

Multiple-Curie-Point Capacitor Dielectrics*

Abstract: This paper reports an experimental study of the preparation of screened printed dielectric materials having high dielectric constants and a controlled temperature characteristic. The technique uses mixtures of sintered bodies which have different Curie points and which retain their identity after processing. Barium-strontium and barium-lead titanate mixtures have been prepared having a dielectric constant of about 500. This process has been used to produce negative-positive-zero, negative, and positive thermal coefficient bodies over various temperature ranges.

Introduction

One of the most persistent problems in the development of microelectronic computer circuitry is the fabrication of passive elements of reasonably small size yet with characteristics sufficiently precise and controllable to meet the needs of modern digital circuitry.¹⁻⁵

Proper capacitance is usually obtained by attaching discrete elements, such as chip capacitors,³ to the carrier substrate using anodized or evaporated films,^{2,3} or by using the junction capacitance of a back-biased diode.³ The chip capacitor is probably the most popular since it does not have the problems of the film capacitor (pinholes and low voltage breakdown) nor the poor tolerances and temperature characteristics of the diodes. However, the chip capacitor itself has certain disadvantages. Since it has to be self-supporting and strong enough to handle, it has to be relatively thick (10 to 30 mils), thus adding height to the module. There also have been sporadic problems with delamination of the internal layers and end plates. Moreover, the dielectric materials used are often extremely temperature-dependent.

In many commercial bodies this temperature dependence is overcome with varying degrees of success by making additions to the titanate base which act as Curie-point suppressants. This approach works well for the manufacture of ceramic chip capacitors with fairly flat temperature characteristics and an average dielectric constant in the range 800 to 1200. This temperature characteristic, however, is fixed and is not controllable with respect to positive or negative thermal coefficients in a desired temperature range.

Other work has been done on silk screening and firing titanate materials on ceramic substrates to form capacitive elements. Although the capacitances obtained are high,

there are certain drawbacks to this approach. These titanate materials mature in the range 1200° to 1500°C. This temperature range limits the usable metallizing systems to members of the platinum family. It also limits the usable substrate materials to refractory oxides such as alumina and beryllia, eliminating many materials with good electrical or thermal characteristics, e.g., alumina porcelains, steatite and cordierite. There is also the problem of thermal expansion mismatch between the titanate and the substrate, leading to both mechanical and electrical failure.

This paper describes a Multiple Curie Point (MCP) system that has a high dielectric constant and forms a thick film capacitor, either printed directly onto the circuit substrate or made into a thin, discrete chip. This system is based on the blending of various ferroelectric materials having different Curie points and fusing them in a glass matrix in a manner that permits them to retain their identities. The thermal characteristics within a variety of desired operating temperature ranges can be controlled to give bodies with negative-positive-zero (NP0), positive (P), or negative (N) thermal coefficients of capacitance. This control is achieved by varying the number present and/or the weight ratio of the sintered binary ferroelectric bodies within the MCP mix.

Barium titanate (BaTiO_3) has transition temperatures at 120°C, 5°C, and -80°C. The highest of these transition temperatures is the ferroelectric Curie point, above which barium titanate is nonferroelectric and is characterized by a cubic crystal structure. The crystal structure is tetragonal in the temperature range between 5°C and 120°C, orthorhombic in the temperature range between -80°C and

* Presented in part at IEEE Electronic Components Conference, Washington, D. C. May 3, 1967.

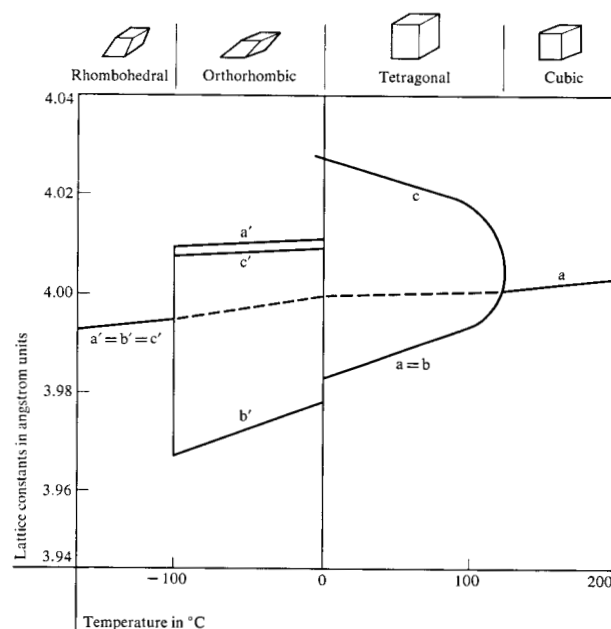


Figure 1 Temperature variation of the lattice parameters of barium titanate showing the various crystallographic transformations (After Megaw, *Proc. Roy. Soc. A*189, 261 (1947)).

5°C, and rhombohedral below -80°C . These phases are shown in Fig. 1. In the neighborhood of each of the transition temperatures, the dielectric constant of barium titanate is increased and ranges from 4,000 at the lowest transition temperature to 10,000 at the Curie point for single crystals. Between the two transition temperatures, however, the dielectric constant drops considerably.

As is well known, the Curie temperature of barium titanate can be changed when it enters into the solid solution with other materials. For example, the addition of strontium titanate (SrTiO_3) lowers the Curie temperature. The addition of lead titanate (PbTiO_3) increases the Curie temperature. In this manner, particular compositions can be obtained which have a Curie temperature (and thus a high dielectric constant) at or near a specified temperature. The Curie-point shift as a function of additive is shown in Fig. 2. A sintered mixture of the respective combinations of materials is characterized by a particular Curie temperature as solid solution occurs, resulting in a single homogeneous composition. The dielectric constant is still highly temperature-dependent, particularly in the neighborhood of the Curie point, as is shown in Fig. 3. A thorough discussion of ferroelectrics is given in Ref. 6.

The present work shows that a composition having a controllable temperature dependence can be obtained from a mixture of two or more of these ferroelectric materials in powdered form if they are kept separate from one another during the fabrication process. The resultant composition

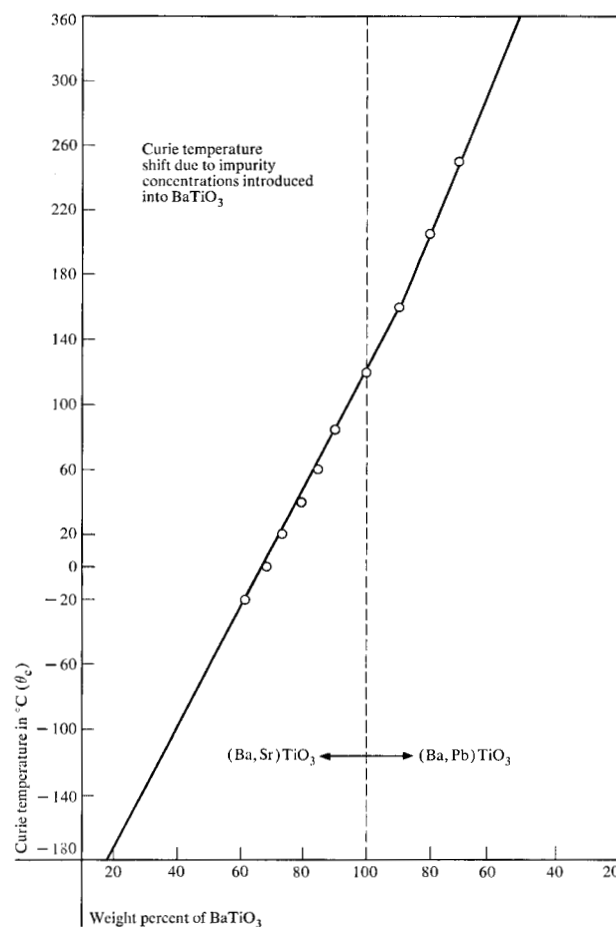
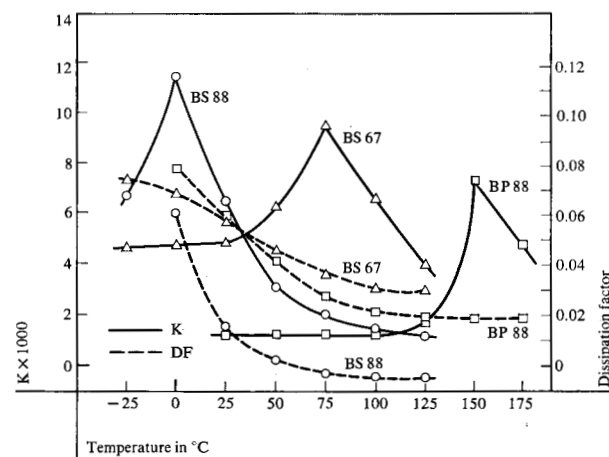


Figure 2 The Curie-point temperature shift as a function of additive.

Figure 3 Sintered mixture binary systems of Ba,SrTiO_3 and Ba,PbTiO_3 bodies: BS88 (88% Ba -12% Sr) TiO_3 ; BS67 (67% Ba -33% Sr) TiO_3 ; BP88 (88% Ba -12% Pb) TiO_3 .



is thus a mixture of discrete granular particles separated from one another by an appropriate binder material, such as glass. This type of composite mixture is not characterized by a single Curie point, at which the dielectric constant is a maximum, but rather is characterized by a dielectric constant that can be described as being approximately proportional to the log sum of the dielectric constants of the individual material particles. Thus, if it is required to increase the dielectric constant of the composition for a particular operating temperature range, one can add an appropriate quantity of a ferroelectric material having a maximum in the dielectric constant in that temperature range. The log sum rule is explained in the section entitled "Materials evaluation."

Device fabrication

The materials used in this study were either C. P. or the (commercial) electronic grade. The appropriate quantities of barium titanate and strontium or lead titanate were weighed out and blended in a water slurry. The slurry was dried to a powder which was subsequently calcined at 1000°C for two hours. The calcined material was reground and remixed. It was then pressed into a compact pellet and fired at 1425°C with a five-hour rise time and a two-hour soak. The fired bodies were crushed to pass through a 105 mesh screen, ball milled for four hours in tetrachloroethylene using Burundum* balls, and dried.

To make the silk screening paste for capacitor fabrication, appropriate amounts of the individual bodies were weighed out according to the desired formulations. Then the glass needed to form the binding matrix was added and the mixture ball milled in tetrachloroethylene for 48 hours. The dried powder was then dispersed in a organic carrier of β -terpineol and ethyl cellulose[†] in the ratio by weight of 75 percent dry powder and 25 percent carrier.

In order to provide adequate reliability under conditions of high humidity, it was found necessary to coat the capacitors with an overglaze, which was also made into a silk-screening paste in the manner outlined above. It is a lead zirconate-titanate and glass composition and was developed to be compatible with respect to thermal expansion and inertness.

All capacitors were fabricated on 96% alumina substrates. Most units were fabricated into parallel-plate type devices with a fired dielectric thickness of about 0.001" to 0.002". A bottom plate and its associated lead were printed using a gold-platinum metallizing paste such as duPont 7553[‡]. This was fired at 760°C for 20 minutes. A layer of dielectric was then screened and dried at 150°C for 10 minutes and fired at 1000°C for 15 minutes. A second dielectric layer

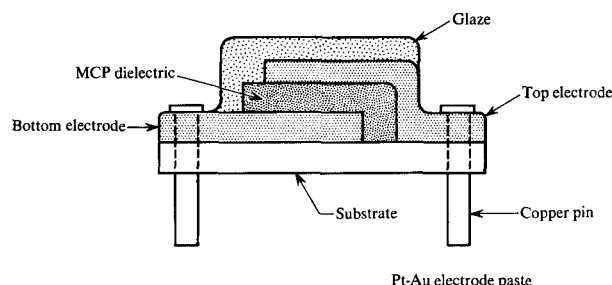


Figure 4 Typical printed parallel-plate capacitor device fabricated by silk screening methods.

was screened and dried, and the top plate and its associated lead were screened and dried. The unit was then fired at 1000°C for 45 minutes. Finally, the glaze was screened, dried at 150°C for 10 minutes and the entire assembly fired at 760°C for 20 minutes.

To provide leads for most samples, copper pins were staked through the alumina substrate, and the substrate was dip-soldered in 10/90 Sn:Pb solder to provide contact between the capacitor leads and the pins (Fig. 4).

Materials evaluation

• Thermal characteristics

The variation of capacitance with temperature was determined by allowing the units to come to equilibrium in a temperature chamber controllable to $\pm 1/2^\circ\text{C}$. The capacitance and dissipation factor at 1 KHz was measured and the dielectric constant calculated using the formula

$$K \equiv \frac{\epsilon}{\epsilon_0} = \eta \frac{Ct}{A},$$

where C is the capacitance, A and t are the plate area and dielectric thickness, and η is a dimensional conversion factor.

The results of these measurements are shown in Figs. 5, 6 and 7. Figure 5 shows the curve for dielectric 121C together with the curves for the individual bodies comprising it. For a comparison the individual bodies were also fabricated as silk-screened capacitors using 6.5% Corning 7059 glass as a matrix. The curves for the individual bodies show that, while the glass (and also some porosity) reduces the dielectric constant considerably, the essential shape of the curve is not changed. That is, the dielectric constant is still strongly temperature dependent and the Curie points, though depressed, are well defined. Dielectric 121C shows the degree of temperature independence obtainable by combining appropriate amounts of the various bodies. The dielectric constant does not vary more than 1% over the range 0° to 100°C .

* Trade name of Carborundum Corp.

† Reausche 163C Squeegee Medium.

‡ Silver-bearing electrode pastes could not be used. A small amount of porosity in the dielectric may allow silver migration under humid conditions with resultant shorting of the capacitor.

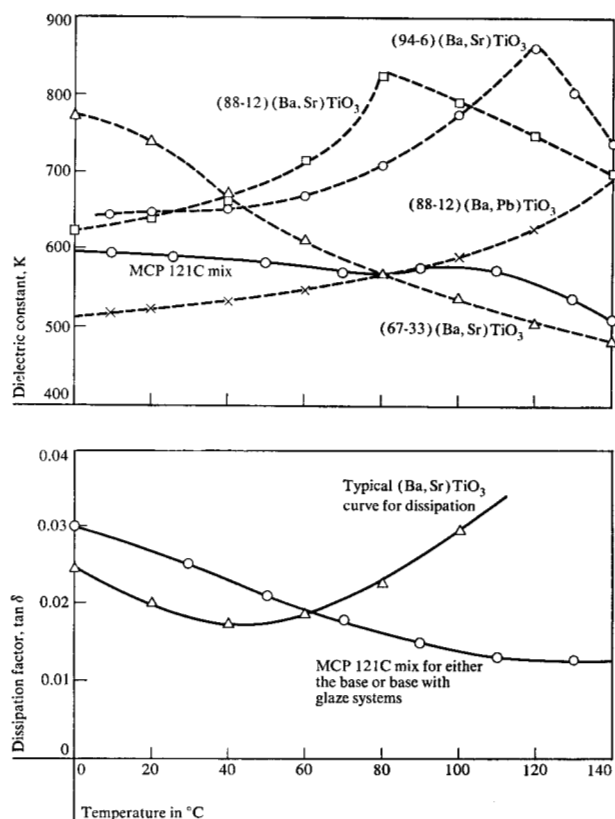


Figure 5 Description of the MCP effect showing both the individual components and the mixture. Mixed-Curie-Point formulation No. 121C:

93.5% $\begin{cases} 94-6 \text{ (Ba, Sr)TiO}_3-20\% \\ 88-12 \text{ (Ba, Sr)TiO}_3-25\% \\ 67-33 \text{ (Ba, Sr)TiO}_3-25\% \\ 88-12 \text{ (Ba, Pb)TiO}_3-30\% \end{cases}$
6.5% Corning 7059 Glass.

Figure 6 shows the variations in temperature characteristics obtained by varying the components in the mixture. Dielectric "B" omits the 150°C Curie-point body and adds bodies with Curie points at 25° and 50°C. The slight dip in K shown by dielectric 121C in the range 25° to 80°C is smoothed out but the K of dielectric "B" drops off rapidly above 75°C.

The effect of varying the amounts of the individual bodies is shown in Fig. 7. Dielectric "D" has equal amounts of each body while "E" has larger amounts of the higher-temperature Curie point bodies. This gives a dielectric which has an almost linear increase in dielectric constant over the range -25° to +40°C. This type of dielectric could be useful in the fabrication of temperature-compensating capacitors.

Examples of the temperature tailoring characteristics of the MCP system are:

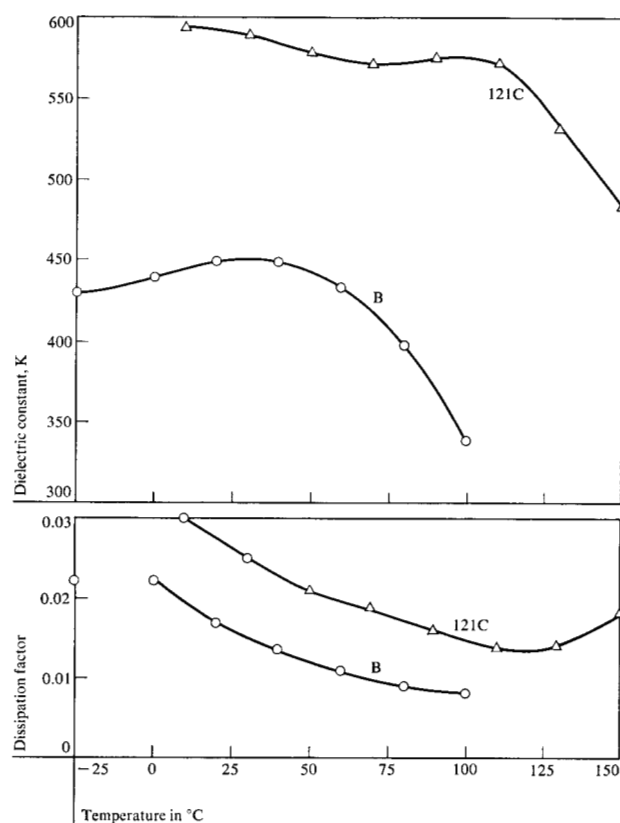


Figure 6 Comparison of 121C and "B" dielectric bodies. Composition of 121C: see caption for Fig. 5. Composition of body "B":

$\begin{cases} 67-33 \text{ (Ba, Sr)TiO}_3-25\% \\ 74-26 \text{ (Ba, Sr)TiO}_3-25\% \\ 81-19 \text{ (Ba, Sr)TiO}_3-25\% \\ 88-12 \text{ (Ba, Sr)TiO}_3-25\% \end{cases}$
93.5%
6.5% Corning 7059 Glass

Body	Temperature Range	Thermal Coefficient (parts per million per °C)
121C	0° to 100°C	~NP0
B	25° to 100°C	N3000
E	0° to 80°C	P3300

• Effects of glass binder

The effect of the matrix material on the resultant dielectric for materials with widely different dielectric constants was also evaluated. The relationship between the dielectric constant of the mixture (K_m) and the constants of the individual components (K_j) at a given temperature is found to be given to a good approximation by Lichtenecker's log mixing rule

$$\log K_m = \sum_{j=1}^N \theta_j \log K_j,$$

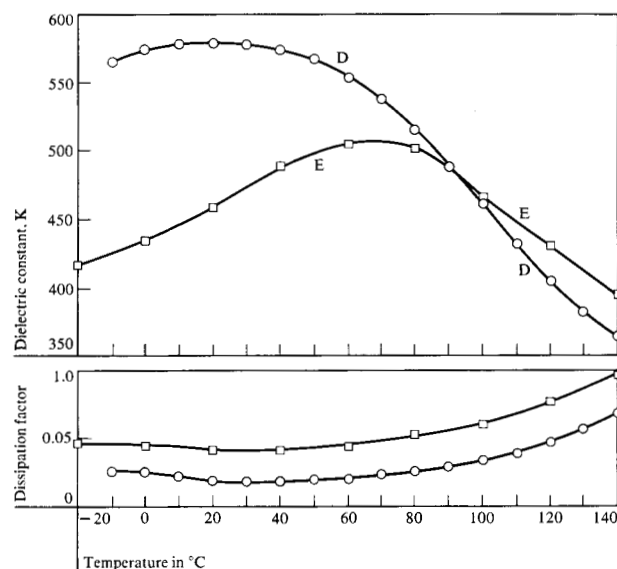


Figure 7 Comparison of "D" and "E" dielectric bodies. Composition of "D":

80% { 67-33 (Ba,Sr)TiO₃-25%
74-26 (Ba,Sr)TiO₃-25%
81-19 (Ba,Sr)TiO₃-25%
88-12 (Ba,Sr)TiO₃-25%
20% 167 JQ Glass.

Composition of "E":

80% { 67-33 (Ba,Sr)TiO₃-12.5%
74-26 (Ba,Sr)TiO₃-12.5%
81-19 (Ba,Sr)TiO₃-37.5%
88-12 (Ba,Sr)TiO₃-37.5%
20% 167 JQ Glass.

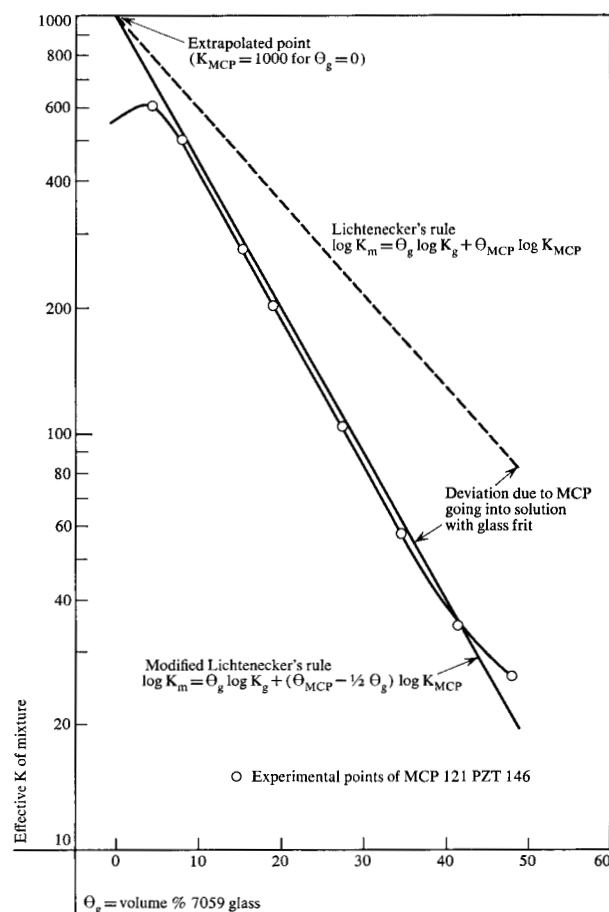


Figure 8 Matrix effect of MCP-glass dielectric system. Note the selectivity of either high or low K which this system offers and its exact predictability.

where θ_j is the volume fraction. This relationship assumes no interactions between the various phases and negligible dielectric media going into solution with the glass frit.

To determine the experimental relationship between percent of the matrix material and composite dielectric constant, the various barium-strontium and barium-lead titanate bodies were mixed together in the manner explained earlier. To this mixture was added a glass frit (Corning 7059 glass) in varying percentages by volume: 0, 4, 8, 13, 17, 21, 29, 37, 44 and 50%. The densities of the glass frit and MCP mixes were evaluated as 2.8 and 6.5 grams/cubic centimeter, respectively.

It was determined that the major interaction was that of the dielectric material going into solution in the glass frit. Figure 8 shows Lichtenecker's log relationship based on a K_m (for zero glass volume fraction) of 1000, which was determined by extrapolation of the experimental curve back to the ordinate axis. Assuming the deviation to be entirely due to this interaction, a modified Lichtenecker's log rule was calculated to be

$$\log K_m = \theta_g \log K_g + (\theta_{MCP} - 1/2\theta_g) \log K_{MCP},$$

where $m \equiv$ dielectric mix; $g \equiv$ glass frit; and MCP $\equiv$ multiple Curie point mixture.

Above about 10 percent by volume of glass, a decrease in the amount of glass results in an over-all increase in the dielectric constant of the composite. However, below 10 percent by volume a further decrease in the amount of glass results in a decrease in the dielectric constant. This is attributed to the amount of glass being too small to fill the voids between the titanate particles. The resultant porosity (introduction of air with a dielectric constant of 1) tends to decrease the over-all dielectric constant.

• Shelf life

The MCP system, like all ferroelectric systems, is subject to aging.⁷⁻⁹ To determine the magnitude of the aging effect, the 121C dielectric was held at 250°C for 5 minutes, then withdrawn, and cooled to room temperature rapidly in a desiccator. Measurement began at exactly 1 hour after withdrawal and terminated, after several readouts, at 1152

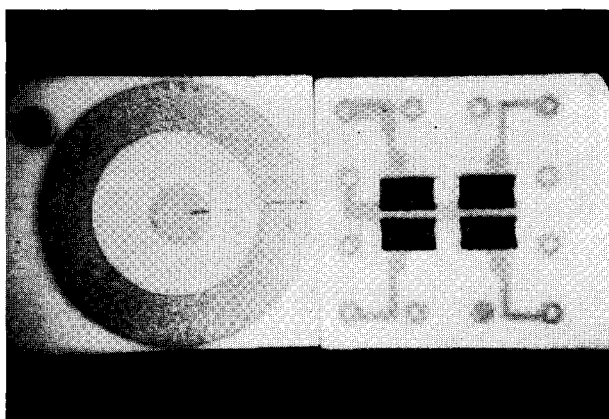


Figure 9 Concentric bullseye capacitor pattern used for all frequency evaluation testing. Innermost disc is top electrode; middle disc is dielectric body; and outer disc is lower electrode. Effective capacitor plate area is the same as the area of the top electrode.

hours. Except for readouts, these units were continuously stored in a desiccator supplied with fresh desiccant at frequent intervals. Results show that aging effects in percent per decade of time are about -1 to -1.5% for the dielectric constant; -10 to -12% for dissipation; and -2 to $+25\%$ for dielectric resistivity.

This aging characteristic is to be regarded as follows: if fabricated capacitors are aged (i.e., stored at 25°C under dry conditions) for 1000 hours (six weeks) prior to actual use, then they will drift less than 1% in capacitance during the first 14 months of operation and less than 2% during a period of 11 years of operation.

• Thermal shock

Samples were placed in a programmed temperature control chamber and cycled between 0°C and 100°C with a 1 minute rise time, 2 minute soak time, 2 minute fall time, and 2 minute lapse time to complete one cycle.

No failures were noted, and drifting of capacitance and dissipation factor was less than $\pm 1\%$.

• Dielectric strength

Samples were individually placed in series with calibrated precision $1\text{M}\Omega$ resistors. A voltage bias was applied from a Keithley Model 241 constant high dc voltage supply ($\pm 0.05\%$ accuracy). The voltage across the precision resistor was monitored with a high-impedance digital voltmeter readable to $1\mu\text{V}$, thus giving a capability of measuring the dc resistance of the capacitor from $10^{12}\Omega$ to breakdown. Measurements were taken at 25° and 75°C (only test capacitors were subjected to heat). A dielectric strength of between 50 and 100 kV/cm was obtained for the various mixtures evaluated, independent of test temperature. The dc resistance decreased by a little more than an order of magnitude up to breakdown.

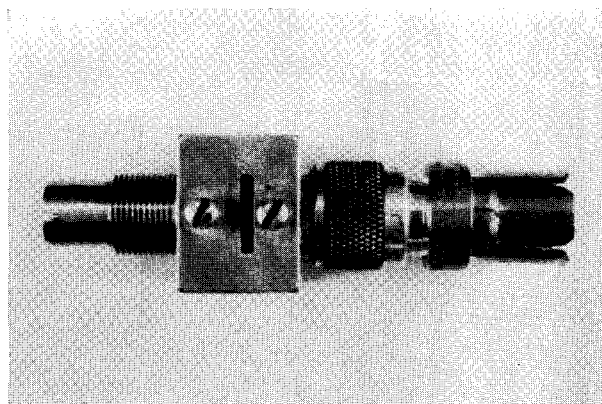


Figure 10 Jig assembly used to measure samples shown in Fig. 9. A spring-loaded copper ball connected to the inner line of the coaxial fixture makes contact to the inner electrode, while the outer lip of the fixture contacts the outer electrode. The screw presses the sample onto both contacts.

• Frequency characteristics

A capacitor test pattern was used that would yield the dielectric response independent of geometry. This pattern should be such that it does not exhibit any series lead or plate resistance or inductance. The pattern chosen is shown in Fig. 9. It is equally important to use a jig assembly which also does not appreciably exhibit either series resistance or inductance. Neither the bullseye pattern nor the jig assembly exhibited any indication of series resistance or inductance up to 100 MHz. The jig assembly used is shown in Fig. 10.

The MCP 121C type capacitor system was measured by standard methods as follows: 100 Hz to 10 kHz on the General Radio 1615A capacitor bridge; to 5 MHz on the Wayne Kerr B601 Radio Frequency Bridge; and to 1000 MHz on the General Radio 1602B Admittance Meter.

The results are shown in Figs. 11 and 12. The salient feature of these curves shows that the MCP thick film system exhibits very nearly bulk capacitor characteristics. The only unusual feature is a maximum in the dissipation factor at about 200 MHz.

Sample devices with encapsulating glass shrouds were subjected to initial dry and wet life testing at 85°C and 25 V dc stress bias for 1000 hours. The results of this testing are shown in Fig. 13.

Because of this initial success, further life testing was performed under greater accelerating conditions:

Temperature ($^{\circ}\text{C}$)	Bias (V dc)	Humidity (% R.H.)
85	25, 50	dry
125	25, 50	dry
175	storage	dry
85	25	98

No failures were recorded and all drift patterns were within Class II* specifications.

*See EIA Standard RS-198

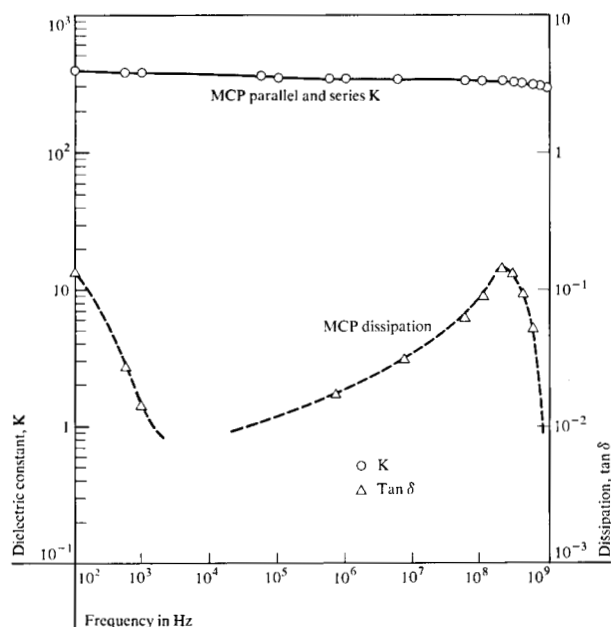


Figure 11 Dielectric constant and dissipation frequency response for MCP mix 121C.

Figure 12 Frequency response for impedance parameters, MCP mix 121C.

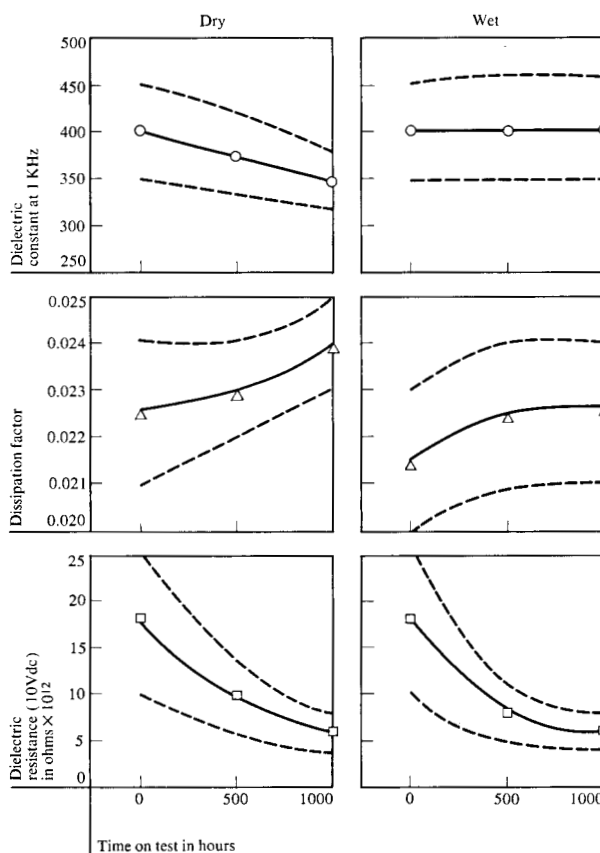
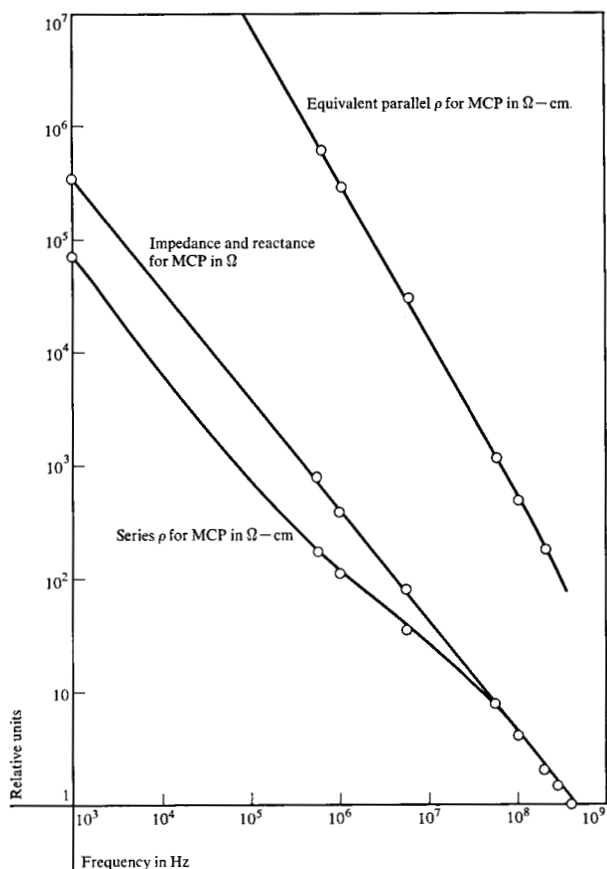


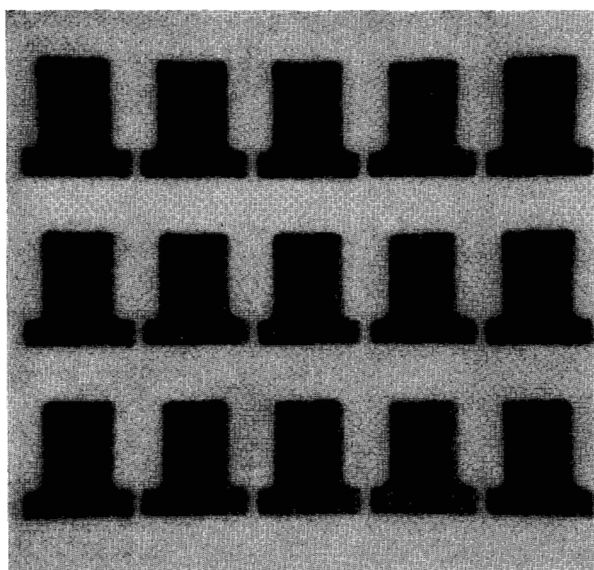
Figure 13 Reliability test results. Dotted lines show spread of results. (Test conditions: 85°C, 25Vdc bias).

• Discrete devices

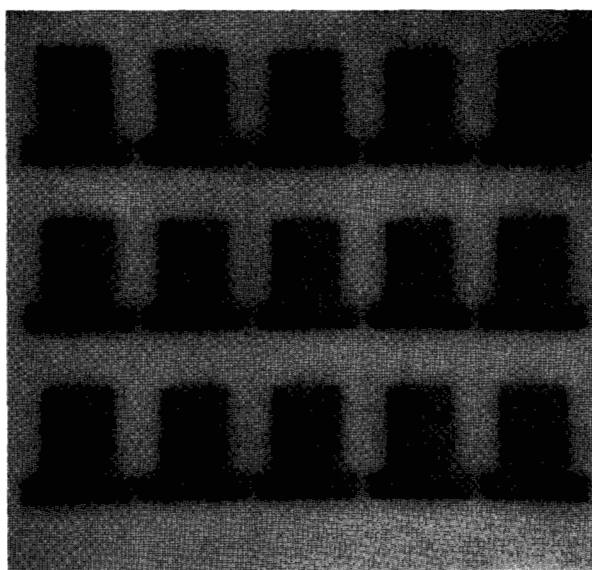
In order to determine feasibility of fabricating discrete devices for hybrid high-density modules, a chip capacitor version of the above process was successfully developed. An illustration of typical operations appears in Fig. 14. The chips shown are 0.065" by 0.085" and have an effective capacitor area of 0.045" square. These units were all hand screened.

Conclusion

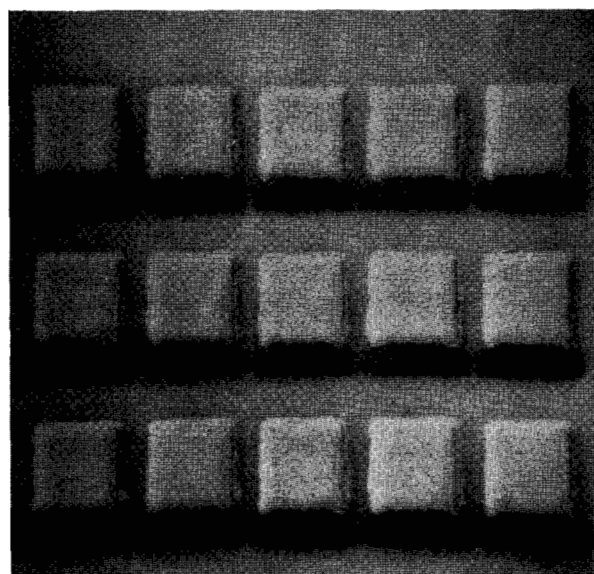
The multiple-Curie-point concept leads to a family of composite materials which can be used to fabricate capacitors with preselected temperature characteristics. The dielectric constant of these composites can be varied from a peak of about 600 to a low of 20 to 30, depending mainly on the amount of glass used. Capacitors from the low-picofarad to the low-nanofarad range can be made, depending upon the dielectric constant of the composite used and the plate area available. These capacitors have been made by silk-screening techniques directly on the substrate which holds the printed circuitry and the screened resistors and semiconductor chips. They have also been made on substrates that were subdivided after scoring to form individual "chip" capacitors, which could later be attached to the rest of the



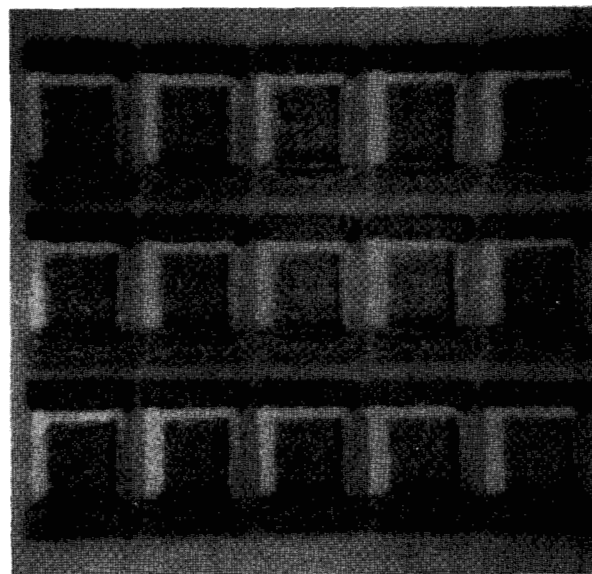
(a)



(b)



(c)



(d)

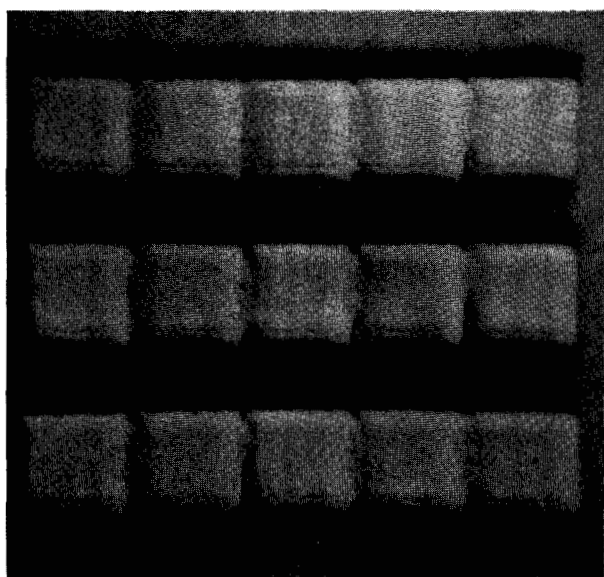
Figure 14 Chip capacitor formulation: (a) bottom electrode dried, (b) fired, (c) 2 layers dielectric—1st fired, 2nd dried, (d) top electrode fired.

circuitry by solder reflow, etc. Chip capacitors can also be made by using the standard ceramic-tape techniques now widely used in the capacitor industry or by dry pressing the composite and firing.

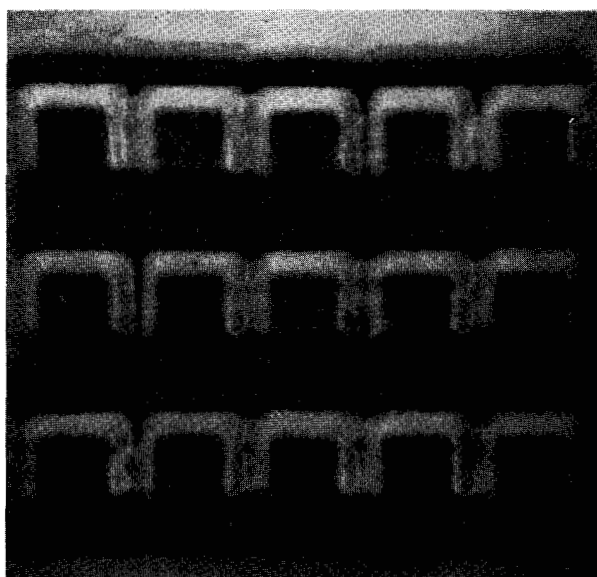
Because of the basic nature of the titanates used, only Class II capacitors can be made by this method. In addition, they are subject to degradation when exposed to high humidity. However, the glaze mentioned in this paper overcomes this humidity problem. The formulation and applications of this glaze will be the subject of another paper.

Because of the unique ability to tailor the temperature characteristics of these capacitors, they should be useful in temperature compensating networks. Since they can be formed on the circuit substrate and have no "flying" leads, these units are extremely rugged and should find useful application in high-mechanical-stress devices such as missile hardware.

In general, MCP systems should find a wide variety of applications where a rugged, low-cost capacitor with tailored temperature characteristics is needed.



(e)



(f)



(g)

Figure 14 Chip capacitor formulation: (e) glaze dried, (f) glaze and assembly fired, (g) completed chip capacitors.

Acknowledgments

The authors appreciate the assistance of R. Spielberger and J. Williams rendered in the fabrication and measurement of test devices used in this investigation.

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Received January 4, 1967.