

Microstructure dependent thermophysical properties of Ni–Zn ferrite–BaTiO₃ functionally graded ceramics

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The purpose of this work was to examine the microstructure dependent thermophysical properties of a mixture of two materials. These were a dielectric powder based on BaTiO₃ and a magnetic Ni–Zn ferrite. The thermophysical properties of the ceramics were studied as a function of the dielectric volume fraction in the magnetic powder. For the thermal expansion coefficient, the experimental results were compared with different theoretical models used for functionally graded materials. The percolation theory was found to be a good model for Ni–Zn ferrite–BaTiO₃ functionally graded ceramics. Two percolation thresholds were found and a fourth-order polynome fitted all the experimental data of the thermomechanical properties. © 1999 Kluwer Academic Publishers

1. Introduction

Functionally graded materials (FGM) are a new class of materials [1] in which it is possible to have a changing value for a property, which cannot be obtained in any monolithic material. For this reason, several modelling studies have been performed in order to predict the thermophysical properties of FGM [2, 3]. The purposes of most of these studies, which have been carried out on ceramic–metal FGM [4–7], have been made to minimize the residual stresses in the material and to determine the composition of a crack-free FGM.

In this study, some mixed composition powders of Ni–Zn ferrite–BaTiO₃ were prepared by ball milling and then sintered. The thermophysical properties were measured and the microstructures were examined by scanning electron microscopy (SEM). Several models were considered to fit the experimental results. The calculations show a close dependence between microstructural and thermophysical properties. The percolation theory was found to be a good model for Ni–Zn ferrite–BaTiO₃ functionally graded materials.

1.1. Percolation theory

The complex microstructure of FGM can be described by the percolation theory [2]. In fact, with a small amount of a second phase in the host phase, the microstructure of the mixture is a dispersed grain structure, i.e. the second phase is discretely and uniformly dispersed within the matrix. With increasing amounts of the second phase, the second phase forms some aggregations, called clusters, of a definite size. This is an aggregated grain structure. Finally, the volume fraction of the second phase reaches a critical value, called the

percolation threshold. At this volume fraction, a continuous cluster is formed creating grain interconnection of the second phase.

One well known example of this theory is a two-phase mixture between an insulator and a conductor. With increasing volume fraction of the conductor within the insulator, the conductivity increases slowly at low volume fractions followed by an abrupt increase at the percolation threshold. The relationship between the conductivity, σ , and the volume fraction above the percolation threshold according to this theory is

$$\sigma \propto \sigma_m (V - V_c)^t$$

where t is the percolation exponent, σ_m the conductivity of the matrix, V the volume fraction of the minor phase, V_c the critical volume fraction or percolation threshold.

According to this equation, the conductivity, σ , is directly proportional to the conductivity of the matrix, σ_m , and the slope of the linear variation of the logarithm of the conductivity with the logarithm of the difference between the volume fraction of the minor phase, V , and the critical volume fraction, V_c , is equal to the percolation exponent, t .

2. Experimental procedure

2.1. Preparation of the mixed composition powders

The mixed composition powders were prepared by ball milling. The pure powders had a characteristic grain size (around 1 μm) and did not contain a binder. Thus 2 wt % binder, Mobil CERQ (based on wax microemulsion), was therefore added and the powders were ball

milled together in demineralized water for 4 h. The slurry was filtered and then dried at 100 °C in a drying oven. For characterization of the mixed composition samples, pellets and beams were pressed using 127 and 55 MPa, respectively. All specimens were sintered under the same conditions at 1120 °C for 3 h.

2.2. Characterization of the mixed composition ceramics

2.2.1. Microstructure

SEM was performed on a JSM-840 microscope on polished and gold-coated samples. The microstructure of the different compositions was examined using back scattered electrons to differentiate the two phases. The pictures obtained were analysed (PC-image, Forster Findlay) in order to calculate the fraction of each phase present. Thus, the ratio between the two phases of the samples was confirmed and an idea of the distribution of the grain in the microstructure for each phase in the ceramics was obtained.

2.2.2. Thermophysical properties

The thermophysical properties measured were the density using Archimedes' method in water, the thermal expansion coefficient, using dilatometry, the permittivity, using a capacitance bridge, and the elastic constants (Young's modulus, E , and Poisson's ratio, ν) using four-point bending test.

3. Results and discussions

3.1. Microstructure

As shown in Fig. 1a, for the micrograph of the sample containing 9 vol % dielectric in the mixed composition, the dielectric grains (white) are discretely and randomly dispersed in the ferrite matrix (grey). For specimens with 18 vol % dielectric, the dielectric grains start to form a network (Fig. 1b). Whereas Fig. 1c shows that the network is fully developed at 28 vol %. According to these observations and the percolation theory, the critical volume fraction is around 18 vol %. This critical volume fraction corresponds with the formation of a dielectric network. On these pictures an analysis of the amount of the two phases was made by transforming the light and dark phases into a binary image where the two networks can clearly be observed. From Fig. 2a–c, the percentage area of each of these phases was then calculated. The values obtained for the percentage area of the ferrite are lower than expected, while the values for the percentage area of the pores are higher. This is attributed to a difficulty in polishing the samples, due to the fact that the dielectric is harder than the ferrite. As a consequence of this, the ferrite particles are more easily removed from the surface during polishing. This is clearly demonstrated in Fig. 3, where large pores were observed. A representative micrograph of a mixed composition with high dielectric content was therefore difficult to obtain. On the binary image of 89 vol % dielectric (Fig. 4), the size of the ferrite clusters are larger than for the dielectric phase with 9 vol % composition.

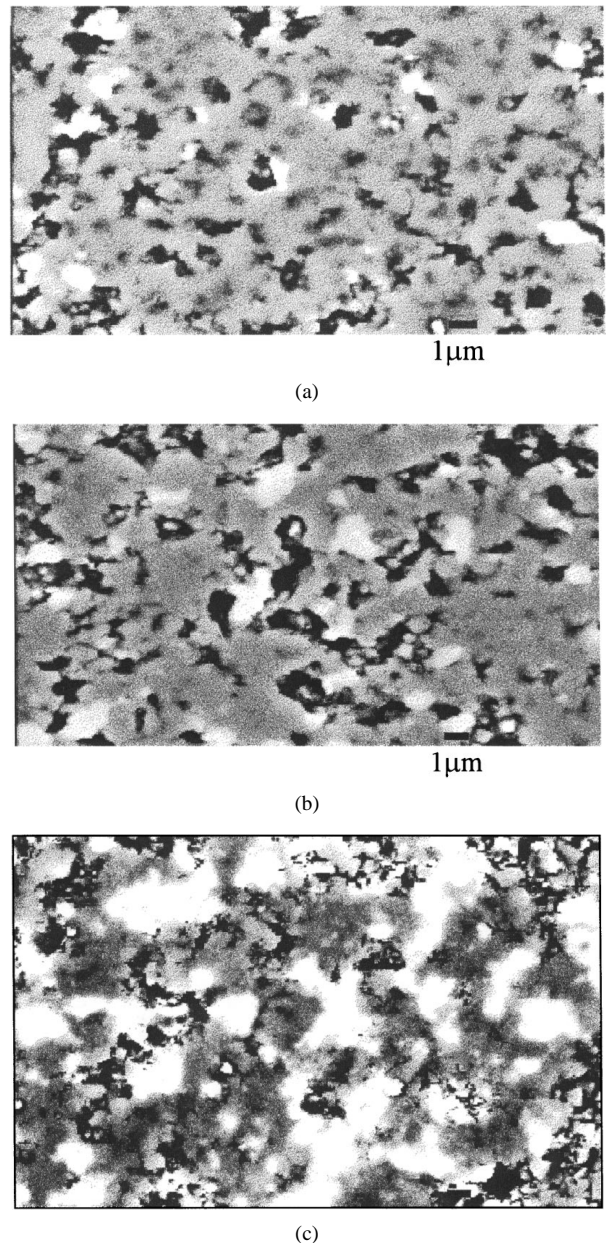
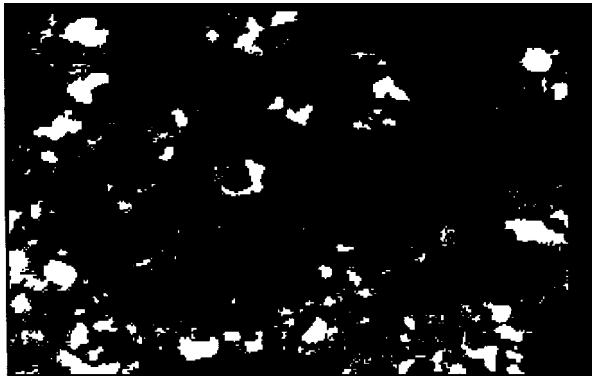


Figure 1 Microstructure of 9 vol % BaTiO₃ in A (a), 18 vol % (b) and 28 vol % (c). Scale bar is 1 μm.

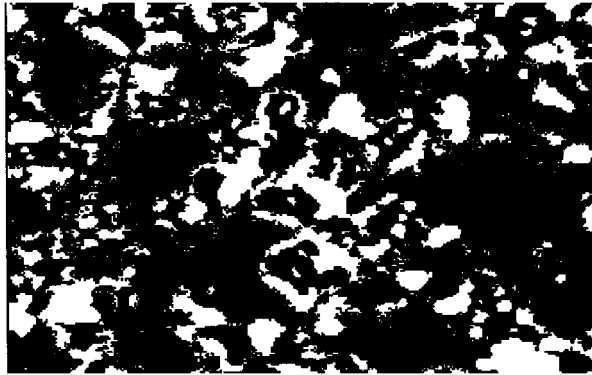
As we have observed, during formation of a dielectric network, a ferrite network is also formed. With increasing amount of dielectric, the amount of ferrite decreases and the ferrite network is reduced until we have only ferrite particles inside the dielectric matrix. There is therefore also a critical volume fraction of dielectric, beyond which a ferrite network no longer forms. At 89 vol %, the ferrite network does not exist anymore, therefore, the critical volume fraction is lower or equal to 89 vol % (Fig. 4).

3.2. Thermal expansion coefficient

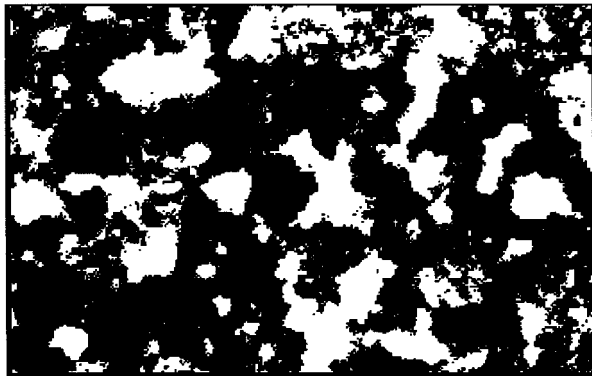
The thermal expansion coefficient was calculated for each composition by cooling from 1000 to 100 °C. The theoretical values predicted by the well known Voigt formula [2, 4], which is a simple arithmetic rule, were calculated. Comparisons between the experimental results and the calculations are shown in Fig. 5. The



(a)



(b)



(c)

Figure 2 Binary image of 9 vol % BaTiO₃ in A (a), 18 vol % (b) and 28 vol % (c).

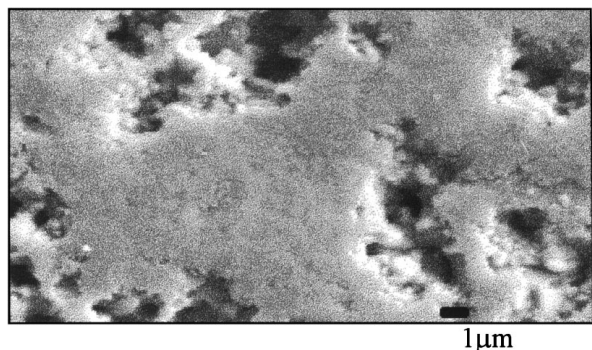


Figure 3 Microstructure of 89 vol % BaTiO₃ in A. Scale bar is 1 μm.

experimental results obtained for the mixed composition ceramics are below the calculated values. Classical micromechanical-based models, such as the Fahmi and Ragai [8], Turner [9] and Kerner [9] models, were used

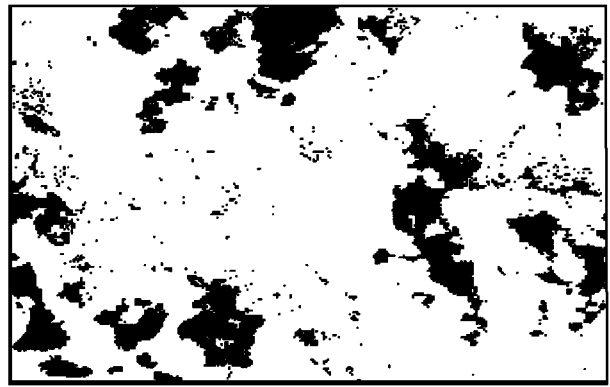


Figure 4 Binary image of 89 vol % BaTiO₃ in A.

to fit the data, but none of these fitted the experimental data well. In fact, it can be seen from Fig. 5 that for samples with up to 18 vol % dielectric in ferrite A, there is no variation of the thermal expansion coefficient. This confirms that the critical volume fraction, V_c , is around this value for the dielectric phase. Another change in the shape of the curve is visible at 89 vol % dielectric. This could indicate that the percolation threshold for the ferrite is around this value.

Considering the percolation theory, a large change in the properties is generally observed at the critical volume fraction, which is equivalent to the percolation threshold [10, 11]. Thus, mathematically an inflexion point should be found around this volume fraction. Therefore, a fourth-order polynome was chosen to fit the data (Fig. 5). The first inflexion point, i.e. the first change in properties, corresponds to the formation of the dielectric network. The critical volume fraction corresponding to this inflexion point therefore had a lower value than this inflexion point; whereas the second inflexion point, i.e. the second change in properties, corresponds to the formation of the ferrite network. The critical volume fraction then had a higher value than this inflexion point. The inflexion points calculated from the fourth-order equation are 31 and 62 vol %. This is in accordance with the micrographs. A linear variation of thermal expansion coefficient is furthermore observed between 18 and 89 vol % dielectric. Thus, the percolation threshold for the dielectric is about 18 and 89 vol % for the ferrite.

3.3. Electrical properties

The samples on which the electrical properties were studied were pellets with a diameter of 9 mm and a thickness of 1.5 mm. Both sides of the pellets were painted with silver paste and the capacitance, C , was measured. The permittivity value, ϵ'_r , was then calculated according to the formula [12]

$$\epsilon'_r = \frac{C \times t}{S \times \epsilon_0}$$

where t is the thickness, S the surface of the electrodes and ϵ_0 the permittivity in air.

The calculation of the inflexion points for the fourth-order equation found are 31 and 57 vol % (Fig. 6). This

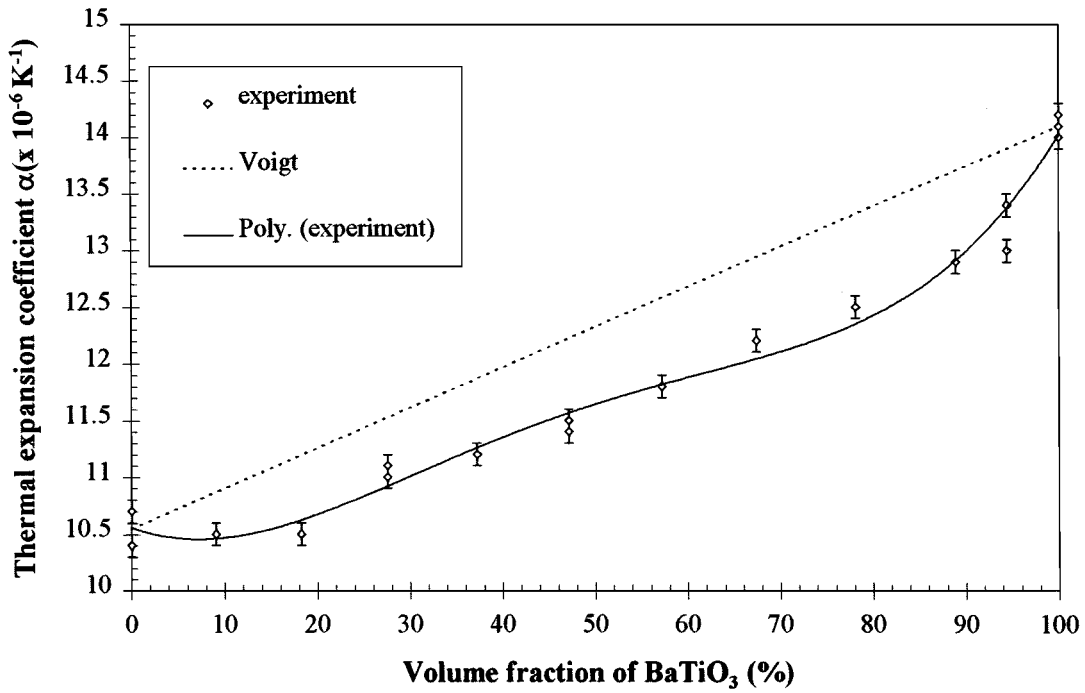


Figure 5 Variation of the thermal expansion coefficient with the volume fraction of BaTiO₃ in A.

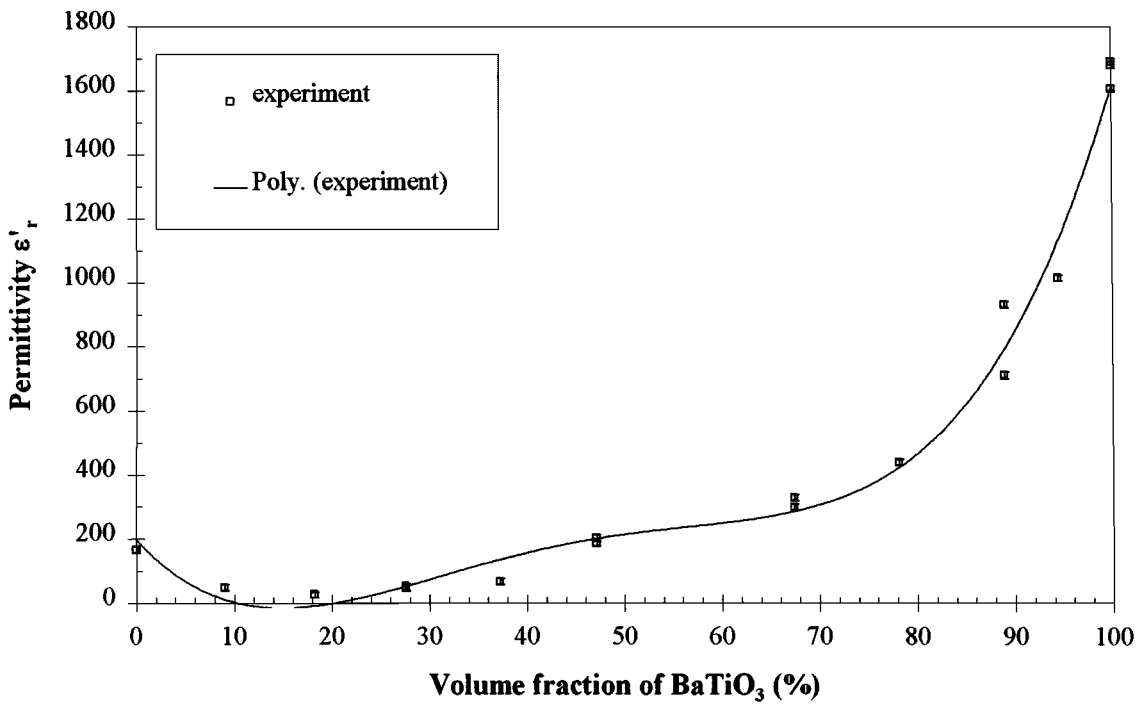


Figure 6 Logarithmic variation of permittivity with the volume fraction of BaTiO₃ in A.

is close to the value observed from the micrographs and from the thermal expansion coefficient curve. In this case, linear logarithmic variation of permittivity is also observed from 18 to 89 vol %. This corresponds to the mixing rule for a diphasic dielectric with a continuous connected phase [13]. The percolation theory was used to fit the data. The percolation exponent calculated, assuming that the critical volume fraction of the dielectric is 18 and 89 vol % for the ferrite, from Fig. 7 is equal to 1.45, which corresponds to a three-dimensional network [10, 11].

3.4. Elastic properties

The samples on which the elastic properties were measured were beams with dimensions of $30 \times 7 \times 2 \text{ mm}^3$. Each sample was polished on both sides to avoid twisting, and a strain gauge was glued onto the bottom surface in the centre of the sample. No significant variation of Poisson's ratio (the value for pure materials is 0.29, and it varies from 0.22 to 0.35 for mixed ceramics) was detected, whereas a large variation was observed for Young's modulus. The experimental results of the Young's modulus obtained with the ferrite A/(BaTiO₃)

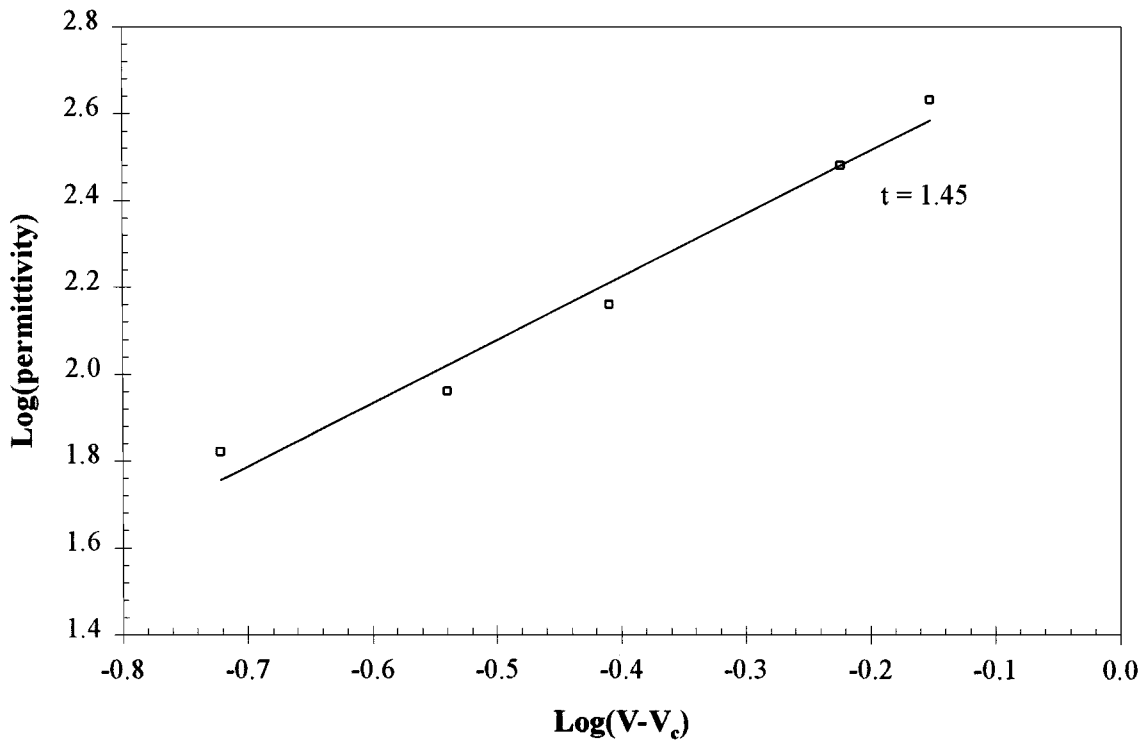


Figure 7 Log-log graph for calculation of the percolation exponent.

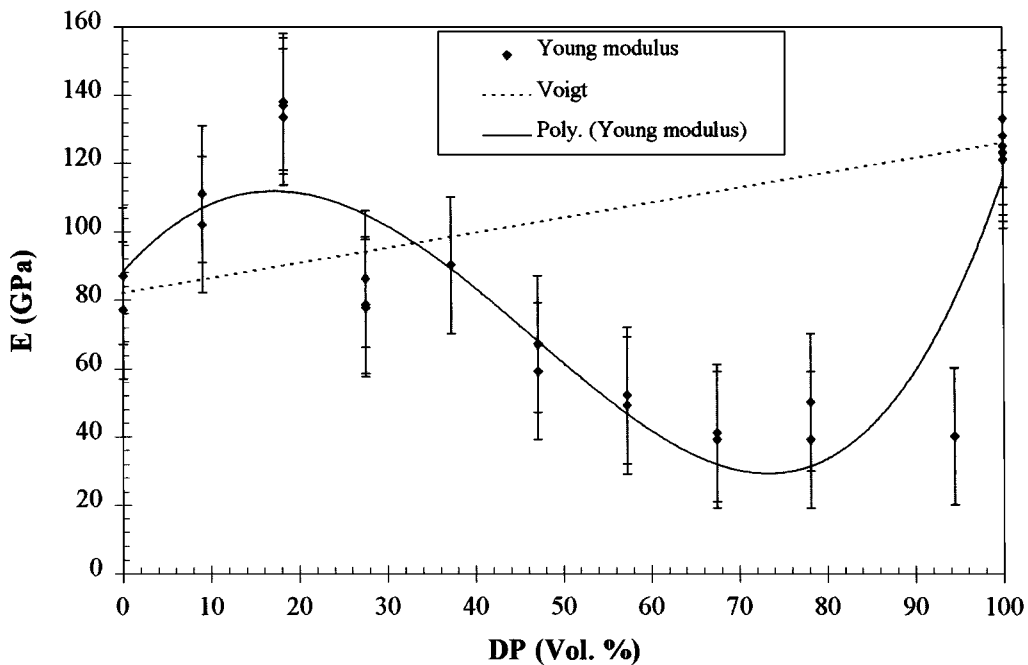


Figure 8 Variation of Young's modulus with the volume fraction of BaTiO₃ in A.

system are compared with the Voigt formula calculations in Fig. 8. It is also well known that the elastic properties depend on the porosity of the materials [14]. Therefore, the density of the samples was measured and compared with theoretical values (Fig. 9). As there is no significant variation of the porosity versus the volume fraction of dielectric, the influence on the elastic properties is small. However, the Young's modulus for 95 vol % is quite low compared with the theoretical curve, as seen from Fig. 8. According to Fig. 4, large pores can be observed for a high content of dielectric and this leads to a decrease in Young's modulus of the

sample. Two big changes are observed in Fig. 8: the first, corresponding to a maximum, is around 17 vol % and the second, corresponding to a minimum, is around 72 vol %. These changes are attributed to the percolation threshold of the dielectric and the ferrite, respectively. This is in accordance with previous data. The linear variation of Young's modulus between 18 and 89 vol % is, however, less evident than for the thermal expansion coefficient and for the permittivity. This can be attributed to the formation of pores during polishing, which induces a decrease in the elastic properties depending on the percentage porosity [14].

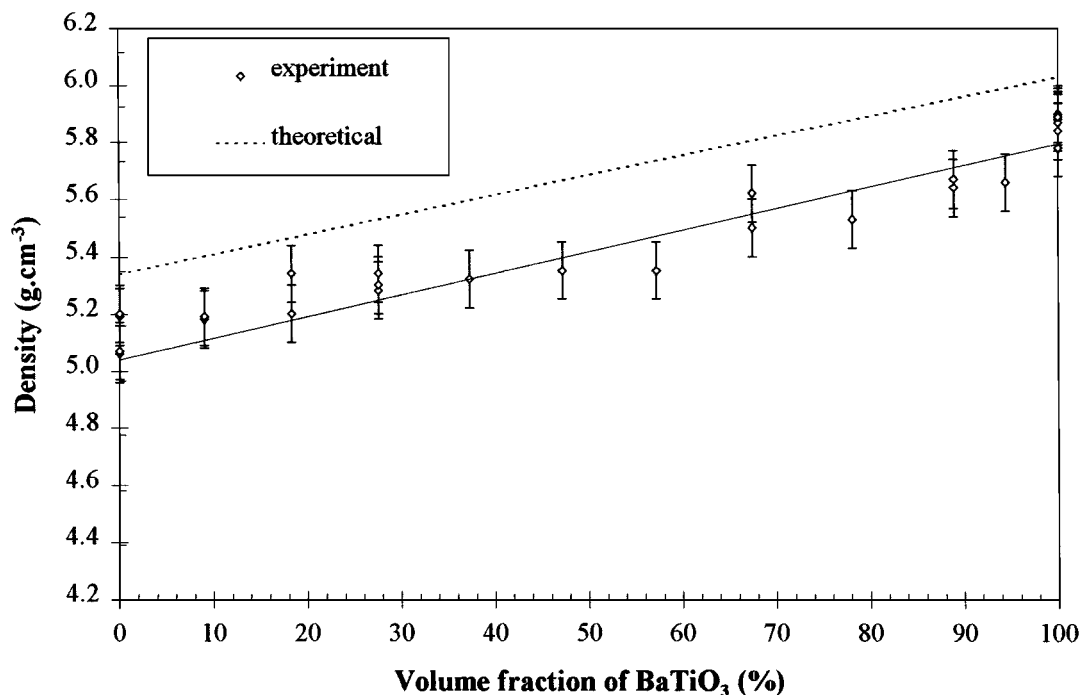


Figure 9 Variation of density with the volume fraction of BaTiO₃ in A.

4. Conclusions

The thermophysical properties, such as the thermal expansion coefficient, permittivity and Young's modulus, of the mixed composition samples show two variations with the dielectric volume fraction. A fourth-order polynome fits all the experimental data for these properties. No significant variation was found for the density and the Poisson's ratio.

Two percolation thresholds are observed in Ni-Zn ferrite-BaTiO₃ functionally graded ceramics: one corresponding to the formation of a dielectric network at 18 vol % and the other corresponding to the formation of a ferrite network at 89 vol %. The percolation exponent calculated from the dielectric measurements corresponds to a three-dimensional network. Crack free functionally graded ceramics were fabricated [15].

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