

Figure 1. Relative polarizability contributions to permittivity in glasses and glass-ceramics (Ref. 2).

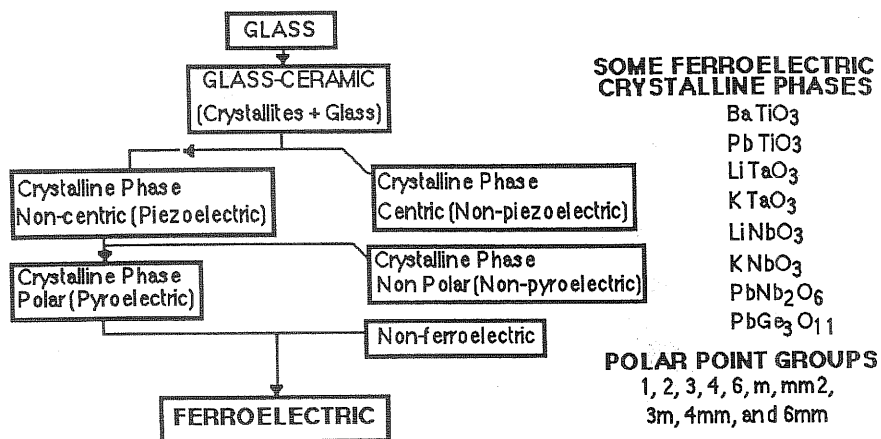


Figure 2. Route to High-Permittivity Glass-ceramics (Ref. 7)

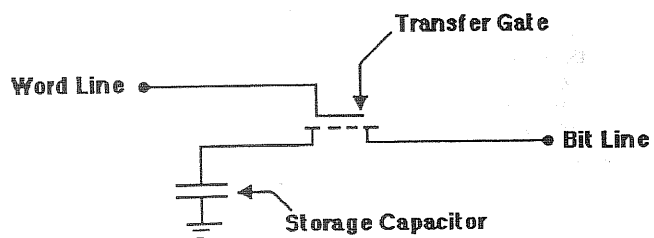


Figure 3. Schematic of a one-transistor DRAM cell with a storage capacitor (Ref. 20).

LIQUID PHASE ASSISTED SINTERING OF CERAMIC DIELECTRIC FOR LOW FIRED MLC APPLICATION

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ABSTRACT

The incorporation of only a few percent of an appropriate glass forming flux in a ceramic dielectric can significantly reduce its sintering temperature. The role of some popular flux additives in enhancing sintering and their subsequent effect on the physical and electrical properties of low fired dielectric (Z5U, X7R and COG) for MLC applications are reviewed.

The solid solubilities of bismuth compounds of titanate, zirconate and stannate with barium titanate were investigated using a cadmium silicate flux as sintering aid. Electron spectroscopy chemical analysis (ESCA) has shown that a limited amount of bismuth (<4m%) can be incorporated with BaTiO₃ when a charge compensation additive is included. In the system BaTiO₃-Bi₂Ti₂O₇ approximately the first 1m% of bismuth tended to enter the lattice as Bi⁺⁵, presumably on the titanium site, and causes an upward shift in curie temperature. Above 1m%, the bismuth tended to enter the lattice as Bi⁺³, presumably on the barium site,

and causes a downward shift in curie temperature. In the system $\text{BaTiO}_3-(2\text{Bi}_2\text{O}_3:3\text{ZrO}_2)$ and $\text{BaTiO}_3-(\text{Bi}_2\text{O}_3:3\text{SnO}_2)$, bismuth appeared to incorporate mostly as Bi^{+3} , and to cause a downward shift in curie temperature.

LOW FIRED DIELECTRICS

Introduction

The dramatic increase in the cost of palladium, the metal commonly used in the mid-1960s for the internal electrode of MLC capacitors, provided the catalyst to search for alternative electrode systems. Significant advances have been made on several fronts. These include the use of base metal electrode⁽¹⁾, lead injected electrode⁽²⁾, and high silver (Ag-Pd) electrode⁽³⁾.

This paper reviews work performed on the latter system at the Research and Development Center of Sprague Electric Company. In order to take advantage of the lower cost of the Ag-Pd system, it was necessary to reduce the sintering temperature of the dielectric, which was mostly high fired MLC sintered at 1350°C, to less than 1150°C. The popular electrode system commonly used for low fired MLC dielectrics is a 70 Ag/30 Pd.

Additives that are low melting temperature fluxes (Table 1), or others that can form low temperature

eutectic with the dielectric⁽⁴⁾, have been used in the manufacture of ceramic dielectric base MLC capacitors. For a Z5U type dielectric, it is desirable that the flux react with the dielectric to form a solid solution resulting in grain growth via liquid phase re-precipitated mechanisms^(3,5,6). On the other hand, for X7R and COG type dielectrics, the flux need only react at the surface of the grain to enhance sintering without significantly increasing the size of the grains or solid solubility among the components in the dielectrics⁽³⁾.

Common Flux Additives

The flux additives commonly used as sintering aids in many dielectric compositions are summarized in Table 1. There are undoubtedly many other combinations and permutations that can be used to achieve the desired physical and electrical properties. Many of these systems are reported elsewhere^(15,16). The development of these dielectrics over the past twenty years is summarized in Table 2. The progress made in improving the dielectric constant and reducing the dielectric thickness of the MLC is also described.

Z5U Dielectrics

In the early development stage of this dielectric system, the flux additives constituted between 8 and 12w% of the total composition. Even with this high concentration, a respectable dielectric constant in the range of 4500 to 6500 was achieved. A simplifica-

tion of the flux composition and better understanding of mechanisms involved^(4,18,17), resulted in a reduction of the flux content to less than 4w%. This, in turn, increased the dielectric constant to over 8000 without changing the sintering temperature. The dielectric properties of this system are still being improved by using high purity and fine powder starting materials (Figure 1).

X7R Dielectrics

Development of the X7R dielectric has also taken a course similar to that described for the Z5U. However, the availability of fine powder barium titanate with controlled stoichiometry and optimum surface area has resulted in low fired compositions that nearly equal high fired counterparts in properties. In these systems, a dielectric thickness as low as 6 microns with exceptional electrical properties has already been reported⁽¹⁸⁾. Typical characteristics of such a dielectric are described in Figure 2.

COG Dielectrics

In the COG class of dielectric two systems are commonly used; one is a stable high "K" system, and the other is a low "K" system for high frequency applications.

The high "K" composition was based on a BaO-Nd₂O₃-TiO₂ ternary system while that for low K was based on calcium modified MgZnTiO₃. Unlike the Z5U

and X7R, the incorporation of flux additive in the ternary system not only allowed the sintering temperature to be reduced but also gave a much higher dielectric constant. Additional details on these systems are described elsewhere^(3,9,19).

Bismuth oxide and/or bismuth compounds are used as additives in the composition of many low fired dielectrics. In the second part of this paper the effect of bismuth dopant on the Curie Temperature of BaTiO₃ will be described.

ROLE OF BISMUTH DOPANT ON THE CURIE TEMPERATURE OF LOW-FIRED BARIUM TITANATE BASE DIELECTRIC

As has been shown in the previous section, many of the additives that have been used in the composition of low fired dielectric contain bismuth. In the early stages of the dielectric development fluxes used for all three classes of dielectric contained significant amounts of bismuth⁽³⁾. Bismuth oxide or bismuth compounds have been added to BaTiO₃ to enhance sintering without grain growth, in order to achieve an X7R type characteristic^(20,21). In the case of the high "K" COG dielectric based on the BaO-Nd₂O₃-TiO₂ system, the addition of bismuth played a major role in enhancing sintering and providing the temperature coefficient requirement of $\pm 30\text{ppm}/^\circ\text{C}$ ^(19,22).

In this paper, the role of bismuth dopant on the curie temperature of low fired barium titanate base dielectric will be described. Part of this work was presented earlier⁽²³⁾.

Experimental Samples

Samples were prepared by blending 100 grams of barium titanate with additives and flux in an organic binder/solvent system, using polyethylene bottles and high density barium titanate balls, for six hours. After drying the solvent, the cake was granulated through a 40 mesh nylon screen and discs were hydrostatically pressed at 10^8 Pa. The discs were baked to 800°C on an open zirconia slab to remove the binder, then were stacked in a high purity alumina crucible with cover. Sintering was performed at 1100°C for three hours at peak temperatures. The starting composition consisted of relatively high purity stoichiometry BaTiO_3 with an average particle size of 0.9 micron. The bismuth compound additives were all electronic grades ($\text{Bi}_2\text{O}_3 \cdot 2\text{TiO}_2$), ($2\text{Bi}_2\text{O}_3 \cdot 3\text{ZrO}_2$) and ($\text{Bi}_2\text{O}_3 \cdot 3\text{SnO}_2$). The flux consisted of $5\text{CdO} \cdot 2\text{SiO}_2$. All these additives had average particle size between 1 and 1.6 microns.

In the experimental samples the flux was kept constant at 1.25m% and the bismuth compound additives were varied as follows:

$$0.9875 [(1-x) \text{BaTiO}_3 + x \text{B}] + 0.0125 (5\text{CdO} \cdot 2\text{SiO}_2)$$

where: B = Bismuth compounds

x = Varied between 0.0 and 0.05 mole fraction.

After sintering the samples were processed to generate the electrical properties. The as-fired grain structure was examined with SEM. The solubility of Bi, Cd, Zr and Sn dopants in the grains was determined by Electron-Microprobe analysis. The substitution of the bismuth in the BaTiO_3 lattice was determined by Electronic Spectroscopy Chemical Analysis (ESCA).

RESULTS AND DISCUSSION

Effect of Bismuth Compound Additives on the Curie Temperature (T_c) Shift of BaTiO_3

The change in capacitance with temperature (TCC) was determined for each of the compositional series. The results are shown in Figure 3. As can be seen from the data, bismuth titanate additive shifted T_c upward, while both bismuth zirconate and bismuth stannate showed an initial small shift upward followed by a sharp down shift in T_c with increasing dopant concentration. It should be noted that the sample with BaTiO_3 and flux only showed no shift in T_c but with significant precipitation of semiconducting cadmium phase (blue) dispersed throughout the dielectric.

Grain Structure

The as-fired grain structure, as a function of composition for bismuth titanate and bismuth zirconate, is shown in Figures 4 and 5 respectively.

In the case of the bismuth titanate additives, the grain showed a maximum size in the range of 10-15 microns at about 1.5m% addition, while for the bismuth zirconate the grains showed maximum growth near 1m%. A similar grain structure variation was observed for bismuth stannate additive, with maximum grain growth occurring near 2m%.

Grain Composition

The concentration of Bi, Cd, Zr and Sn in samples with large uniform grains was determined using electron microprobe analysis. The results are summarized in Table 3. Each entry represents an average of ten measurements.

As can be seen from the data, all the added bismuth appeared to have been incorporated in the barium titanate; similarly, the ZrO_2 and SnO_2 also entered the barium titanate matrix. However, only about one-third of the CdO has gone into solution with $BaTiO_3$, the remainder most likely segregating in a glass phase at triple points.

As the concentration of additive was increased, from 0 to over 4m%, the grain structure varied from fine to large to fine grain, then finally, the sample became porous near the upper limits. Also the level of the semiconducting cadmium phase was reduced and then disappeared as the amount of additive was increased.

Site Occupation of the Bismuth in the $BaTiO_3$ Lattice

The site occupation of bismuth in the barium titanate lattice was determined by ESCA⁽²⁴⁾. The binding energy of Carbon C_{1S} was used as a reference, (Figure 6). The ESCA spectrum for samples with bismuth titanate, and bismuth zirconate are shown in Figures 7 and 8 respectively. As can be seen from the data, for the first mole % of bismuth titanate addition, a significant portion of the bismuth appeared to be a Bi^{+5} , most likely occupying a Ti^{+4} lattice site. However, further increases in the additive tended to show an increase in the Bi^{+3} and less of Bi^{+5} with occupancy most likely on the Ba^{+2} lattice site (See Figure 7).

In the case of bismuth zirconate additives, a small portion of the bismuth was incorporated as Bi^{+5} but the major portion was incorporated as Bi^{+3} (See Figure 8).

No ESCA determination was done on the samples with bismuth stannate. However, it is believed that the bismuth will incorporate into the $BaTiO_3$ lattice in a manner similar to that of the bismuth zirconate additive.

Henning et al.⁽²¹⁾ have also observed a shift in the T_c upward when a few mole percent of Bi_2O_3 was substituted in the $BaTiO_3$. However, the mechanisms for this shift were attributed to the formation of a layered pervoskite of $Bi_4Ti_3O_{12}$ with a reported T_c of

+675°C. The works of Burn^(8,17) and Maher⁽⁴⁾ show that in these large grain solid solution systems, the bismuth Bi^{+3} or Bi^{+5} are donor ions with respect to the BaTiO_3 and are charge compensated with Cd^{+1} as an acceptor large cation substituting on the Ba^{+2} lattice site.

In this study and from Table 3, only a few of the compositions showed that enough cadmium was dissolved in the lattice to charge compensate for bismuth. Therefore in those samples where the molar ratio of $\frac{\text{Bi}^{+5} + \text{Bi}^{+3}}{\text{Cd}^{+1}}$ is greater than 1.1, then an additional charge compensation mechanism must be involved, possibly the creation of barium vacancies. Further study will be needed in this area.

SUMMARY

The availability of high purity and fine grain ceramic powder and a better understanding of the affect of flux additives on the sintering characteristics of the dielectrics have resulted in the development of a variety of compositions with reduced sintering temperature while maintaining excellent physical and electrical properties. In a barium titanate-based system, a dielectric constant near 10,000 with dielectric thickness between 10 to 15 microns are realistic targets for Z5U applications at sintering temperatures no higher than 1100°C.

Similarly, for an X7R, a dielectric constant near 3500 with dielectric thickness between 6 and 10 microns has also been demonstrated.

For COG application, systems that are mostly based on the alkaline earth-rare earth-titanates would likely give a dielectric constant near 100. The inherent stability and capability of this dielectric would also lend itself to thin layer (6 to 10 microns) MLC design.

In many of these classes of dielectrics, the bismuth compound additive not only acted as a sintering aid, but was also found to incorporate into the barium titanate lattice. In those systems containing bismuth titanate, zirconate or stannate, with cadmium silicate flux as sintering aid, the ESCA data suggest that the bismuth may substitute as Bi^{+5} presumably on the Ti^{+4} and as Bi^{+3} on the Ba^{+2} lattice site. The electrical data also suggest that in the Bi^{+5} state the bismuth tended to shift the T_c upward, while in the Bi^{+3} state, it shifted the T_c downward.

ACKNOWLEDGEMENT

Most of this study was done at the Sprague Research and Development Center (presently MRA Laboratories). The author is very grateful to all who have contributed to this work.

REFERENCES:

1. Burn, I. & Maher, G. H. "High Resistivity BaTiO₃ Ceramics Sintered in CO-CO₂ Atmospheres", J. Materials Science 10:633-640, 1975.
2. Rutt, P.C., U.S. Patent 3,619,220, 1971.
3. Maher, G.H. "Improved Dielectrics for Multi-Layer Ceramic Capacitors", Proceedings of the 27th Electronic Components Conference, 391-399, 1977.
4. Maher, G.H. "Ceramic Capacitors and Method for Making the Same", U.S. Patent 4,266,265, 1981.
5. Maher, G.H. "Method of Forming a Glass-Reacted-Ceramic Component", U.S. Patent 3,885,941, 1975.
6. Burn, I. "Method for Making a Glass-Reacted-Ceramic", U.S. Patent 3,120,677, 1978.
7. Sarkar, S.K. et al., "Liquid Phase Sintering of BaTiO₃ by B₂O₃ and PbB₂O₄" Mat. Res. Bull., 24: 773-779, 1989.
8. Burn, I. "Flux-Sintered BaTiO₃ Dielectrics" Journal of Materials Science 27:1398-1408, 1982.
9. Maher, G.H. "Low Firing High Q Monolithic Ceramic Capacitor" U.S. Patent 4,533,974, 1985.
10. Payne, D. et al "Heterophasic Ceramic Capacitor" U.S. Patent 4,158,219, 1979.
11. Chowdray, K.R. and Subbarao, E.C. "Liquid Phase Sintered BaTiO₃" Ferroelectrics 37:689-692, 1981.
12. Armstrong, T.R. et al., "Dielectric Properties of Fluxed Barium Titanate Ceramic with Zirconia Additions" J. American Ceramic Soc. 73[3]:700-706, 1990.
13. Desgardin, G. et al., "BaLiF₃ - A New Sintering Agent for BaTiO₃-Based Capacitor" American Ceramic Society Bulletin 64[4]:564-570, 1985.
14. Hennings, D.F "Control of Liquid-Phase-Enhanced Discontinuous Grain Growth in Barium Titanate" Journal of the American Ceramic Society 70[1]:23-27, 1987.
15. Maher, G.H. "A New PLZT Dielectric for Use in Characteristic X7R Multilayer Ceramic Capacitors" IEEE Trans on CHMT, CHMT-6[4]:372-376, 1983.
16. Shrout, T. et al. "Lead Based Pb(B₁B₂)O₃ Relaxors vs. BaTiO₃ Dielectrics for Multilayer² Capacitors" Ceramic Transactions 8:3-19, 1990.
17. Burn, I. "Low Firing Monolithic Ceramic Capacitor with High Dielectric Constant" U.S. Patent 4,283,753, 1981.
18. Maher, G.H. "MLC Capacitors with 6 microns Active Dielectrics and X7R Electrical Characteristics" Ceramic Transactions 11:429-435, 1990.
19. Maher, G.H. "Method for Making a Bismuth Doped Neodymium Barium Titanate" French Patent, 2,581,683, 1990.
20. Rawal, G. et al., "Grain Core Shell Structures in Barium Titanate-Based Dielectric" Advances in Ceramics 1:172-188, 1981.
21. Hennings, D. et al "Temperature-Stable Dielectrics Based on Chemically Inhomogeneous BaTiO₃", J. Amer. Cer. Soc. 67[4]:249-254, 1984.
22. Roup, R. "Ceramic Compositions for High Stability Capacitors" U.S. Patent 3,775,142, 1973.
23. Maher, G.H "Influence of Bi⁺³, Bi⁺⁵ doping on the Curie Temperature of BaTiO₃" Amer. Cer. Soc. Bull. 60:401, 1981 (Abstract only).
24. ESCA Analysis was performed by Structure Probe, Inc., Metuchen, N.J.

Table 1
Common Flux Additives

Oxides Glass Formers	Oxides Glass Modifiers		
	Strong	Intermediate	Moderate
B ₂ O ₃	PbO	ZnO	Al ₂ O ₃
SiO ₂	Bi ₂ O ₃	BaO	Sb ₂ O ₃
GeO ₂	CdO	CaO	MoO ₃
	Li ₂ O	SrO	WO ₃

Few Reported Flux Systems Additives

CdO-Bi ₂ O ₃ -PbO-ZnO-B ₂ O ₃ -SiO ₂
PbO-B ₂ O ₃ ; PbO-Bi ₂ O ₃ -B ₂ O ₃
CdO-B ₂ O ₃ ; CdO-Bi ₂ O ₃ -B ₂ O ₃
ZnO-B ₂ O ₃ ; ZnO-Bi ₂ O ₃ -B ₂ O ₃
CdO-ZnO-B ₂ O ₃
CdO-SiO ₂
PbO-GeO ₂
Bi ₂ O ₃ -B ₂ O ₃
CaO-Al ₂ O ₃ -B ₂ O ₃
LiF; BaLiF ₃

References

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Table 2
Development of Low Fired Dielectrics

Class	System	High Fired T > 1250°C 1950 - 60's	First Generation Low Fired 1000 - 1100°C 1970 - 80's	Second Generation Low Fired 1050 - 1100°C 1980 - 1985	Third Generation Low Fired 1050 - 1120°C 1985 ->
Z5U (Ba, Sr, Ca, Pb)(Ti,Zr)O ₃		K = 6000-8000 AD = 25-50 μm	K = 4500-6000 AD = 20-30 μm	K = 7000-9000 AD = 20-30 μm	K ≥ 10,000 AD = 10-15 μm
X7R BaTiO ₃ +Nb ₂ O ₅ BaTiO ₃ +Bi ₂ Ti ₂ O ₇ BaTiO ₃ +2Bi ₂ O ₃ ·3TiO ₂		K = 1600-2500 AD = 25-50 μm	K = 1450-1650 AD = 20-30 μm	K = 2000-2500 AD = 20-30 μm	K = 2600-3500 AD = 6-10 μm
COG - High "K" BaO-Nd ₂ O ₃ -TiO ₂		K = 45-60 AD = 25-50 μm	K = 60-70 AD = 20-34 μm	K = 80-90 AD = 15-25 μm	K = 80-110 AD = 6-10 μm
- Low "K" (Mg, Zn, Ca)TiO ₃		K = 15-25 AD = 25-50 μm		K = 15-25 AD = 20-30 μm	K = 7-20 AD = 20-30 μm

Table 3
Electron Probe Micro-analysis (at 20 KV, 80 ma)
for Bi, Cd, Zr, Sn in the grain W%

Exp. #	Bi ₂ O ₃	CdO	ZrO ₂	SnO ₂	M
79-628	1.94 +/- .08 (1.88)*	1.02 +/- .10	-	-	1.05
79-63A	3.18 +/- .15 (3.11)	1.25 +/- .05	-	-	1.367
79-62D	2.45 +/- .10 (2.40)	1.07 +/- .04	0.91 +/- .07 (0.95)	-	1.236
79-63C	4.03 +/- .11 (3.94)	1.37 +/- .13	1.50 +/- .06 (1.56)	-	1.579
80-6D	2.42 +/- .2 (2.50)	0.97 +/- .04	-	2.16 +/- .3 (2.43)	1.421
80-8A	2.73 +/- .1 (2.80)	1.03 +/- .06	-	2.57 +/- .2 (2.72)	1.496
80-8B	3.66 +/- .6 (3.17)	1.00 +/- .18	-	2.72 +/- .03 (3.09)	1.743

* Values in parenthesis indicate the amount in W% of the bismuth compound added
Actual data represent an average of 10 measurements
M = Approximate molar ratio in grains of BiO_{1.5}/CdO

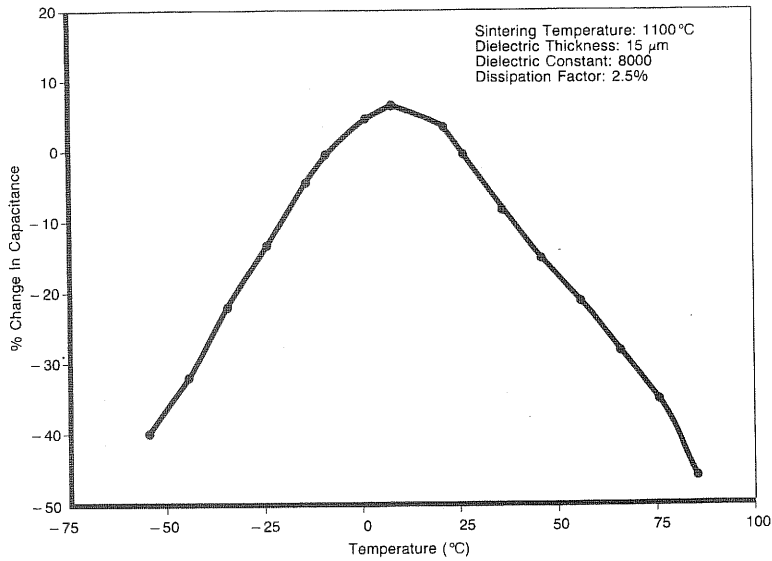


Figure 1: Variation of Capacitance with Temperature (TCC) for a Z5U type Low Fired MLC Capacitor

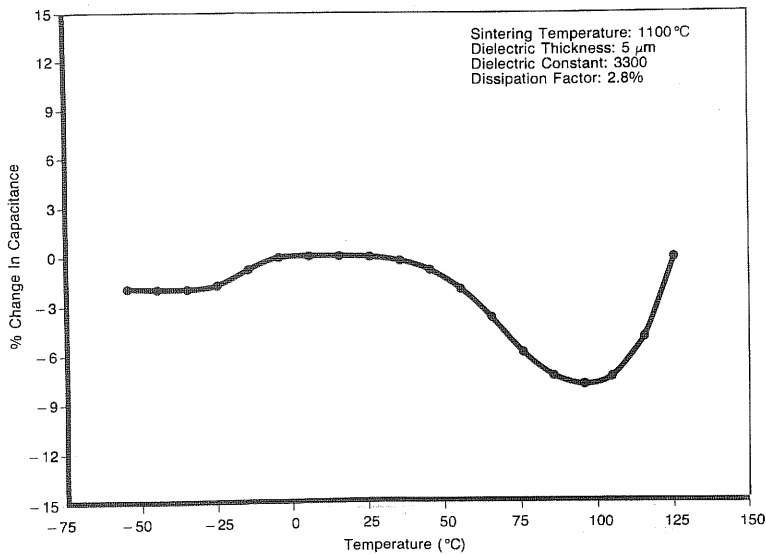


Figure 2: Variation of Capacitance with Temperature for an X7R Type Low Fired MLC Capacitor

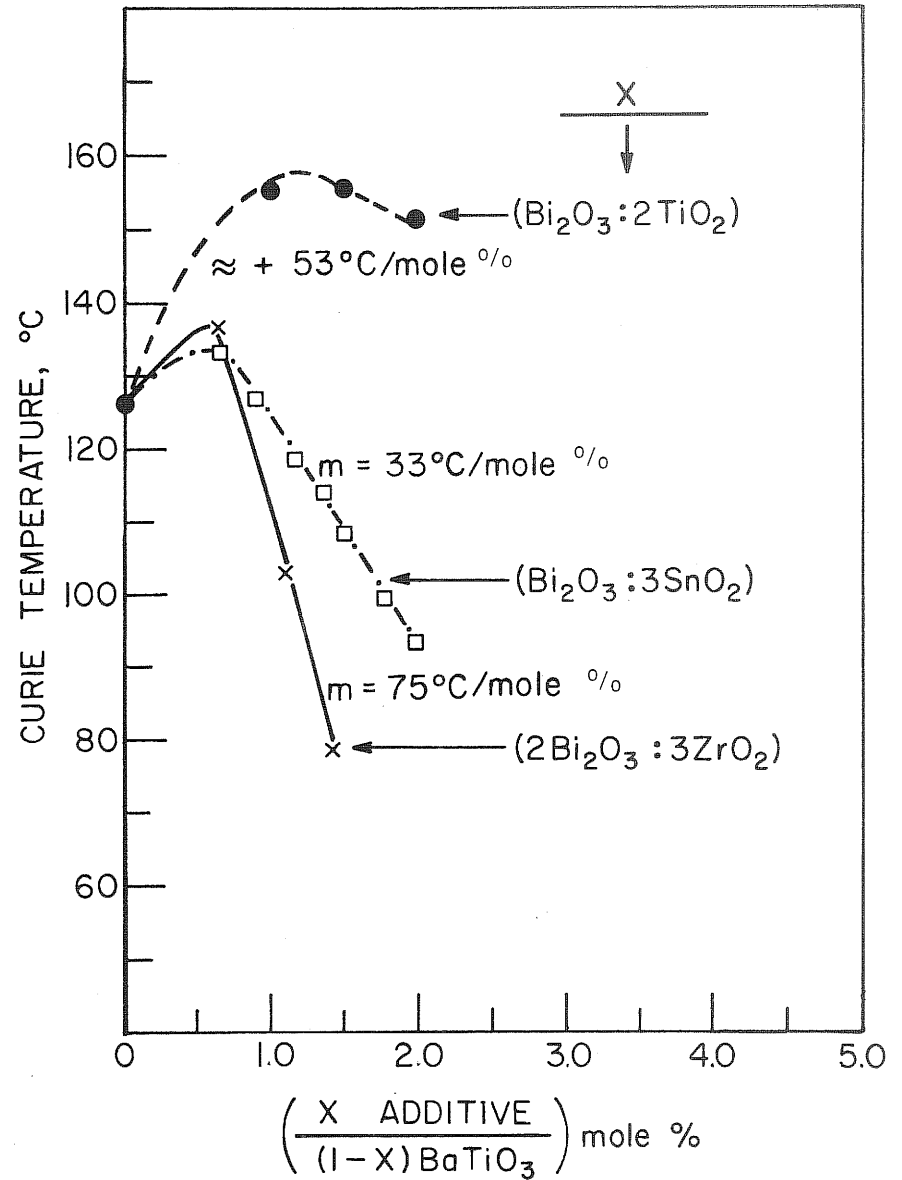
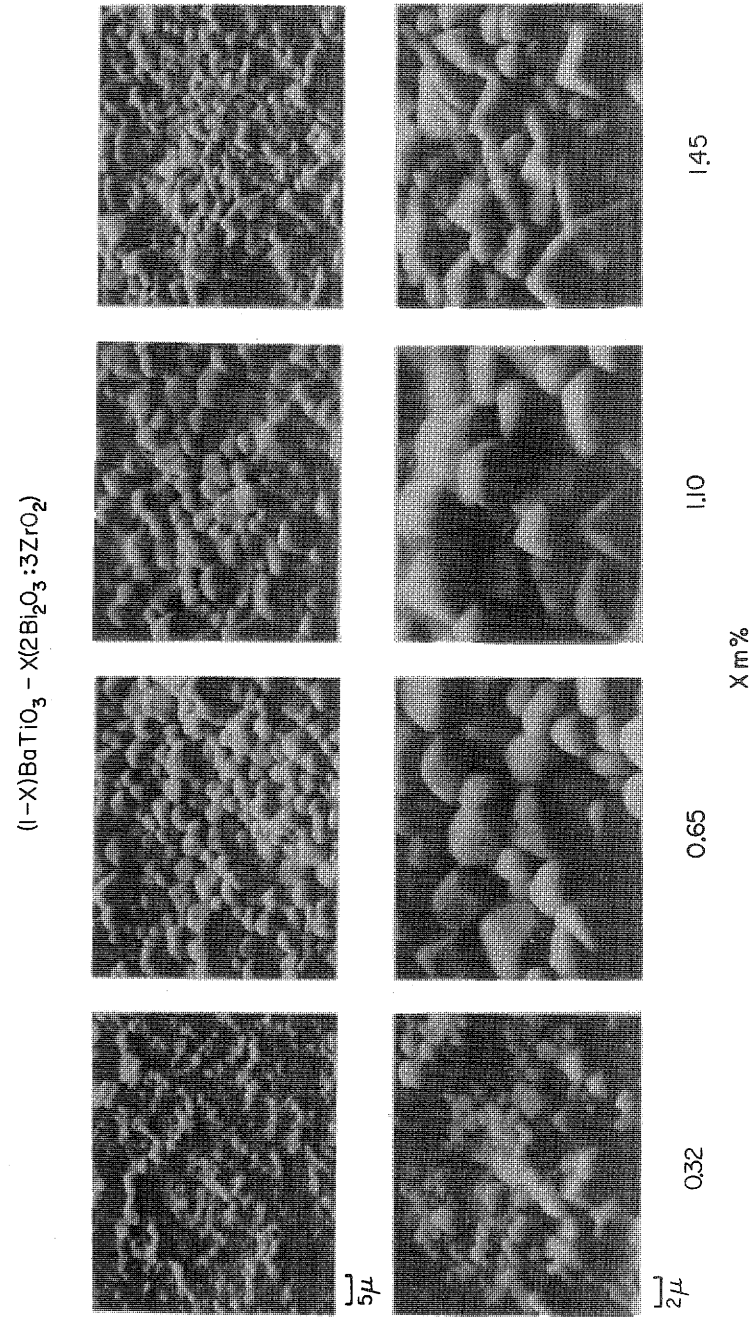
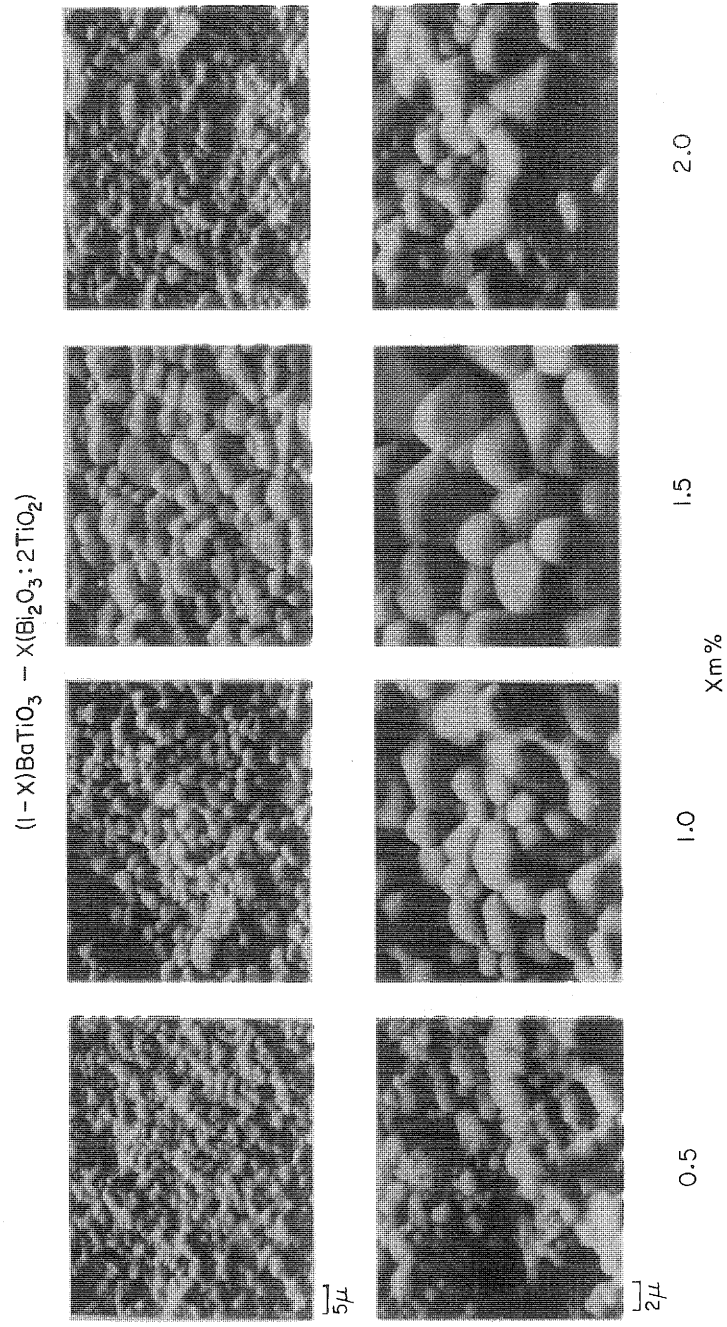


Figure 3: Shift in the Curie Temperature (T_c) of Barium Titanate for Different Bismuth Compound Additives Sintered at 1100°C



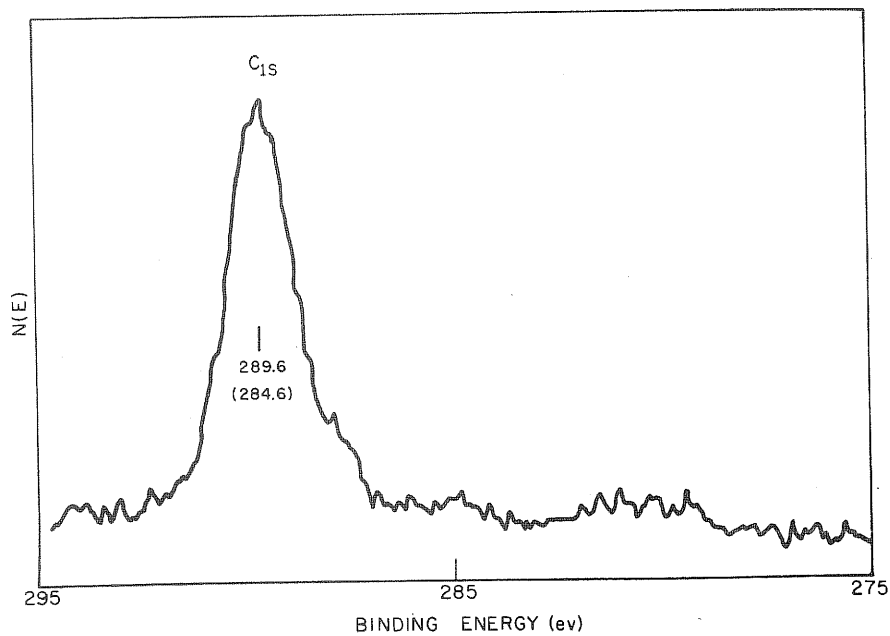


Figure 6: ESCA Spectrum of Binding Energy of Carbon, C_{1s}, used as a Reference for Barium Titanate Sample

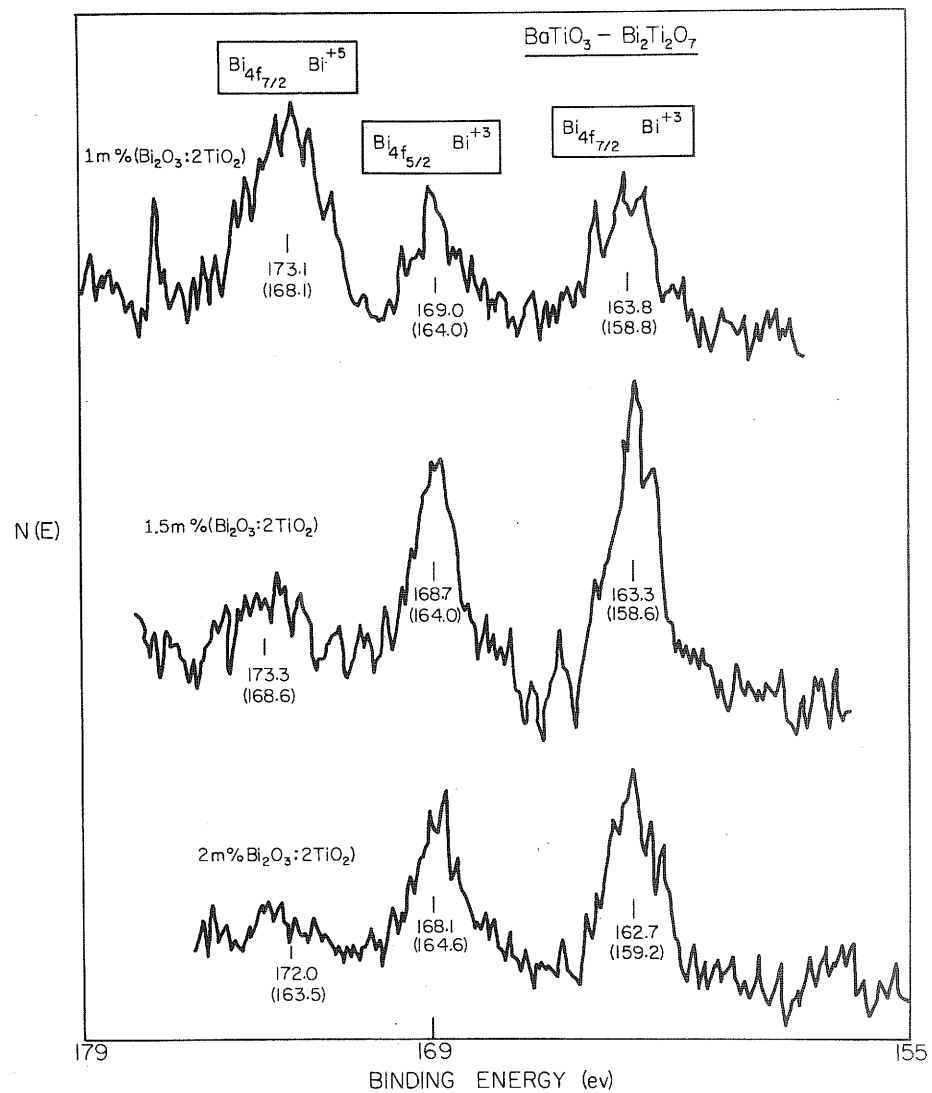


Figure 7: ESCA Spectrum of Binding Energy of Bismuth in BaTiO₃ Grains with Different Concentration of Bi₂Ti₂O₇

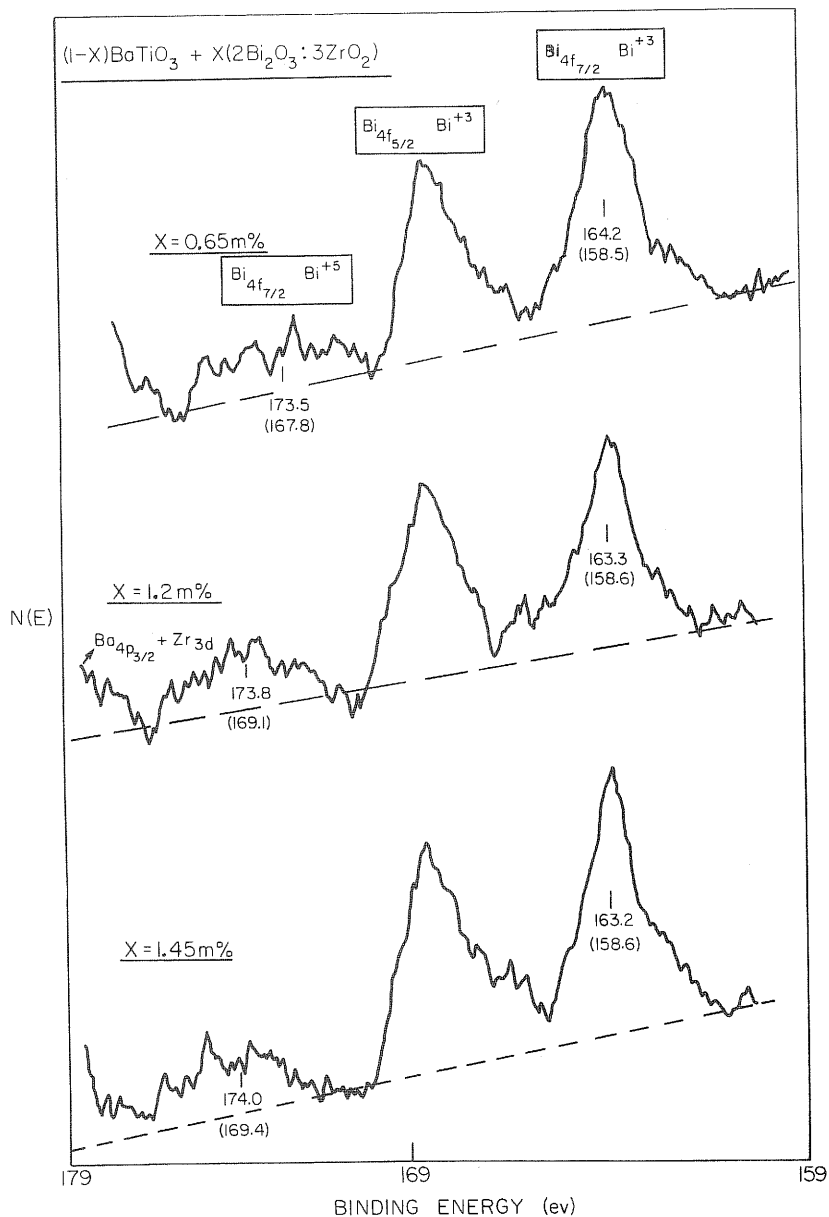


Figure 8: ESCA Spectrum of Binding Energy of Bismuth in BaTiO₃ Grain with Different Concentration of (2Bi₂O₃:3ZrO₂)

LOW FIRING TEMPERATURE GLASSES FOR ELECTRONIC APPLICATIONS

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ABSTRACT

Glasses and glass-composites are often used in many electronic components as barriers, binders, or sealants. Damage to the functioning of electronic components during the glassing operation can be reduced if the firing temperature of the glass is low, preferably lower than 400 °C. Such firing would also allow the use of glass as a cost-effective molding encapsulant, and may even compete with and replace the organic polymers. Some technology segments where a need for low firing temperature glasses exists and the general requirements for those applications are identified. Some examples and prospects of low temperature durable glasses in the oxide, oxy-halide, halide, and chalcogenide systems are discussed.

INTRODUCTION

Glasses and glass-composites are used for a broad-range of applications critical to the function, performance, and reliability of the IC devices, and packaging components. Some major applications include the use of glasses and glass-ceramics as passivation layers, insulation dielectrics, capacitor elements, die attach adhesives, binders in metallizations, solder glasses in cerdip packages, sealing glasses for metal housings, thin-film and thick-film substrates, and cofired multilayer multichip modules. In some cases, such as the die attach and cerdip sealing, the IC (silicon) devices are subjected to the glass flow temperatures of up to 450°C to achieve bonding or sealing, and, for improved device reliability, it is desirable to lower these firing temperatures.

Lowering of the glass flow temperatures to below 400°C would further provide opportunities for the application of glasses in the areas where, traditionally, the organic polymers dominate. Some low temperature soft solders also fall in this category for applications where the non-insulating