of conventional PZT ceramics because of the existence of the non-piezoelectric air phase.

Figure 4 shows the scanning electron micrographs of porous PZT ceramics of both high and low porosity (PZT/PEO: 50/50, 80/20). It shows that, when amount of PEO increases the porosity also increases; this subsequently increases the interconnectivities between the

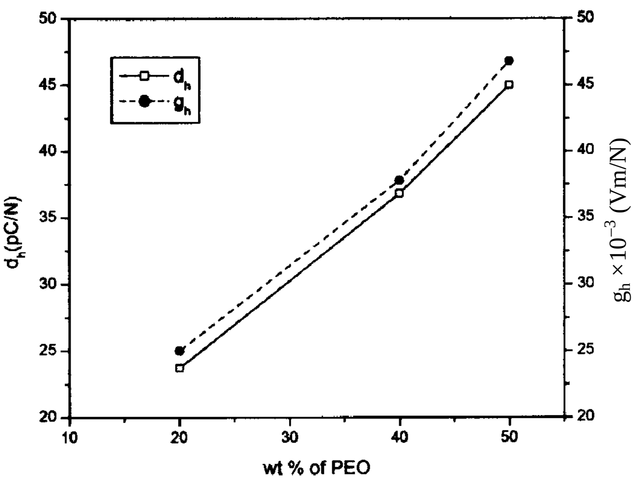

Figure 2. Effect of PEO (wt%) on hydrostatic charge (d_h) and voltage (g_h) coefficients.

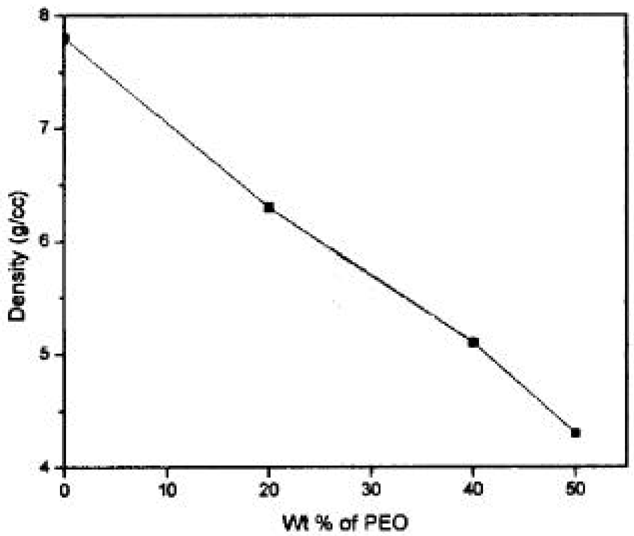

Figure 1. Effect of PEO (wt%) on density.

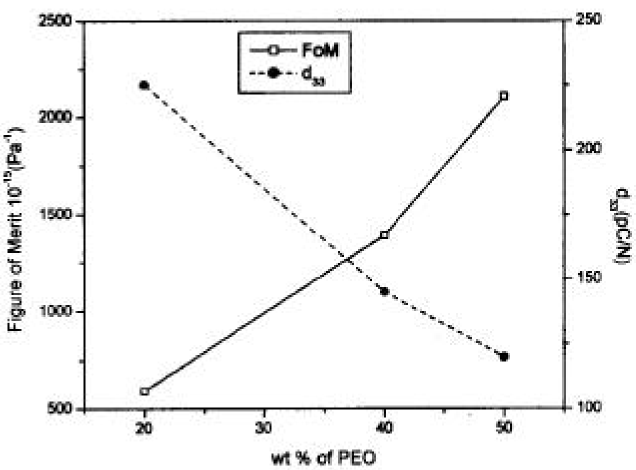

Figure 3. Effect of PEO (wt%) on figure of merit (FoM) and piezoelectric charge coefficient (d_{33}).

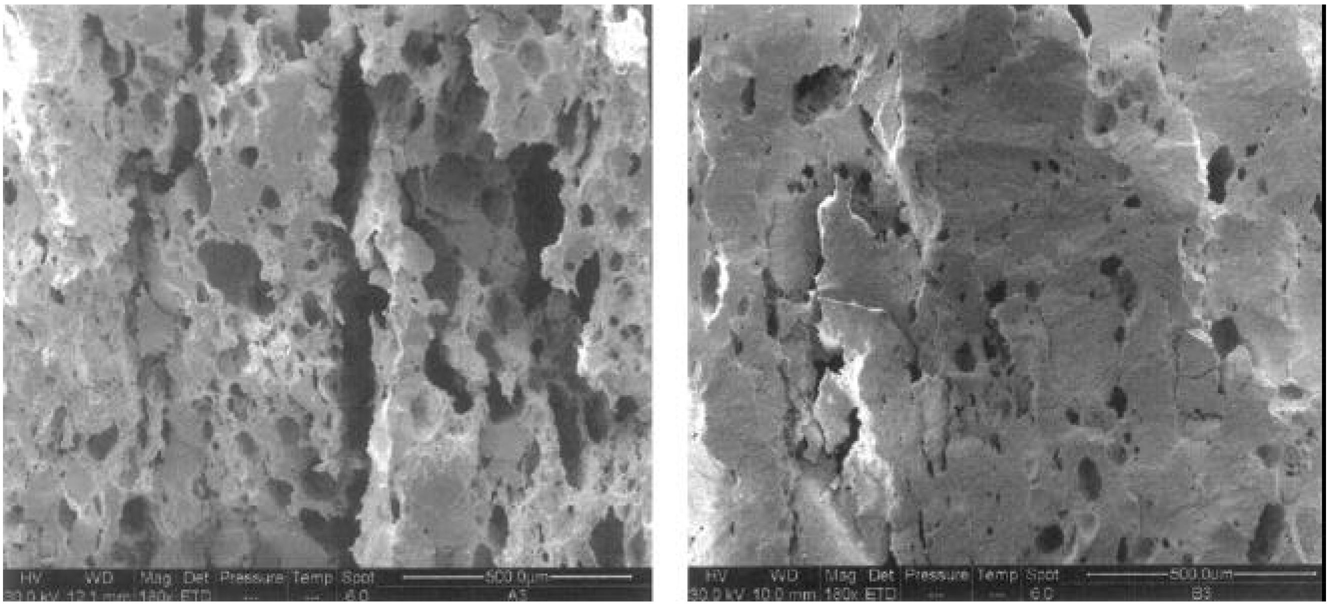

Figure 4. Scanning electron microstructures of high porosity PZT/PEO: 50/50 (3–3 connectivity) and low porosity PZT/PEO: 80/20 (mixture of 0–3 and 3–3 connectivity) porous PZT ceramics.

pores and pore sizes. Irregular distribution of pores (mixture of 3–3 and 0–3 connectivity) is seen in the low porosity microstructure whereas uniform distribution of pores (3–3 connectivity) is seen in high porosity microstructures. It also shows wide range of pore distribution varying from small micro pores to few macro pores. This change in microstructure is due to the amount of pore forming agent used during the processing of porous PZT ceramics.

4. Conclusions

In the present work, porous PZT ceramics were developed by using varied amounts of PEO as the pore-forming agent. At a given sintering temperature, porosity increases with increase in PEO content and both hydrostatic coefficients and FoM increase, with increase in the amount of PEO, whereas piezoelectric charge coefficient decreases with the increase in the amount of PEO. Prominent 3–3 connectivity is seen only in highly porous PZT ceramics (PZT/PEO: 50/50). This porous PZT ceramics with passive air phase could be suitable for the development of high sensitivity hydrophones.

Acknowledgements

The authors are thankful to Shri A S Rajagopal, Director, Armament Research and Development Establishment (ARDE), Pune, for constant encouragement during this work and Dr R Ramesh, NPOL, Kochi, for technical discussions.

References

Bowen C R and Topolov V Yu 2003 *Acta Mater*. **51** 4965
Chen Y C and Wu S 2004 *Ceram. Int*. **30** 69
Haertling G H 1999 *J. Am. Ceram. Soc*. **82** 797
Li J F, Takagi K, Ono M, Pan W, Watanabe R, Almajid A and Taya M 2003 *J. Am. Ceram. Soc*. **86** 1094
Newnham R E 1997 *Mater. Res. Bull*. **22** 20
Newnham R E and Ruschau G R 1991 *J. Am. Ceram. Soc*. **74** 463
Praveenkumar B, Kumar H H and Kharat D K 2004 *Proc. of international conference on advanced materials and processing ISAMAP 2K4* (Kharagpur: IIT) Vol. 11, p. 1151
Ramesh R, Kara H and Bowen C R 2004 *Com. Mater. Sci*. **30** 397
Roncari E, Galassi C, Cracium F, Capiani C and Piancastelli A 2001 *J. Eur. Ceram. Soc*. **21** 409
Waller D and Safari A 1988 *Ferroelectrics* **87** 189