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Characterisation of barium titanate-silver composites part II: Electrical properties

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Barium titanate-silver composites were manufactured with silver contents ranging from 0 wt.% to 30 wt.%. The electrical properties were systematically characterised in terms of relative permittivity, conductivity, piezoelectric properties (d_{33}, d_{31} and coupling coefficient), polarisation-field measurements and electrical breakdown strength. The electrical properties are strongly influenced by the conducting phase, with an increase in relative permittivity, conductivity, coercive field and remnant polarisation measured. A decrease in breakdown strength and piezoelectric coefficients were observed.

1. Introduction

The study of two-phase ceramic composites consisting of one phase that is highly conducting and another phase that is insulating has been reported in a number of papers due to the potential advantageous changes in dielectric properties. The most common observation for these particular systems is an enhancement in the permittivity of the material. Both Feng Li *et al*. [1] and Duan *et al*. [2] reported an increase in the relative permittivity for lead zirconate titanate-platinum, PZT-Pt, composites. Yu *et al*. [3] observed a high dielectric constant with a frequency dispersion in barium titanate-$(Ni_{0.3}Zn_{0.7})Fe_{2.1}O_4$ materials, which was attributed to a Maxwell-Wagner polarisation (interfacial polarisation). An improvement in the relative permittivity has also been reported on adding silver to PZT [4]. Enhanced permittivity, with a weak frequency and temperature dependence, has been observed in the $Na_{0.5}Bi_{0.5}TiO_3$ composites with silver particles [5].

We have studied barium titanate-silver, $BaTiO_3$-Ag, composites as a model system due to the well characterised behaviour of barium titanate and the relative ease of manufacture of the composite materials. The aim of this work is to present a detailed and thorough characterisation of the mechanical and electrical properties of a dielectric-conductor composite system. This is particularly important if these composites are to replace conventional materials in specific applications. For example, if a high permittivity metal-dielectric composite is to be considered in a capacitor application, the influence of the conductive phase on breakdown field must be known, since this limits the operating voltage. For actuator and sensor applications, the potential change in piezoelectric properties (e.g. d_{31} or d_{33}) as a function of metal content must also be considered.

The method of manufacturing $BaTiO_3$-Ag, composites, along with microstructural and mechanical characterisation, has been reported in Part I [6]. In summary, silver particles were found intergranularly and intragranularly and observed to impinge on domains and generate microcracks. An increase in tensile strength (typically from 100 to 140 MPa) was observed by incorporating silver particles into a barium titanate matrix. In addition, since no reaction phases were observed by X-ray diffraction or transmission electron microscopy, this system is able to provide interesting data on the electrical properties of metal-dielectric composites. The modelling of conductive defects in a random resistor-capacitor network to explain some of the changes in the observed properties will be reported in a future paper.

2. Experimental procedure

Barium titanate composites with 0, 1.3, 3.2, 6.4, 9.5, 12.7, 15.7 and 19.1 wt.% silver (0, 0.7, 1.8, 3.7, 5.6, 7.6, 9.7 and 11.8 vol.%) were fabricated, as detailed elsewhere [6]. The disc samples were ground to remove a thin depleted outer layer of silver approximately 50 μm deep. Electrical measurements were conducted on polished samples (3 μm finish) using silver electrodes. The capacitance, resistance and dielectric loss were measured using a Hewlett

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Packard 4263B LCR meter with a 1 V signal at 1 kHz. The relative permittivity and conductivity of the samples were calculated from the capacitance and resistance. The piezoelectric coefficients, d_{33} and d_{31}, was measured using a Piezometer (Take Control Ltd.), 24 h after samples had been corona poled. The dielectric strength was determined by application of an increasing potential difference (DC) across the samples using steel spherical electrodes while immersed in transformer oil. Dielectric breakdown was considered to have occurred when a rate of current change greater than 3 mA/s was detected across the sample. Impedance analysis of poled samples using a Solartron 1296 Dielectric Interface with 1260 Impedance Analyser was carried out to determine the effective coupling coefficients, K_{eff}, and mechanical quality factor, Q_m, of the composites, using Equations 1 and 2 [7], where f_a and f_r are the anti-resonant and resonant frequencies, respectively; $|Z_m|$ is the impedance value at resonance and C_O the free cell capacitance, taken as the capacitance at 1 kHz.

$$K_{\text{eff}} = \left[\frac{f_a^2 - f_r^2}{f_a^2}\right]^{0.5} \tag{1}$$

$$Q_m = \left[2\pi f_r \left|Z_m\right| C_0 K_{\text{eff}}^2\right]^{-1} \tag{2}$$

Polarisation-electric field loops were measured to establish the complete electric field behaviour. Impedance analysis was undertaken using a Solartron 1260 and 1296 Dielectric Interface on monolithic and composite samples at a range of temperatures from 10 Hz to 10^6 Hz in order to determine their permittivity and conductivity frequency dependence. The temperatures used were 25, 186, 242 and 310°C were chosen to allow comparison with previously reported results on pure barium titanate [8].

3. Results and discussion

3.1. Permittivity, conductivity and dielectric loss

The monolithic barium titanate had a relative permittivity of 1500, typical for the material, where values range from 950–1740 [9, 10]. The change in relative permittivity on addition of silver particles is shown in Fig. 1. At low silver contents the increase is small. However, with 25 wt.% silver a significant increase to ~4800 was measured. Feng Li *et al.* [1] stated that Maxwell's equation, below, can be used to predict the effective composite permittivity, $\varepsilon(V_f)$, as a function of metal volume fraction, V_f.

$$\varepsilon(V_f) = \varepsilon_m \left[\frac{(1 + 2V_f)}{(1 - V_f)}\right] \tag{3}$$

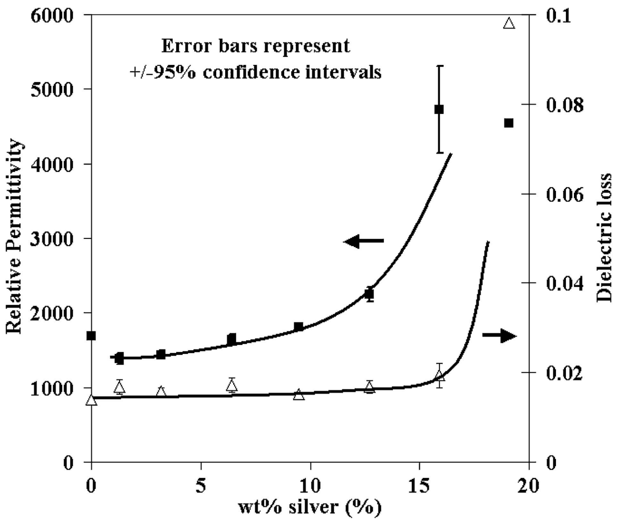

Figure 1 Variation of relative permittivity and dielectric loss with silver content. Error bars indicate 95% confidence limits.

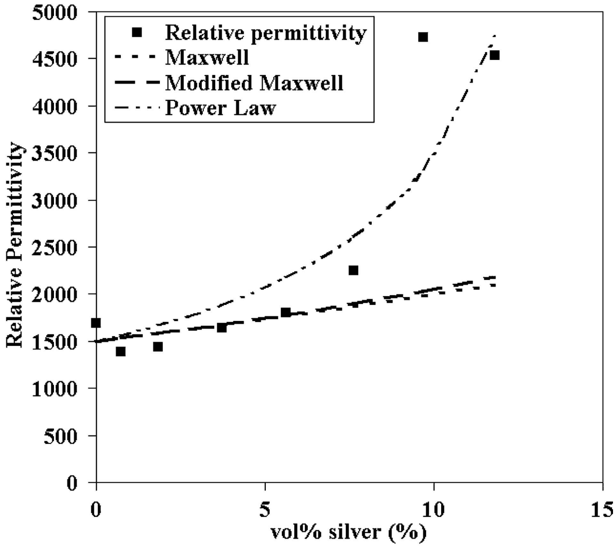

Figure 2 Relative permittivity as a variation of metal particle volume content, with lines representing the power law, modified and un-modified Maxwell equations.

Where ε_m is the relative permittivity of the matrix material (in this case barium titanate). Fig. 2 shows the results plotted against Equation 3, using a value ε_m of 1500. The observed increase in permittivity has been suggested to be due to the silver particles acting as 'internal' electrodes within the barium titanate and increasing the local electric field. Kwan *et al.* proposed a modified Maxwell equation, equation 4, for a non-continuous metallic phase to fit to this process [11].

$$\varepsilon(V_f) = \frac{\varepsilon_m}{(1 - V_f)^3} \tag{4}$$

This equation has also been plotted in Fig. 2. It is apparent that the experimental results are similar to the prediction by both modified and un-modified Maxwell equations at low silver volume fractions. Above ~5–8 vol.% silver the

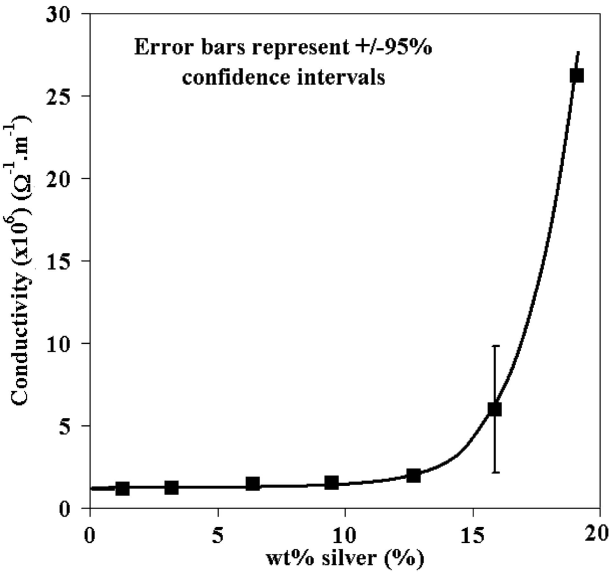

Figure 3 Variation of conductivity with silver content. Error bars indicate 95% confidence limits.

experimental increase in the relative permittivity is greater than predicted. Moya *et al.* [12] have observed a large increase in permittivity near the percolation threshold, since the composite consists of conducting silver particles surrounded by a thin layer of barium titanate. The large increase in permittivity near percolation is given by a power law [13], equation 5.

$$\varepsilon(V_f) = \varepsilon_m \left[\frac{V_c - V_f}{V_c}\right]^{-q} \tag{5}$$

Where ε_m is the matrix permittivity, V_c is the percolation threshold and q is a critical exponent. Equation 5 is also plotted in Fig. 2, with agreement at high silver contents using a percolation threshold of 0.16 (the theoretical value for a random composite) and $q = 0.86$ as used by Pecharroman *et al.* [12] in $BaTiO_3$-Ni composites.

The dielectric loss is also shown in Fig. 1, which indicates a dielectric loss value of ∼0.01, typical of monolithic barium titanate [10]. No significant change in dielectric loss with silver content was observed until silver contents reached ∼20 wt.%. At this composition the silver particles begin to interconnect, leading to a large increase in conductivity, as shown in Fig. 3. The addition of silver increases the conductivity compared to that of the barium titanate matrix ($1.25 \times 10^{-6}\ \Omega^{-1}\ m^{-1}$), although the increase is relatively small with silver contents of up to 12 wt.%, where the silver particles are isolated (Fig. 3). At higher silver contents the silver particles percolate leading to a large increase in conductivity. It is of interest to note that near percolation (∼16 wt.% silver) some scatter is observed in the measured conductivity, presumably due to the fact that individual samples have a greater or lesser degree of percolated metallic particles.

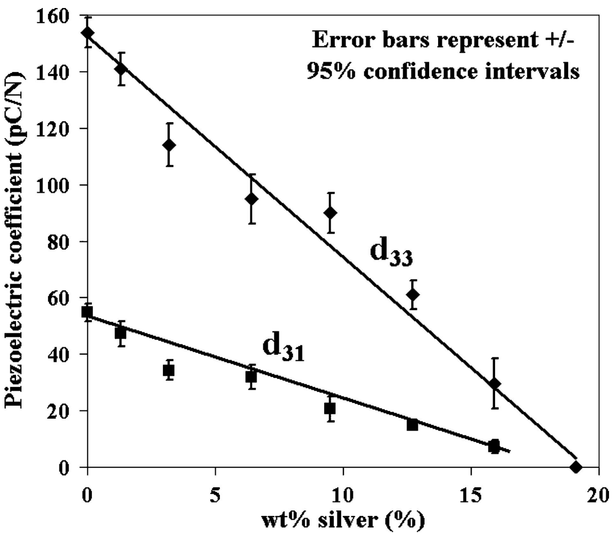

Figure 4 Piezoelectric coefficients, d_{33} and d_{31}, of barium titanate with various silver particle contents.

3.2. Piezoelectric coefficients (d_{31} and d_{33})

When the dielectric barium titanate matrix was continuous, the samples could still be poled (typically <20 wt.% silver). Samples were corona poled using a temperature of 130°C and a potential greater than 7.5 kV with a tip height of 2 cm. Domain alignment achieved saturation when the samples where cooled in the field. Piezoelectric coefficient measurements of the monolithic barium titanate confirmed that domain reorientation occurred under the poling field with d_{33} and d_{31} values of ∼170 pC/N and ∼−55 pC/N, respectively, typical of barium titanate [14]. The piezoelectric coefficients decreased linearly with increasing silver additions, as indicated in Fig. 4. This decrease is probably due to the fact that some of the mechanical load, which is applied during testing, is supported by the silver phase, which is not piezoelectric (i.e. $d_{33} = 0$). The load transferred into the silver phase depends on volume fraction and elastic modulus, however while there are a number of models for piezoelectric-polymer composites, no detailed theoretical investigations into the effect of conducting particles on the piezoelectric properties of a piezoelectric matrix have been conducted [1]. An additional reduction in the piezoelectric coefficients could be due to the increasing porosity encountered with silver addition. However, it has been widely reported that d_{33} only decreases significantly at relatively large values of porosity [15]. An improved internal electric field due to the silver particles, however, would have been expected to increase the efficiency of domain re-orientation.

3.3. Dielectric breakdown strength and coupling coefficient

The electrical breakdown strength (dielectric strength) of these materials has been rarely reported, for monolithic barium titanate the value (9.5 kV/mm) was similar to that

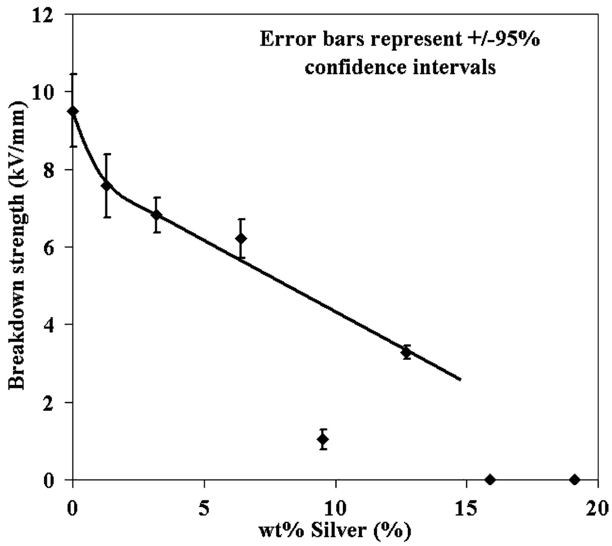

Figure 5 Reduction of breakdown strength with increasing silver content in a matrix of barium titanate.

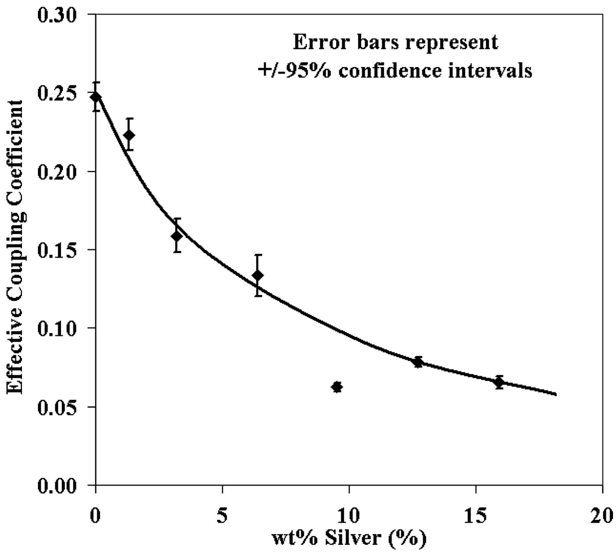

Figure 7 Reduction of the effective coupling coefficient with the addition of silver to a matrix of barium titanate.

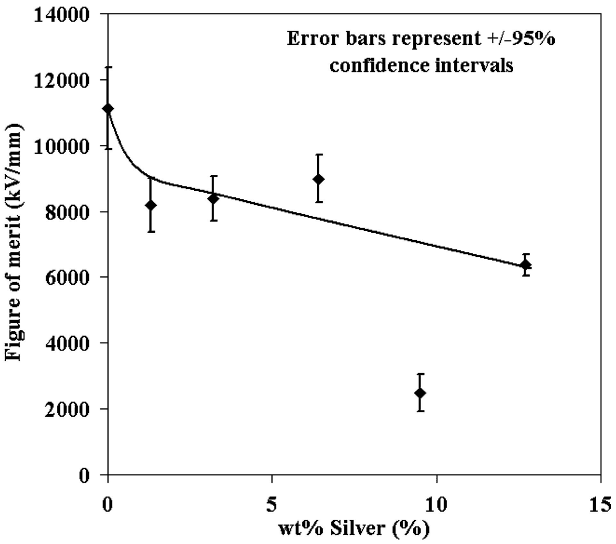

Figure 6 Figure of merit versus silver content in barium titanate.

reported in the literature (7.4 kV/mm)[16]. The influence of silver particle additions on the breakdown strength of the barium titanate composites is shown in Fig. 5. The variability in the results was analysed using Weibull statistics and the Weibull modulus was below 10 for all compositions. The breakdown strength decreased with increasing silver content, which is consistent with the assumption that the conductive particles shorten the internal electrode distance, leading to an increase in effective electric field [17]. As a comparison, the breakdown strength was reduced by nearly a third to a value of 3.5 kV/mm at a silver content of 13 wt.%. No values of dielectric strength were obtained for 17 wt.% silver and above, due to the high conductivity of the composites.

The breakdown strength could be improved by increasing the sample density so that corona discharges within pores, that initiate breakdown, could be reduced. While the increase in permittivity may be initially advantageous and metal-dielectric composites have been reported as a possible material for manufacturing multilayer capacitors [17], or the new supercapacitor materials [18], any decrease in dielectric strength limits their operating voltage. A figure of merit was calculated to take into account the increase in permittivity (beneficial) and decrease in breakdown strength (detrimental) of the composites and assess if composites offer advantages compared to the monolithic materials. The figure of merit is defined as the relative permittivity multiplied by the breakdown strength, which is a measure of the maximum charge stored by a capacitor of fixed dimensions. It appears that the reduction in breakdown strength, or the rise in permittivity is not sufficiently strong, to improve the figure of merit, by the addition of silver (Fig. 6). Barium titanate-silver composites, and other metal-dielectric systems, may have an opportunity for low voltage applications that require high permittivity. Optimising the sintering and processing in order to increase the sintered density may also improve the low dielectric strength values. Increasing the composite density (reducing porosity) would allow an improved figure of merit to be achieved by increasing the permittivity and dielectric breakdown strength.

The variation of the effective coupling coefficient with silver content in barium titanate, as determined by impedance analysis, is given in Fig. 7. It was observed to decrease systematically for the silver composites, with a value below 0.1 measured for a composition of 9.5 wt.% silver (Fig. 7). Similar observations were reported for PZT-Pt composites [1]. No significant change in the mechanical quality factor (Q_m) was observed with the addition of silver to barium titanate.

3.4. Polarisation-field response

In terms of polarisation-field response of the composites, Table I provides the maximum polarisation, remnant po-

TABLE I Measured property responses for an electric field amplitude of 1.5 kVmm^{-1}

Property	0 wt.% silver	1.3 wt.% silver	6.4 wt.% silver
Maximum polarisation (Cm^{-2})	0.095	0.086	0.126
Remnant polarisation (Cm^{-2})	0.025	0.026	0.056
Coercive field (kVmm^{-1})	0.23	0.30	0.35
Hysteresis loss (Jm^{-3}) ($\times 10^4$)	7.2	7.5	18.0

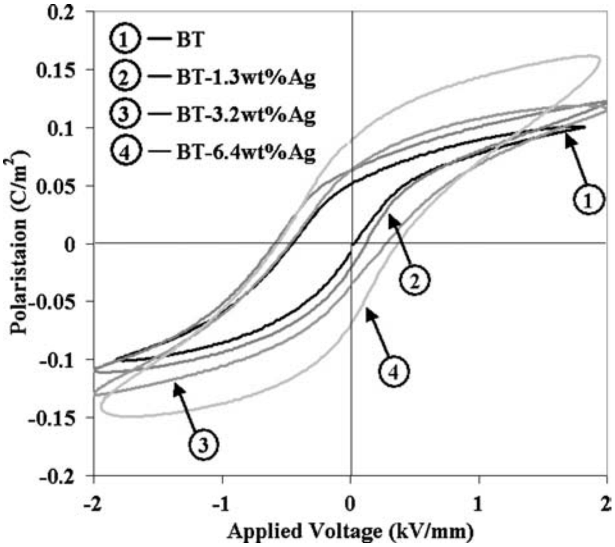

Figure 8 Change in polarisation-electric field behaviour of barium titanate with the addition of silver.

larisation, coercive field and hysteresis loss for an applied field of 1.5 kV mm^{-1}. Compositions with silver contents greater than 6.4 wt.% were not tested, due to the reduced dielectric strength, to avoid damaging the equipment. Fig. 8 shows the change in the hysteresis loop shape with silver addition. The polarisation-field loops of pure barium titanate were typical, with a polarisation of ∼0.12 Cm^{-2} for a field level of 2 kVmm^{-1} [19]. The addition of silver is observed to increase the remnant polarisation in comparison to barium titanate, for contents up to 6.4 wt.%. The coercive field and hysteresis loss was also increased, suggesting that the silver particles may be reducing the domains motion under the application of an electric field. The effect of small silver particles within the barium titanate matrix grains in the investigated composites were reported in Part I [6]. These small silver particles can interact with the domain walls, by hindering their motion when an electric field is applied. The reduction of barium titanate grain size with silver particle addition would be expected to decrease the coercive field, due to the formation of a simpler domain structure [20, 21]. Evidence suggests that incorporation of silver particles into the barium titanate matrix produces an electrically ‘harder’ material.

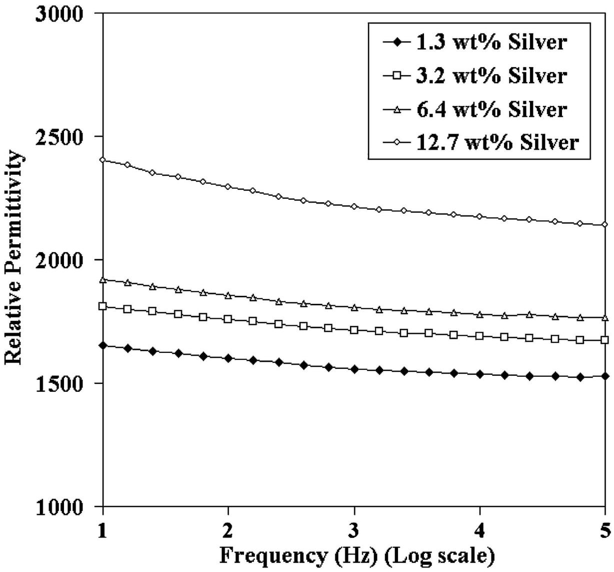

Figure 9 Relative permittivity as a function of frequency for composites at room temperature.

3.5. Frequency response

The relative permittivity as a function of frequency was carried out on monolithic material and the composites. Room temperature measurements are shown in Fig. 9, showing an increase in permittivity with metal content across the whole frequency range studied and a gradual decrease in permittivity with frequency. Lin *et al.* stated that the gradual permittivity decrease with frequency was due to an interfacial relaxation [5], although this is typical of resistor-capacitor electrical networks [22].

Samples were also heated to increase the conductivity (ionic) of the dielectric matrix into a range that would allow observation of the high and low permittivity plateaus. These plateaus have been ascribed to correspond to the high permittivity of the grain boundary at low frequency, and the low permittivity plateau at higher frequency [8] with a rapid decrease in the permittivity between these plateaus. Figs 10 and 11 show the permittivity and conductivity as a function of frequency for composites at a temperature of 242°C. As expected from the 1 kHz measurements (Fig. 2), the permittivity increased with the addition of silver to the barium titanate. The results indicate that this increase occurs over a wide frequency range. The low frequency (<100 Hz) decrease in conductivity is due to ionic charge build up on the electrodes. For the conductivity-frequency results, the conductivity increases with silver content and a convergence at high frequency is observed.

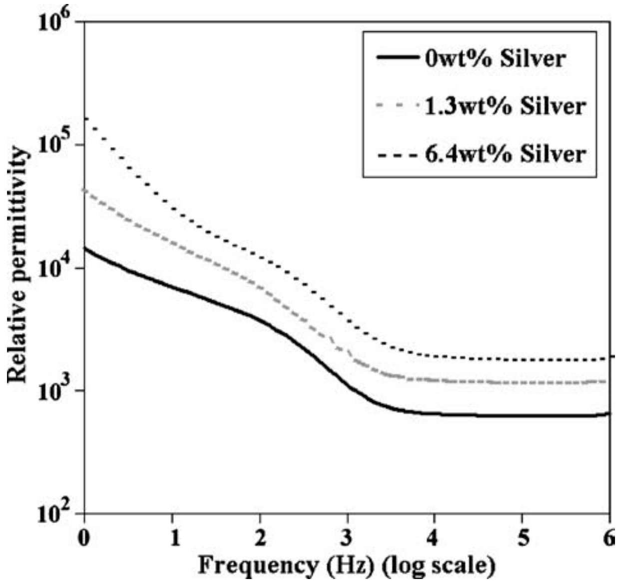

Figure 10 Increase in relative permittivity with the addition of silver to barium titanate at a temperature of 242°C over a frequency range of 1 Hz–1 MHz.

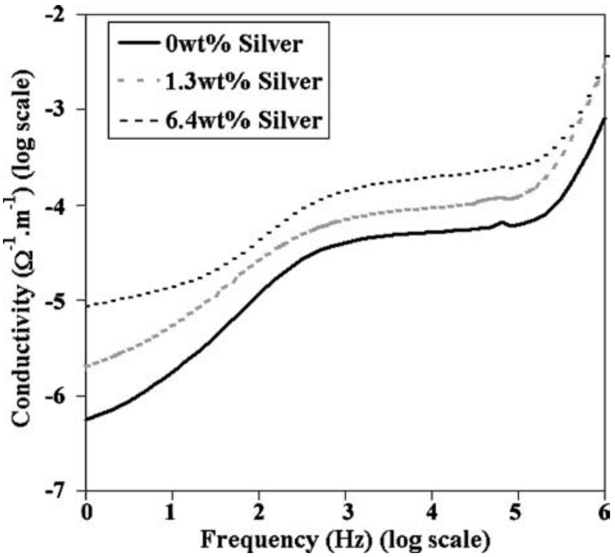

Figure 11 Increase in conductivity with the addition of silver to barium titanate at a temperature of 242°C over a frequency range of 1 Hz–1 MHz.

4. Conclusions

The permittivity was significantly increased across a broad frequency range with the addition of more than 10 wt.% silver, with no corresponding increase in dielectric loss. The monolithic permittivity value of ∼1500 doubled with a 15 wt.% silver particle content. It is suggested that this increase is due to the metallic particles acting as internal electrodes and concentrating the local electric field. Although the composite conductivity increased with the addition of the metallic silver particles, poling was still possible and the piezoelectric coefficients, d_{33} and d_{31}, were observed to decrease linearly with increasing silver content. The coupling coefficient on the other hand was lowered continuously, but at a decreasing rate, with silver particle addition. While the dielectric permittivity improved, the dielectric strength decreased with silver particle addition. A calculated figure of merit indicated that the composites show no benefit for capacitor application, but may be useful for low field applications. Optimising the fabrication process to reduce the porosity of high silver content composites could increase the dielectric breakdown strength to allow use at higher electric fields.

The incorporation of silver increased the coercive field and remnant polarisation of barium titanate. It is proposed that the barium titanate has become 'harder' due to the silver particles inhibiting domain wall motion. Microscopy (Part I) revealed domains impinged on silver nano-particles within the barium titanate grains. Measurement of the permittivity with frequency for the composites revealed that the permittivity improvement is similar at all frequencies in the frequency range tested. The conductivity-electric field frequency behaviour of the composites was observed to converge at high frequency.

If metal-dielectric composites are to replace existing monolithic materials due to enhanced properties such as strength and permittivity for application such as high strength actuators and sensors, multilayer capacitors or supercapacitor materials the possible degradation of other important properties such as breakdown strength, resistivity, piezoelectric and coupling coefficients must also be carefully considered.

Acknowledgments

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References

1. J.-F. LI, K. TAKAGI, N. TERAKUBO and R. WATANABE, *Appl. Phys. Lett.* **79** (2001) 2441.
2. N. DUAN, J. E. TEN ELSHOF, H. VERWEIJ, G. GREUEL and O. DANNAPPLE, *ibid.* **77** (2000) 3263.
3. Z. YU and C. ANG, *J. Appl. Phys.* **91** (2002) 794.
4. H-J. HWANG, T. NAGAI, T. OHJI, M. SANDO, M. TORIYAMA and K. KIIHARA, *J. Am. Ceram. Soc.* **81** (1998) 709.
5. Y. LIN, C-W. NAN, J. WANG, G. LIU, J. WU and N. CAI, *ibid.* **87** (2004) 742.
6. S. PANTENY, C. BOWEN and R. STEVENS, *ibid.* (2005) .
7. European standard prEN 50324-2:1999E Piezoelectric properties of ceramic materials and components; Part 2: methods of measurement and properties — low power (1999).
8. N. HIROSE and A. WEST, *J. Am. Ceram. Soc.* **79** (1996) 1633.
9. G. ARLT, D. HENNINGS and G. DE WITH, *J. Appl. Phys.* **58** (1985) 1619.
10. A. J. MOULSON and J. M. HERBERT, in "Electroceramics – Materials, Properties & Applications" (Chapman & Hall, London, 1990).
11. S. KWAN, F. SHIN and W. TSUI, *J. Mater. Sci.* **19** (1984) 4093.
12. C. PECHARROMAN, F. ESTEBAN-BETEGON, J. F. BARTOLOME, S. LOPEZ-ESTEBAN and J. S. MOYA, *Adv. Mat.* **13** (2001) 1541.
13. A. L. EFROS and B. I. SHKLOVSKII, *Phys. Stat. Sol. B* **76** (1976) 475.

14. C. NEAR, Morgan Technical Publication TP-226 (2003).
15. C. R. BOWEN, A. PERRY, H. KARA and S. MAHON, *J. Euro. Ceram. Soc.* **21** (2001) 1463.
16. B.-C. SHIN and H-G. KIM, *Ferroelectrics* **77** (1988) 161.
17. N. HALDER, A. SHARMA, S. KHAN, A. SEN and H. MAITI, *Mat. Res. Bull.* **34** (1999) 545.
18. C. PECHARROMAN and J. MOYA, *Adv. Mater.* **12** (2000) 294.
19. J. NOWOTNY, in "Electronic Ceramic Materials" (Transtech Publishing, UK, 1992).
20. G. ARLT, *Ferroelectrics* **76** (1987) 451.
21. K. WU and W. SCHULZE, *J. Am. Ceram. Soc.* **75** (1992) 3385.
22. D. P. ALMOND and C. R. BOWEN, *Phys. Rev. Lett.* **92** (2004) 157601-1

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