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Flux-sintered $BaTiO_3$ dielectrics

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$BaTiO_3$ modified with $BaZrO_3$ or $SrZrO_3$ was sintered at 1100° C with the aid of various fluxes. The objective was to identify compositions in the system $CdO–Bi_2O_3–PbO–B_2O_3$ that would permit growth of the ceramic grains during sintering to produce dielectric constants greater than 5000 at room temperature. By studying binary, and then ternary flux systems initially, the roles of the flux components were identified and classified according to their solubility and mode of substitution in the titanate crystal lattice. This, together with close control of cation stoichiometry, resulted in the discovery of flux systems with other oxides substituting for CdO, Bi_2O_3 or B_2O_3 that produced similar results.

1. Introduction

Polycrystalline barium titanate, and its modifications that are often used as capacitor dielectrics, are normally prepared by sintering powder compacts at temperatures near 1350° C. However, barium titanate ceramics with sintering temperatures down to about 1000° C have been reported in the literature and these are of important commercial application in monolithic capacitors [1]. In general, the approach has been to add to the ceramic powder small amounts of fluxing agents, or a quantity of low-melting glass powder, to promote densification by liquid phase sintering at lower temperatures. For example, the use of the following types of fluxes has been described: lithium fluoride [2], boron oxide [3], copper oxide [4–6], lead germanate [7, 8], cadmium silicate [9], or mixtures of cadmium oxide and bismuth oxide [10]. Alternatively, various borosilicate glass powders containing appreciable amounts of heavy-metal oxides such as PbO, BaO, Bi_2O_3, CdO and ZnO have been used [11–15].

Unfortunately, lower sintering temperatures are often accompanied by a significant decrease in dielectric constant, K. This decrease results mainly from dilution of the high dielectric constant ceramic with low dielectric constant flux or glass powder, and/or because of formation of low dielectric constant compounds by reaction of the ceramic with the low melting phase [16]. In some cases, however, the reaction between the ceramic and flux was found to produce dielectric properties advantageous for use in capacitors [1, 2, 12].

In obtaining materials with high room-temperature dielectric constants ($K \geqslant 4000$), a key step appeared to be the adjustment of the barium titanate ceramic or flux-glass composition to permit grain growth during sintering [1, 12, 17]. During grain growth, certain ions from the low melting phase were found to be incorporated into the titanate lattice, modifying the ceramic properties and reducing the volume fraction of low dielectric constant phase.

The ceramic and/or flux compositions described in the literature have generally been complex so that adjustments made to produce grain growth during low-temperature sintering have been largely empirical. Some measure of simplification can be made to the ceramic composition by using barium titanate mixed with simple Curie-point shifters such as $BaZrO_3$ or $SrZrO_3$. These modifiers are introduced into the titanate structure during liquid phase sintering if grain growth occurs [18]. This procedure was used in the present work with the main objective of elucidating the factors involved in obtaining grain growth with fluxes containing CdO, Bi_2O_3 and PbO. By studying relatively simple systems first, however, an explanation of the compositional requirements for grain growth has been obtained that is applicable

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not only to CdO–Bi_2O_3–PbO fluxes but to a wide variety of other flux-sintered barium titanate ceramics.

2. Experimental procedure

2.1. Materials

Commercial barium titanate* of adequate purity and cation stoichiometry was used. It contained $\leqslant$ 1.0% SrO (by weight), $\leqslant$ 0.2% Al_2O_3 and $\leqslant$ 0.1% SiO_2 as major impurities. A small amount of Nb_2O_5 (0.25%) was also present to neutralize most of the impurities soluble in the titanate crystal structure as acceptors [19], and the cation stoichiometry (A/B site ions) was close to 1.00. The relevance of these properties will be dicussed presently. The zirconate materials used as barium titanate modifiers were also available commercially†.

The flux systems were chosen from combinations of a glass-forming oxide with one or more of the modifiers listed in Table I. Boron oxide was used mainly as the glass-forming oxide because of the many low melting compositions containing this compound. Glass-former cations are practically insoluble in perovskite titanates because of incompatible size and charge, but Type I modifiers are very soluble, and Type II modifiers are slightly soluble ($\leqslant$ 5 mol%) depending on the overall composition and sintering conditions. This classification of the flux modifiers was adopted for the present purposes because it was found that the solubility of Type II modifiers in barium titanate ceramics, and the distinction between Type II (A) and Type II(B) modifiers, had an important bearing on the experimental results.

The fluxes were prepared mainly by blending reagent grade oxides or carbonates of the constituents along with the ceramic powder during ball milling (with $BaTiO_3$ balls). Compared with pre-reacting the flux components, as for example in a glass, and then comminuting before mixing with the ceramic, the above procedure did not always lead to the highest ceramic density at a given sintering temperature, but the effect of the composition on grain growth was essentially the same and it reduced appreciably the time required for materials preparation.

TABLE I Flux component classification

Glass former	Modifier (type)		
	I	II(A)	II(B)
B_2O_3	PbO	CdO	Bi_2O_3
SiO_2	BaO	ZnO	Y_2O_3
GeO_2	SrO	Li_2O	Sb_2O_3
	CaO	CuO	WO_3
			Nb_2O_5

2.2. Preparation of samples

Samples were prepared for the most part in the form of plates approximately 10 mm × 10 mm × 0.5 mm in size by the doctor blade technique, and were then sintered mainly at 1100° C for 2 h. Compositions that contained volatile components (e.g. CdO, PbO) were fired in closed alumina containers after burning out the organic binders. This helped in maintaining a constant composition during the sintering process [17, 20]. Electrical properties could be checked by coating the major faces of the plates with Ag–Pd electrode paste before firing, or by refiring at 750° C with Ag electrode paste applied.

Materials that densified well at 1100° C could be used in monolithic capacitors with 70 wt% Ag–30 wt% Pd electrodes [1], and several compositions were tested in devices of this type with dielectric thicknesses down to 25 μm.

3. Results and discussion

3.1. CdO–B_2O_3 fluxes

These fluxes were examined first because of the reported influence of CdO on grain growth of barium titanate during sintering [12, 21]. The ceramic composition was a mixture of 90.8 mol% $BaTiO_3$ and 9.2 mol% $SrZrO_3$, and the densification and compositional homogenization obtained for various CdO plus B_2O_3 additions were examined following sintering at 1100° C. The important parameters were (a) the total quantity of flux, which was kept to a minimum to avoid excessive dilution of the high dielectric constant phase, and (b) the molar CdO/$BO_{1.5}$ ratio.

It was found that about 4 wt% flux was needed to obtain densification, and that grain growth with optimum compositional homogenization occurred when the molar amounts of CdO and $BO_{1.5}$ were approximately equal, i.e. for compositions close to $2CdO{\cdot}B_2O_3$, one of the three stable cadmium borate compounds [22]. Compositional homogenization of the ceramic phases was judged by evidence of grain growth ($\geqslant$ 5 μm grains, Fig. 1)

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*TICON COF grade, TAM Ceramics Inc. Niagara Falls, New York, USA.

†Transelco Division, Ferro Corporation, Penn Yan, New York, USA.

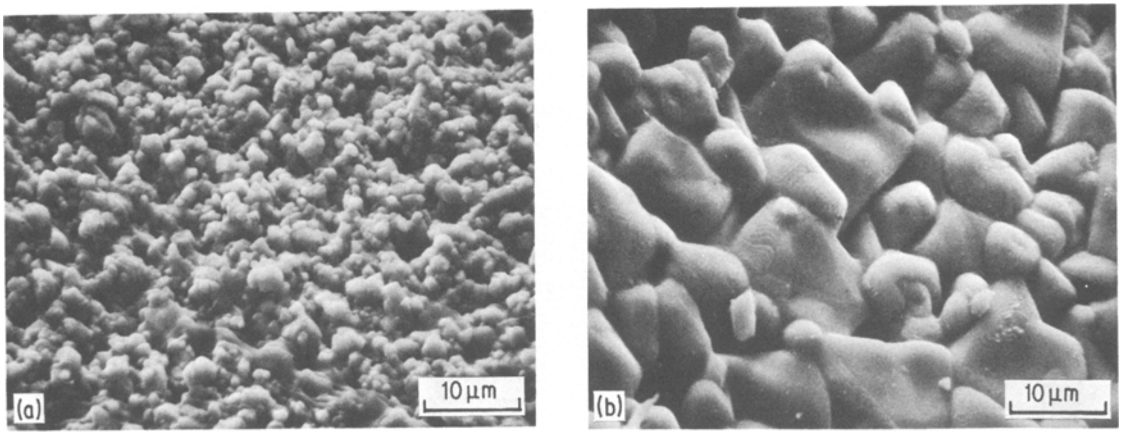

Figure 1 Typical microstructures of flux-sintered ceramics fired at 1100° C; (a) without grain growth, (b) with grain growth.

and by the sharpness of the permittivity against temperature peak (Fig. 2). Excess cadmium oxide (chocolate colour) precipitated within the material for Cd/B $\geqslant$ 1.3, and surprisingly, because the total amount of flux was increasing, densification began to decrease for a given CdO level at Cd/B $\leqslant$ 1.

It is interesting to note that the fluxes producing the best results (i.e. Cd/B = 1.0 ± 0.2) correspond to $CdO-B_2O_3$ compositions of 18.4 to 25.3 wt% B_2O_3, which is outside the reported glass-forming region in this system (30 to 46 wt% B_2O_3 [23]). Glass forming ability is therefore not necessarily advantageous for ceramic dielectric fluxes and could account for the relatively low dielectric constant ($K < 2000$) obtained by Biggers *et al.* [14] who chose a $CdO-B_2O_3-SiO_2$ composition as a sintering aid on the basis of its ability to form a glass.

3.2. $CdO-B_2O_3-Bi_2O_3$ fluxes

As bismuth oxide was added to $CdO-B_2O_3$ fluxes the Cd/B ratio had to be readjusted for optimum grain growth and homogeneity of the ceramic during sintering. As before, too high a Cd level suppressed grain growth and resulted in precipitates of cadmium oxide within the ceramic but now they were black, apparently chemically reduced, rather than chocolate brown. On the other hand, increasing the level of B_2O_3 past a certain limit also suppressed grain growth, but in this case there was an abrupt change from large grain to small grain, accompanied by a substantial decrease in dielectric constant, in a narrow critical region which was named the extinction zone. The range of suitable compositions was a relatively small portion of the total system and is shown as Region A in Fig. 3.

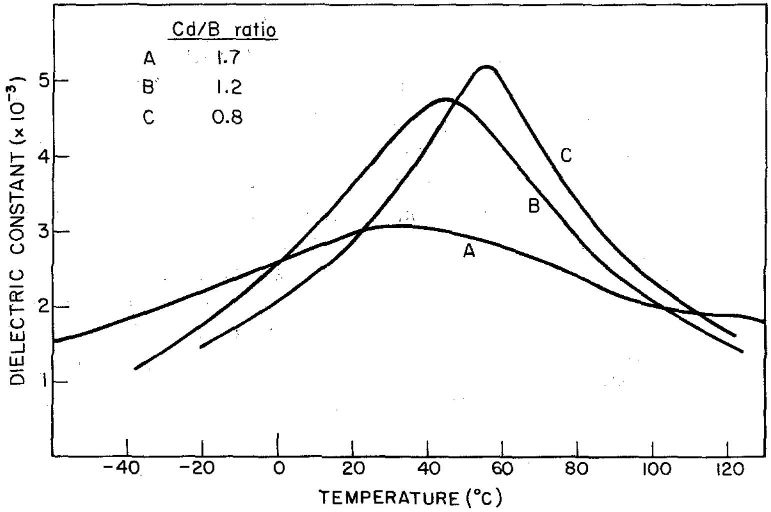

Figure 2 Influence of Cd/B ratio on the permittivity of a $BaTiO_3-SrZrO_3$ ceramic sintered at 1100° C with various cadmium borate fluxes.

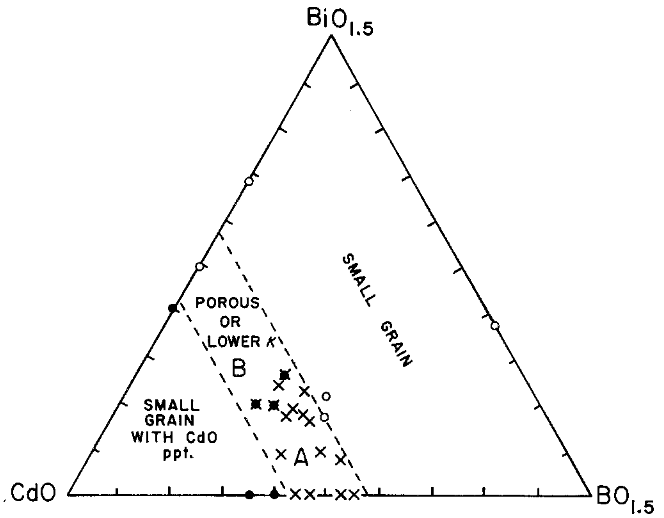

Figure 3 Composition range of CdO–B_2O_3–Bi_2O_3 fluxes permitting homogenization of a $BaTiO_3$–$SrZrO_3$ ceramic during sintering at 1100° C. Key: X = good grain growth; ⊕ = grain growth with some CdO precipitates; ● = heavy CdO precipitates, poor grain growth; ○ = negligible grain growth.

It should be emphasized that the data in Fig. 3 apply to ceramic compositions that had overall stoichiometry in large and small cations, i.e. the molar amount of Ba^{2+} plus Sr^{2+} was closely equal to the molar amounts of Ti^{4+} plus Zr^{4+} because stoichiometric raw materials ($BaTiO_3$, $SrZrO_3$) were used. The influence of non-stoichiometry was apparent by adding extra large or small cations. For example, additions of BaO with the flux produced CdO precipitation and poor homogenization at lower CdO levels, and addition of TiO_2 (or ZrO_2) allowed higher CdO levels, but induced the cessation of grain growth at lower B_2O_3 content. When this was realized and taken into account, it was found possible to use various compounds of the flux components such as bismuth zirconate or cadmium titanate instead of the oxides [24].

With bismuth oxide present, the ceramic densified with lower amounts of CdO–B_2O_3 flux and could tolerate higher Cd/B ratios in the flux, a situation characteristic of small cation additives such as TiO_2 or ZrO_2, as mentioned above. This suggested the possibility that the bismuth could have substituted in the ceramic on titanium sites at Bi^{5+}. Electron-probe analysis of the ceramic grains of samples sintered with good compositional homogeneity (fluxes in Region A of Fig. 3) indicated essentially complete absorption of the bismuth from the flux into the ceramic, and partial incorporation of the cadmium, which increased by an amount (in moles) approxi-

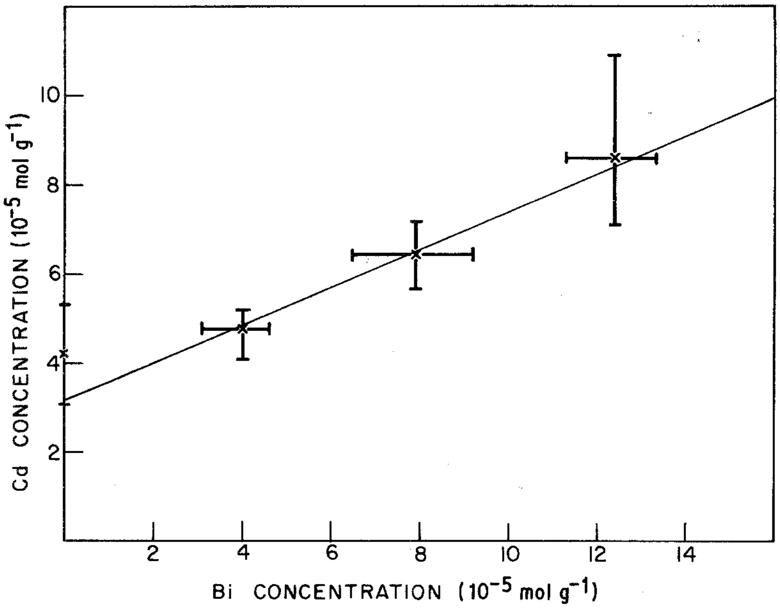

Figure 4 Concentration of Cd and Bi in the grains of a $BaTiO_3$–$SrZrO_3$ ceramic sintered with grain growth at 1100° C (CdO–B_2O_3–Bi_2O_3 flux).

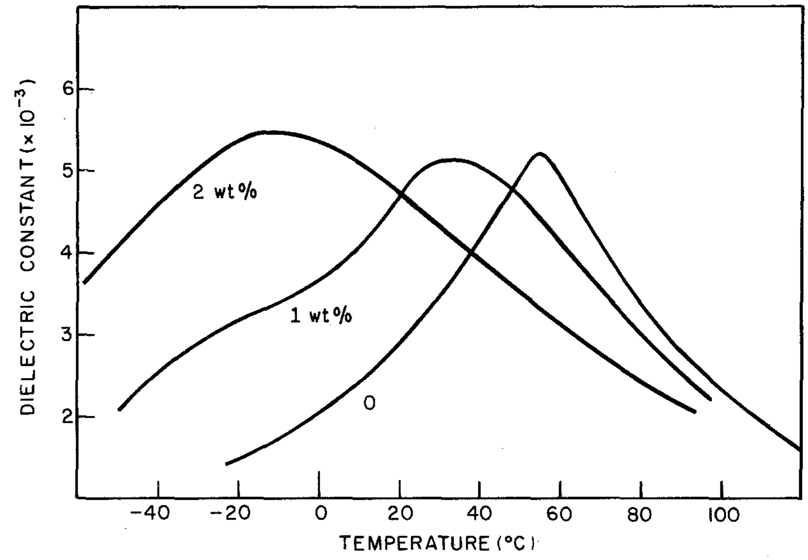

Figure 5 Influence of bismuth oxide (in wt%) on the permittivity of a $BaTiO_3$–$SrZrO_3$ ceramic sintered, with grain growth, at 1100° C using cadmium borate fluxes.

mately one half (0.4 ± 0.1) that of the bismuth (Fig. 4). For these dielectrics, therefore, the flux compositions could be written approximately as

$$x\,2CdO \cdot B_2O_3 + y\,Bi_2O_3 \cdot CdO \qquad (x > y).$$

Although flux compositions could be formulated in Region B ($x < y$) to produce grain growth during sintering for the ceramic composition being studied, either the boron oxide level was too low for adequate densification at 1100° C, or the bismuth oxide level was too high ($\geqslant 3$ wt%) for optimum values of dielectric constant. At high Bi_2O_3 levels the permittivity peak was depressed below room temperature and broadened as shown in Fig. 5. However, the permittivity peak could be adjusted by changing the $SrZrO_3$ level for a given bismuth oxide content, as illustrated in Fig. 6 for 2 wt% Bi_2O_3. An interesting aspect of these curves is the apparent suppression of the orthorhombic–tetragonal transition. Typical data for a monolithic ceramic capacitor are given in Table II (Composition 1).

Although the way in which Bi and Cd were incorporated in the barium titanate grains was not clear, the cadmium in the flux appeared to have a dual role:

(a) to produce with the glass-former a suitable liquid phase that could promote densification and grain growth by a solution and re-precipitation process [25, 26],

(b) to assist solution of the Bi into the ceramic, either by a redox reaction of the type

$$Bi^{3+} + 2Cd^{2+} \rightarrow Bi^{5+} + 2Cd^{+}, \qquad (1)$$

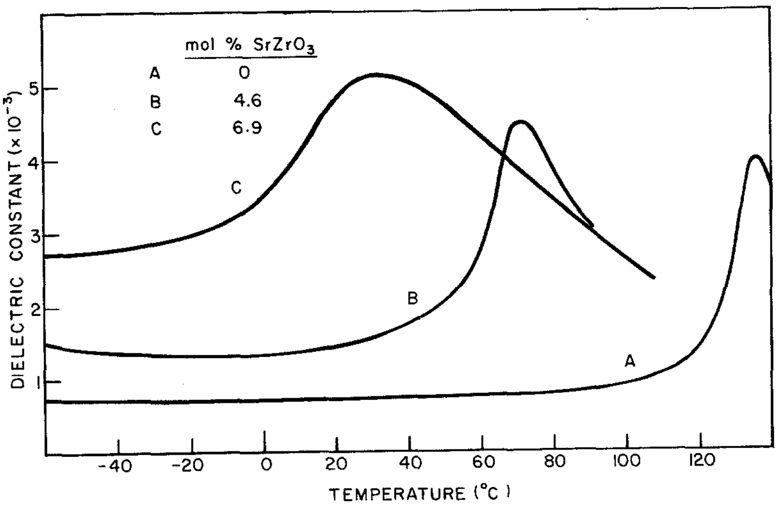

Figure 6 Influence of $SrZrO_3$ on the permittivity of $BaTiO_3$ sintered at 1100° C with grain growth using a cadmium–bismuth–borate flux.

TABLE II Ceramic compositions and properties of monolithic ceramic capacitors with 70 wt% Ag–30 wt% Pd electrodes sintered at 1100° C for 2.5 h

Flux composition					Ceramic additives to $BaTiO_3$*		K (± 200) at 25° C	Curie temperature (° C)
Composition number	Composition	Wt% (of total composition)	Vol%	Mol%	Composition	Mol% (of ceramic)		
1	CdO	3.1	2.3	5.3	$SrZrO_3$	9.2	5400	−6
	$BO_{1.5}$	0.50	1.2	3.1	TiO_2†	2.4		
	$BiO_{1.5}$	2.1	1.4	1.9				
2	ZnO	1.5	1.6	4.1	$BaZrO_3$	9.7	6000	6
	$BO_{1.5}$	0.56	1.3	3.6				
	$BiO_{1.5}$	1.5	1.0	1.4				
3	$CuO_{0.5}$	0.60	0.59	2.0	$BaZrO_3$	10.6	5500	11
	GeO_2	0.50	0.70	1.1				
	$BiO_{1.5}$	1.5	1.0	1.5				
4	Li_2O	0.7	2.1	5.0	$BaZrO_3$	9.4	6400	19
	SiO_2	1.0	2.1	3.3				
	$BiO_{1.5}$	1.5	1.0	1.4				
5	CdO	3.0	2.2	5.2	$SrZrO_3$	8.3	6200	11
	$BO_{1.5}$	0.57	1.4	3.6	$PbTiO_3$	2.5		
	$BiO_{1.5}$	2.0	1.4	1.9				
6	ZnO	1.4	1.5	3.9	$SrZrO_3$	8.8	7800	25
	$BO_{1.5}$	0.39	0.97	2.5	$PbTiO_3$	10.5		
	$NbO_{2.5}$‡	0.90	1.2	1.5	BaO†	2.3		

* All compositions also contained 0.2 mol% Mn [18].

† Stoichiometry adjustment.

‡ The Nb was present in the barium titanate used.

or by a charge-balancing mechanism in the titanate lattice, e.g.

$$Cd^{+}_{Ba} + Bi^{5+}_{Ti} + 3O^{2-}_{O} \qquad (2)$$

or

$$Bi^{3+}_{Ba} + Cd^{+}_{Ba} + 2Ti^{4+}_{Ti} + 6O^{2-}_{O}\,, \qquad (3)$$

where the subscripts refer to lattice sites.

Since none of these mechanisms appeared to fit all of the experimental observations described above, experiments with other fluxes were carried out in an attempt to clarify the situation.

3.3. Fluxes without cadmium oxide

3.3.1. Zinc oxide fluxes

Because of the chemical similarity between CdO and ZnO, fluxes with CdO replaced by ZnO were tried. With simple $ZnO–B_2O_3$ fluxes, densification

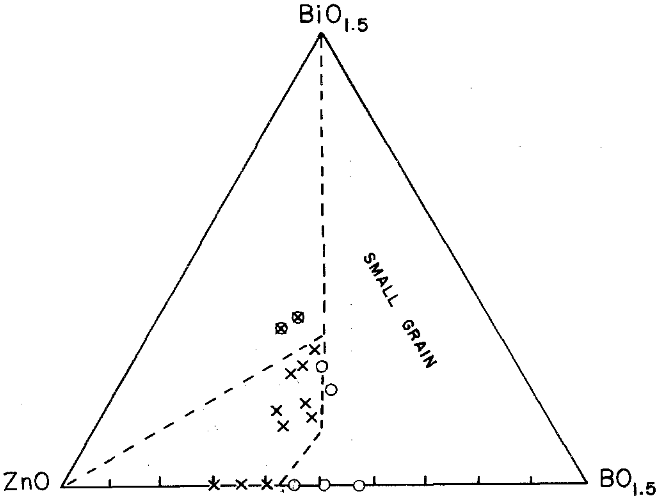

Figure 7 Composition range of $ZnO–B_2O_3–Bi_2O_3$ fluxes permitting homogenization of a $BaTiO_3–SrZrO_3$ ceramic during sintering at 1100° C. Key: × = good grain growth; ○ = poor grain growth; ⊗ = grain growth but porous.

at 1100° C was achieved with as little as 2.5 wt % flux. Optimum compositional homogeneity of the ceramic phase, as judged by uniformity of grain growth during sintering and sharpness of the permittivity peak, occurred for Zn/B molar ratios of 2.0 ± 0.2. It is worth noting again that the glass formation range Zn/B = 0.5 to 1.0, including the eutectic (961° C) composition Zn/B = 0.81 [27], was outside the necessary range for grain growth.

When bismuth oxide was included in the flux, optimum ceramic homogenization occurred at lower Zn/B ratios (≥ 1.0) such that, as shown in Fig. 7, a similar optimum flux composition zone was found with CdO replaced by ZnO in Region A of Fig. 3. When excess ZnO was present in the flux, however, it could not be easily detected in the sintered ceramic by its colour, as was the case for CdO. A typical composition useful for monolithic ceramic capacitors is included in Table II (Composition 2).

Some of the flux was again absorbed into the ceramic grains during sintering, as indicated in Fig. 8. These data are difficult to interpret without knowledge of the valence states of the Bi and Zn. One possible explanation, however, is that the zinc occupied Ti^{4+} sites as Zn^{2+} in the absence of bismuth, but began to occupy Ba^{2+} sites as Zn^{+} at a concentration level that increased at a rate of approximately one half that of the bismuth. This effect would then be similar to the reduction of CdO in $CdO–Bi_2O_3–B_2O_3$ fluxes. Also, by making small additions of ZnO to $CdO–Bi_2O_3–B_2O_3$ fluxes with compositions close to the extinction zone, it was observed that ZnO generally behaved as a large cation (A site) additive.

3.3.2. Copper oxide fluxes

Copper oxide fluxes were investigated because cupric oxide (Cu^{2+}) is readily reduced to cuprous oxide (Cu^{+}) and the ionic size of the latter (0.096 nm) is similar to that of Cd^{+} and of Zn^{+}. Compositions containing Bi_2O_3 and selected in Region A of Fig. 3 with cadmium replaced by copper, once again resulted in useful fluxes, producing densification and good compositional homogenization of the ceramic dielectric. This was also the case when SiO_2 or GeO_2 was used instead of B_2O_3, with relatively small amounts of glass-forming oxide being required (≤ 1 mol% total). An example of a $Cu_2O–Bi_2O_3–GeO_2$ flux used in a monolithic capacitor sintered at 1100° C is given in Table II (Composition 3).

Grain growth was achieved for binary fluxes of Cu_2O with a glass former only at relatively high copper oxide/glass former ratios (i.e. ≥ 5). On the other hand, grain growth occurred readily for binary $Cu_2O–Bi_2O_3$ fluxes at low bismuth levels (≤ 1.5 mol% total), but such fluxes were less effective in producing good densification than those containing a glass forming oxide. The sintering of barium titanate ceramics with copper oxide fluxes has also been studied recently by Hennings [4–6], although the problem of obtaining dielectric materials with high dielectric constant at room temperature was not addressed specifically.

Electron-probe analysis of the ceramic grains indicated that most of the bismuth from the flux had entered the barium titanate lattice, accompanied by a smaller amount of copper. For example, at a bismuth level of 1.0 mol%, the copper concentration in the ceramic grains was

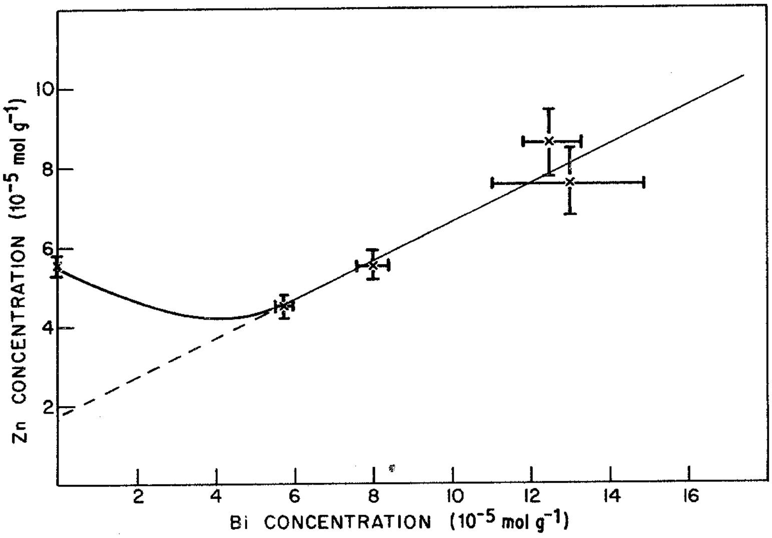

Figure 8 Concentration of Zn and Bi in the grains of a $BaTiO_3–SrZrO_3$ ceramic sintered with grain growth at 1100° C ($ZnO–B_2O_3–Bi_2O_3$ flux).

0.75 ± 0.05 mol%, compared with approximately 0.3 mol% Cu for compositions without bismuth.

The resistivity of the sintered dielectric was lowered when the flux contained an excess of copper oxide. This appeared to result either because of conduction via precipitates of copper oxide or because of "hopping" via Cu^{2+} and Cu^{+} ions in the grain-boundary phase, as can occur in glasses containing copper oxide [28].

3.3.3. Alkali metal oxide fluxes

Alkali metal oxides are well known for their fluxing action in ceramic materials so it was of interest to determine if fluxes containing ions that were clearly monovalent behaved similarly to those described above. Lithium oxide was used mainly because of its relatively low vapour pressure, but a few experiments with Na_2O gave qualitatively similar results. Low melting phases with liquidus temperatures below 1100° C are obtainable in the binary systems Li_2O–B_2O_3, Li_2O–GeO_2 and Li_2O–SiO_2 [29] so that any one of these sytems (or their mixtures) appeared appropriate.

Suitable binary compositions were determined using the same criteria as before. For example, Li_2O–B_2O_3 fluxes appeared to produce the best compositional homogeneity of the ceramic phase during sintering at Li/B ratios $\simeq 3$ (i.e. $3Li_2O \cdot B_2O_3$), whereas Li_2O–SiO_2 compositions were best close to the orthosilicate composition ($2Li_2O \cdot SiO_2$). Once again these compositions did not correspond to eutectic compositions and were outside the glass formation ranges [29].

When bismuth oxide was added to the flux, densification of the ceramic improved with very similar dielectric properties being obtained as before for flux compositions containing comparable (molar) amounts of Li_2O instead of CdO or ZnO (e.g. Table II, Composition 4). These experiments indicated that even if redox reactions of the type discussed above did take place in some flux systems, they did not play an essential role in the incorporation of the bismuth into the titanate lattice.

3.3.4. Alkaline-earth oxide fluxes

Because of resistance to chemical reduction, barium borate and other alkaline-earth borate and aluminoborate fluxes or glasses have been used to lower the sintering temperature of ceramic dielectrics co-fired with base-metal electrodes in atmospheres of low oxygen content [13, 30]. In the present work binary BaO–B_2O_3 fluxes were briefly reinvestigated to determine the optimum Ba/B ratio for compositional homogenization in ceramic systems with close cation stoichiometry, and to examine the effect of bismuth oxide additions. These experiments indicated that fluxes close to the composition $BaO \cdot 2B_2O_3$ produced the best ceramic homogeneity in simple $BaTiO_3$–$BaZrO_3$ or $BaTiO_3$–$CaZrO_3$ formulations fired in air at 1100° C.

In contrast to the flux compositions discussed earlier, however, additions of Bi_2O_3 suppressed grain growth for the wide range of Ba/B ratios investigated. This prevented homogenization of the ceramic phase so that dielectric constants were $\leqslant 3000$. This behaviour was interpreted as typical grain growth suppression by donor doping [26, 31], and although the effect is not well understood, it can be avoided by donor–acceptor compensation [19, 31]. It seems likely, therefore, that for fluxes containing monovalent elements, some of the ions from the flux are incorporated in the titanate lattice as acceptors (Cd^{+}, Cu^{+}, etc.), at least in the presence of bismuth oxide. This suggests in turn that high dielectric constants are difficult to achieve in fluxes containing bismuth oxide when based on strictly divalent (Class I) modifiers (Ba^{2+}, Ca^{2+}, Pb^{2+}, etc.).

3.4. Fluxes without bismuth oxide

Because of the indication that grain growth was related to donor–acceptor compensation, experiments were carried out with other well known donor dopants such as Nb^{5+} and Y^{3+}. While such substitutions were not expected to have the same fluxing action as produced by Bi_2O_3 it was nevertheless of interest to examine the effect on grain growth and dielectric properties.

When $BiO_{1.5}$ was replaced by $NbO_{2.5}$ or $YO_{1.5}$ in cadmium borate fluxes selected from Region A of Fig. 3, grain growth could generally be obtained in the ceramic during sintering and there was a downward shift in Curie temperature as before, although the permittivity curves tended to be sharper than when bismuth was used (Fig. 9). Some care with stoichiometry was necessary, however, particularly for donor levels $\geqslant 1.5$ mol% (total). For example, when yttrium oxide, a recognized large cation donor dopant in titanates, was added to cadmium borate fluxes at Cd/B ratios $\geqslant 1.2$, cadmium oxide precipitates were observed in the ceramic after sintering, whereas

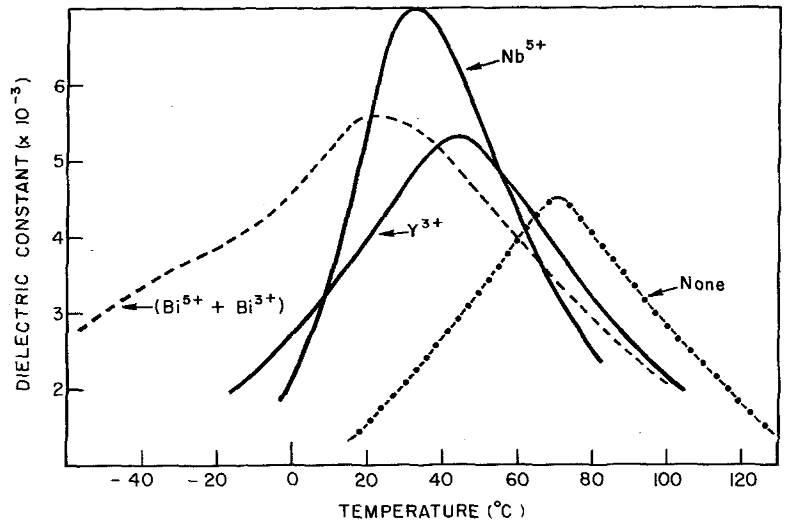

Figure 9 Effect of various donors (1.5 mol%) on the permittivity of a $BaTiO_3$–$BaZrO_3$ ceramic sintered with grain growth at 1100° C (CdO–B_2O_3 flux).

when niobium, a commonly used small cation donor dopant, was added at Cd/B ratios $\leqslant 1.2$ the ceramic usually had small grains. These effects could be avoided by adjusting the Cd/B ratio or by compensating with small or large cations as discussed earlier. By using adjustments of this kind it was thought possible to identify the lattice site occupancy of bismuth in the titanate lattice by comparing the influence on stoichiometry of bismuth with that of Y^{3+} and Nb^{5+}. This approach indicated that the bismuth was substituting both as large and small cation donors (Bi^{3+} and Bi^{5+}), but mainly as Bi^{5+}. The site occupancy of bismuth in similar ceramic dielectrics has also been discussed recently by Maher [32].

Experiments with other donors such as Sb^{5+} and W^{6+}, either with cadmium oxide or other acceptors, also resulted in flux sintered bodies with good grain development provided that stoichiometry was adjusted when necessary, and the following approximate relationship between the molar amounts of acceptors, N_A, donors, N_D, and glass formers, N_G, was used [24].

$$N_A \simeq aN_D + bN_G \qquad \text{with } N_D \leqslant N_G, \qquad (4)$$

where a describes the effective donor–acceptor compensation (e.g. $a = 1/2$ for Bi, $a = 1$ for Nb^{5+}, $a = 2$ for W^{6+}, etc.), and $b \simeq 1$ for CdO, ZnO, $CuO_{0.5}$ and Li_2O for donor levels in the ceramic $\geqslant 1$ mol%.

3.5. Fluxes containing lead oxide

Polycrystalline ceramics containing major amounts of PbO, such as those based on lead niobate [33], usually have relatively low sintering temperatures, and lead oxide has been a common ingredient in low melting compositions used as sintering aids for barium titanate ceramics [7, 8, 11, 15]. Because Pb^{2+} is an example of what we have called a Type I modifier, i.e. a readily soluble isovalent substitute for Ba^{2+} (Table I), it was found possible to include lead oxide in any of the flux compositions described in the preceding sections without altering the grain-growth characteristics significantly, provided that stoichiometry was maintained. This could be accomplished conveniently by partial substitution of $BaTiO_3$ with $PbTiO_3$, for example, and was simpler than the alternative approach of investigating the fluxing action and grain growth properties of ceramics sintered with various PbO/glass-former compositions [7, 8].

Inclusion of lead oxide in the ceramic generally improved densification so that sintering in some cases could be carried out either with lower amounts of glass-former, an advantage when trying to obtain materials with high dielectric constant, or at lower temperatures. Because most of the lead oxide was incorporated in the titanate lattice when grain growth took place during sintering, the dielectric properties were influenced in the manner typical for Pb^{2+} substitution in barium titanate, i.e. broadening of the permittivity peak with a displacement of the Curie point to higher temperatures, as illustrated in Fig. 10. The permittivity curve could of course be readjusted for a given lead content by appropriate choice of zirconia and/or donor level. Typical compositions containing PbO producing high dielectric constants in multilayer capacitors are included in Table II

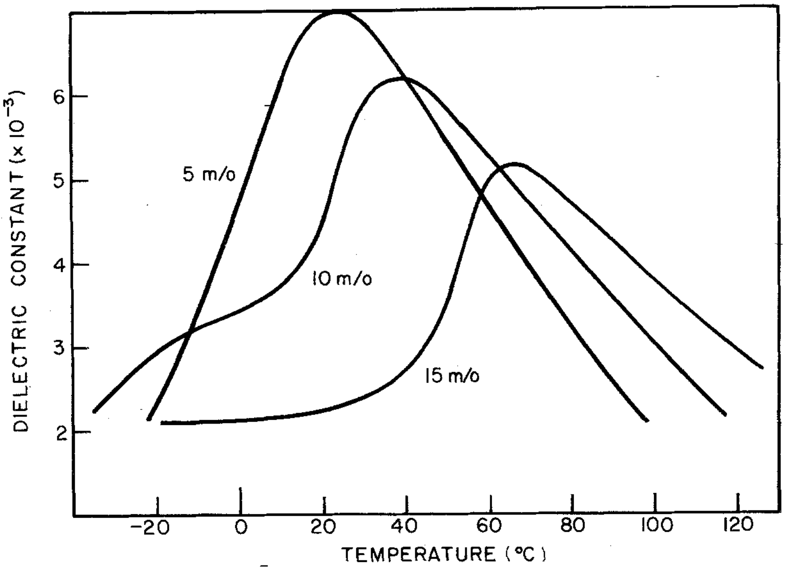

Figure 10 Influence of $PbTiO_3$ substitution for $BaTiO_3$ in a $BaTiO_3$–$BaZrO_3$ ceramic sintered with grain growth at 1100° C (CdO–B_2O_3–Nb_2O_5 flux).

(Compositions 5 and 6), and others are given in the patent literature [9, 24].

4. Summary and conclusions

A study has been made of the compositional requirements for fluxes in the CdO–Bi_2O_3–PbO–B_2O_3 system necessary for producing grain growth in barium titanate ceramics during sintering at 1100° C. The ceramic and flux composition were considered as a whole, and the components classified according to the way in which they were incorporated in the ceramic grains. Cadmium oxide was found to play a key role in these compositions, producing a relatively insoluble intergranular phase in combination with B_2O_3 that provided the vehicle for grain growth via liquid phase sintering, and also assisting dissolution of Bi_2O_3 by a donor–acceptor compensation mechanism.

The composition zone in the CdO–Bi_2O_3–B_2O_3 system, suitable for producing grain growth and compositional homogeneity of barium titanate ceramics sintered at 1100° C, was identified for ceramic compositions of controlled cation stoichiometry, and was valid regardless of whether the cadmium or bismuth had been added as oxides, or in a glass, or as compounds such as titanates of zirconates, provided that cation stoichiometry was adjusted appropriately. Lead oxide generally improved the sintering characteristics of the ceramic and had little influence on grain development when included as a stoichiometric compound such as $PbTiO_3$.

Identification of the roles and classification of the flux components resulted in ceramic materials with similar dielectric constants ($\geqslant 5000$) when CdO was replaced by other acceptor (Type II (A)) materials such as ZnO, Cu_2O or Li_2O; or Bi_2O_3 was replaced by other donor (Type II (B)) materials such as Nb_2O_5, Y_2O_3, Sb_2O_5 or WO_3; or when other glass formers such as SiO_2 or GeO_2 were used.

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