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A quantitative analysis of the complex dielectric constants of binary mixtures of lead magnesium niobate–pyrochlore

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Abstract. The general effective media (GEM) equation is shown to quantitatively describe the complex dielectric constants of a binary mixture of lead magnesium niobate and pyrochlore as a function of the volume fraction, over the entire range of composition, and for all temperatures between −100 °C and 150 °C. The parameters of the GEM equation, the morphology parameters ϕ_c and t and the complex dielectric constants of the two components $(\epsilon_h'(T) + i\epsilon_h''(T))$ and $(\epsilon_l'(T) + i\epsilon_l''(T))$, are determined from the experimental data at each temperature. Within the accuracy of the data, ϕ_c and t are found to be temperature independent, which implies that the connectivity of the two components does not change with temperature.

1. Introduction

The behaviour of both the conductivity and the permittivity, or dielectric constant, of binary composites has been the subject of both experimental and theoretical studies for a very long time. An extensive review of the conductivity of inhomogeneous media had been given by Landauer (1978) and more recently by McLachlan *et al* (1990). Reviews of previous work on the dielectric constant have been given by van Beek (1967) and Payne and Cross (1977). Unfortunately, except in very special cases, no single theory that satisfactorily models the experimental results for either the conductivity or dielectric constant, over the entire composition range has previously existed.

Effective media theories (Meredith and Tobias 1962, Landauer 1978, McLachlan *et al* 1990), are always valid when there is only a very small volume fraction of one component. Theories such as Bruggeman's symmetric and asymmetric effective media theories are valid for the entire composition range for particular well specified geometries of both components. Mixing rules, such as those of Wiener (1904) and Lichtenecker (1926), which cover the entire composition range have also been extensively used, with some success.

In binary composites, where one component has a very high conductivity (σ_h) or dielectric constant (ϵ_h) with respect to the other component (σ_l or ϵ_l) and, in the volume fraction range where the σ_h or ϵ_h component has just or is about to form a continuous percolating network or infinite cluster, one can in principle use percolation theory. However, the main problem with using percolation theory in practical cases

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is that it is only strictly valid when σ_h/σ_l or ϵ_h/ϵ_l is infinite. Percolation theory is briefly reviewed by Landauer (1978), Zallen (1983) and McLachlan *et al* (1990) and in more detail by Stauffer (1985). Other wide ranging reviews on percolation and related phenomena are given in a fairly recent review book (Deutcher *et al* 1983) in which Straley (1983) discusses the limits of the validity of percolation theory when the ratio σ_h/σ_l is finite.

The principal objective of this paper is to show that is it possible to model the results for a mixture of lead magnesium niobate (PMN) (ϵ_h) and pyrochlore (PC) (ϵ_l) over the entire composition range, using the general effective media (GEM) equation (McLachlan 1987, McLachlan *et al* 1990). The equation was originally used to model conductivity results (McLachlan 1987, McLachlan *et al* 1990) but, as with any valid effective media theory, it also holds for gaseous diffusion (Perng and Altstetter 1986), permeability (McLachlan and White 1987, Deprez *et al* 1988) and permittivity (McLachlan 1989, McLachlan *et al* 1992). One of the previous papers on permittivity concerned emulsions, which are aerosol–OT (sodium di-2-ethylhexylsulfosuccinate)-coated conducting water droplets dispersed in oil (van Dijk 1985, Eiche *et al* 1986). The dielectric behaviour of the AOT-covered conducting water droplets is dominated by the imaginary component, the oil is virtually lossless and the emulsions can only be measured over for a limited volume fraction range ($\leqslant 0.3$) of droplets. McLachlan *et al* (1992) successfully modelled the results for the complex dielectric constant for carbon–polymer and conducting polymer–air (or water) composites, for small volume fractions of the conductor, at microwave frequencies using the GEM equation. In this work it was clearly shown that the GEM equation is better able to fit the data than the, widely used in this field, equation of Looyenga (1965), Kraszewski (1977), Grosse and Greffe (1979) and Bottcher (1945). In contrast to the two previous examples the present system spans the entire concentration range for a mixture where the PMN has a very high real dielectric constant (ϵ_h') and the pyrochlore a somewhat lower real component (ϵ_l'). Above about 0 °C, the transition temperature from ferroelectric to paraelectric for the PMN, both components have small lossy components (ϵ_h'' and ϵ_l''), while below 0 °C ϵ_h'' for PMN increases dramatically.

The experimental work of Chen and Harmer (1990) was carried out because the relaxor ferroelectric lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ designated PMN, exhibits excellent dielectric properties and a high electrostrictive coefficient, thus making the PMN system promising for various dielectric and electrostrictive applications. (Smolenskii and Agranovskaya 1960, Swartz *et al* 1984, Shrout and Hulliyal 1987, Uchino 1986.) One of the problems with PMN ceramics is the difficulty in producing a single-phase material consisting of only the perovskite structure. Improper processing results in the formation of a lead niobate-based pyrochlore phase. This pyrochlore phase has a much lower dielectric constant, and it is commonly believed that pyrochlore causes lower than optimum dielectric permittivity in PMN ceramics (Agranovskaya 1960, Shrout and Halliyal 1987, Ling *et al* 1989).

The objective of the paper by Chen and Harmer (1990) was to demonstrate the intrinsic effect of pyrochlore phase on the permittivity of PMN. The phase distribution and the dielectric properties of the two-phase mixture (PMN + pyrochlore) were investigated by examining the full range of compositions from nearly pure PMN to pure pyrochlore. The amount of pyrochlore within the PMN matrix was controlled by adjusting the Mg/Nb ratio in the starting composition. X-ray diffraction methods were used to determine the amount of pyrochlore present in each composition; the morphology and phase distribution was determined from SEM micrographs.

2. Theory

In using GEM equation to model the data the following parameters are used at each temperature: $\epsilon_h = \epsilon_h' + i\epsilon_h''$ for the dielectric constant of PMN, whose volume fraction is designated ϕ, ϕ_c the critical volume fraction where the PMN first forms a continuous percolating network or infinite cluster, and $\epsilon_l = \epsilon_l' + i\epsilon_l''$ for the dielectric constant of the pyrochlore whose volume fraction is $f = 1 - \phi$ and $f_c = 1 - \phi_c$. As in percolation theory ϕ_c and an exponent t characterize the microstructure of the composite. In terms of these parameters the GEM equation, written in terms of the dielectric constant is (McLachlan 1987),

$$(1-f)(\epsilon_h^{1/t} - \epsilon_m^{1/t})/\left\{\epsilon_h^{1/t} + [(f_c/1-f_c)]\epsilon_m^{1/t}\right\} + f\left(\epsilon_l^{1/t} - \epsilon_m^{1/t}\right)/\left\{\epsilon_l^{1/t} + [f_c/(1-f_c)]\epsilon_m^{1/t}\right\} = 0 \quad (1)$$

Here ϵ_m is the complex dielectric constant of the medium, mixture or composite.

The GEM equation reduces to the Bruggeman symmetric equation (Landauer 1978, McLachlan 1987, McLachlan *et al* 1990) when $t = 1$ and to the appropriate Bruggeman asymmetric equation (Meredith and Tobias 1962, Landauer 1978, McLachlan *et al* 1990) if $\epsilon_l = 0$ and $f_c = 1$ or when $\epsilon_h = \infty$ and $f_c = 0$. Although $\epsilon_l = 0$ is clearly unphysical, this situation is approximated when $\epsilon_h(\sigma_h) \gg \epsilon_l(\sigma_l)$ and $f_c = 1$. In the latter case the equation is better written in terms of the reciprocal ϵs. If $\epsilon_l = 0$ and $\phi_c \neq 0$ or if $\epsilon_h = \infty$ and $\phi_c \neq 1$ the GEM equation has the mathematical form of one of the percolation equations (McLachlan 1987, McLachlan *et al* 1990) and can be regarded as an interpolation formula between these two equations (McLachlan *et al* 1990).

Replacing $\epsilon_l^{1/t}$ in the GEM equation by $\epsilon_l^{1/t} = K_l^{1/t}\exp(i\theta_l/t)$, with $\epsilon_l = \epsilon_l' + i\epsilon_l'' = K_l\exp(i\theta_l)$, making a similar substitution for $\epsilon_h^{1/t}$ and then solving this expression for $\epsilon_m^{1/t}$ one obtains the actual equation used to fit the data in this paper:

$$\epsilon_m^{1/t} = K_m^{1/t}\exp[i\theta_m/t] = 1/2A\big[a(f)K_l^{1/t}(\exp i\theta_l/t) + b(f)K_h^{1/t}\exp(i\theta_h/t)) + \{[a(f)K_l^{1/t}\exp(i\theta_l/t) + b(f)K_h^{1/t}\exp(i\theta_h/t)]^2 + 4AK_l^{1/t}\exp(i\theta_l/t)K_h^{1/t}\exp(i\theta_h/t)\}^{1/2}\big] \quad (2)$$

where $a(f) = A(1-f) - f$, $b(f) = Af - (1-f)$ and $A = f_c/(1-f_c)$. The quantities ϵ_m' (calc) and ϵ_m'' (calc) are then obtained from

$$(\epsilon_m^{1/t})^t = K_m\exp[i\theta_m] = K_m\cos\theta_m + iK_m\sin\theta_m = \epsilon_m' + i\epsilon_m''.$$

Owing to the $\sigma^{1/t}$ or $\epsilon^{1/t}$ terms in the GEM equation, this is a non-linear interpolation equation in which a physically sensible root always has to be chosen. Therefore the Kramers–Kronig relations are probably violated.

The programme used for fitting the experimental data in terms of the relevant fixed and variable parameters minimized the quantity

$$\chi^2 = \sum_n \{C'[(\epsilon'(\text{calc}) - \epsilon'(\exp t))/0.01\epsilon'(\exp t)]^2 + C''[(\epsilon''(\text{calc}) - \epsilon''(\exp t)/0.01\epsilon''(\exp t)]^2\} \quad (3)$$

where the actual values of the weighting factors C' and C'' used are discussed below.

The quantity δ is $\sqrt{\chi^2/(n-p)}$ where n is the number of data points and p the number of variable parameters.

3. Results

The dielectric data as taken by Chen and Harmer (1990) consisted of quasi continuous curves of ϵ'_m and ϵ''_m versus T between about −150 °C and 150 °C for various volume fractions of pyrochlore. Data were extracted from the quasi continuous curves, obtained at 100 Hz, by linear extrapolation at the following fixed temperatures: −100, −75, −50, −37.5, −25, −12.5, 0, 12.5, 25, 37.5, 50, 100 and 150 °C. At each particular temperature, the data were fitted to the GEM equation. For temperatures above and including 0 °C only the parameters ϵ'_h, ϵ'_l, f_c and t were varied and C' was put equal to one with C'' equal to zero. This is because of the low values of and the large uncertainties in the ϵ''_m data. At and above 0 °C ϵ''_h and ϵ''_l were fixed at values obtained by extrapolating the extreme data points. Below 0 °C all six parameters were varied with $C' = 0.667$ and $C'' = 0.333$. This somewhat arbitrary choice was made as the ϵ'_m experimental data are considerably more accurate. Very similar fits and parameters are obtained if $C' = C'' = 0.5$. It was then observed that at all temperatures, except for −12.5, −25 and −37.5 °C, most of the values of ϕ_c and t lay within one standard deviation of the mean and that all lay within two standard deviations of the mean. As it is highly unlikely that ϕ_c and t will change their values over a small temperature range and then return to the same value, it was decided to fix the value of ϕ_c and t at these values, which are $\phi_c = 0.302 \pm 0.005$ and $t = 1.703 \pm 0.053$. The somewhat different values of ϕ_c and t lie in the temperature range where there is a sharp increase in ϵ''_m due to the paraelectric to ferroelectric phase transition. This contention is supported by the fact that the χ^2 and δ values are also considerably higher in this range. The results of the fits with $\phi_c = 0.302$ [$f_c = 0.698$] and $t = 1.703$ are given in table 1, where underlined numbers represent fixed parameters. The somewhat higher δ values at 0 °C and above are due to there being effectively only half the number of data points (i.e. only ϵ'_m).

Table 1. The temperature-dependent ϵ_{PC} and ϵ_{PMN} values obtained from the GEM equation.

Temp (°C)	ϵ'_{PC}	ϵ''_{PC}	ϵ'_{PMN}	ϵ''_{PMN}	δ
150	132.5	1.0	2591.1	4	3.98
125	136.0	1.0	3498.4	4	4.05
100	139.9	0.9	4892.8	4	4.11
50	148.7	1.0	10107	4	4.75
37.5	151.0	1.1	12015	5	4.92
25	153.3	1.3	14138	10	5.05
12.5	155.8	1.5	16412	25	5.25
0	157.8	1.9	18754	53	5.50
−12.5	162.2	1.400	20054	641.0	15.9
−25	163.9	1.085	16439	1315	10.5
−37.5	165.0	0.916	11237	928.5	5.46
−50	171.7	0.343	7940.7	647.6	2.98
−75	179.5	0.017	4468.7	345.5	2.61
−100	188.2	0.016	2689.7	194.1	2.70

Figure 1 shows the ϵ'_m data and GEM fits at 50 °C. Figures 2 and 3 show ϵ'_m and ϵ''_m data and fits at −25 and −50 °C respectively. It must be emphasized that figures 2 and 3 are simultaneous fits with the same microstructure parameters ϕ_c and t.

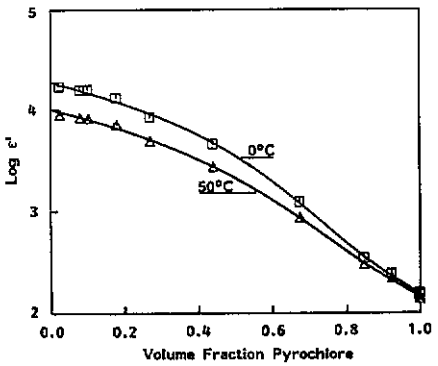

Figure 1. The experimental results, measured at 100 Hz, at 0 and 50 °C are plotted at □ and Δ respectively. The continuous curves are the GEM equation with $\phi = 0.302$ and 1.703 together with the values of ϵ_h and ϵ_l at 0 and 50 °C given in table 1.

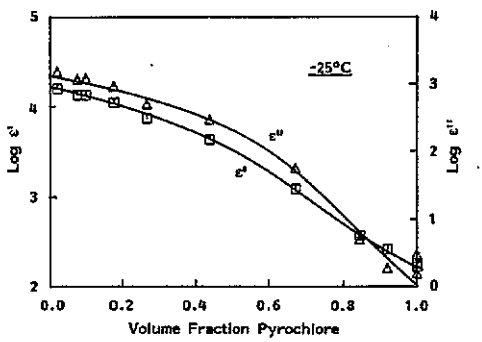

Figure 2. The experimental results, measured at 100 Hz, for ϵ' and ϵ'' at −25 °C are plotted as ■ and Δ respectively. The continuous curves are the GEM equation with $\phi = 0.302$, $t = 1.703$ together with the values of ϵ_h and ϵ_l at −25 °C given in table 1.

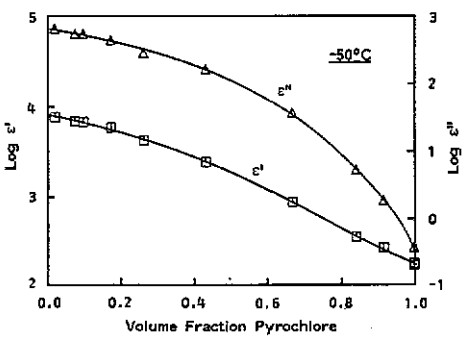

Figure 3. The experimental results, measured at 100 Hz, for ϵ' and ϵ'' at −50 °C are plotted as □ and Δ respectively. The continuous curves are the GEM equation with $\phi = 0.302$, $t = 1.703$ together with the values of ϵ_h and ϵ_l at −50 °C given in table 1.

Figures 4 and 5 shows some of the quasi continuous ϵ'_m and ϵ''_m experimental results for volume fractions of 0.174 and 0.669 pyrochlore as dotted lines, with the results from the GEM fits given as discrete points. If theoretical or phenomenological expressions for $\epsilon_h(T)$ and $\epsilon_l(T)$ exist it should be possible to determine the param-

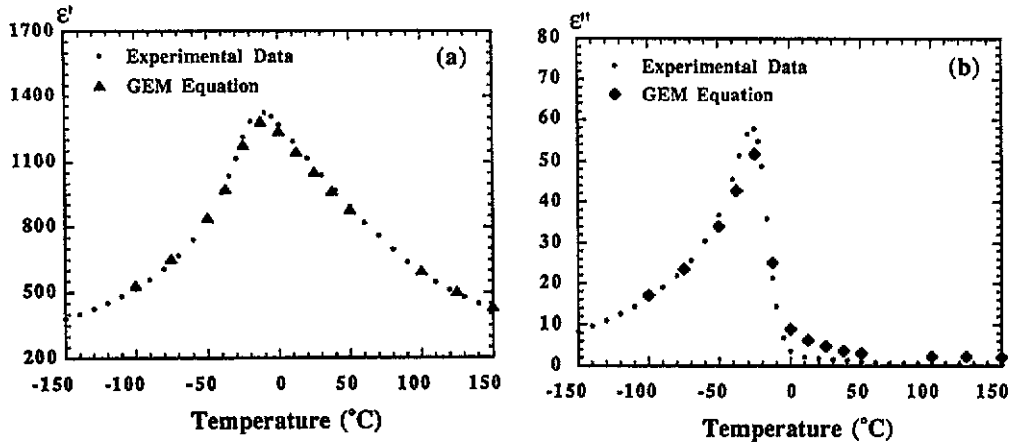

Figure 4. Quasi continuous plots of (*a*) ϵ'_m and (*b*) ϵ''_m, measured at 100 Hz, versus the temperature as dotted lines for $f = (1 - \phi)$ 0.174. The points (Δ) are the values calculated using $\phi = 0.302$, $t = 1.703$ and the values of ϵ_h and ϵ_l at the temperatures given in table 1.

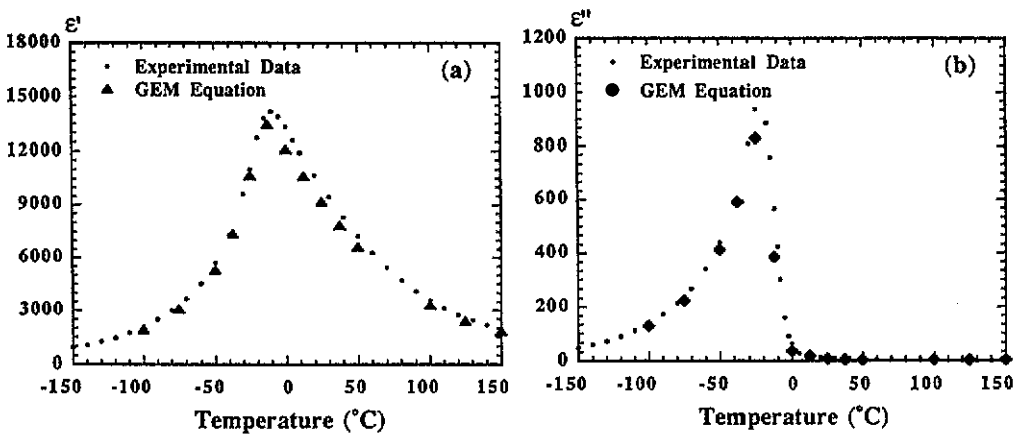

Figure 5. Quasi continuous plots of (*a*) ϵ'_m and (*b*) ϵ''_m, measured at 100 Hz, versus the temperature as dotted lines for $f = (1 - \phi) = 0.669$. The points (Δ) are the values calculated using $\phi_c = 0.302$, $t = 1.703$ and the values of ϵ_h and ϵ_l each temperature given in table 1.

eters of these theories by fitting the data using the GEM equation. The theoretical GEM curves could then be plotted as continuous lines.

As is clearly shown in figure 2, some of the inaccuracies in fitting result from the values of ϵ'' measured for the 0.999 and 1.0 pyrochlore samples often being higher than for that for a 0.911 volume fraction sample, which is against the general trend of the data. As there was no valid reason for discarding the pure pyrochlore data, all data were treated equally. This problem is also apparent in figure 5(*b*) where a lower value of ϵ'' for pure pyrochlore would give better agreement between the data and the fit. However as the main aim of this paper is to show the ability of the GEM equation to model binary dielectric data and not to study discrepancies peculiar to

the PMN–PC system this anomaly is merely accepted in this paper.

While the agreement in these figures is obviously not perfect, due to either experimental inaccuracies or the inadequacy of the GEM equation, these curves represent a considerable advance in the modelling and understanding of the dielectric constant over the entire composition range in this case (from pure PMN to pure pyrochlore). Compare for instance figures 1, 2 and 3 with figures 13 and 14 in Chen and Harmer (1990), and figures 7.6 in Chen (1991) where the data are also modelled using Wiener's (1904) and Lichtenecker's (1926) mixing rules.

The composition for which the experimental data deviated strongly from Wiener's (1904) rule was interpreted by Chen and Harmer (1990) as the PMN percolation threshold. Subsequent stereological analysis by Chen (1991) using SEM confirmed that the value of ϕ_c obtained by this method was approximately 0.17. This differs from the value of 0.302 deduced from the application of the GEM equation. One possible cause of this discrepancy could be that very thin layers of pyrochlore (undetectable by SEM) may exist between a fraction of the PMN grains. This would have the effect of raising the percolation threshold (ϕ_c) for the PMN grains significantly. However, there is clearly a need for additional work in this area.

4. Conclusion

The GEM equation is at present the best available equation to quantitatively model the dielectric properties over the entire mixture range from pure PMN to pure pyrochlore. Based on the results of this paper, the authors feel confident that it can also be used to analyse many other two-phase dielectric mixtures of this nature. Furthermore, due to its ability to model the dielectric constants of conductor in insulator mixtures, (McLachlan 1989, McLachlan *et al* 1992) the GEM equation can probably be used to analyse a wide variety of binary dielectric composites.

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