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Dielectric behaviours of multi-doped $BaTiO_3$/epoxy composites

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Abstract

Multi-doped $BaTiO_3$/epoxy composites with the different types of treated ceramic powders are under investigation. The ceramic/epoxy composite with the 900°C treated ceramic powder has the highest dielectric constant, while lower values for those with powders treated at higher temperatures. Longer grinding of 20 h can have different heat-treated composites with similar dielectric constants. Dielectric properties of these composites were measured as functions of temperature and frequency. The increase of dielectric loss at frequencies above 1 MHz is due to the mechanism of domain-wall motion. The composite with semi-conducting fillers can have a limited increase in dielectric constant, but a large increase in dielectric loss. To have the best dielectric properties of the multi-doped $BaTiO_3$/epoxy composite thick films for the printed wiring boards, the ceramic ratio need to be maximized without losing the board flexibility. A proper powder treatment is required to maximize the powder loading and performance. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$; Composites; Dielectric properties; Epoxy materials

1. Introduction

Most multichip modules (MCM's) fabricated today require decoupling capacitors to suppress the power distribution noise.[1,2] These surface mount capacitors are large in size, occupy space, and have large parasitic capacitance. The integration of capacitors with other passive components on a substrate especially on a printed wiring board (PWB) are being considered for use in MCM applications to reduce substrate size and to improve functionality and manufacturing cost.

Materials with relative dielectric constant in the range of 25–170 are required for advanced decoupling capacitors. Composite materials consisting of ferroelectric ceramics and polymers have aroused much attention for advanced capacitors because their properties can be adjusted by changing the fractions of the constituents. Epoxy is a suitable polymer for its compatibility with PWB's. Furthermore, epoxy materials are not attacked by the electroless plating solution of the capacitor electrodes. Barium titanate ($BaTiO_3$), a well-known ferroelectric material, has a high dielectric constant (K) around 6000 at a fine grain size of ~1 μm, and of 1500–2000 at a coarse grain size.[3,4] The dielectric constant of $BaTiO_3$ at the Curie point of ~120°C can reach a peak value as high as 10,000, but decrease as the temperature decreases. Chemical additives or so-called shifters have been applied to $BaTiO_3$ to move the Curie peak value towards room temperature to improve the dielectric constant, and to smooth the Curie peak to obtain a lower temperature coefficient of the dielectric constant. Isovalent and aliovalent shifters can either decrease or increase the Curie point and change the dielectric constant. Strontium (Sr)-doped and lanthanum (La)-doped $BaTiO_3$ have the dielectric constants of 10,000–19,000, at room temperature.[5] For most barrier-layer capacitors, the effective permittivity is 10,000–20,000 and up to 50,000 for $SrTiO_3$-based and $BaTiO_3$-based electroceramics, respectively.[6] High dielectric constants of 50,000–100,000 were reported for the barrier-layer $BaTiO_3$-based materials.[7]

Dielectric properties of $BaTiO_3$ ceramics are highly dependent upon the grain size, phase content of the ceramic body and also the type of dopants used. For

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$BaTiO_3$ powder, its behavior also is related to the particle size, phase content, and the dopants added. Cubic $BaTiO_3$ (c-$BaTiO_3$) powder transforms to the tetragonal phase (*t*-$BaTiO_3$) if its size is larger than 30 nm.[8] Powder with a size of 40–80 nm contains a single domain. Crystallites with a size larger than 80 nm will be multidomain t-BaTiO3.[9] Arlt[10] reported that the increase of the permittivity is possibly caused by a summation of the domain size and the stress effect. He also mentioned that the width of ferroelectric 90° domains decreases proportional to the square root of the grain diameter for grains with size <10 μm. The removal of grain boundaries, i.e. elimination of constrained forces from neighboring grains and a drop in domain density as the particle size decreases, may reduce the dielectric constant of the $BaTiO_3$ powders. With increasing particle size, unsintered powder eventually becomes a ceramic-like body and possesses similar properties as the ceramics.[11] Therefore, ceramics and powders of $BaTiO_3$ can show a different dielectric behavior, depending on the particle size.

In this study, different ceramic/polymer composite thick films were fabricated by screen printing. These films, composed of a laboratory-synthesized multi-doped $BaTiO_3$ filler and an epoxy matrix, were studied by varying the filler amount and filler properties. The variation of dielectric properties of these composite thick films with testing temperature and frequency was measured.

2. Experimental procedure

Multi-doped $BaTiO_3$ ceramic powder was prepared by a polymeric route in order to have uniformly distributed components. La, Mg, and Sr ratios in the multi-doped $BaTiO_3$ are in the range of 1–5, 1–5 and 10–30%, respectively. In this polymeric method, metal acetates and nitrates in deionized water were mixed with titanium-*n*-butoxide in ethylene glycol to form a clear solution. This clear solution was added with the solution of citric acid and ethylene glycol to form a new clear solution. Followed by homogenization, chelation, and drying, the polymeric intermediate was pyrolyzed at 900°C to obtain the required ceramic powder. After ball milling, drying, and sieving, the calcined and multi-doped $BaTiO_3$ powder was ready for the following studies.

Different treatments were conducted on the calcined powder to change its particle size. Powders fired at 900, 1000, 1200, 1300 and 1400°C for 1 h were ball milled for 1, 4, 10 and 20 h. Powders fired at 1400°C for 1, 5, and 10 h were ball milled for 4 h. Different amounts of the prepared powder were mixed with a solution of epoxy (Bisphenol F), curing agent (dicyandiamide) and catalyst (2-methylimidazole) at volume fractions of 10, 20, 30 and 40 to form the screen-printing ink. The thick films were prepared on copper foils by screen-printing. A maximum of 40 vol.% $BaTiO_3$ in the epoxy could be obtained. A higher ceramic volume fraction formed a thick film with poor quality. To measure the dielectric properties as a function of frequency, slurry-cast bulk samples instead of screen-printed thick films were chosen due to the test failure at high frequency (in MHz range) for the thick films with copper foil as a substrate.

To understand the semi-conducting and barrier-layer effects of multi-doped $BaTiO_3$ powder on the dielectric properties of the ceramic/polymer thick films, the calcined $BaTiO_3$ powder was treated at 1300°C for 1 h under vacuum to become semi-conductive. The ground semi-conducting powder was oxidized at 500°C for 1 h to form a barrier-layer powder with their outer surface oxidized. The ground semi-conducting powders also were coated with silica using a solution of tetraethyl orthosilicate. These coated powders were heat treated at 500 and 1000°C for 1 h to form an insulating silica shell. These treated powders are labeled by R-1300, R-1300-500, R-1300-S-500, and R-1300-S-1000, where R represents the reduction under vacuum, S the SiO_2 and the numbers the temperatures, and were used for the preparation of ferroelectric/epoxy composites. A 1300°C heat-treated powder was prepared for comparison.

Porosity was obtained by comparing the measured density with the theoretical density. The surface morphology of the films was examined by a scanning electron microscope (SEM, Hitachi model S-3500H). Their relative dielectric constants and loss tangents were measured from 25 to 90°C by employing a HP 4285A LCR meter (Hewlett-Packard, USA) in the frequency range of 75 kHz–32 MHz at an average voltage of 1 V.

3. Results and discussion

3.1. Properties of ferroelectric/epoxy composite thick films with un-treated fillers

The calcined and ground $BaTiO_3$ powder was mixed with epoxy to form composites with 10, 20, 30 and 40 vol.% ceramic filler. The dielectric constants of these screen-printed films are shown in Fig. 1. The dielectric constants measured at 100 kHz are 13, 14, 26.5 and 44 for 10, 20, 30 and 40% composites, respectively. The dielectric losses are 0.021, 0.028, 0.027 and 0.028 for these thick films. Sintered $BaTiO_3$ has the highest dielectric constant of ~25,000 and dielectric loss of 0.3 at 25°C. For epoxy matrix, relative dielectric constant remains ~5.7 and dielectric loss is 0.018 at 25°C. The relative dielectric constant of epoxy is not a strong function of temperature in the range of 25–90°C, but dielectric loss decreases with increasing temperature. PWB-compatible ceramic/polymer composites have been studied.[1,2] Chahal et al.[1] reported dielectric constants of 39 and 22 for 55 vol.% ceramic/polyacrylonitrile and for the 50% ceramic/polynorbornene composites, respectively. Bhattacharya et al.[2] reported dielectric constants of 9 and 34 for two kinds of PWB-compatible composites at a filler loading of 21 and 46%, respectively. The dielectric constant of 44 at a filler loading of 40% in this study thus compares favorably with these literature data. Fig. 2a–d shows the surface morphology of the 10, 20, 30 and 40% slurry-cast composites, respectively. From microstructural examination of bulk samples, it was found that internal pores start to appear when the filler volume ratio reaches 20%. Interfacial pores between ceramic particle and epoxy also occur in the 40% composite.

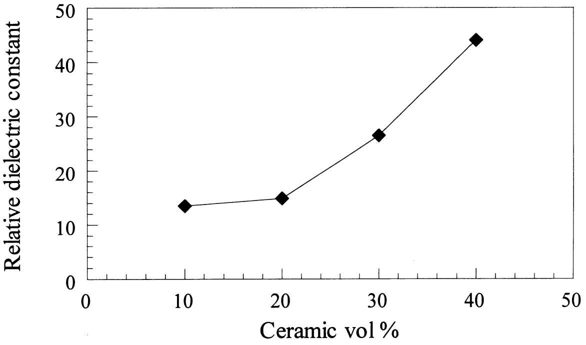

Fig. 1. Relative dielectric constants of the ferroelectric/polymer composite thick films, measured at 25°C and 100 kHz, as a function of the volume fraction of the ferroelectric phase.

3.2. *Properties of 30 vol.% ferroelectric/epoxy thick films with heat-treated fillers*

3.2.1. *Effect of heat treatment temperature*

The dielectric properties of the 30% ferroelectric/epoxy composite thick films with the multi-doped $BaTiO_3$ fillers heat treated at 900–1400°C for 1 h are demonstrated in Fig. 3. While the dielectric constant of the sintered multi-doped $BaTiO_3$ decreases with temperature,[12] it is independent of temperature for the composite thick film (Fig. 3a). The independent behavior is also similar to that of epoxy matrix.[12] The dielectric loss of the thick film is less than 0.03 and decreases with increasing test temperature (Fig. 3b), which is close to that of the epoxy matrix but ten time less than that of sintered multi-doped BaTiO3.[12] Basically, the temperature dependence of the dielectric behaviors of the composite thick film is similar

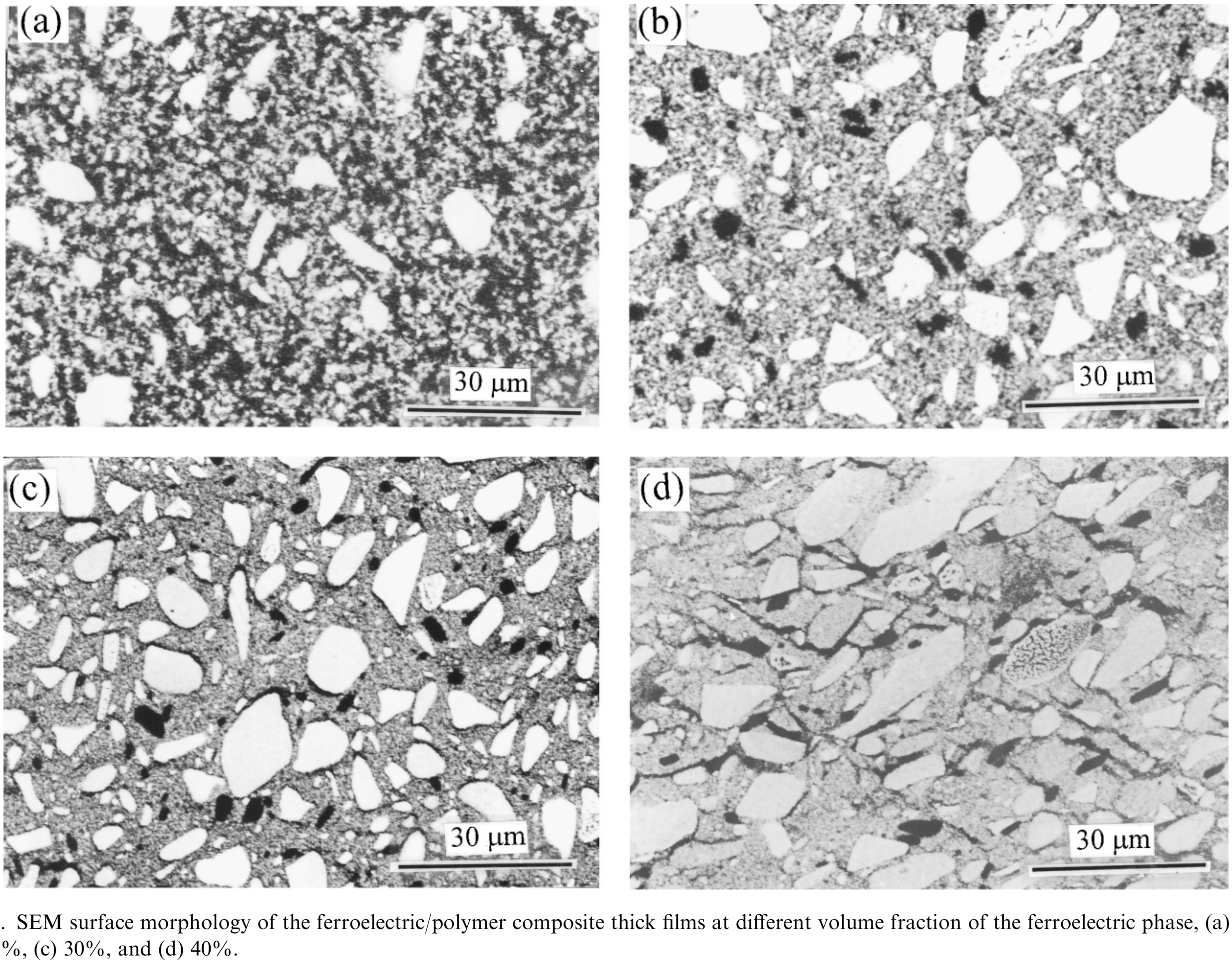

Fig. 2. SEM surface morphology of the ferroelectric/polymer composite thick films at different volume fraction of the ferroelectric phase, (a) 10%, (b) 20%, (c) 30%, and (d) 40%.

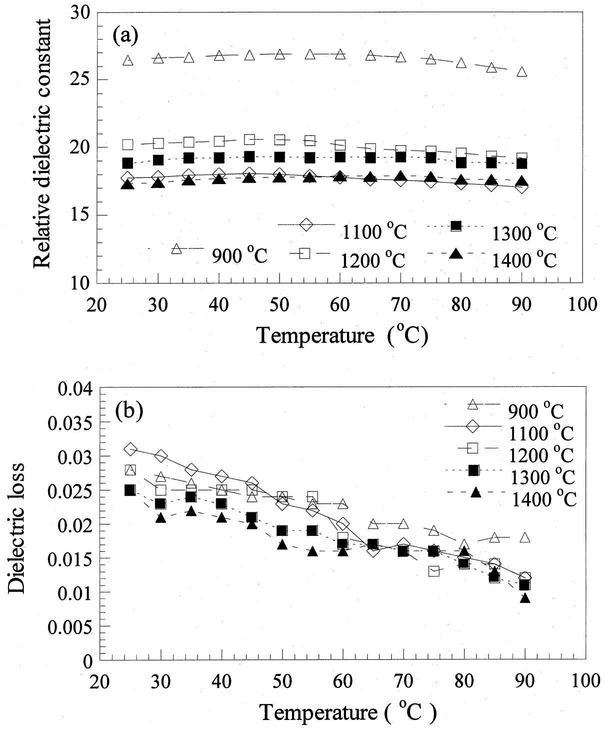

Fig. 3. Variations of (a) relative dielectric constant and (b) dielectric loss of the 30 vol.% ferroelectric/polymer composite thick films with test temperatures for multi-doped ferroelectric fillers heat treated at 900–1400°C for 1 h followed by 4 h milling. Measured at 100 kHz.

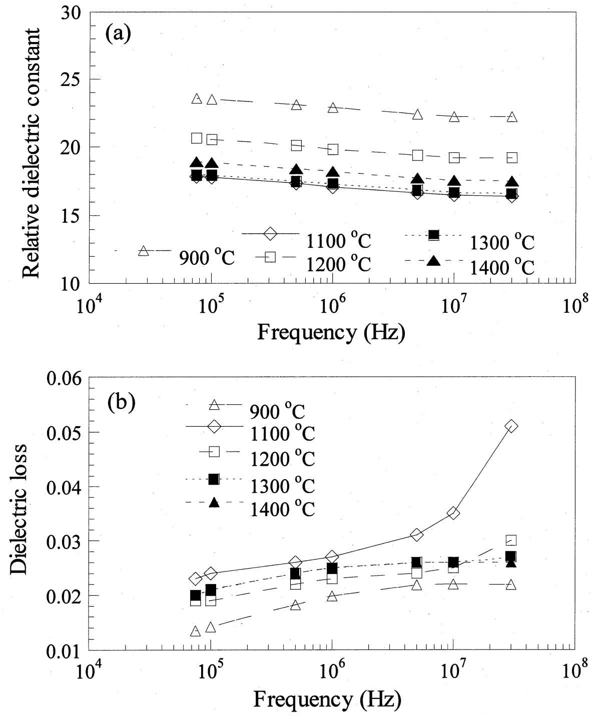

Fig. 4. Frequency dependence of (a) relative dielectric constant and (b) dielectric loss for the 30 vol.% ferroelectric/polymer bulk composites on ceramic fillers heat treated at 900–1400°C for 1 h followed by 4 h milling. Measured at 25 °C.

to those of epoxy. The second phase of the multi-doped $BaTiO_3$ is surrounded by the epoxy. The epoxy is contact with the electrodes to induce the bound charges on the electrodes. For the above reason, the temperature effect on the relative dielectric properties of composite thick films is similar to that of epoxy only.

The frequency dependence of dielectric properties for the composites in the bulk form with different heat-treated ceramic fillers is shown in Fig. 4. The slight difference in dielectric constants between Figs. 3 and 4 is attributed to the different composite forms: one is in the thick film and the other is in the bulk form.

In the films obtained by the screen printing, trapped bubbles can escape out of slurry. In the freely cast bulk form the air bubbles remain trapped in the specimen and this leads to lower dielectric constants. The dielectric constant decreases slightly and dielectric loss increases slightly as the test frequency increases. It has been reported that the loss tangent values (tan δ) are high at low frequencies up to 1 kHz and are very low at frequencies from 10 kHz to 1 MHz. The dielectric losses increase again at frequencies higher than 1 MHz. The behavior of dielectric loss at low frequencies below 1 kHz is attributed to domain motion and inhomogeneous conductivity, and that at high frequencies above 1 MHz to domain-wall motion.[12] The increase of the loss tangent with frequencies in Fig. 4 can be related to the mechanism of domain-wall motion. The higher dielectric loss for the 1100°C-heat treated sample is due to its higher porosity of 0.093. The higher porosity causes a sharp increase in dielectric loss at high frequency.

3.2.2. *Effect of holding time at 1400°C*

The purpose of firing multi-doped $BaTiO_3$ powder at 1400°C for 1, 5 and 10 h is to increase grain size. To facilitate screen-printing, the heat treated powders are milled to break the aggregates before preparing the printing ink. Fig. 5 shows the dielectric properties of the 30%-ferroelectric composites with the ceramic fillers heat treated at 1400°C for different duration of 1, 5 and 10 h. The dielectric constants are 17.2, 17.2 and 18.5 for the duration of 1, 5 and 10 h. Basically, the high temperature duration to enhance grain growth is not a major factor to increase the dielectric constant, as we compare with Fig. 1 of the volume-ratio effect. These ferroelectric/epoxy composites still demonstrate an independence of dielectric constant upon temperature. Their dielectric loss is less than 0.03 and decreases with increasing test temperature. The frequency dependence of dielectric properties for these composites is similar to those in Fig. 4.

3.2.3. *Grinding effect at different heat treatment temperatures*

The temperature dependence of dielectric constants for the composite thick films with ceramic fillers milled for different duration after heat treated at 900, 1100, 1300 and 1400°C for 1 h is shown in Fig. 6a–d, respectively. Their dielectric constants are not a strong function of temperature. The behavior of dielectric loss is similar to the results in Fig. 3. The influence of the milling time on the dielectric constant (measured at 25°C) is plotted in Fig. 7, demonstrating that there is an optimized particle size at different heat treatment temperatures to reach an optimized dielectric constant. The slight deviation of the data point for 1100°C at 4-h milling relates to complex factors such as surface energy and shape of ceramic powder, mixing of ceramic and epoxy, viscosity of the screen-printing slurry etc.

The frequency dependence of dielectric constants of the bulk composite samples with ceramic fillers milled for different duration after heat treated at 900–1400°C for 1 h is similar to those in Fig. 4, i.e. dielectric constants

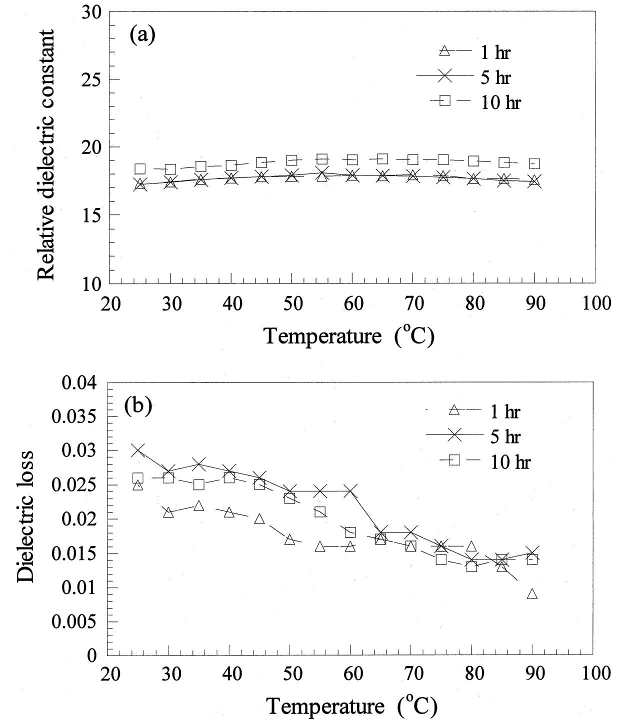

Fig. 5. Temperature dependence of (a) relative dielectric constant and (b) dielectric loss of the 30%-ferroelectric composite thick films on the ceramic fillers heat treated at 1400°C for different duration of 1, 5 and 10 h followed by 4 h milling. Measured at 100 kHz.

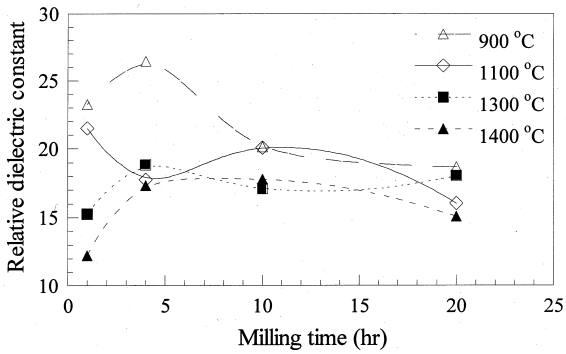

Fig. 7. The dependence of relative dielectric constants of the 30%-ferroelectric composite films on the ceramic fillers which were heated at 900–1400°C for 1 h followed by different milling times. Measured at 25°C and 100 kHz.

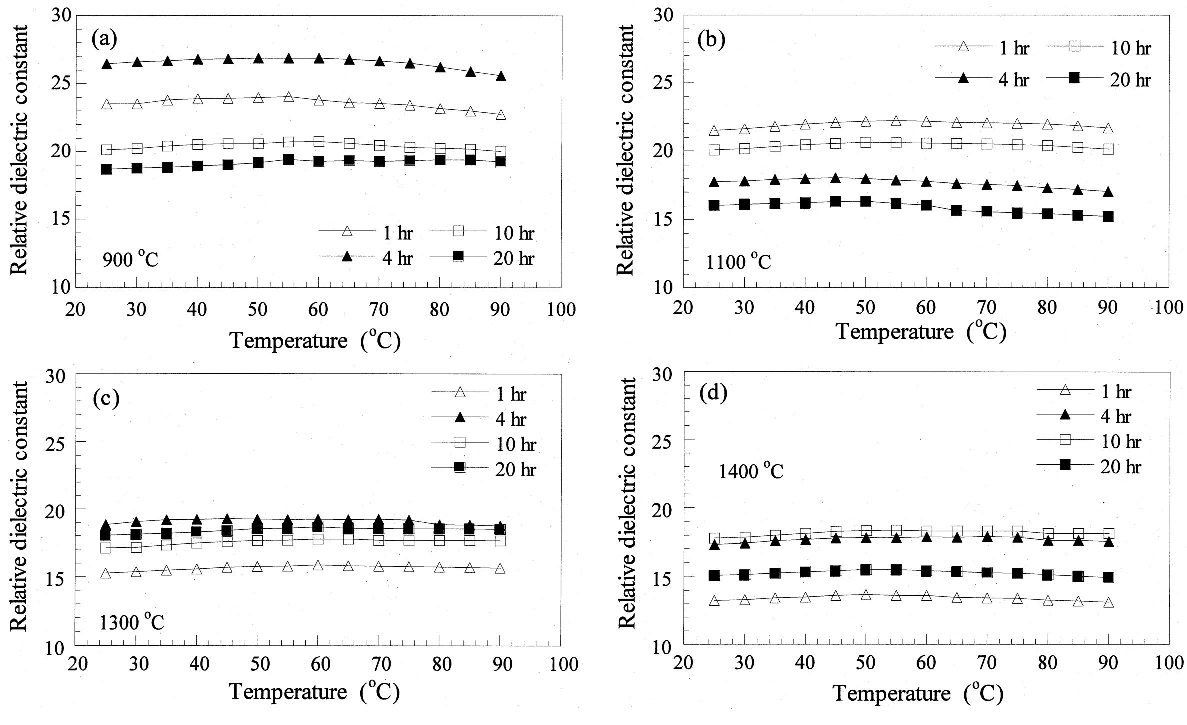

Fig. 6. Temperature dependence of relative dielectric constants of the 30%-ferroelectric composite thick films with ceramic fillers milled at different duration of 1, 4, 10 and 20 h, after heat treated at (a) 900°C, (b) 1100°C, (c) 1300°C, and (d) 1400°C for 1 h. Measured at 100 kHz.

slightly decrease as frequency increases. From the data measured at 100 kHz, the influence of grinding time on the dielectric constant for the samples in the bulk form is shown in Fig. 8, as compared to Fig. 7 for samples in the thick-film form. From both figures, we can find that the dielectric properties approach similar values at long milling time, no matter how high the ceramic powders are heat treated. The frequency dependence of dielectric loss is shown in Fig. 9. The dielectric losses reach saturated values for bulk samples with fillers heat treated at 900°C (Fig. 9a) and 1400°C (Fig. 9d), while they diverge for those heat treated at 1100°C (Fig. 9b) and 1300°C (Fig. 9c). To explain the above behavior, the variation of porosity with milling time was measured and plotted in Fig. 10. The low porosity after 4 h grinding usually corresponds to a lower dielectric loss. The bulk composites with high porosity show a continuous increase in dielectric loss at high frequencies, except for the 1400°C heat-treated composite. The discrepancy for 1400°C heat-treated composite remains further investigation.

3.2.4. *Effect of semi-conducting and barrier-layer treatments*

The variation of dielectric properties with temperature is shown in Fig. 11 for ferroelectric/epoxy composites with five kinds of ceramic fillers: 1300, R-1300, R-1300-500, R-1300-S-500, and R-1300-S-1000. The R-1300

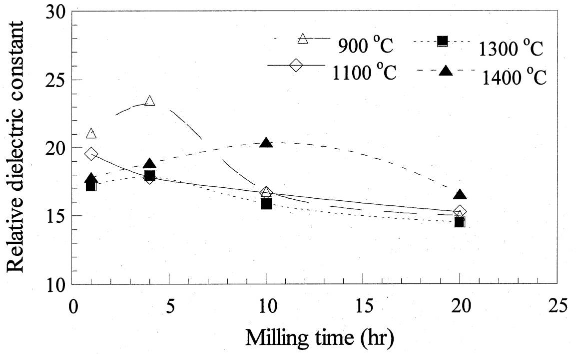

Fig. 8. The dependence of relative dielectric constants of the 30%-ferroelectric bulk composite with the ceramic fillers heat treated at 900–1400°C for 1 h followed by different milling times. Measured at 25°C and 100 kHz.

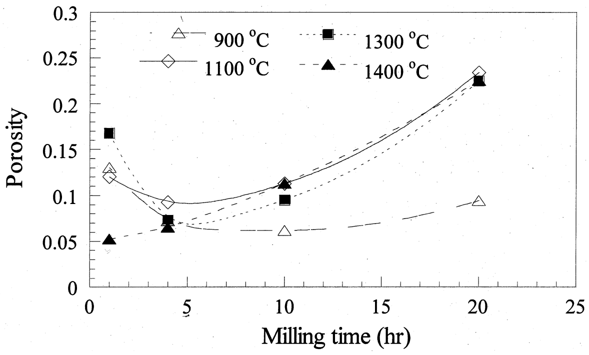

Fig. 10. Dependence of porosity of the 30%-ferroelectric bulk composites with the ceramic fillers heat treated at 900–1400°C for 1 h followed by different milling times. Measured at 25°C and 100 kHz.

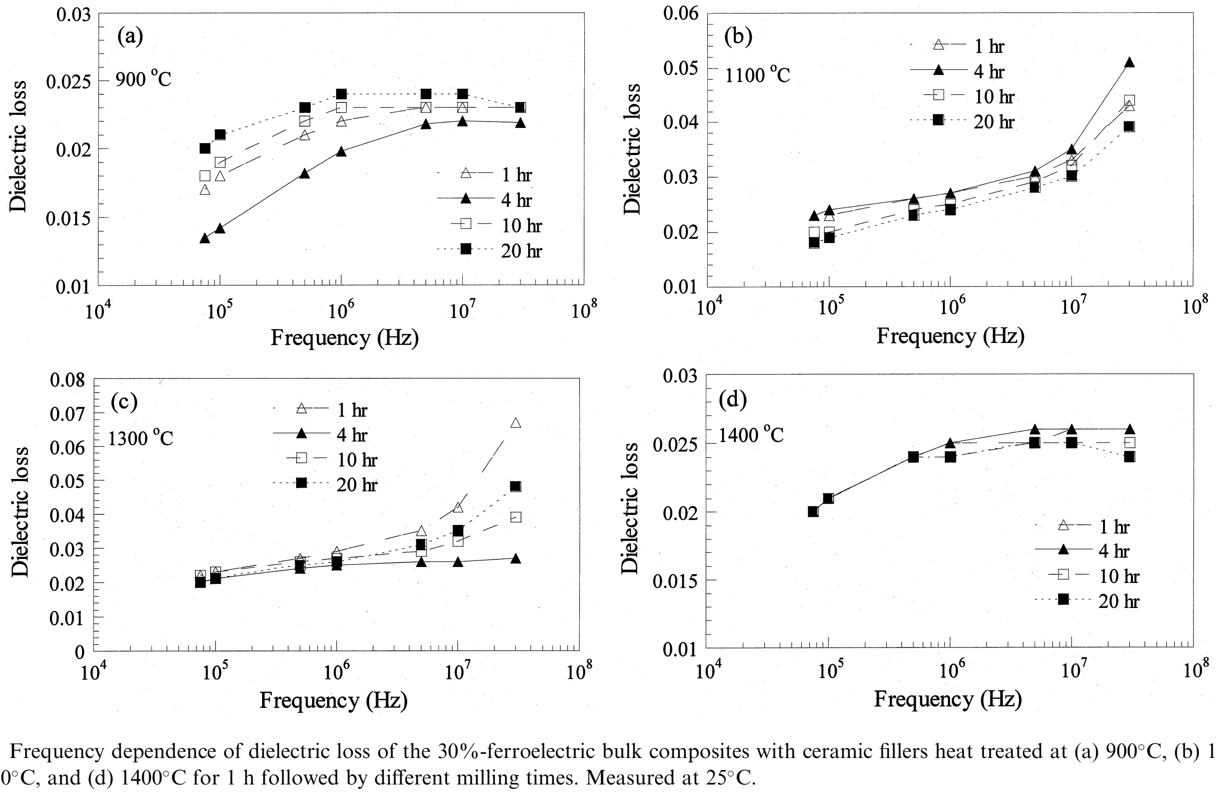

Fig. 9. Frequency dependence of dielectric loss of the 30%-ferroelectric bulk composites with ceramic fillers heat treated at (a) 900°C, (b) 1100°C, (c) 1300°C, and (d) 1400°C for 1 h followed by different milling times. Measured at 25°C.

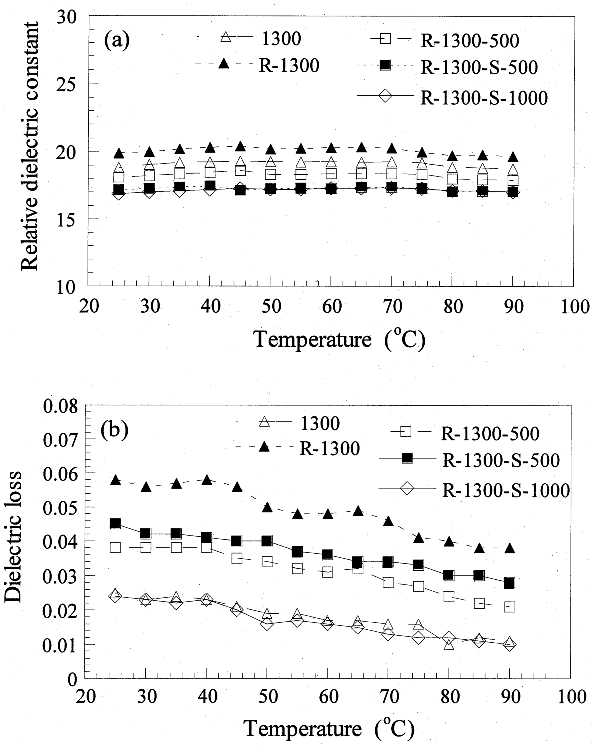

Fig. 11. Variation of (a) relative dielectric constant and (b) dielectric loss of 30 vol.% ferroelectric/epoxy composite thick films with test temperatures for five kinds of treated ceramic fillers: 1300, R-1300, R-1300-500, R-1300-S-500, and R-1300-S-1000. Measured at 100 kHz.

composite shows a higher dielectric constant and loss. The silica-coated composites have lower dielectric constants and losses. The frequency effect of these treated composites on dielectric properties is similar to those in Fig. 4, i.e. dielectric constant decreases slightly with frequency and dielectric loss increases slightly with frequency. The only exception is the sharp decrease of dielectric loss of the R-1300 composite with frequency. The loss mechanism for the composite with the semi-conducting powders can be the inhomogeneous conductivity,[13] which causes the dielectric loss decreases at frequencies above 1 MHz.

4. Conclusions

Multi-doped $BaTiO_3$/epoxy composites with the different types of treated ceramic powders have been investigated and discussed. These treatments include 900–1400°C firing for different duration followed by grinding, vacuum firing to make $BaTiO_3$ powder semi-conducting, and forming an insulating shell by coating and oxidizing the semi-conducting powder. The composite with the 900°C treated ceramic filler has the highest dielectric constant, while the values were lower for those with ceramic powders treated at higher temperatures. Longer grinding can have finer ceramic powder. Longer grinding also causes the dielectric properties of the different treated composites reaching a similar value. The dielectric constants of the composites remain constant, while dielectric losses decrease with temperatures. The influence of the test frequency between 75 kHz and 32 MHz was limited, but an increase of dielectric loss with increasing frequency is observed, probably due to the mechanism of domain-wall motion. The composite with semi-conducting fillers can have a limited increase in dielectric constant, but a higher increase in dielectric loss. Its dielectric loss decreases with increasing frequency due to the inhomogeneous conductivity.

Increasing the amount of ferroelectric ceramic in a ceramic/polymer composite can increase dielectric constant quickly. Modifying filler properties by different treatments can further adjust dielectric properties of composites to an optimized condition. To have the best dielectric properties of the multi-doped $BaTiO_3$/epoxy composites for the printed wiring boards, the ceramic ratio need to be maximized without losing the board flexibility. A proper powder treatment is required to maximize the powder loading and dielectric properties.

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