SHORT COMMUNICATION

Processing of Lead Zirconate Titanate-graphite 3-3 Piezocomposites

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ABSTRACT

The lead zirconate titanate (PZT)-graphite piezocomposites have potential for higher piezoelectric sensitivity, lower acoustic impedance, higher piezoelectric voltage constants, higher electromechanical coupling coefficient, and higher hydrostatic coefficients as compared to dense PZT materials. In addition, the properties of piezocomposites can be tailored for various weight percentage of graphite powder. To study the phenomena, PZT-graphite 3-3 composites were prepared by mixing calcined PZT and commercially available graphite powder. The mixed powder was compacted, sintered, and poled by corona poling technique. Scanning electron microstructures were recorded to study the effect of graphite on processing of 3-3 piezocomposites. The polarising behaviour, piezoelectric and dielectric properties of PZT-graphite composites were studied.

Keywords: PZT, BURPS process, corona poling technique, piezoelectric, lead zirconate titanate, PZT-graphite composites, piezocomposites, pervoskite structure

1. INTRODUCTION

Lead zirconate titanate (PZT) is a ferroelectric material with pervoskite structure and has important applications in piezoelectric devices, ferroelectric memory devices, high dielectric capacitors, and infrared pyroelectric detectors due to their piezoelectric, ferroelectric, and pyroelectric properties[1]. Recently, porous PZT ceramics have received attention due to their possibility in enhancing their parameters with dense materials. Moreover, porosity in the material can reduce the effective acoustic impedance, and consequently improve the acoustic matching with media through which signals could be transmitted or received[2]. Secondly, an increase in the amount of porosity leads to a decrease in the transverse piezoelectric coefficient $(-d_{31})$ relative to longitudinal piezoelectric coefficient (d_{33}). This produces an increase in hydrostatic strain coefficient, d_h $(= d_{33} + 2d_{31})$, so that higher electric charges are generated per unit hydrostatic force. Finally, the increase in porosity reduces the permittivity (ε) of the material because air replaces the high dielectric constant PZT phase and increases the hydrostatic voltage coefficient, g_h $(= d_h/\varepsilon)$, which is a measure of electric field generated per unit hydrostatic stress.

Combining active piezoelectric material with passive polymer can form a variety of new piezoceramic connectivities[3]. In 3-3 connectivity, where both PZT phase and porosity are interconnected in the three directions, is preferred for low-frequency hydrophone applications because of its low density, improved acoustic matching with water, high compliance for damping, and high figure of merit[4,5]. These porous PZT ceramics are developed using BURPS process because of its ability to control porosity and ease of manufacture at larger scale[6,7]. In author's earlier studies, the effect of various pore-forming

agents such as polyvinyl chloride, polyethylene oxide, and polymethyl methacrylate on processing of porous PZT composites has been reported[8].

In sequence of the authors' earlier work, graphite has been used as pore-forming agent due to its fine semiconducting properties[9]. PZT-graphite composites were prepared by BURPS process using graphite powder as a pore-forming agent. The graphite powder was mixed with PZT powder and which allowed the binder, to burn out to leave the pores in the ceramic material and was followed by sintering and poling. The porous PZT ceramic with varied amount of graphite was investigated for microstructure, dielectric, and piezoelectric properties.

2. EXPERIMENTAL DETAILS

In this work, commercially available soft PZT powder was used as a base material. An appropriate quantity of this powder was weighed and mixed using a ball mill using zirconia balls as a grinding medium and water as a solvent for milling for 24 h. After milling, the mixture was calcined at 1000 °C for 4 h. The calcined PZT powder was then mixed with 10, 30, and 50-volume per cent of graphite for 1 h using agate pestal mortar. The specimens were designated as PZT/10GP, PZT/30GP, and PZT/50GP respectively. Approximately, seven weight per cent of polyvinyl alcohol was added to the mixture as a binding agent. The powder was then uniaxially pressed to produce 22 x 3.5 mm disk specimens. The specimens were subsequently fired at 500-600 °C for 10 h to remove graphite. The porous specimens were then stacked in an alumina crucible and sintered at 1260 °C and soaked for 1 h.

The densities of the sintered specimens were measured from their mass and dimensions. The sintered specimens were then poled by corona poling technique.[10] Copper foils were applied on the specimens to measure the dielectric and piezoelectric properties. To study the microstructure, scanning electron micrographs of the sintered specimens were recorded using SEM, JSM 5800 (Jeol, Japan). The piezoelectric longitudinal charge coefficient was recorded using Berlincourt, d_{33} piezometer (UK). The dielectric properties and hydrostatic charge (d_h), and voltage coefficient (g_h) were measured usingdual-range

piezometersystem, PM 35 (Take Control, UK).

3. RESULTS AND DISCUSSION

The variation of density as a consequence of addition of graphite is shown in Fig. 1. This plot indicates that the density (ρ) of the specimen decreases with increase in graphite content, leading to the subsequent decrease in the acoustic impedance (z) of the material since the acoustic impedance is a product of density and the sound velocity (c) of the material, i.e., $z = \rho c$. Further as the density of material decreases, the porosity increases, which subsequently affects the dielectric constant and hydrostatic coefficients in line with Eqn (1).

$$\text{Porosity } (P) = (1 - \rho/\rho_o) \text{ x } 100 \ (\%) \qquad (1)$$

where ρ_o is the theoretical density of PZT (7.82 g/cc) and ρ is the density of porous PZT. In this case, graphite develops the porosity in the material when specimens were heated at 500–600 °C. As graphite content increases, the porosity in the material also increases, and subsequently reduces the density of the material ($\rho = 6.1$ g/cc, PZT/ 50GP).

Figure 2 shows the effect of dielectric constant (k) and longitudinal piezoelectric charge coefficient (d_{33}) as a function of different amount of graphite added in the soft PZT material. Both dielectric constant and piezoelectric charge coefficient decrease with increase in graphite content. This is mainly due to the increased porosity (PZT/50GP specimens) observed due to the introduction of air-filled pores in the matrix. The trend shows that the PZT composite with high porosity retards the domain wall motion of grains compare
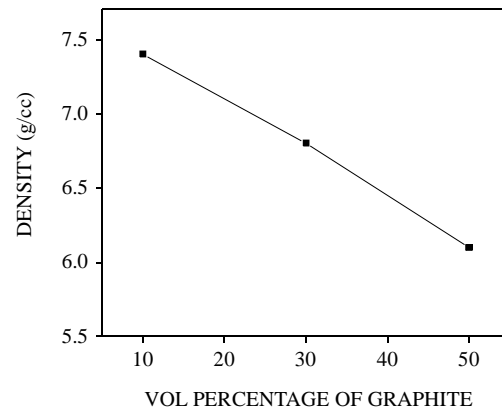

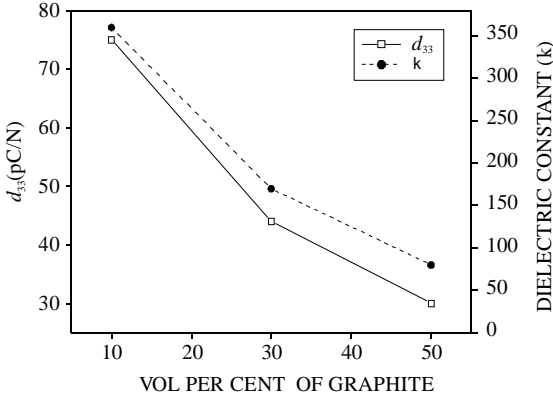**Figure 1. Variation of density with addition of graphite.**

Figure 2. Variation of d_{33} and k with addition of graphite.

Figure 3. Variation of d_h and g_h with addition of graphite.

to low-porous specimens and decreases the dielectric constant with an increase in porosity[11].

Piezoelectric charge coefficient decreases with increase in porosity because of its difficulty in poling, as large part of high dielectric constant PZT phase is replaced by low dielectric constant air phase, and large part of voltage is wasted across the air (porosity) phase. Also graphite-ash content in the porous PZT composite, may affect both the dielectric constant and piezoelectric charge coefficient.

It was reported in the authors' earlier studies[8] that both the hydrostatic charge (d_h) and voltage coefficient (g_h) increase with increase in amount of pore-forming agent. The effect of graphite pore-forming agent on d_h and g_h has been shown in Fig. 3. It is seen that, both d_h and g_h increase linearly with increase in graphite content, since d_h and g_h values directly depend on the amount of porosity and connectivity. Figure 3 also shows that,
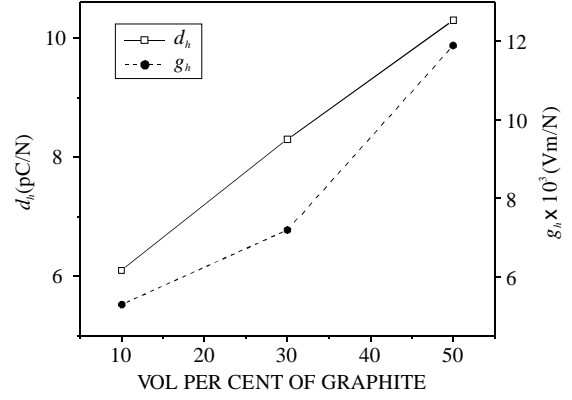
d_h and g_h values are relatively low in the case of the PZT-GP composite in comparision to PZT-PMMA and PZT-PEO composites[8]. This clearly shows that order of porosity (less open pores) and 3-3 connectivity in case of graphite specimens was relatively low because of its fine particle size (20 µm).

Figures 4 (a) and 4(b) show the scanning electron microstructures of unpoled specimens with 50 per cent and 30 per cent of graphite content, sintered at 1260 °C for 1 h. Figure 4(a) shows the presence of low porosity in the specimen, which is mainly due to less amount of graphite (30 %). Figure 4(b) shows slightly high porosity which has contributed for an increase in the hydrostatic coefficient and decrease in the dielectric constant. The following observations were made in the microstructure: (i) lower order of porosity (less open pores), (ii) fine particle size of graphite (20 µm), (iii) non-uniform pore and pore size distribution, (iv) absence of
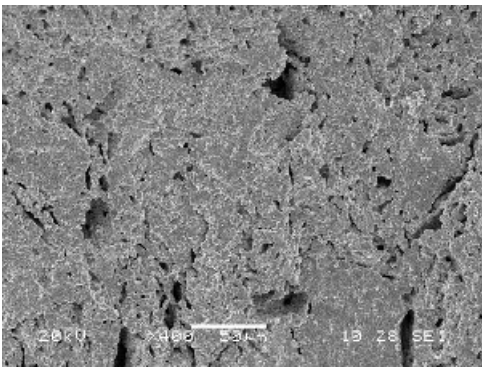
(a)
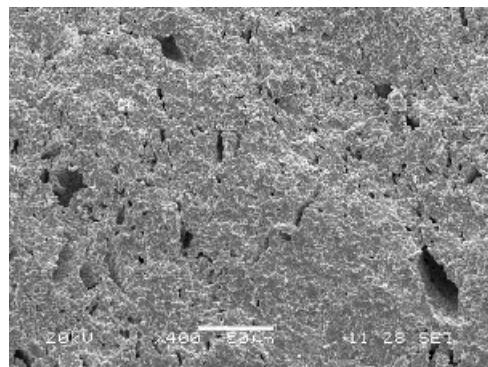
(b)

Figure 4. SEM of: (a) unpoled sintered PZT/50 GP, and (b) unpoled sintered PZT/30 GP.

3-3 connectivity in the microstructure, and (v) absence of cracks. These may be some of the reasons for decrease in hydrostatic coefficients of PZT-GP specimens compared to PZT-PMMA and PZT-PEO specimens.

4. CONCLUSION

The processing and characterisation of 3-3 PZT-graphite composites with different graphite ratios (10 %, 30 %, and 50 %) suitable for hydrophone applications were studied. The density, dielectric constant, and piezoelectric charge coefficient of the specimens decreases with the addition of graphite, mainly because of porosity. However, the hydrostatic charge and voltage coefficient increase with increase in the amount of graphite added.

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