

Development of Temperature-Stable Thick-Film Dielectrics: II. Medium- K Dielectric

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Abstract—A temperature-stable, medium dielectric constant ($K = 100$) thick-film dielectric is developed for high-temperature electronic instrumentation. A theoretical model predicts a temperature-insensitive dielectric in the glass- $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - SrTiO_3 system, while experimental results suggest an optimum composition in the glass- SrTiO_3 - BaTiO_3 system. Interfacial polarization is the major factor which causes the deviation. The medium- K dielectric, when properly fired, terminated, and heat-treated, can work adequately from 25°C to 400°C.

I. INTRODUCTION

LOW-LOSS, medium dielectric constant ($K = 100$), temperature-stable dielectrics are needed in some high-temperature microelectronic instrumentation. Thick-film capacitors are logical candidates for high-temperature operations, because they are processed at elevated temperatures. However, with present-day thick-film technology, there are few commercial thick-film dielectrics with properties suitable for high-temperature applications, especially for applications where dielectric constants larger than 30 are required [1]–[3].

The objective of this research is to develop a medium- K dielectric for thick-film capacitors. The capacitors should retain useful electrical properties in a wide temperature range (e.g., 25°C to 350°C or 500°C), and remain stable for an extended period of time at elevated temperature.

The approach to the development of a medium- K dielectric is to have a sufficient quantity of a vitreous phase to assure complete densification, and to load this vitreous phase with two temperature-compensated, crystalline phases to obtain the desired properties in the temperature range of interest.

The material system employed in this study are glass G2- $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - SrTiO_3 and glass G1- SrTiO_3 - BaTiO_3 , where glass G1 and G2 are two types of glass developed for high-temperature thick-film systems [4]–[6]. The compositions of G1 and G2 are listed in Table I. Both types of glass have a positive temperature coefficient of dielectric constant (PTK). The crystalline phases used are: SrTiO_3 , BaTiO_3 , and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. SrTiO_3 is a paraelectric material with a negative temperature coefficient of dielectric constant (NTK); while both BaTiO_3 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are ferroelectric materials with a

PTK from room temperature to their Curie temperatures (T_c) and an NTK at temperatures above T_c .

II. DIELECTRIC PROPERTIES OF MULTIPHASE SYSTEMS—THEORETICAL

The dielectric behavior of a mixture of two components is a function of volume fractions, shape, size, and dielectric constants of each component particle. Theoretical calculations are most easily made for systems where the components are arranged in a regular array, but normal mixtures show a random arrangement of components. Two models commonly applied to a diphasic mixture are a dispersion of discrete volumes of one phase within the continuously connected matrix of a second phase [7], or both phases continuously connected [8]. Both models can be reduced to an approach commonly known as “effective medium theory” (EMT). By the effective medium theory, the average effect of the dispersed phase in a heterogeneous system can be expressed by giving all of the dispersed particles a single dielectric constant K and by choosing K such that the effects of changing any one dielectric constant back to its true value will, on the average, cancel out. Based on the effective medium theory, the dielectric constant of the multiphase system can be derived from the following equation:

$$\sum_{i=1}^n V_i \frac{K - K_i}{K_i + (z/2 - 1)K} = 0 \quad (1)$$

where

- K dielectric constant of the multiphase system;
- K_i dielectric constant of phase i ;
- V_i volume fraction of phase i ;
- n number of phases in the system;
- z coordination number of the system, which is the number of neighbors of an atom or a cluster in the microstructure network; $z = 4$ for a square network; $z = 6$ for a cubic network.

Effective medium theory was employed to calculate the dielectric constant of a multiphase system. The material network is three-dimensional so the coordination number was assumed to be 6 in this study.

The materials selected for calculation of anticipated dielectric behavior of heterogeneous systems were glass types G1, G2, SrTiO_3 , and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The dielectric constant of each

Manuscript received October 5, 1988; revised May 15, 1989. This work was supported by Sandia National Laboratories and the U. S. Department of Energy under Contract 28-7200.

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IEEE Log Number 8930374.

TABLE I
COMPOSITION OF GLASSES EMPLOYED IN THIS STUDY

Glass Designation	PbO	B ₂ O ₃	SiO ₂ (mol %)	Al ₂ O ₃	CaO	BaO
G1	29	36.5	20.4	13.7		
G2		38	20	12	21	9

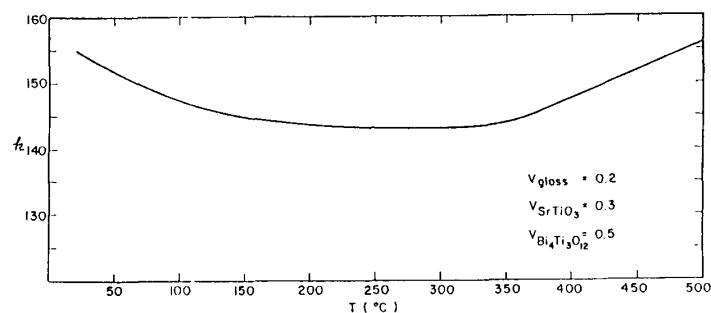


Fig. 1. Predicted temperature dependence of dielectric constant for the system 50 vol % Bi₄Ti₃O₁₂-30 vol % SrTiO₃-20 vol % Frit G1.

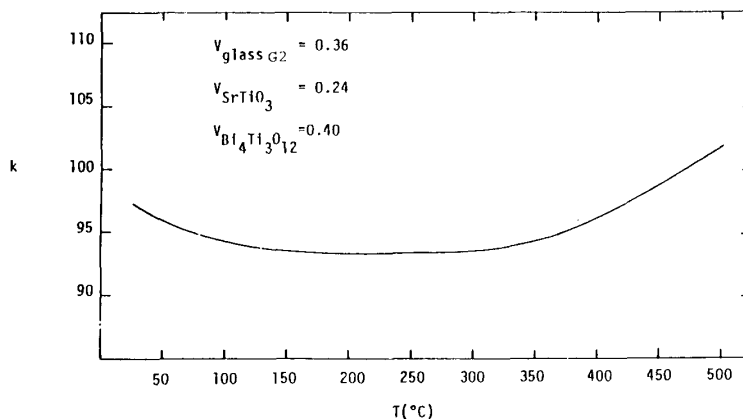


Fig. 2. Predicted temperature dependence of dielectric constant for the system 40 vol % Bi₄Ti₃O₁₂-24 vol % SrTiO₃-36 vol % Frit G2.

material as a function of temperature was approximated as [5]

$$\begin{aligned}
 \text{glass G1} & K = 6.0 + 0.0032 (T - 273) \\
 \text{glass G2} & K = 10 + 0.0013 (T - 648), \quad 298 \text{ K} \leq T \leq 648 \text{ K} \\
 & K = 10 + 0.0032 (T - 648), \quad 648 \text{ K} \leq T \leq 773 \text{ K} \\
 \text{SrTiO}_3 & K = 42.7 + 6.78 \times 10^{-4} / (T - 44) \\
 \text{Bi}_4\text{Ti}_3\text{O}_{12} & K = 180 + 0.2154 (T - 298), \quad T \leq 623 \text{ K} \\
 & K = 250 + 0.4 (T - 623), \quad T > 623 \text{ K}.
 \end{aligned}$$

Fig. 1 shows the calculated temperature dependence of dielectric constant for the three-phase system: 50 vol % Bi₄Ti₃O₁₂-30 vol % SrTiO₃-20 vol % Frit G1. The average dielectric constant predicted for this heterogeneous system is 150 with a variation of ± 4 percent over the temperature range 25°C-500°C. Fig. 2 shows the calculated temperature dependence of the dielectric constant for the three-phase system: 36 vol % Frit G2-24 vol % SrTiO₃-40 vol % Bi₄Ti₃O₁₂. The dielectric constant is 95.41 ± 2.64 , which is equivalent to a variation of 2.77 percent over the temperature range. If all the

phases of these systems retain their properties after firing, both dielectric systems will function adequately from 25°C to 500°C.

III. EXPERIMENTAL PROCEDURE

Dielectric formulations were prepared by combining appropriate amounts of SrTiO₃ (<45 μm), Bi₄Ti₃O₁₂ (<45 μm), BaTiO₃ (<45 μm), Frit G1 (<20 μm), and Frit G2 (<45 μm). The mixed powders were blended with 50 to 70 vol % screening agent consisting of 10 percent N-300 ethyl cellulose (Hercules) in butyl carbitol solvent for 2 h on a glass-sleeved roll mill. Engelhard A3770 Au/Pd conductor was printed and fired on AlSiMag 614 (3M Co.) substrates for bottom electrodes. Dielectric formulations were printed through a 200-mesh stainless-steel screen, allowed to level off at room temperature, dried at 150°C for 15 min to remove the solvent, burned out at 400°C for 15 min to remove the ethyl cellulose, and fired in the temperature range 700°C-1020°C for times

varying from 5 to 35 min. In some instances, a second (or even third) layer of dielectric was printed and dried in the same manner, and fired in the temperature range 700°C–1020°C for times varying from 12 to 20 min. Counter electrodes of Du Pont 4119 Au conductor were then printed and fired at 700°C for 10 min to give a one square capacitor pattern (3 mm × 3 mm).

IV. RESULTS AND DISCUSSION

The first system studied experimentally was 36 vol % Frit G2–24 vol % SrTiO₃–40 vol % Bi₄Ti₃O₁₂, however, a severe pinhole problem was encountered unless three successive printing and firing cycles were applied. Hence the total firing time for this system was 75 min at 1000°C (20 min on the first two firings and 35 min on the last one). Another problem was discovered when a preliminary experiment with X vol % SrTiO₃ powder and (100 – X) vol % Frit G2 ($X = 1, 3, 5, 10$) showed that SrTiO₃ dissolved completely in the glass in 75 min at 1000°C. Therefore, the firing time had to be reduced in order to produce the desired microstructure in the dielectric.

One of the approaches investigated to reduce the firing time was to use smaller particle size Frit G1 instead of Frit G2. The strain point of G1 is lower than that of G2, so G1 has lower viscosity than G2 under the same firing temperature. The presence of G1 will help in eliminating pinholes in the dielectrics.

The first composition studied in the Frit G1–SrTiO₃–Bi₄Ti₃O₁₂ system was 20 vol % Frit G1–30 vol % SrTiO₃–50 vol % Bi₄Ti₃O₁₂; however, instead of a 4-percent variation, a relative capacitance change of greater than 100 percent was observed over the temperature range of interest. Extensive studies of the Frit G1–SrTiO₃–Bi₄Ti₃O₁₂ system, involving variations in the ratio of the three constituents, in the firing conditions as well as the fabrication processes, were then carried out. For most of the compositions studied in the Frit G1–SrTiO₃–Bi₄Ti₃O₁₂ system, the relative capacitance change with temperature showed an increase after the initial decrease and the temperatures corresponding to a minimum dielectric constant ranged from 75°C to 250°C. The deviation from the anticipated dielectric behavior may be due to factors such as interfacial polarization between the electrodes and the dielectric and/or among different phases in the dielectric. An approach investigated to temperature-compensate the dielectric in this temperature range was to replace Bi₄Ti₃O₁₂ with a ferroelectric material with a Curie temperature (T_c) between 75°C and 250°C. The presence of the low- T_c ferroelectric should yield positive temperature dependence on the dielectric constant from room temperature to T_c and negative temperature dependence from T_c to 500°C. Barium titanate (BaTiO₃) is a ferroelectric material with $T_c \sim 120^\circ\text{C}$ and was selected as one of the medium- K components.

Studies of the Frit G1–SrTiO₃–BaTiO₃ system involved variations in the ratio of the three constituents, in the firing conditions, in the fabrication processes, and in the addition of the fourth constituent. The most promising results obtained are capacitors with dielectric 35 vol % Frit G1–25 vol % SrTiO₃–40 vol % BaTiO₃ fired at 800°C for 10 min and 1000°C for 15 min, and furnace-cooled to room temperature

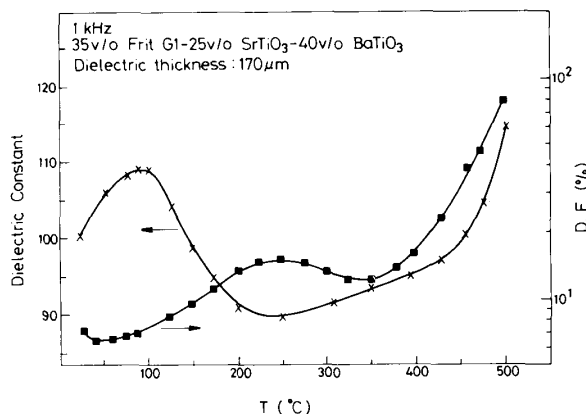


Fig. 3. Dielectric properties of a medium- K dielectric as a function of temperature.

after the counter electrode was applied. Fig. 3 is a typical result for the temperature dependence of the dielectric properties of this composition. The 1-kHz dielectric constants are 100, 107.8, 92.4, and 114.4 at 25°C, 85°C, 350°C, and 500°C, respectively. This corresponds to a relative capacitance change of +7.8 percent (25°C–85°C), –7.6 percent (25°C–350°C), and +14.4 percent (25°C–500°C). The dissipation factors are smaller than 16 percent in the temperature range 25°C–400°C, but increase to a value of 80 percent at 500°C. These results suggest that the medium- K dielectric 35 vol % Frit G1–25 vol % SrTiO₃–40 vol % BaTiO₃ is a good candidate for 400°C thick-film application.

The initial increase followed by a decrease of $\Delta C/C_0$ may be attributed to the presence of crystalline BaTiO₃. Barium titanate, a ferroelectric material with a Curie temperature (T_c) near 120°C, has a positive temperature dependence of dielectric constant (K) at temperatures below T_c , a maximum K at T_c , and a negative temperature dependence of K at temperatures above T_c . A tall, narrow peak in K is observed at T_c for pure BaTiO₃. The lowering and broadening of the peak observed in this medium- K dielectric may be partially due to the presence of the glassy phase, but a more probable cause is the formation of BaTiO₃ solid solutions. Strontium titanate is a paraelectric material, and any solid solution of SrTiO₃ and BaTiO₃ should have a Curie temperature below 120°C. Formation of SrTiO₃–BaTiO₃ solid solution in this dielectric composition was observed from the cell constant change obtained by X-ray diffraction experiments, but the standard dielectric firing condition of 1000°C for 15 min is too short to reach the equilibrium state. Instead of a definite composition of SrTiO₃–BaTiO₃ solid solution, continuous compositions of solid solutions are thus formed (i.e., the composition varies from pure SrTiO₃ to pure BaTiO₃ with many different ratios of SrTiO₃ and BaTiO₃ in between) [9]. Therefore, a distribution of Curie temperatures is expected, which would lead to the observed flattening and broadening of the Curie peak.

The increase in the relative capacitance change observed at the highest temperatures contradicts what is expected for the paraelectric materials in the system, i.e., BaTiO₃ and SrTiO₃. This increase may be caused by factors such as dissolution of crystalline phases into glassy phase during firing, thermal

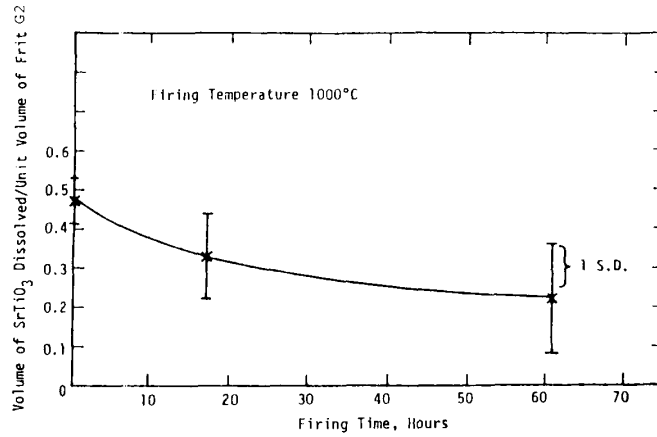


Fig. 4. Dissolution of SrTiO₃ into Frit G2 as a function of firing time at 1000°C.

stresses among different components in the system, changes in defect structure, and interfacial polarization between the electrode and the dielectric material and/or among the different components of the dielectric material. Possible factors that affect the dielectric properties of the Frit G1-SrTiO₃-BaTiO₃ system are investigated and the results discussed in the following.

A. Dissolution of the Crystalline Phase into Glass during Firing

Dissolution of the crystalline phase into glass during firing is one possibility which may cause the positive temperature dependence of the medium-K system at high temperatures. This possibility was evaluated by studying the dielectric properties of a SrTiO₃ saturated glass. The solubility of SrTiO₃ into glass was determined by firing powders consisting of 35 vol % Frit G2-65 vol % SrTiO₃ at 1000°C for different times, and analyzing the X-ray diffraction patterns of the samples after firing. Barium titanate was used as a standard to calculate the amount of SrTiO₃ left. The results of these experiments (Fig. 4) show that for a firing condition comparable to that of most dielectrics studied, i.e., 10 min at 800°C and 15 min at 1000°C, 0.47 unit volume of SrTiO₃ dissolves into one unit volume of Frit G2. As the firing time is increased, some of the SrTiO₃ precipitates to form larger grains, and the solubility of SrTiO₃ decreases as the firing time increases until it reaches an equilibrium value of 0.22. Based on these results, a glass with composition 20 vol % SrTiO₃-80 vol % Frit G2 was prepared, and its dielectric properties measured to produce the results shown in Fig. 5. The dielectric constant at 25°C is 14.7, the relative capacitance change is 7.0 percent to 350°C and 12.7 percent to 500°C, and the dissipation factor at 500°C is 6.4 percent. These results indicate that it is not the dissolution of SrTiO₃ into the glass which causes the increase of $\Delta C/C_0$ and DF at high temperature.

B. Effect of Thermal Stress among Different Components

Dielectric properties of capacitors as-fabricated and after annealing for 5 min at 500°C and after slow cooling were measured and compared in order to study the effect of thermal

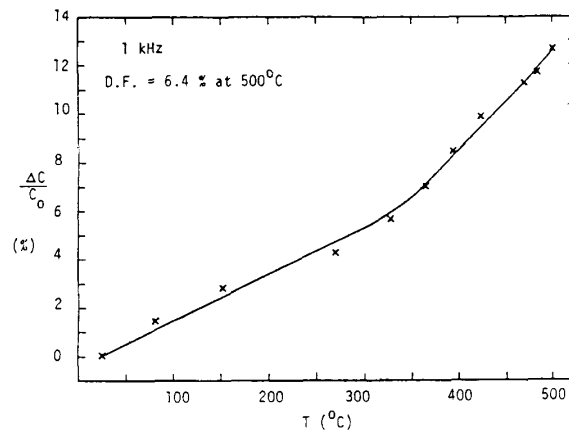


Fig. 5. Relative capacitance change as a function of temperature for a glass dielectric of composition 20 vol % SrTiO₃-80 vol % Frit G2.

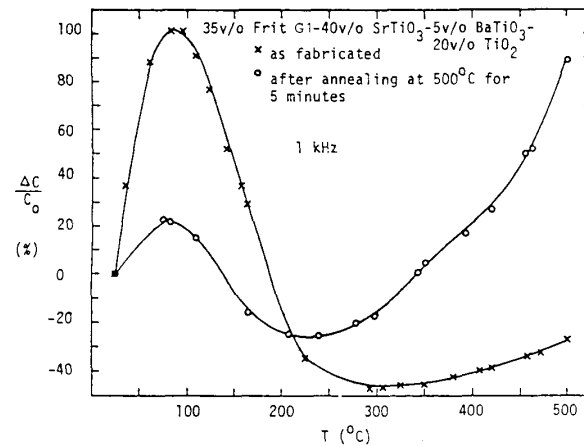


Fig. 6. Effect of annealing on relative capacitance change as a function of temperature for a medium-K dielectric.

stress caused by rapid cooling of capacitors at room temperature, in addition to any other effects which may be associated with the annealing process. A typical result is shown in Fig. 6. The annealed capacitor has a much smaller increase in $\Delta C/C_0$ than the as-fabricated one below 100°C, a smaller decrease

TABLE II
RELATIVE CAPACITANCE CHANGE AT DIFFERENT FREQUENCIES AND VARIOUS TEMPERATURE RANGES FOR CAPACITORS
MADE WITH DIELECTRIC 35 vol % FRIT G1-25 vol % SrTiO₃-40 vol % BaTiO₃ FIRED AT 1000°C

Temperature Range	Frequency			
	120 Hz	1 kHz (%)	10 kHz	1 MHz
25°C-85°C	—	7.8	—	6
25°C-100°C	—	3.9	—	6.1
25°C-120°C	—	-0.5	—	5.9
25°C-200°C	—	-15	—	-4
25°C-350°C	-6.5	-7.6	-13.2	-14
25°C-500°C	+51	+14.4	-5	-21

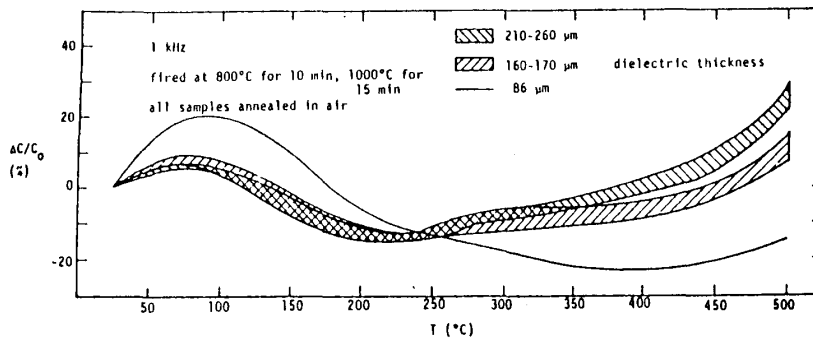


Fig. 7. Effects of dielectric thickness on relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

between 100°C and 300°C, and a much larger increase from 300°C to 500°C. This result suggests that thermal stresses caused by the rapid cooling of the capacitors from the top electrode firing temperature (700°C) to room temperature, and residual thermal stress among different components in the system do affect the relative capacitance change of the medium-*K* capacitor. However, a detailed study of the thermal stress effects on this multiphase system is beyond the scope of this research.

In most cases, the annealed capacitors give more consistent and reproducible results than the as-fabricated ones. Therefore, the annealing process is applied to all the medium-*K* capacitors.

C. Interfacial Polarization Effects

Interfacial polarization occurs when two materials of different conductivities are brought into contact. Blocking of charge carriers happens across the interface, this will manifest itself as an increase in the capacitance to the outside observer. The polarization of any material is both frequency- and temperature-dependent, and interfacial polarization normally becomes important only at low frequency and high temperature. One way to test whether or not interfacial polarization effects are contributing to the increase in the 1-kHz $\Delta C/C_0$ at high temperatures is to measure the relative capacitance change at higher frequency, e.g., at 1 MHz, and compare to the 1-kHz $\Delta C/C_0$; at 1 MHz, the interfacial polarization effect should be negligible in the temperature range of interest.

Table II summarizes the relative capacitance change at different frequencies and various temperature ranges for

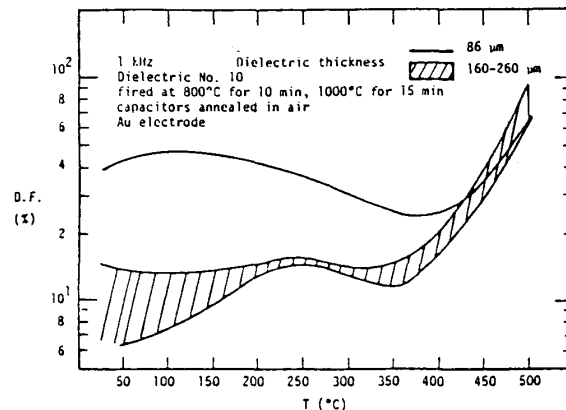


Fig. 8. Dissipation factor as a function of temperature for dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

capacitors made with 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃ fired at 1000°C. At temperatures above the Curie point, the 1-MHz $\Delta C/C_0$ decreases monotonously as temperature increases; this is the expected behavior based on the intrinsic properties of the dielectric materials. Hence, the interfacial polarization effect is indeed one of the important contributors to the increase of the 1-kHz $\Delta C/C_0$ at high temperatures.

The dielectric properties of this medium-*K* compositions as a function of dielectric thickness was investigated. The results for temperature dependence of the dielectric properties for different thickness of this medium-*K* dielectric fired at 800°C for 10 min and 1000°C for 15 min are shown in Figs. 7 and 8

TABLE III
THE 1-kHz DIELECTRIC PROPERTIES OF DIELECTRIC 35 vol % FRIT G1-25 vol % SrTiO₃-40 vol % BaTiO₃ WITH Au ELECTRODES FOR DIFFERENT DIELECTRIC THICKNESS

Capacitor number	1	2	3	4	5	6
Dielectric thickness (μm)	86	160	170	170	210	260
$\Delta C/C_0$ (%) (25°C-500°C)	-15	8	14	14	22	30
Dielectric constant ($K_{25^\circ\text{C}}$, $K_{500^\circ\text{C}}$)	(308, 263)	(120, 130)	(101, 116)	(123, 141)	(123, 149)	(124, 161)
500°C, DF (%)	67	66	80	71	88	90

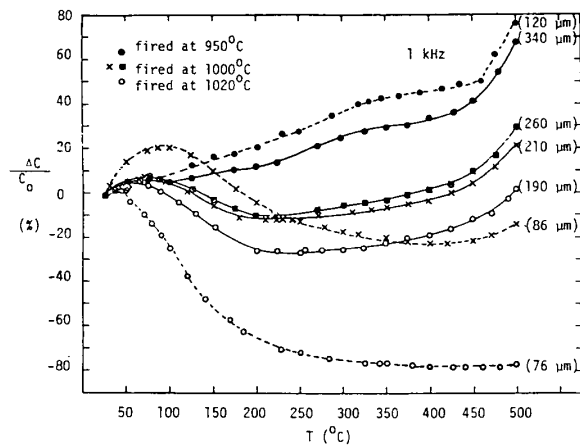


Fig. 9. Effects of firing temperature and dielectric thickness on the relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

and summarized in Table III. Initially, $\Delta C/C_0$ increases as temperature increases until it reaches a maximum value between 75°C and 100°C, then decreases as the temperature increases, before again increasing at still higher temperatures. Both the initial increase and the following decrease are accentuated with decreasing dielectric thickness, and $\Delta C/C_0$ from 25°C to 500°C showed a monotonic increase with increasing dielectric thickness. This observation suggests that if interfacial polarization is contributing to the positive TCC of the medium-K composition, the effect of interfacial polarization between phases and grains in the bulk of the dielectric is larger than that induced by interfacial polarization between the electrodes and the dielectric.

The dielectric properties of dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃ as a function of dielectric firing temperature was also investigated. The dielectrics were fired in air for 10 min at 800°C, followed by 15 min at 950°C, 1000°C, or 1020°C. The counter electrodes were then fired and annealed in air as described previously. The results of these experiments are shown in Figs. 9 and 10 and summarized in Table IV. For comparable dielectric thicknesses,

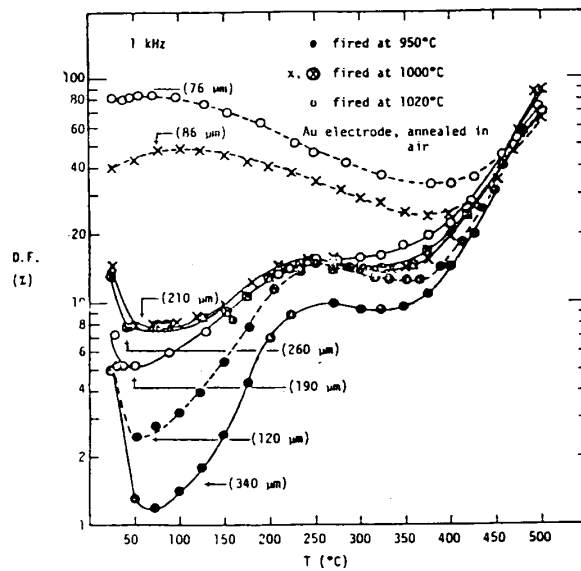


Fig. 10. Effects of firing temperature and dielectric thickness on the dissipation factor as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

$\Delta C/C_0$ is more negative and DF is smaller for the dielectric fired at higher temperatures, and increases as the firing temperature decreases. For the same firing conditions, in general $\Delta C/C_0$ increases and DF decreases as the dielectric thickness increases.

The results shown in Figs. 9 and 10 are consistent with a contribution of interfacial polarization between grains in the bulk of the dielectric to the relative capacitance change. For the same firing time, a dielectric fired at a higher temperature will have larger crystalline grains and, hence, less interfacial area and fewer grain boundaries. Therefore, for the same dielectric thickness, higher firing temperatures will lead to a smaller interfacial polarization effect. If interfacial polarization is contributing to the increase in $\Delta C/C_0$ at high temperature, a more negative $\Delta C/C_0$ for higher firing temperatures would be expected, as is observed.

TABLE IV
THE EFFECT OF FIRING TEMPERATURE AND DIELECTRIC THICKNESS ON THE 1-kHz DIELECTRIC PROPERTIES OF DIELECTRIC 35 vol % FRIT G1-25 vol % SrTiO₃-40 vol % BaTiO₃, Au ELECTRODE, CAPACITORS ANNEALED IN AIR

Capacitor number	1	2	3	4	5	6	7
Firing temperature (°C)	950	950	1000	1000	1000	1020	1020
Dielectric thickness (μm)	120	340	86	210	260	76	190
Dielectric constant (K _{25°C} , K _{500°C})	(75, 132)	(70, 118)	(308, 263)	(123, 149)	(124, 161)	(1275, 292)	(140, 141)
ΔC/C ₀ (%) (25°C-500°C)	76	68	-15	22	30	-77	1.4
Dissipation factor (%) (DF _{25°C} , DF _{500°C})	(4.8, 86)	(5.1, 86)	(40, 67)	(14.5, 90)	(13, 87)	(80, 74)	(7.2, 70)

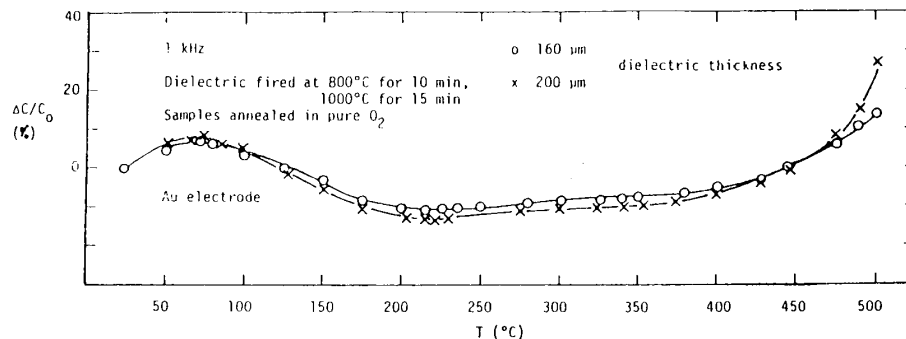


Fig. 11. Relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

The other general feature observed in Figs. 9 and 10 is that the temperature corresponding to the Curie temperature peak of the dielectric fired at 1020°C is lower than that of the dielectric fired at 1000°C. Since the molar ratio of BaTiO₃ to SrTiO₃ in this composition is 1.48 to 1, if all the BaTiO₃ and SrTiO₃ in the dielectric formed a complete solid solution, the Curie temperature for this equilibrium solid solution would be -21°C. Formation of solid solution would be more complete at the higher firing temperature, and the temperature of ΔC/C₀ peak should be lower, as is observed.

D. Effects of Defect Structure

In order to investigate the possible contribution of changes in defect structure during firing to the relative capacitance change at high temperature, two capacitors were prepared using the same firing conditions as the previous ones (Figs. 7 and 8) except that the counter electrodes were fired and annealed in pure O₂. The increased oxygen partial pressure during firing will decrease the concentration of oxygen vacancies in the dielectric. The results obtained for these two capacitors are shown in Figs. 11 and 12, and summarized in

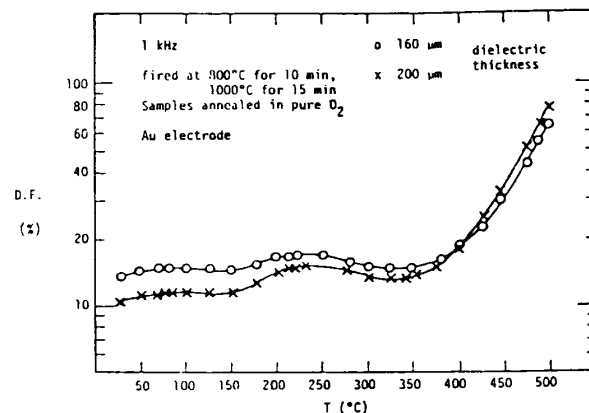


Fig. 12. Dissipation factor as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

TABLE V
THE 1-KHZ PROPERTIES OF DIELECTRIC 35 vol % FRIT G1-25 vol % SrTiO₃-40 vol % BaTiO₃, Au ELECTRODE, CAPACITORS ANNEALED IN PURE O₂

Capacitor number	1	2
Dielectric thickness (μm)	160	200
ΔC/C ₀ (%) 25°C-500°C	14	26
Dielectric constant (K _{25°C} , K _{500°C})	(124, 142)	(130, 160)
DF (%), 500°C	64	78

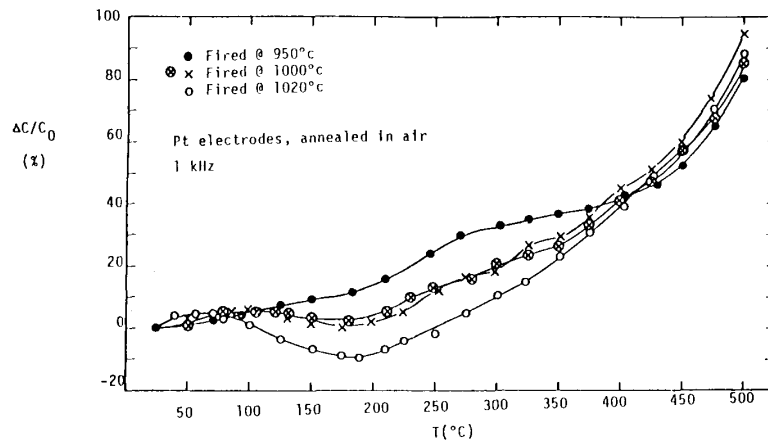


Fig. 13. Effect of firing temperature on the relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

Table V. Comparing Figs. 7 to 11, Figs. 8 to 12, and Tables III to V, there are no apparent differences between the capacitors fired in air and fired in O₂. Thus changes in defect structure do not appear to be significant in causing the positive ΔC/C₀ at high temperatures.

E. Effects of the Electrode Ingredients

The effect of electrode ingredients on the dielectric properties of dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃ was also studied. Platinum electrodes were used and the capacitor dielectrics were fired at 950°C, 1000°C, or 1020°C to compare with capacitors with gold electrodes fired at the same temperatures. Figs. 13 and 14 give the dielectric properties of dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃ fired at different temperatures with platinum electrodes. Comparing Figs. 13 and 14 to Figs. 9 and 10, the dielectric properties of capacitors with Pt electrodes are less sensitive to the firing temperature of the dielectric than those of capacitors with Au electrodes. Figs. 15-17 show the comparisons between the relative capacitance change of capacitors with Au electrodes and those of capacitors with Pt electrodes for different dielectric thickness at three firing temperatures. The results are similar at the lowest firing temperature (Fig. 15), but show increasing divergence at

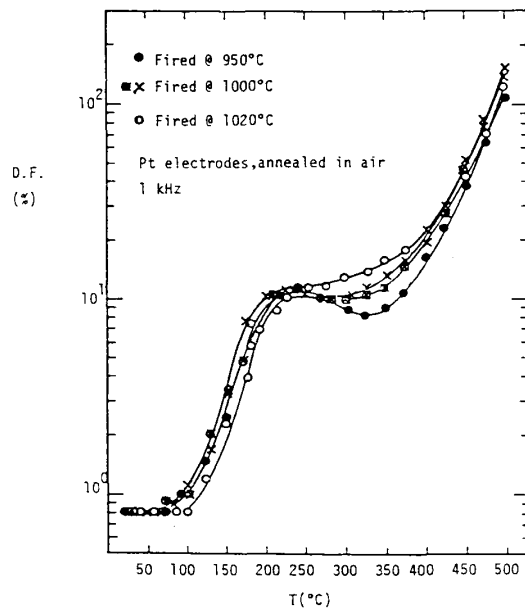


Fig. 14. Effect of firing temperature on the dissipation factor as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

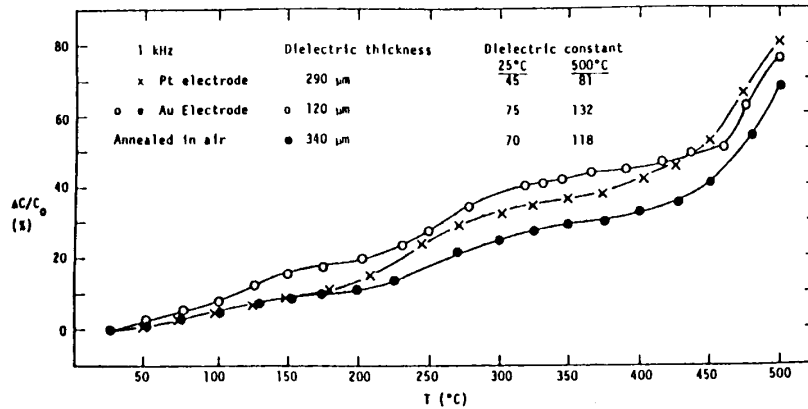


Fig. 15. Effect of electrode material and dielectric thickness on the relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃, fired at 950°C.

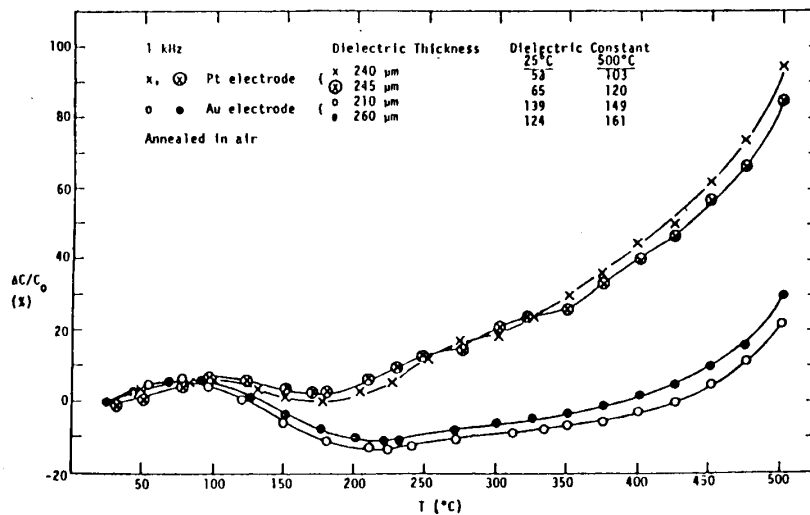


Fig. 16. Effects of electrode material and dielectric thickness on the relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃, fired at 1000°C.

higher firing temperatures (Figs. 16 and 17). The 1-kHz room-temperature dielectric constants calculated for the capacitors with platinum electrodes ranged from 45 to 65, while those for similar capacitors with gold electrodes ranged from 70 to 1075 (Figs. 15-17).

F. Stability of Dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃ after Thermal Storage

Figs. 18-21 give the dielectric properties of capacitors with 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃ after 350°C and 500°C thermal storage. The relative capacitance change from 25°C to 500°C and the dissipation factor at 500°C increase after thermal storage at 350°C or 500°C thermal storage. However, the dissipation factor seemed to be improved after 356-h storage in the temperature range 25°C-300°C. Very little difference is observed between the properties after 356- and 1893-h storage. Besides, the dielectric

properties from room temperature to 350°C are less temperature-sensitive after 250°C or 500°C thermal storage.

On the basis of the thermal storage results, it is concluded that 1) dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃ fired at 800°C for 10 min followed by 1000°C for 15 min is a candidate for 400°C thick-film dielectric, and 2) the thermal stability of capacitors made with the above composition can be improved by storing the capacitors at 500°C for 15 days before the application of the capacitors in high-temperature electronics.

V. CONCLUSIONS

1) A temperature-stable medium-*K* dielectric, consisting of 35 vol % glass G1-25 vol % SrTiO₃-40 vol % BaTiO₃ was developed. The composition of G1 is 29 mole % PbO-36.9 mole % B₂O₃-20.4 mole % SiO₂-13.7 mole % Al₂O₃ which is developed for high-temperature application.

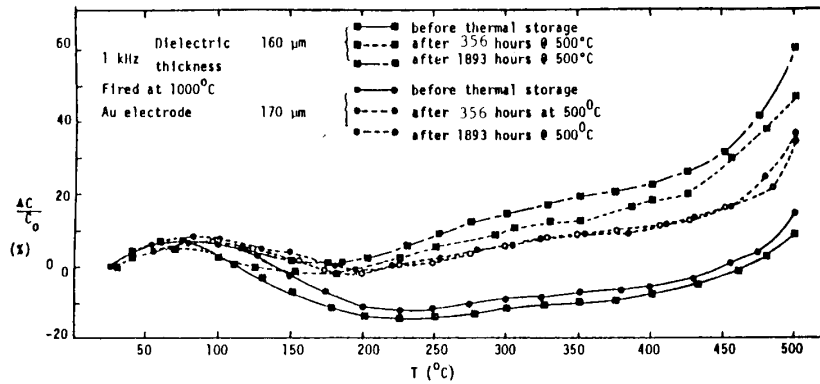


Fig. 19. Effect of 500°C thermal storage on the relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

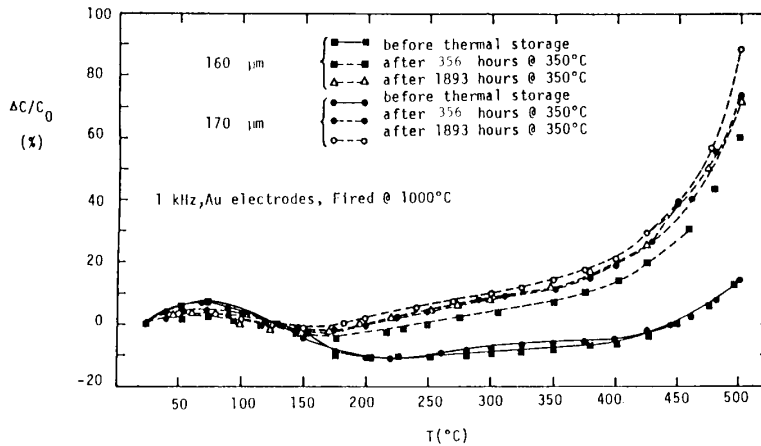


Fig. 20. Effect of 350°C thermal storage on the relative capacitance change as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

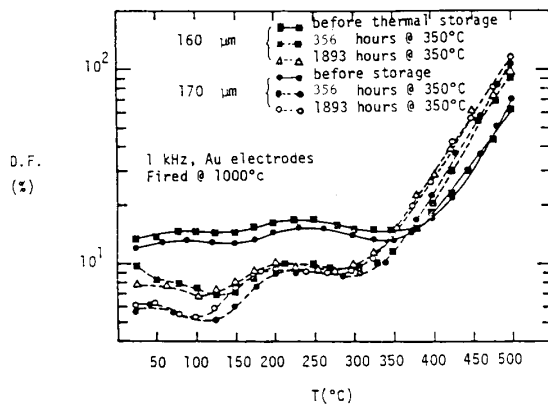


Fig. 21. Effect of 350°C thermal storage on the dissipation factor as a function of temperature for capacitors made with dielectric 35 vol % Frit G1-25 vol % SrTiO₃-40 vol % BaTiO₃.

2) This dielectric, when properly fired, terminated, and heat-treated will work adequately in the temperature range 25°C-400°C for a lifetime longer than 1500 h.

3) The dielectric properties of the multiphase system are divergent from the theoretical prediction. Interfacial polariza-

tion between the electrodes and dielectric and/or among different phases in the dielectric is the major factor that causes deviation.

ACKNOWLEDGMENT

The author wishes to thank Dr. R. W. Vest for helpful discussions.

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