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Sintering and electrical properties of PZT/Pt dual-phase composites

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Abstract

Lead zirconate titanate–platinum dual phase composites, which have been shown to exhibit a very interesting electric field dependence of the dielectric constant, were prepared. The sintering properties and microstructure were analyzed. No chemical reaction between PZT and Pt was found in the composite. Neither did Pt atoms dissolve into the PZT lattice. The behavior of the effective electrical resistivity and the effective dielectric permittivity of the composites were investigated experimentally and theoretically in terms of the metal concentration. The dielectric constant of the composites increases with increasing metal concentration and approaches a maximum near the percolation threshold while the electrical conductivity and the dielectric losses remain small. It is indicative that the composites show a conspicuous effect of the tortuous, near-percolative metal phase. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; Ferroelectrics; Pt; PZT

1. Introduction

Little work[1–3] on lead zirconate titanate (PZT)/metal composites has been reported. It is known that introduction of metallic particles into a matrix improves its mechanical properties due to strengthening at the grain boundaries. However, the electrical properties reported, such as dielectric constant and piezoelectric coefficients, are quite inconsistent. It is commonly known that reinforcement of the mechanical properties of piezoelectrics and ferroelectrics by the addition of some fibers, whiskers and particles usually causes a partial loss of the electrical properties. A fraction of platinum particles can also improve the fatigue properties of composites strongly, but the dielectric properties are slightly decreased by this addition.[2] However, PZT with silver particles dispersed in the matrix has been reported to have both improved mechanical and dielectric properties.[1] In this work large amounts of metallic particles are added to the PZT matrix. We found that the dielectric and ferroelectric properties of PZT are enhanced considerably by this addition.[4] This, we believe, can be attributed mainly to the effect of the tortuous, near-percolative metal phase (called “near-percolative effect” in the remainder of the text) of the composite. Percolative effects are widely known in mixed materials systems, like insulating–conducting mixtures, cermets, and insulating — superconducting mixtures, etc. According to percolation theory, the electrical properties of these disordered systems, e.g. the electrical conductivity and dielectric constant, change strongly with composition when one phase in the mixture is approaching its percolation threshold. This feature may support applications such as capacitors with anomalously high capacitances. These might be used in a variety of applications like electromagnetic shieldings, solid state ionic devices, and antenna systems. In a former work,[4] we found that the dielectric properties of such PZT-Pt composites show a much larger electrical field dependence than single-phase PZT does. Therefore, in the present work this anomalous dielectric behavior is investigated further. We also report on the sintering properties of the composites and analyze the results of the composition dependence of the dielectric constant and the electrical conductivity in terms of percolation theory.

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2. Experimental

Lead zirconate titanate-platinum composites were fabricated by means of the conventional solid state reaction method. Raw materials, PbO (grain size < 14 μm, purity 99.7%, ACROS Organics, USA), ZrO_2 (grain size < 5 μm, purity 97.25%, Philips Research Eindhoven, The Netherlands), and TiO_2 (grain size < 24 μm, purity 99.87%, Philips Research Eindhoven, The Netherlands) were weighed and mixed according to the stoichiometric formula $Pb(Zr_xTi_{1-x})O_3$ of the desired composition with Zr/Ti = 53/47. 0.5 wt.% extra PbO was added to the starting materials to compensate for the evaporation of Pb during sintering. The starting oxides were wet-milled for 24 h in a polyethylene jar using acetone and a combination of 2 mm and 10 mm YSZ balls. The mixed slurry was dried in an oven. To the dried powder mixture 6 wt.% distilled water was added, after which it was sieved through a 300 μm mesh screen. The powder was uniaxially pressed to a green pellet at a pressure of 10 MPa for better calcination at 850°C for 2 h. After grinding the calcined PZT powder down to an average particle size of about 5 μm, commercially available Pt powder (grain size 0.8–2 μm, purity 99.9%, ACROS Organics, USA) with a proper volume amount was added and wet-mixed. Then 8 wt.% PVA was added to the PZT/Pt mixture. Green compacts were made by pressing the powder uniaxially at 10 MPa, followed by cold isostatic pressing at 300 MPa. The polymer adhesive was burned out at 600°C for 1 h. The pellets were subsequently sintered at 1000–1300°C for ~2 h in a sealed crucible, while being surrounded by calcined PZT powder.

The bulk density was determined by the Archimedes method in mercury. The phase purity of the as-sintered samples was checked by X-ray diffraction. Sintered specimens were polished with diamond paste for characterization of the microstructure and electrical properties. Microstructural investigation was performed by scanning electron microscopy. Grain sizes of the composites were determined using the linear intercept technique.[5] Chemical analysis of the phases was performed by energy dispersive X-ray analysis. For the electrical measurements platinum electrodes were sputtered on both sides of the samples. The dielectric permittivity was measured using a HP 4274A multi-frequency LCR meter with an amplitude of 2 V/mm at a frequency of 1 kHz. The electrical conductivity was calculated from the *I–V* curves that were obtained using a Keithley 237 high voltage source and measurements unit.

3. Results and discussion

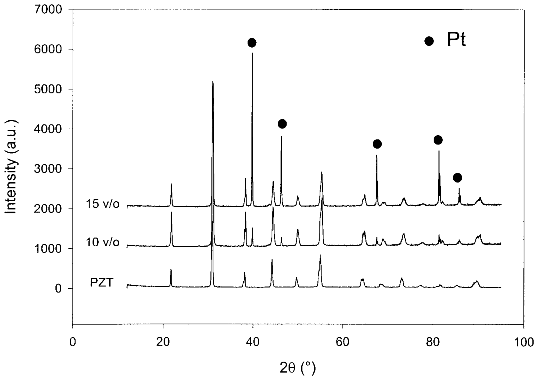

Fig. 1. XRD patterns of samples PZT/Pt with 10 and 15 v/o Pt. Arrows indicate the Pt phase, the other peaks belong to the PZT phase. The split peaks in the XRD pattern for single-phase PZT implies the coexistence of the tetragonal and rhombohedral phases.

Fig. 1 shows the XRD spectra of the as-sintered PZT/Pt composites together with that of single-phase PZT. XRD analysis shows no indications of a chemical reaction between PZT and Pt, and both PZT and the metallic Pt phase have well-defined lattices. Energy dispersive X-ray analysis further showed the absence of diffusion between the two phases. Hence it seems unlikely that Pt atoms will diffuse into the PZT lattice. Another sample, prepared by a wet-chemical method, neither gave indications of diffusion of Pt-ions into the PZT lattice. It is known that the radius of Pt^{2+} ions is 0.80 Å, which is close to Ti^{4+}(0.68 Å) and Zr^{4+} (0.80 Å). However, Pt^{2+} ions have a much larger electronegativity and lower valence than Ti^{4+} and Zr^{4+} ions. Hence, neither Ti^{4+} nor Zr^{4+} are expected to be (partially) replaced by Pt^{2+}. Irrespective of the fact that they have the same valence, Pb^{2+} cannot be substituted for Pt^{2+}, due to both the difference in ionic radius and the difference in electronegativity.

As a representative example, Fig. 2 shows the microstructure of the PZT/Pt composite with 10 vol.% Pt. It can be seen that the PZT grains have an equiaxed shape and that the Pt phase is present as more or less round particles, albeit with a somewhat irregular shape. Pt grain boundaries cannot be observed, but it is expected that the Pt grains have an equiaxed shape similar to that of PZT. No third phase is observed. The average grain size of PZT is about 2–3 μm, which is smaller than the 4–5 μm of monolithic PZT. It should be noted that Pt appears to be agglomerated, which is indicative of the high mobility of Pt atoms during sintering. It has been reported that Pt particles have a large tendency to aggregation, and that the growth of Pt particles occurs by coalescence.[2,6] However, agglomeration caused by the processing procedure cannot be ruled out as a possibility. In the present work the ball-milling method is used to mix the PZT and Pt powders. Thus segregation of the Pt phase during drying of the mixed slurry may occur, due to its density that differs strongly from that of PZT.

The sintering properties of PZT/Pt composites are presented in Figs. 3 and 4. Fig. 3 shows the measured and relative densities as a function of Pt content. The

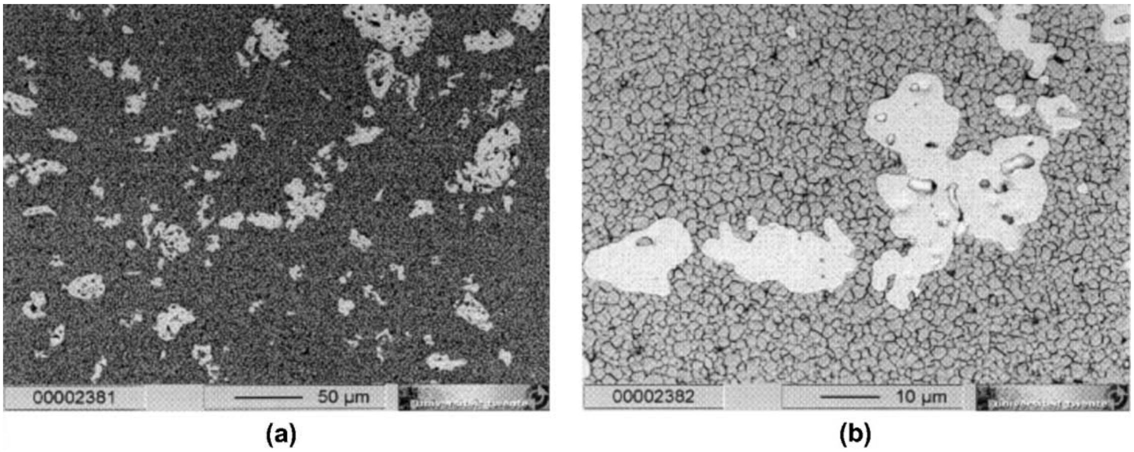

Fig. 2. (a) SEM graph of sample PZT/Pt10. The light gray phase is Pt and the dark gray one is PZT. (b) Details of (a).

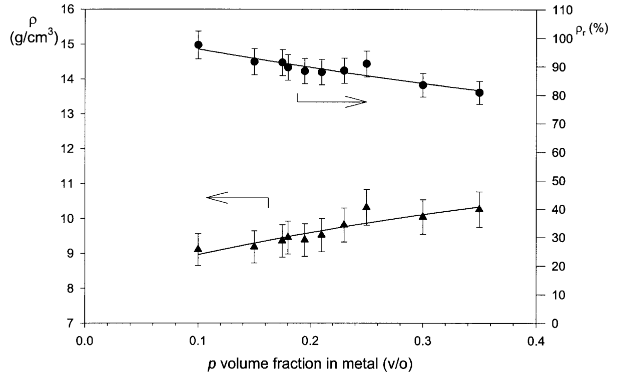

Fig. 3. Measured (triangles) and relative (solid circles) densities in relation to the Pt content. Drawn lines are a guide to the eye.

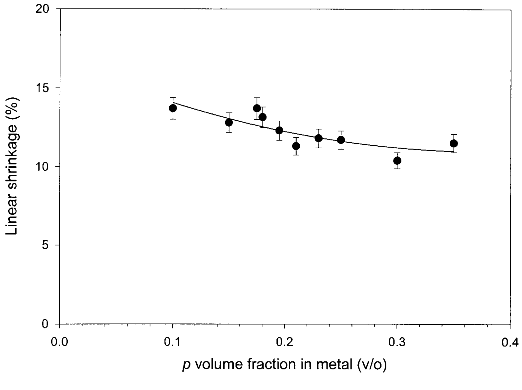

Fig. 4. Linear shrinkage as a function of Pt content.

relative density decreases slightly with increasing Pt concentration under the same processing conditions. The size of the Pt agglomerates does not change much with Pt content. It is expected that the coalescence of Pt particles causes pores, which cannot be removed easily during sintering. Hence, when more Pt agglomerates form, i.e. at higher metal concentrations, a lower relative density is obtained. From Fig. 4, which shows the linear shrinkage during sintering as a function of Pt content, it can be seen that composites with a higher Pt content show slightly less shrinkage. This can be accounted for by the more common occurrence of pore formation with increasing Pt content.

The composition dependence of the dielectric constant and the electrical conductivity of the composites is shown in Fig. 5. The electrical conductivity increases abruptly when the Pt content is between 30 and 35 v/o. The dielectric constant increases nonlinearly with Pt content. Such a composition dependence of the dielectric constant and the electrical conductivity is typically caused by a near-percolative metal concentration. A few models like the effective-medium approximations,[7] including the Claussius–Mossotti formula, the Maxwell–Garnett approximation, the Bruggeman symmetric and asymmetric equations etc., percolation theory,[8] and the general effective media equation[9] may be used to explain the experimental phenomena. In the present work we used the general effective media (GEM) equation and percolation theory to analyze the experimental behavior of the dielectric constant. The general effective media (GEM) equation is given by:

$$\frac{(1-p)\left(\sigma_{\mathrm{f}}^{1/s}-\sigma^{1/s}\right)}{\sigma_{\mathrm{f}}^{1/s}+A\sigma^{1/s}}+\frac{p\left(\sigma_{\mathrm{c}}^{1/t}-\sigma^{1/t}\right)}{\sigma_{\mathrm{c}}^{1/t}+A\sigma^{1t}}=0 \qquad (1)$$

where $A=(1-p_{\mathrm{c}})/p_{\mathrm{c}}$, p_{c} the percolation threshold (volume fraction) in the metal; σ_{c} and σ_{f} are the electrical conductivities of the conductor and the insulator, respectively, σ is the effective electric conductivity of the composite, p the volume Pt content, and t and s are transport exponents related to the microscopic details of the system under consideration.

The theoretical curve fitted with Eq. (1) is shown in Fig. 5(a). The obtained fitting parameters are $s=0.49\pm0.02$, $t=4$, $p_{\mathrm{c}}=0.31\pm0.02$, and $\sigma_{\mathrm{f}}=(1.09\pm0.05)\times10^{-11}$ Ω m^{-1}. The parameter σ_{c} (9.56×10^{6} Ω m^{-1}) was taken

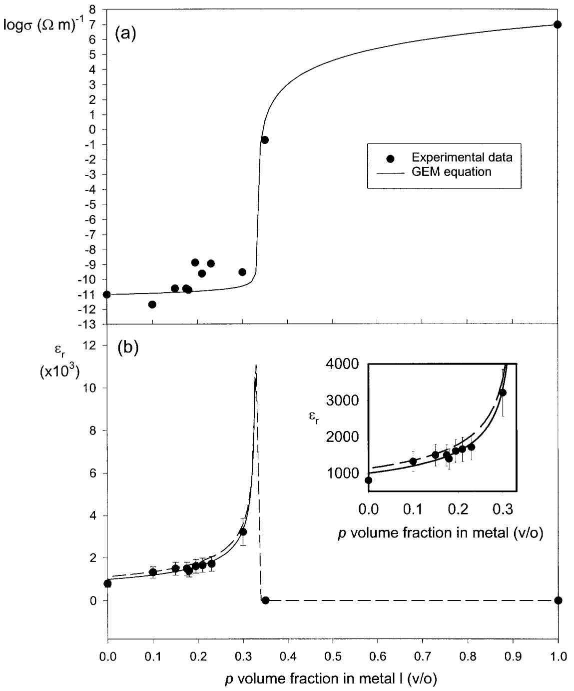

Fig. 5. Effective electrical conductivity (a) and effective dielectric constant (b) as a function of the Pt content. Both solid lines are fits of the GEM equation to the experimental data. The fit parameters are given in the text. The dashed line in Fig. 3(b) is a fit of the normalized percolation theory [Eq. (3)] to the experimental data. The inset in Fig. 3(b) shows the details of the experimental data, where a large increment of the effective dielectric constant of the composites, compared to the single phase PZT, can be clearly seen.

from literature and was kept constant to reduce the number of variables. Due to the lack of experimental data on the $p > p_c$ side, t can not be determined accurately by the above fitting procedure. However, t only affects the slope change on the $p > p_c$ side, which is not the region of interest here.

The effective dielectric constant can be derived from Eq. (1),

$$\varepsilon_{\mathrm{eff}} = -\frac{\mathrm{Im}\sigma}{\omega\varepsilon_0} \tag{2}$$

where ω is the measuring frequency, and ε_0 the vacuum dielectric permittivity.

The theoretical fit of Eq. (2) with the same parameters is plotted in Fig. 5(b), except that σ_f is replaced by a complex number, 1.09×10^{-11}–i 2.18×10^{-9}, obtained from $\sigma_f = \omega\varepsilon_0\varepsilon'' - i\omega\varepsilon_0\varepsilon'$, assuming $\tan\delta = \varepsilon''/\varepsilon' = 0.005$. We can see that the maximum theoretical dielectric constant is about 10 times that of single-phase PZT. The extrapolated dielectric constant for PZT (zero Pt content) is $\sim 11.5\times10^2$, which is close to the experimental value.

The experimental data of the dielectric constant are also fitted with an expression from the normalized percolation theory:[11]

$$\varepsilon_m = \varepsilon_f(1-p/p_c)^{-s} \tag{3}$$

where ε_m and ε_f are the effective dielectric constant of the composite, and the relative dielectric constant of single-phase PZT ceramic, respectively.

The fitting parameters are $s = 0.502\pm0.059$, and $p_c = 0.332\pm0.010$. For ε_f, the fixed value of 1000, which is reasonable for undoped PZT with Zr/Ti = 53/47, was taken. The fitted parameters s and p_c are rather sensitive to the given ε_f value. A good estimate of ε_f can provide a better fit to the experimental data. It is interesting to note that both theoretical fits of Eqs. (2) and (3) result in almost the same s and p_c values. A value for p_c around 0.33, in accordance with the theoretical prediction,[10] implies the two phases in the composite to have fairly similar geometric shapes, namely isometric or round shapes, irrespective of differences in size. This is consistent with the microstructure observed by SEM. The s (~0.5) value is reasonably close to the typical value (normally 0.76–0.89),[11] which further implies that the system has a uniform microstructure without any preferential orientation.

The measured relative dielectric constant of the composite with 30 v/o Pt is about 4 times higher than that of single-phase PZT ceramics with the same Zr/Ti ratio. The theoretical curves in Fig. 5 predict that in theory, when the Pt content approaches p_c, very large effective dielectric constants can be obtained, although it is quite difficult to achieve this in practice.

Another important fact that should be noted is that although the effective dielectric constant has increased remarkably, the electrical conductivities of all these non-percolative samples remain low. This feature ensures good insulating properties of the composites.

4. Conclusions

Dual-phase ferroelectric composites were successfully made in the PZT-Pt system. Within the experimental error of XRD and EDX, no chemical reaction between two phases was found. The dielectric constants of the composites show an apparent near-percolative effect. The dielectric constant increases strongly with the increase of the Pt content when the composites are just below the percolation threshold for the metal phase. At the same time the electrical conductivity remains low. The dielectric behavior is also related to the homogeneity and the microstructure of the composites, or, to be more specific, to the distribution, shape, and grain size of the Pt phase. This can be achieved better by means of a wet-chemical method. This work is under way. Theoretical analysis revealed that 10 times higher dielectric constants than found in monolithic PZT, can be obtained in near-percolative PZT/Pt composites. The calculated percolation threshold value, p_c~0.33, is in agreement with observations from SEM, indicating that the two phases have a comparable geometric shape. It is likely that the p_c value can be lowered by an improved control of the grain size and shape of the Pt phase.

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