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0 – 3 PIEZOELECTRIC – GLASS COMPOSITES

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Abstract Piezoelectric 0–3 ceramic–glass composites have been developed by firing a mixture of modified Lead Zirconate Titanate (PZT) and a lead based glass powder. Composites with 58 to 92 volume percent PZT were fabricated and their dielectric, piezoelectric and hydrostatic properties have been determined. The hydrostatic properties were pressure independent and the material showed good mechanical stability. The measured properties of the composites suggest that they could be useful in hydrophones and also as acoustic backing material.

INTRODUCTION

Electroceramic composites are today being increasingly used as transducer materials. By a suitable choice of the phases and connectivities, the properties of the composites can often be tailored to meet design requirements[1]. The preparation and properties of a large variety of piezoelectric ceramic–polymer composites have been reported[2]. However, the use of a polymer matrix restricts the use of these composites to relatively low temperatures. Grain–oriented glass–ceramics, based on fresnoite, have been developed for piezoelectric applications[3], but they show poor mechanical integrity and their fabrication requires temperature gradient crystallisation which is inconvenient. Conventional glass–ceramic processing has also been used to fabricate piezoelectric glass–ceramics based on Lead Titanate[4]. We have used similar techniques to fabricate piezoelectric glass–ceramic composites using a mixture of Lead Zirconate Titanate and lead based glass powders and, in this paper, we report on the dielectric, piezoelectric and hydrostatic properties of these composites.

MATERIAL FABRICATION

The piezoelectric material chosen was a Navy Type V modified Lead Zirconate Titanate (PZT) composition marketed by Sensor Technology Ltd. as BM 532 material. This material has a high dielectric constant (~3250) and good piezoelectric properties (d_{33} ~ 580 pC/N). The glass used in our composites is a proprietary lead based composition developed by Sensor Technology Ltd. (BM1000) for the production of polarisable glasses. This glass has a relatively low softening temperature, which makes for easier processing; it is chemically compatible with the ceramic particle and it has good electrical insulation properties which makes poling easier.

The PZT and glass powders had a particle size of 2 to 4 μm. The powders were mixed in the desired composition and the mixture was milled in methanol for two hours and pan dried. A 5% solution of poly-vinyl-alcohol (Air Products 107) was added to the powder as a binder and discs, 25 mm in diameter and 2.5 mm thick, were pressed at a pressure of 20 MPa. The binder was burnt out by heating at 500°C and the discs were fired at temperatures of between 550 to 600°C. These sintering temperatures were sufficiently low that no additional precautions were taken regarding the atmosphere during sintering; however, the firing was carried out in covered alumina crucibles. The fired discs were ground to produce uniform dimensions and a silver composition, with a low firing temperature, was applied to form the electrodes. The discs were poled for 30 minutes with an electric field of 5 KV/mm at a temperature of 120°C.

Since the properties of 0-3 composites are known to be a function of their composition, a total of 6 compositions were fabricated with their PZT content in the range of 58 - 92 volume percent.

MATERIAL PROPERTIES

The dielectric constant and the dissipation of our samples were measured at room temperature and at a frequency of 1 KHz. Their values are shown, as a function of PZT content, in Figure 1. The dielectric constant is found to be much lower than the value for the bulk PZT (~ 3250) while the dissipation also is somewhat reduced when compared with bulk PZT value (~ 0.02).

The piezoelectric d_{33} coefficients of the discs were determined by using a Berlincourt type d_{33} Meter. As shown in Figure 2(a), the d_{33} values of the composites show a roughly linear increase as a

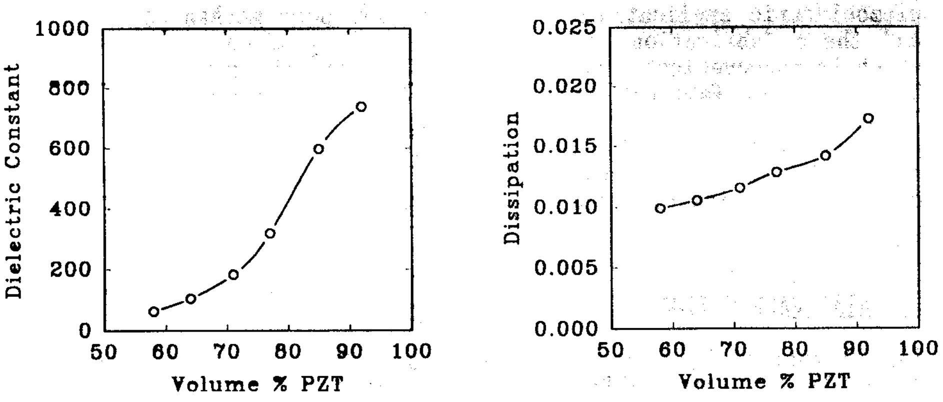
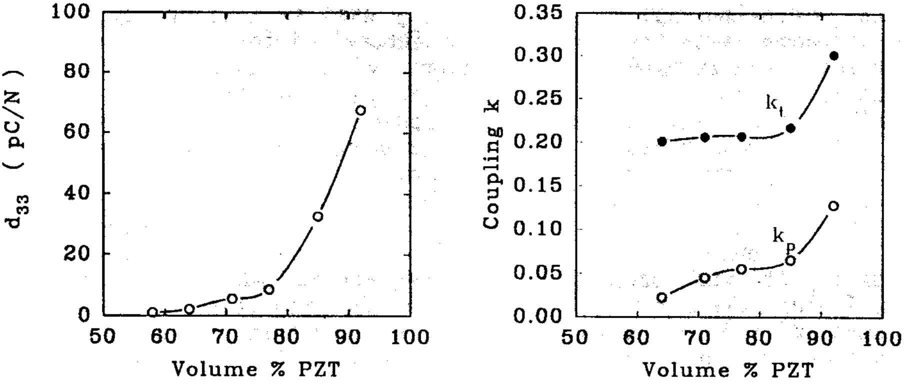


FIGURE 1. The dielectric constant and the dissipation of the composites as a function of PZT volume percent.



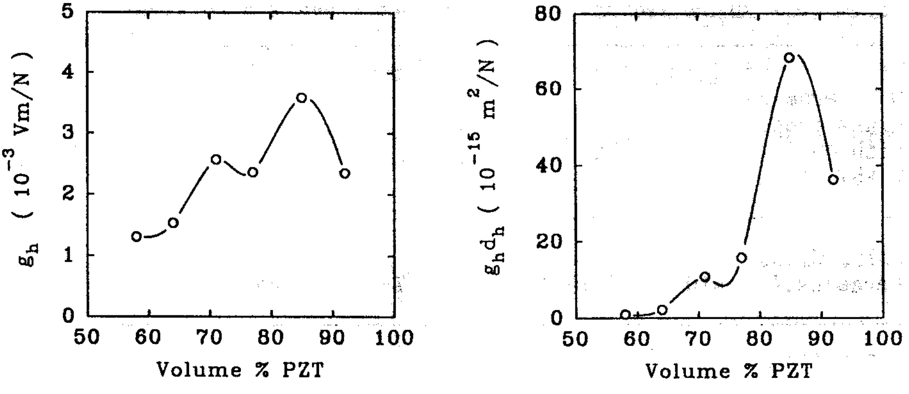
(a) (b)

FIGURE 2. The piezoelectric d_{33} coefficient and the coupling constants of the composites as a function of PZT content.

function of the PZT content until the latter reaches about 80%; but for higher PZT content the d_{33} values increase much more sharply to reach a maximum of about 68 pC/N for the specimen with 92 volume percent of PZT.

The thickness mode electromechanical coupling constant, k_t, and the planar coupling constant, k_p, of the composites were determined from resonance measurements, and the values are shown in Figure 2(b).

A technique similar to that developed by Sims and Henriquez[5] has been used to measure the hydrostatic voltage coefficient, g_h, of our



(a) (b)

FIGURE 3. The hydrostatic voltage coefficient, g_h, and the figure of merit, $g_h d_h$, of our composites as a function of PZT content.

composites, at a pressure of 2 MPa, and the variation of g_h as a function of PZT content in the composites is shown in Figure 3(a). The product of the hydrostatic voltage coefficient and the hydrostatic charge coefficient, $g_h d_h$, is commonly used as a figure of merit for hydrophone materials and has been determined for our specimens. As shown in Figure 3(b), the best figure of merit has been obtained for the sample with 85 volume percent PZT, for which $g_h d_h$ is 68 x 10^{-15} m^2/N. g_h has been measured as a function of hydrostatic pressure and, for pressures up to 14 MPa, g_h has been found to be independent of pressure to within experimental uncertainty.

The acoustic velocity and attenuation of the composites were measured using standard transmission techniques. The discs were precision lapped to provide good contact with the transducers and a standard metal plate was used to calibrate the system. The results are shown in Table 1 which provides a summary of the properties of the PZT–glass composites; for purposes of comparison, the table also gives published data on a few other types of composites and polar glass ceramics.

TABLE I Characteristics of the PZT–glass composites.

Vol % PZT	Diel. Const.	d_{33} $10^{-12}C/N$	g_h $10^{-3}Vm/N$	$g_h d_h$ $10^{-15}m^2/N$	Acoustic Velocity m/sec	Attenuation dB/cm
58	62	1.00	1.3	0.9		
64	104	2.11	1.5	2.0	3395	26
71	183	5.5	2.6	10	3490	26
77	319	8.6	2.4	15	3520	27
85	598	33	3.6	68	3215	30
92	738	68	2.4	36	3340	30
0–3 ceramic–glass comp. with 49 vol. % $PbTiO_3$.[4]	52	8				
Polar Glass Ceramics.[6]	~10	~8–10	83	747	~5000	
0–3 $PbTiO_3$ – rubber composite.[7]	54	60	47	1000		

CONCLUSIONS

Piezoelectric 0–3 ceramic–glass composites have been fabricated by the conventional firing of a mixture of powders of PZT and a lead based glass. The best d_{33} values obtained were comparable to those of some 0–3 ceramic–polymer composites and were an improvement over the d_{33} of similar composites made with Lead Titanate and those of polar glass ceramics. The hydrostatic properties of the composites were pressure independent and they showed good mechanical stability. This type of ceramic–glass composite is easier to fabricate than polar glass ceramics, their dielectric dispersion is less than that of polymer based composites. They can also be used over a much wider temperature range than polymer based composites since the elastic properties of glasses are much less temperature dependent than those of polymers. In addition to their possible use in transducers, the relatively large acoustic attenuation of these materials suggests their possible use as acoustic backing material.

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REFERENCES

1 R.E. Newnham, D.P. Skinner and L.E. Cross, Mat. Res. Bull., 13, 525 (1978).

2 R.E. Newnham, A. Safari, J. Giniewicz and B.H. Fox, Ferroelectrics, 60, 15 (1984).

3 A. Halliyal, A. Safari, A.S. Bhalla and R.E. Newnham, Ferroelectrics, 50, 45 (1983).

4 G.S. Lee, S. Kim and T.R. Shrout, Sensors and Materials, 2, 1, 7 (1990).

5 C.C. Sims and T.A. Henriquez, J. Acoust. Soc. Am., 36, 1704 (1964).

6 A. Halliyal, A. Safari, A.S. Bhalla, R.E. Newnham and L.E. Cross, J. Am. Cer. Soc., 67, 331 (1984).

7 H. Banno, Ferroelectrics, 50, 3 (1983).