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Development of composite dielectrics with high specific capacitance and stable temperature characteristics

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A new alternative of tailoring the dielectric characteristics of a $BaTiO_3$-based ceramic is established in this study. The ceramic dielectrics were made by either two or three constituents having a composition of $(Ba_{0.96}Ca_{0.04})(Ti_{1.0-x}Zr_xMn_{0.01})O_3$ (BCTZ), where x ranges from 0 to 0.22, and sintered with Ni inner electrodes at 1300°C for 4 h in a reducing atmosphere. Both alternative stacking, i.e., layer-by-layer of different compositions, and bulk stacking configurations were prepared by screen-printing, resulting in a composite dielectric of different characteristics. It is obtained that the Curie temperature (T_c) of the BCTZ ceramics decreases with an increase of Zr in the dielectrics, i.e., −8°C per mole of Zr. In addition, the stacking configuration, the proportion and the number of constituents in the composite materials control the dielectric characteristics of the multilayer ceramic capacitors. On the basis of the principles outlined, a multilayer ceramic dielectric having k-value in excess of 8000 with the X7R specification (−55 ∼ +125°C, ±15%), which consists of two BCTZ ceramics with Curie temperatures of −20 and 100°C, was successfully developed.

1. Introduction

Most of the dielectric materials in current use for multilayer ceramic capacitors (MLCs) are based on barium titanate, $BaTiO_3$. For a long time, the dielectric ceramics are cofired with inner electrodes of precious metals such as palladium or palladium-silver alloys. Upon intensive research and development over the years, the manufactures of MLCs are now capable of replacing the expensive noble metals by low-cost base metals, e.g., Fe, Co, Ni and Cu [1–4]. The three most widely used capacitors with capacitance ranging from nF to μF are tantalum capacitors, X7R and Y5V ceramic capacitors. The main disadvantages of tantalum capacitors are poor frequency characteristic, low breakdown voltage and high cost, compared with the ceramic capacitors [5]. Ceramics for MLCs in Class II are classified into two subgroups: stable (X7R) and semi-stable (Y5V), which are differentiated by the temperature coefficients of capacitance and the temperature range of use. In general, the ceramic capacitors exhibit better frequency characteristics than the tantalum capacitors. Although the dielectric characteristic of Y5V ceramic capacitors is comparable to the tantalum capacitors, its capacitance is strongly influenced by temperature and applied voltage. Within the temperature range of −30°C to 85°C, the capacitance of a Y5V ceramic capacitor changes from +30% to −82%, and when a dc voltage is applied from 0 to rated voltage, the capacitance varies from 0 to −90% [6]. In practical applications, especially at high temperatures and high dc voltages, the Y5V ceramic capacitors show very poor performance, i.e., a significant drop of capacitance occurs.

In contrast to the Y5V ceramic capacitors, the X7R ceramic capacitors show very promising performance on frequency, temperature and dc voltage characteristics. However, its low capacitance range and high cost are inferior to competition with tantalum capacitors [7, 8]. The two disadvantages of X7R ceramic capacitors are attributed to their low dielectric constant.

As a result, how to enhance the dielectric constant and retain stable temperature coefficients of capacitance is a major challenge for the X7R ceramic capacitors [9, 10]. In this study, we developed a dielectric composite that satisfies the X7R specification and still remains a high dielectric constant. The composite materials were prepared by combining 2 or more individual components with different Curie temperatures, and then sintered with nickel inner electrodes in a reducing atmosphere.

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2. Experimental

The raw materials for the composite dielectrics were high purity $BaCO_3$ (Nippon Chemical), TiO_2 (Fuji Titanium), $CaCO_3$, ZrO_2 and MnO_2 (Merck) powders weighed to have a composition of $(Ba_{0.96}Ca_{0.04})$ $(Ti_{1.0-x}Zr_xMn_{0.01})O_3$ (BCTZ), where x ranges from 0 to 0.22. Each batch of the powders mixed with 99.5% purity ethanol, was ball-milled in a polypropylene bottle with 2 mm YTZ balls for 4 h and subsequently calcined at a temperature of 1000°C for 4 h in a pure alumina crucible. The calcined powders were further pulverized using a mortar and pestle to have an average particle size of 1.0 μm.

For making the multilayer capacitors, the calcined powders were added with suitable solvent, dispersant and binder to form a slip. The slip was cast on glass plates by a doctor blade to form a tape of thickness about 10 μm. The ceramic tape was then cut into a 0805-sized device and printed with nickel ink. Printed foils were then laminated and pressed into a green plate and sintered at a temperature of 1300°C for 4 h in a reducing atmosphere ($P_{O_2} = 1.18 \times 10^{-10}$ Pa), which was controlled by adjusting the H_2/H_2O ratio. After sintering, these sintered samples were polished and dipped with the Dupont 7095 silver paste. Dielectric properties of the capacitors were evaluated by a digital LCR meter (HP4284A).

3. Results and discussion

3.1. Tailoring the Curie temperature of dielectrics

It is known that the dielectric properties and structural characteristics of $BaTiO_3$-based ceramics are significantly influenced by the addition of Zr and Ca [10]. Fig. 1 shows the variation of Curie temperature (T_c) with Zr concentration in the BCTZ ceramics. It is obtained that the Curie temperature decreases linearly with Zr mole fraction by a slope of approximately −8°C per mole of Zr. The result indicates that the Curie temperature of the BCTZ ceramics can be tailored by controlling the amount of Zr in the dielectric materials. In addition to lowering the Curie temperature of the dielectrics, the temperature dependence of the dielectric constant curve is broadened and flattened by an increase of the Zr content. This phenomenon could be explained by the presence of diffuse phase transition (DPT) in the dielectrics [11]. As the Zr content is increased, a core-shell microstructure composed of the central ferroelectric phase and boundary paraelectric phase, is formed in the dielectrics [10]. The two ferroelectric and paraelectric phases can coexist in a wider temperature range in the dielectric materials at higher Zr content. Based on the information provided in Fig. 1, it is possible to obtain a dielectric with desired T_c by properly adjusting the composition of the BCTZ ceramics. The temperature characteristics of a composite dielectric composed of two BCTZ ceramics with different T_c will be discussed below.

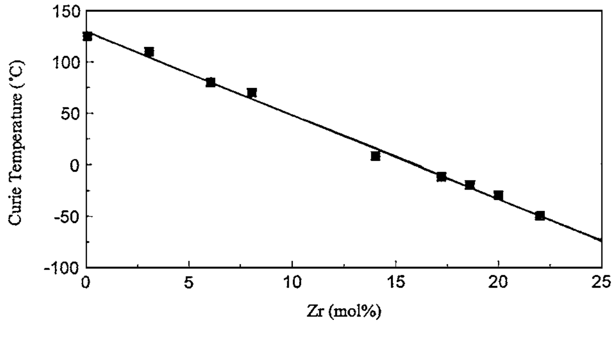


Figure 1 Variation of the Curie temperature with Zr content in the BCTZ ceramic dielectrics.

Fig. 2 gives a schematic of the bulk composite multiplayer capacitors along with their temperature characteristics of the capacitance. It can be seen that when the Curie temperature of the two components, e.g. one has $T_c = 40$°C and the other $T_c = 0$°C, differs equal to or less than 40°C due to a slight difference in their Zr content, a single Curie temperature, $T_c = 20$°C, is obtained for the composite dielectric. On the contrary, as the difference in T_c between the two components is larger than 40°C, corresponding to approximately a 5% difference in the Zr concentration, two distinguishable T_c peaks are observed, as shown in Fig. 2 for the case where the two dielectrics have high and low T_c of 100 and −20°C, respectively. The composite multiplayer capacitor displays two T_c peaks located at 90 and −5°C. The reduction of the T_c between high and low peaks in the composite dielectric is mainly due to the interdiffusion of Zr and Ti in the two components during sintering.

A cross-sectional scanning electron microscopy (SEM) micrograph of the composite capacitor with two T_c peaks located at 90 and −5°C is shown in Fig. 3. It can be seen that the grain size of the BCTZ ceramic with high T_c shown in the upper half is larger than that of the component with low T_c in the lower half of the micrograph. A concentration profile of the Zr and Ti distributions, using the spot mode in the SEM equipped with an energy-dispersive spectroscopy, across the interface region is given in Fig. 4. The Zr concentration is lower in the high T_c material and gradually increases toward the low T_c material, and vice versa for the Ti concentration. This result indicates that interdiffusion of Zr and Ti between the two constituents has occurred in the composite dielectric ceramics during sintering. Suppression of the grain growth in the $BaTiO_3$-based ceramics by the addition of Zr has been reported in the literature [10, 11].

3.2. Effect of the number and proportion of constituents on the T_c curve

Applications of $BaTiO_3$-based dielectrics require high and stable capacitance over the temperature range between −55 to 125°C, or segments within that range. As a result, modification of the T_c curve of dielectric materials to meet specific needs is an important issue in the design of commercial capacitors, in addition to tailoring the Curie temperature. The Curie temperature, as mentioned previously, can be modified by the addition of Zr and Ca, which are also commonly used to broaden and flatten the T_c curve in the $BaTiO_3$-based dielectrics.

In the case of a composite capacitor, broadening and flattening of the T_c curve can be achieved through

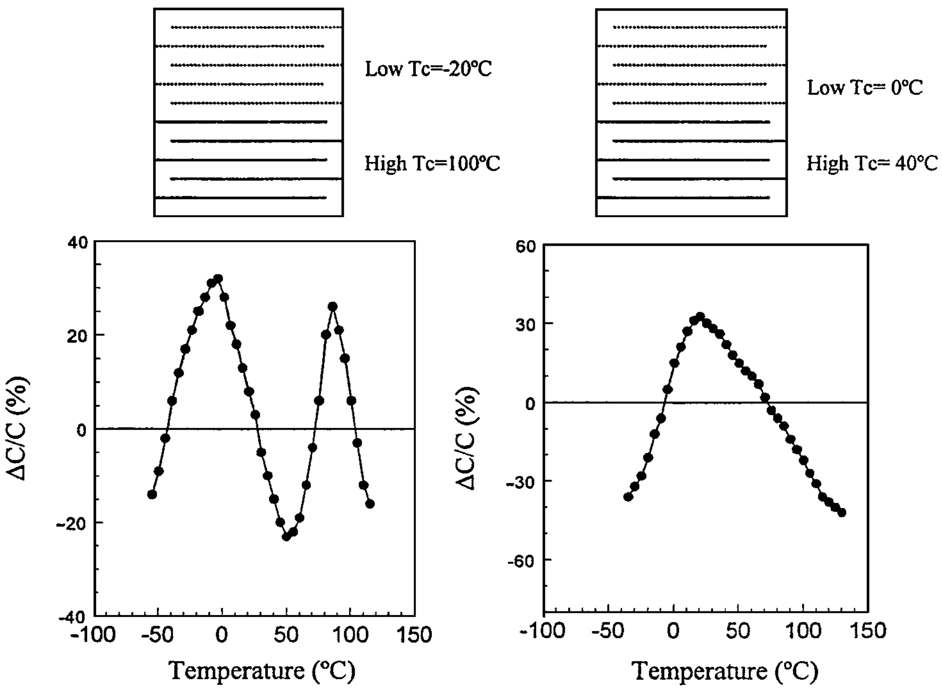


Figure 2 A schematic of the stacking configurations in the two-component multilayer ceramic capacitors and their temperature characteristics.

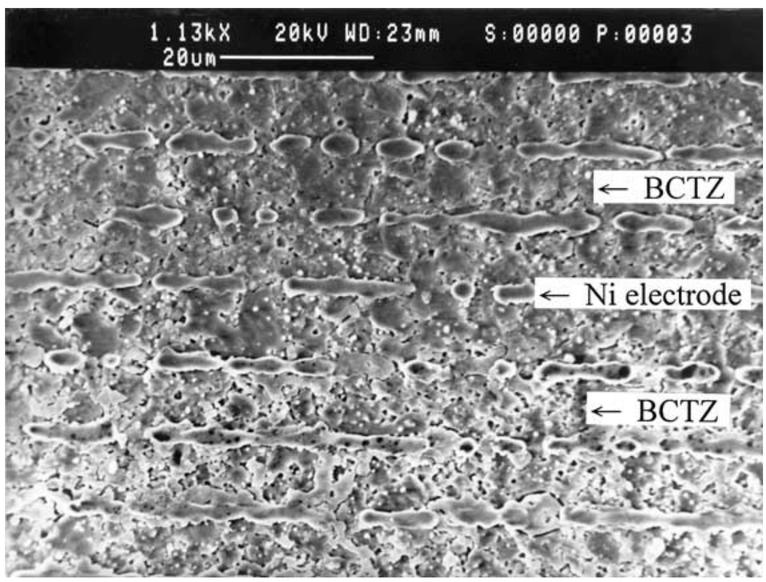


Figure 3 Cross-sectional SEM micrograph of the composite ceramic capacitor with two T_c peaks.

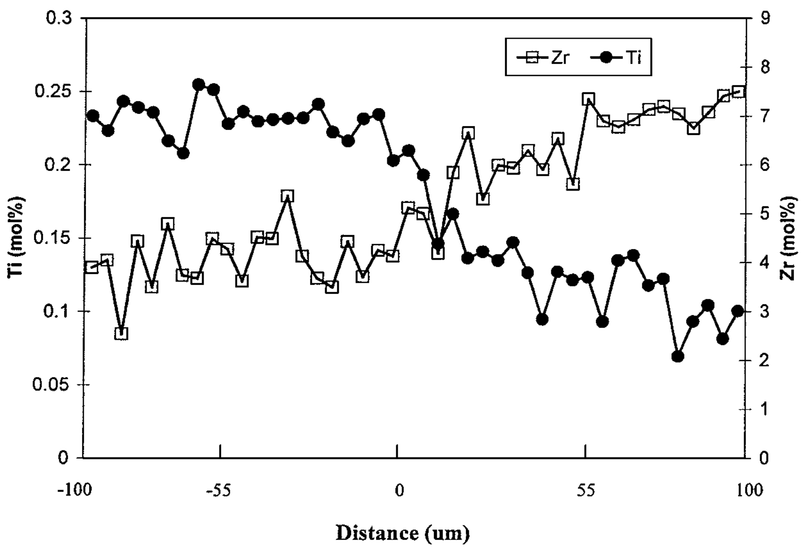


Figure 4 Concentration profiles of the Zr and Ti distributions in the composite capacitor shown in Fig. 3.

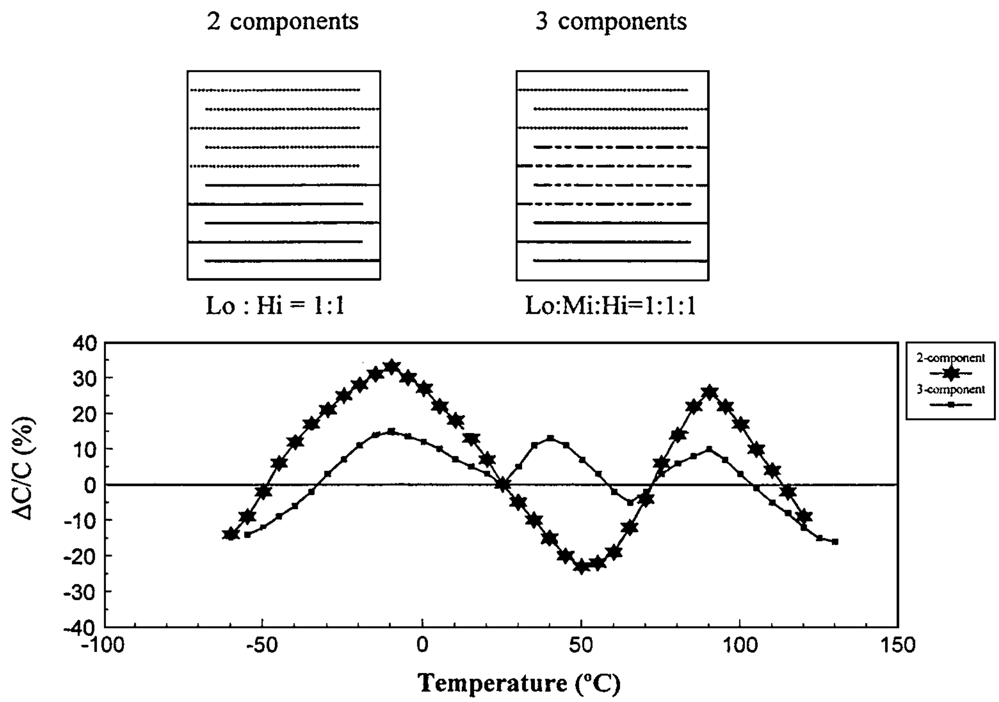


Figure 5 Temperature characteristics of the composite capacitors composed of two components of $T_c = -20$ and 100°C, and three components of $T_c = -20$, 40, and 100°C, along with their stacking configuration.

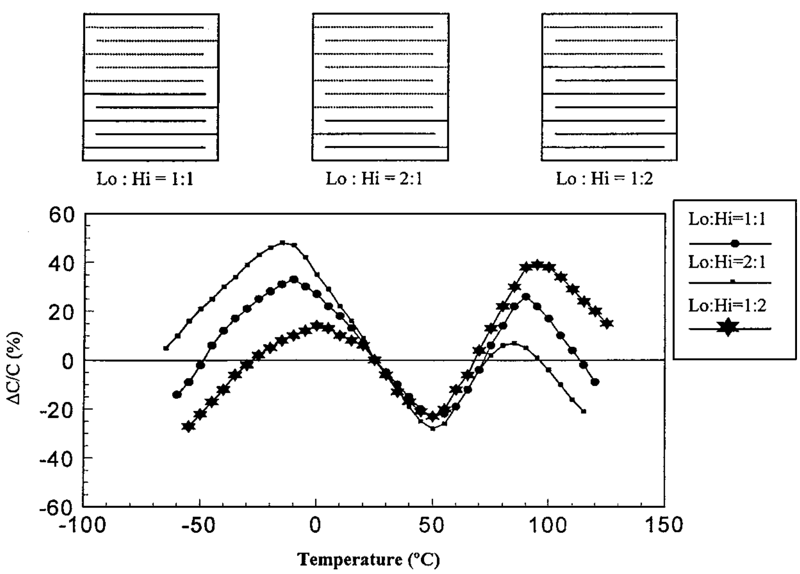


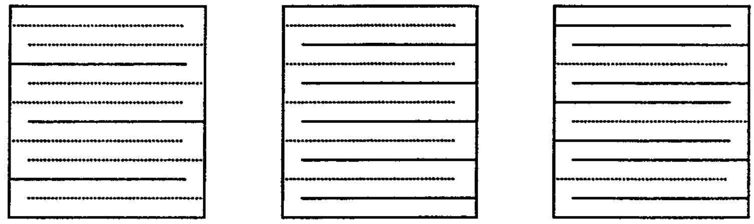
Figure 6 Temperature characteristics of the two-component capacitors with different proportions of the constituents.

increasing the number of individual component as well. Fig. 5 shows the T_c curves of two composite dielectrics composed of either two components with $T_c = -20$ and 100°C, or three components with $T_c = -20$, 40, and 100°C. Since the differences in T_c among each individual component are larger than 40°C, the T_c curves exhibit peaks equal to the number of components in the composite dielectrics. Compared with the two-component dielectric, the variation of capacitance with temperature in the three-component dielectric is much smaller. It is therefore practical to broaden and flatten the T_c curve of a composite dielectric by increasing the number of individual components.

In addition to the number of components, the proportion of each component can have considerable influence on the T_c curve of the composite dielectrics. Fig. 6 shows the variation of capacitance vs. temperature curve for the two-component dielectrics with different proportions. There are two peaks in each T_c curve because the difference in T_c between the two components is larger than 40°C. Although the dielectric characteristics of each component are retained, the T_c peaks of the composites have been shifted slightly toward an intermediate value, as a result of interdiffusion between the constituents.

3.3. Effect of stacking configuration on the Curie temperature

After considering the effect of number and proportion of the constituents on the Curie temperature, it is interesting to explore the stacking sequence of the printed foils on the dielectric characteristics. Ceramic multilayer capacitors composed of two dielectrics with T_c of −20 and 100°C were produced with alternative



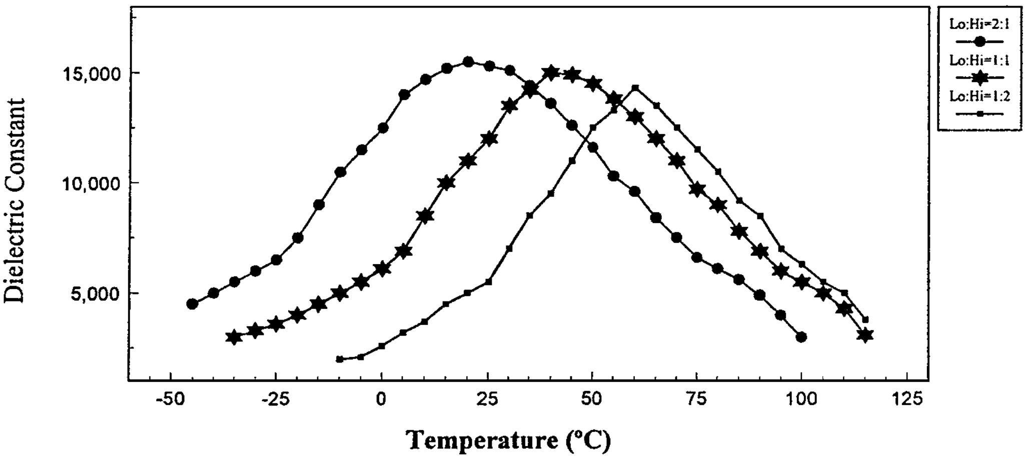


Figure 7 Temperature characteristics of the two-component capacitors with different proportions and alternatively stacking configurations.

stacking configuration and different proportions during screening printing process, as shown in Fig. 7. In contrast to the temperature-dependent dielectric curve shown in Fig. 2 that has two T_c peaks due to a large difference in the Curie temperature between the constituents, the composite capacitors have displayed only one broadened peak. This is because the distance between the two constituents is so short that interdiffusion can readily occur during sintering, resulting in a homogeneous composition with a single intermediate Curie temperature. It is also noted that the peak position and the extent of peak shifting depend upon the proportion of each component. With this method, it is therefore feasible to prepare a multilayer ceramic capacitor with single Curie temperature by stacking two dielectrics with very different Curie temperatures, i.e., larger than 40°C.

3.4. Design of a composite capacitor with X7R characteristics

The EIA's (Electronic Industries Association) specification for the X7R capacitor requires that the capacitance change of the dielectric is less than ±15% over a temperature range from −55 to 125°C. From the previous experimental results, it is realized that this specification can be achieved by using a three-component dielectric composite with equal proportion, as shown in Fig. 5.

From the viewpoint of processing and cost reduction, however, two components would be a better choice. It is feasible, as mentioned in the above section and displayed in Fig. 7, to obtain a capacitor with single intermediate T_c from two components with high and low T_c by varying the stacking configuration and proportion of each dielectric layer. By this way, a three-component composite capacitor can be produced, in which one component with intermediate Curie temperature is, in fact, composed of the other two components with alternative stacking configuration and proportion.

The temperature characteristics of a composite capacitor composed of two components with T_c of −20 and 100°C and with different stacking geometry and proportion are shown in Fig. 8. The major difference between the type II and III capacitors is the proportion of the high and low T_c components in the middle section of the capacitors. It can be seen that the type II capacitor is fully satisfied with the X7R specification, whereas the variation of the capacitance at high temperature region ~100°C is beyond the scope of the X7R specification for the type III capacitor. This is because the type III capacitor has a higher proportion of the high T_c component in the middle layer.

3.5. Comparison of the dielectric properties of the X7R, C-X7R and Y5V 0805/1.0 μF capacitors

3.5.1. Temperature characteristics

It is interesting to compare the capacitor performance of the multilayer dielectrics prepared by the above-mentioned method, called the composite-X7R, with those of current use commercially, the X7R and Y5V capacitors. Fig. 9 shows the temperature characteristics of the X7R, composite-X7R, and Y5V 0805/1.0 μF capacitors, in which the X7R and Y5V capacitors were made by the ceramic powders from Udden Co. It can be seen that both the X7R and the composite-X7R capacitors satisfy the EIA's specification, i.e. the variation of the capacitance over the temperature range from −55°C to 125°C is within ±15%. It is clear that the temperature-dependent capacitance of the X7R and composite-X7R capacitors is much more stable than

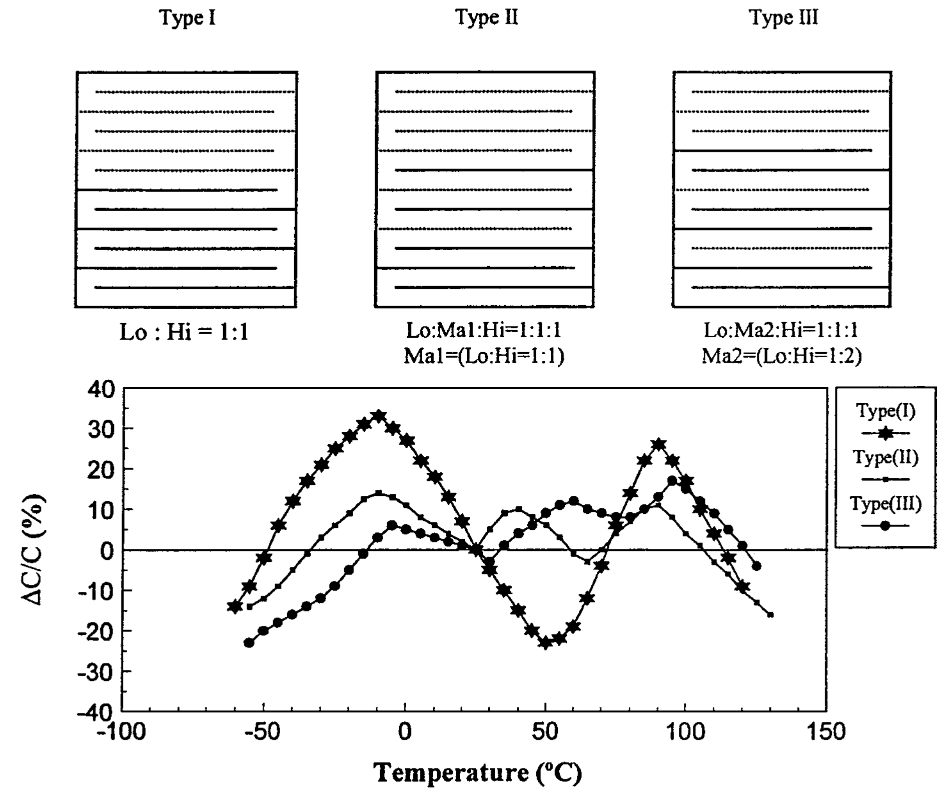


Figure 8 Temperature characteristics of the three-component capacitors, in which one of the components is made of the other two with different proportions and alternatively stacking configurations.

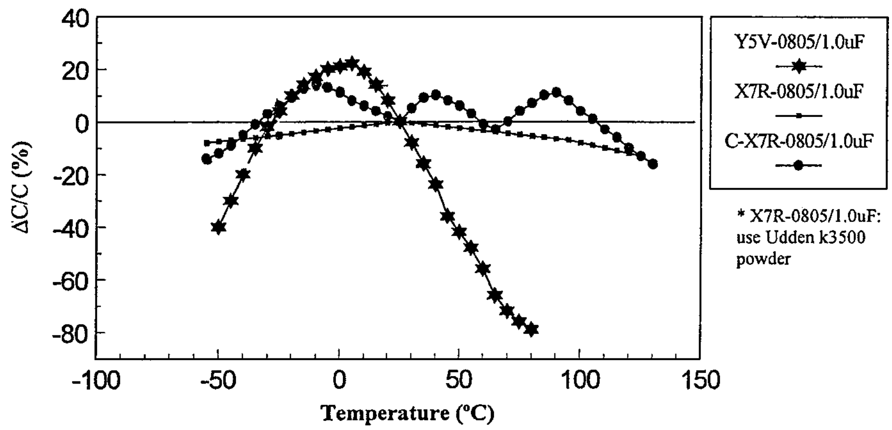


Figure 9 Temperature characteristics of the X7R, composite-X7R, and Y5V multiplayer ceramic capacitors.

that of the Y5V capacitor, +30% to −82% over the temperature range of −30°C to 85°C.

3.5.2. Dielectric strength

The maximum permissible operating voltage is one of the engineering parameters used to evaluate the performance of a dielectric capacitor. When the applied electrical field across a dielectric reaches a critical value, the dielectric strength, an electron avalanche is produced and an electrical current passes through the dielectric. The breakdown voltage depends on the geometry of the test specimens, electrode materials, microstructure and thickness of the dielectrics. The test results of the breakdown voltage for the X7R, composite-X7R and Y5V 0805/1.0 μF capacitors are shown in Fig. 10. It is noted that the Y5V capacitor demonstrates the highest average breakdown voltage among the three categories

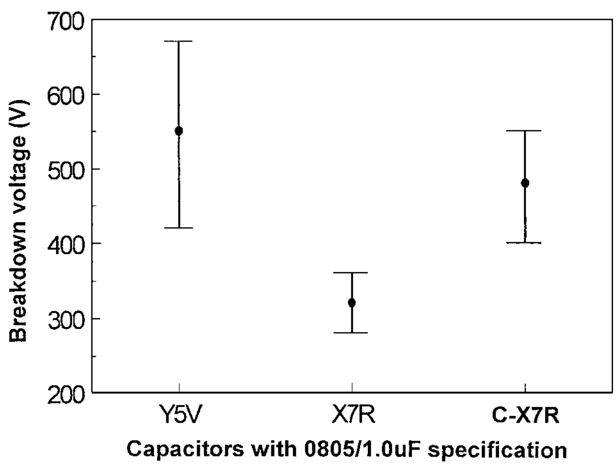


Figure 10 Dielectric strength of the X7R, composite-X7R, and Y5V 0805/1.0 μF multiplayer ceramic capacitors, in which the thickness of the dielectric layers is 6, 7, and 10 μm, respectively.

of capacitors. On the contrary, the commercial X7R capacitor has the lowest average breakdown voltage.

The difference in the breakdown voltage for the three categories of capacitors can be explained by their differences in the thickness of the dielectric layers [12]. In general, the breakdown voltage increases with the thickness of the dielectrics. To achieve the 0805/1.0 μF specification among the three categories of capacitors, the number of the dielectric layers is least and the thickness of the dielectric layers is highest in the Y5V capacitor because its constituent has the largest dielectric constant ($\sim$12000). On the other hand, the X7R has lower dielectric constant ($\sim$3000), therefore the number of the dielectric layers must be increased and the thickness of the dielectric layers is decreased. The dielectric constant of the composite-X7R ($\sim$8000) is in between, so do the dielectric thickness and the breakdown voltage.

4. Conclusions

It has been demonstrated that the Curie temperature of a $BaTiO_3$-based ceramic dielectric is controlled by the amount of Zr content in the materials. The temperature characteristics of a composite capacitor composed of either two or three constituents with different Curie temperatures can be tailored by the stacking configuration and proportion of the constituents in the dielectric capacitors. The principles outlined in this paper are applied successfully to produce a multilayer ceramic capacitor satisfying the X7R specification.

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References

1. I. BURN and G. MAHER, *J. Mater. Sci.* **10** (1975) 633.
2. J. DANIELS, K. H. HARDTL, D. F. K. HENNINGS and R. WERNICKE, *Philips Research Reports* **31** (1976) 487.
3. D. F. K. HENNINGS and H. SCHREINEMACHER, *J. European Ceram. Soc.* **15** (1995) 795.
4. S. SATO, Y. NAKANO, A. SATO and T. NOMURA, *ibid.* **19** (1999) 1061.
5. C. C. WU, M. KAHN and W. MOY, *J. Amer. Ceram. Soc.* **79** (1996) 809.
6. I. BURN, M. T. RAAD and K. SASAKI, *Ceram. Trans.* **8** (1993) 20.
7. J. V. BIGGERS, G. L. MARSHALL and D. W. STRICKLER, *Solid State Technol.* **13** (1970) 63.
8. Y. YAMASHITA, O. FURUKAWA, H. KANAI, M. IMAI and M. HARATA, *Ceramic Trans.* **8** (1993) 35.
9. D. F. K. HENNINGS and A. SCHNELL, *J. Amer. Ceram. Soc.* **65** (1982) 539.
10. T. R. ARMSTRONG, L. E. MORGENS, A. K. MAURICE and R. C. BUCHANAN, *ibid.* **72** (1989) 605.
11. Y. SAKABE, K. MINAI and K. WAKINO, *Japan J. Appl. Phys.* **20** (1981) 147.
12. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics," 2nd edn. (John Wiley & Sons, New York, 1976).

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