

TEMPERATURE-STABLE BARIUM TITANATE CERAMICS CONTAINING NIOBIUM PENTOXIDE

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Niobium is known to lower the Curie point and broaden the permittivity peak of barium titanate. However, the distribution of niobium in sintered barium titanate is often not homogeneous, being influenced by such preparation variables as large cation/small cation stoichiometry and firing conditions. In addition to these factors, it was found that, at least up to about 5 mol % Nb, the distribution of niobium in the barium titanate grains could be regulated by small amounts (<1 mol %) of oxides of Co, Mg, Ni or Mn. These oxides appear to form niobates that produce high permittivity solid solutions in the "skins" of the barium titanate grains and permit dielectrics to be obtained with permittivity $K \approx 2000$, stable to within $\pm 10\%$ over the temperature range -55°C to 125°C .

1 INTRODUCTION

The influence of niobium on the temperature dependence of the permittivity of barium titanate has been described by several authors.¹⁻³ Some inconsistencies in the earlier data^{1,2} have been explained by Kahn³ who found that the addition of Nb to prereacted barium titanate resulted in a homogeneous distribution only under conditions of grain growth during sintering. When little grain growth occurred, the permittivity vs. temperature curves indicated the presence of Nb-free barium titanate in the grain cores.⁴

As pointed out by Plessner and West⁵ and Rutt,⁶ if an additive that lowers the Curie temperature of barium titanate is distributed in a non-homogeneous but controlled manner, the material can be of practical use as a high permittivity ($K \approx 2000$) temperature-stable dielectric. Dielectrics of this type have been described that contain several mol % NaNbO_3 ⁷⁻⁹, as well as some in which the niobium distribution was regulated by additions of Li or Fe^{8,10}, or Mg.^{8,11} It was found in the present work that certain other additives also modify the niobium distribution and an attempt has been made to explain this effect.

2 EXPERIMENTAL PROCEDURE

The barium titanate was a commercial material† with a reported BaO/TiO₂ mole ratio of 1.015 and containing 1.4 (mol) % Sr, 1.0% Al and 0.4% Nb as

principal impurities. A small amount of work was also done with a similar barium titanate‡ with comparable impurity level but small BaO/TiO₂ ratio (0.99). Up to about 5 mol % niobium oxide ($\text{NbO}_{2.5}$) was added to the barium titanate powder together with various other oxides in amounts less than 1 mol %.

In most cases about 100 gms of powder were ball-milled for 12 h. in a suitable organic binder at roughly 77 wt % solids in a 200 cc capacity porcelain mill containing alumina balls. This procedure resulted in efficient mixing with negligible mill contamination but little comminution of the initial particle size, which was less than about 2 μm . The slip was cast on a glass plate after milling, using the doctor-blade technique, and when dry was cut into small squares approximately $10 \times 10 \times 0.5$ mm. In a few instances the powder was spray dried and pressed into discs of similar thickness to the squares. The samples were fired in a tube furnace in air mainly at 1400°C with a 5 h. soak. Electrodes of commercial silver paste were then painted or screen-printed on both sides of the squares or discs and matured in the usual way (750°C ; 1 h. cycle).

The electroded samples were allowed to age for one day and then the change in capacitance at 1 kHz over the range -60°C to 130°C was measured. This was accomplished by first balancing an impedance comparator with the sample at 25°C , cooling the

†COF grade from TAM Division of NL Industries Inc.,
Niagara Falls, N.Y.

‡5018 grade also from TAM Division of NL Industries.

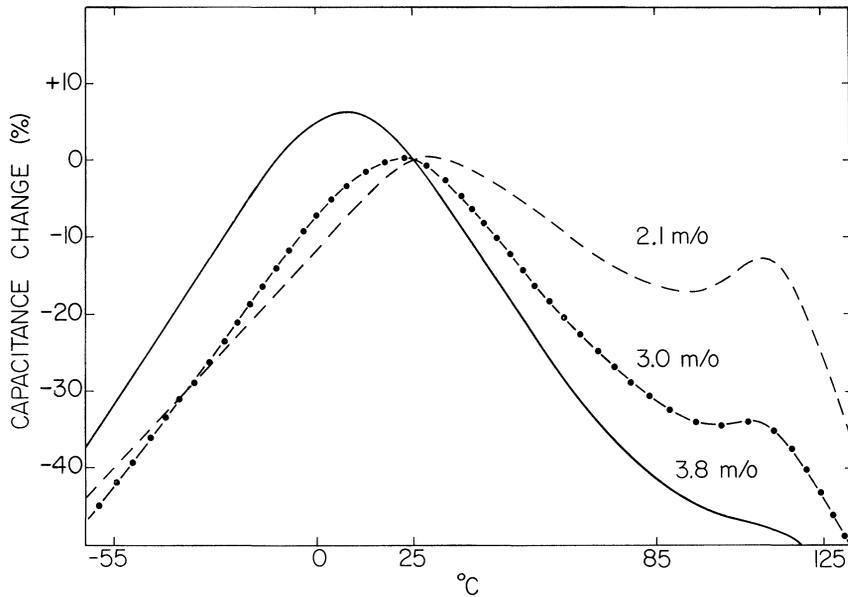


FIGURE 1 Influence of niobium oxide on the permittivity of barium titanate sintered 5 h. at 1400°C.

sample to -60°C , and heating at roughly $3^{\circ}\text{C}/\text{min}$. while continuously recording the change in capacitance.

3 RESULTS

Figure 1 shows how the permittivity varied with temperature for increasing additions of niobium to the (COF) barium titanate. When the niobium was less than about 3 mol %, some connected porosity was apparent in the ceramic for the firing conditions used, and the presence of some unreacted barium titanate was evident from the secondary capacitance peak. Although a dense ceramic was obtained for 3.8% Nb, there was no evidence of any significant grain growth during sintering (Figure 2), and some unreacted barium titanate could still be detected.

Figure 3 illustrates how small additions of cobalt oxide could modify the permittivity-temperature characteristics for 3.8 mol % Nb. As the cobalt was increased, the presence of unreacted barium titanate became more evident, and as seen from Figure 4 the amount of porosity increased. Figure 5 compares data (obtained from pressed discs) for the different grades of barium titanate and shows that the effect of the cobalt addition was qualitatively similar in both cases. However, a smaller amount of Co was needed for

optimum temperature stability in the case of the 5018 grade barium titanate. Judging by the high temperature permittivity peak, the latter material appeared to have a more uniform crystallinity and a higher purity than the COF barium titanate in the cores of the grains. Dielectric constant at room temperature was 1800 ± 50 in the case of the COF-based material and 2050 ± 50 for that using the 5018 barium titanate. The slightly lower capacitance at -55°C obtained for pressed discs compared with the cast squares (Figures 3 and 5) was perhaps due to

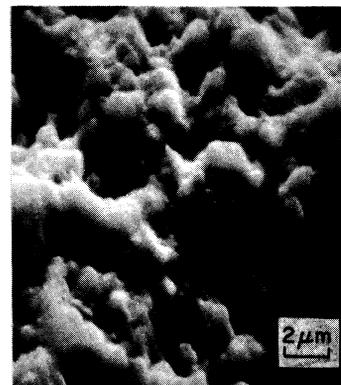


FIGURE 2 Surface microstructure of barium titanate with 3.8 m/o Nb sintered 5 h. at 1400°C.

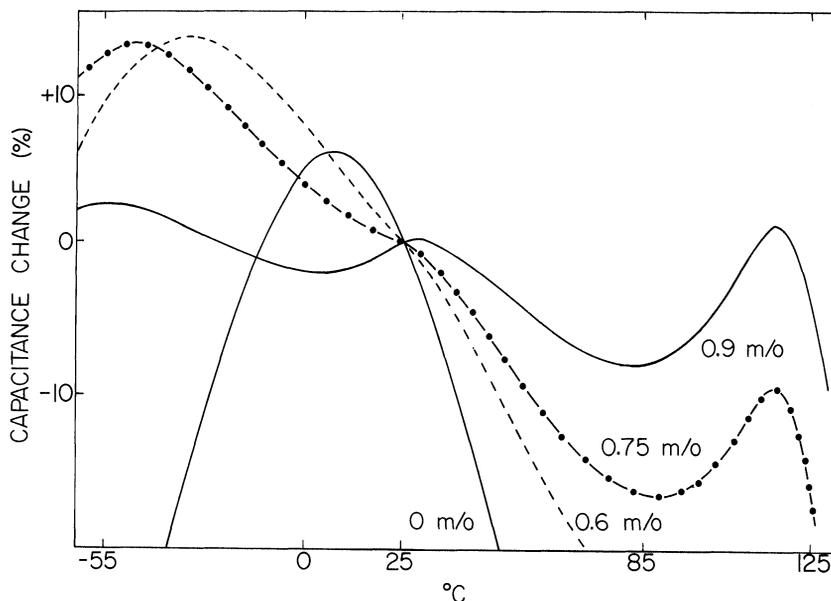


FIGURE 3 Influence of cobalt oxide on the distribution of Nb (3.8 m/o) in barium titanate sintered 5 h. at 1400°C.

a difference in packing density in the green state. When the cobalt was added together with a similar amount of TiO_2 , densification was improved and the degree of reaction between the barium titanate and the niobium was slightly diminished (Figure 6).

As shown in Figure 7, virtually identical permittivity characteristics were obtained when the same molar amounts of magnesium oxide were used instead of cobalt oxide. When the amount of niobium was increased to approximately 5 mol %, dense temperature-stable dielectrics could be obtained

following firing at 1400°C for periods of less than 5 h. (Figure 8). These were essentially similar to those described by Prokopowicz⁸ and by Rutt.¹¹

Nickel oxide produced similar results to those for Co and Mg, as did manganese oxide, though the latter was slightly less effective in modifying the niobium reaction with the barium titanate (Figure 9). It can also be seen from Figure 9 that equivalent amounts of iron had little influence on the permittivity-temperature characteristics, and this was also true for Cr, as well as for Ba or Ca.

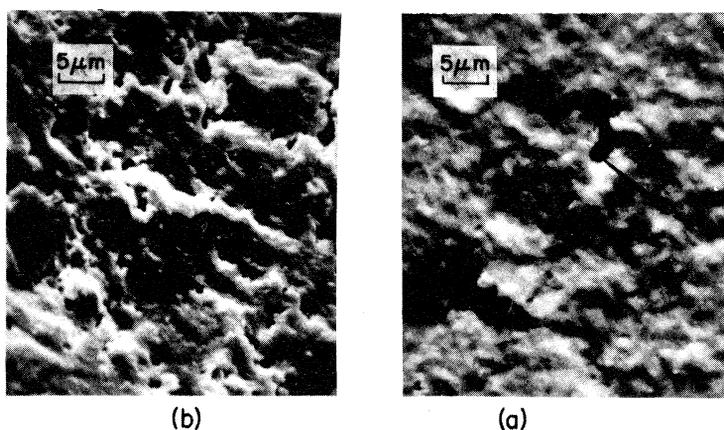


FIGURE 4 Increase in porosity with cobalt oxide additions to barium titanate with 3.8 m/o Nb sintered 5 h. at 1400°C. (a) 0 m/o Co, (b) 0.9 m/o Co. Fractured surfaces.

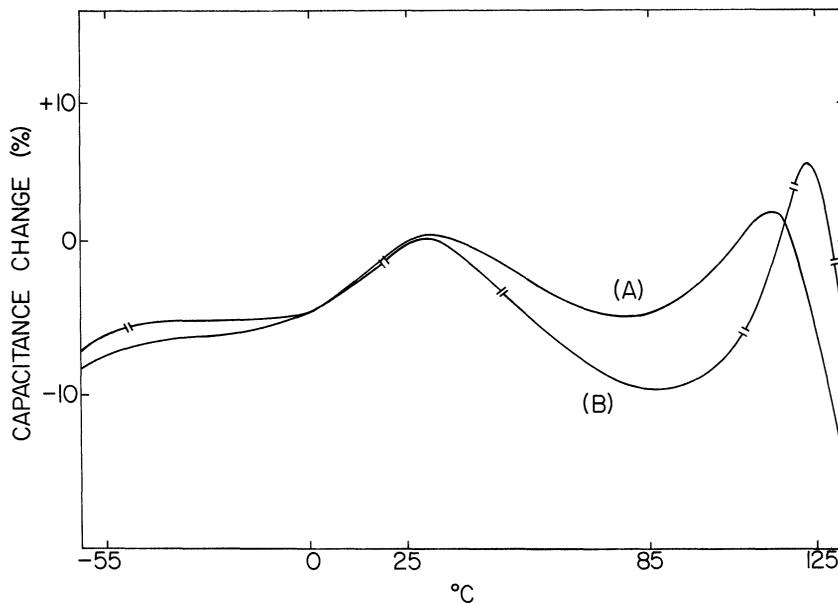


FIGURE 5 Temperature-stable dielectrics obtained from different types of barium titanate containing 3.8 m/o Nb with additions of cobalt oxide and sintered 5 h. at 1400°C: (A) COF barium titanate with 0.9 m/o Co, and (B) 5018 grade barium titanate with 0.6 m/o Co.

4 DISCUSSION

The experimental data pose two main questions:
 (1) Why was densification of the barium titanate made easier as the amount of niobium was increased;

and (2) Why did additives such as Co, Mg, Ni or Mn modify solid solution of the niobium and retard densification, while equivalent amounts of Fe, Cr, Ca or Ba, for example, apparently did not? Additions of TiO_2 , and ions that substitute for Ti^{4+} in the titanate

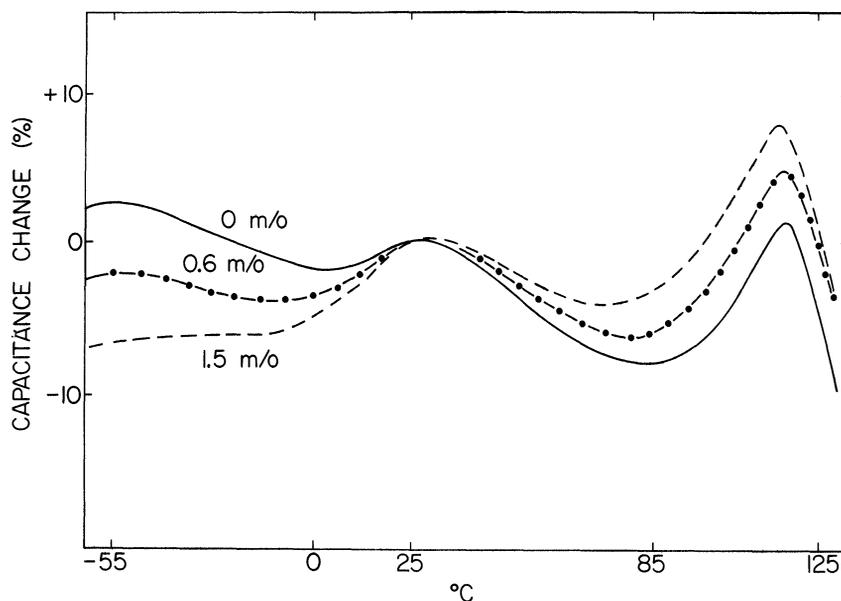


FIGURE 6 Influence of TiO_2 additions on the permittivity of barium titanate with 3.8 m/o Nb and 0.9 m/o Co sintered 5 h. at 1400°C.

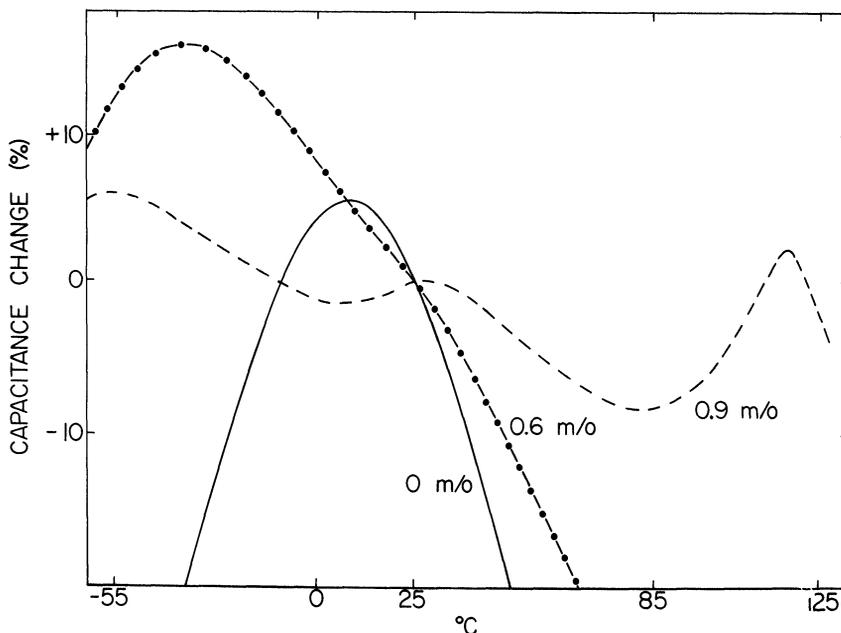


FIGURE 7 Influence of magnesium oxide on the distribution of Nb (3.8 m/o) in barium titanate sintered 5 h. at 1400°C.

lattice, generally improve the sinterability of barium titanate that is closely stoichiometric in Ba and Ti. This is because formation of a liquid titanate phase is encouraged at the temperatures commonly used for

sintering ($\approx 1350^\circ\text{C}$).^{1,2} Conversely, additions of BaO or additives that substitute for Ba (e.g. Ca) generally retard sintering. In the present case, it seems probable that a liquid niobate phase, as well as a liquid titanate

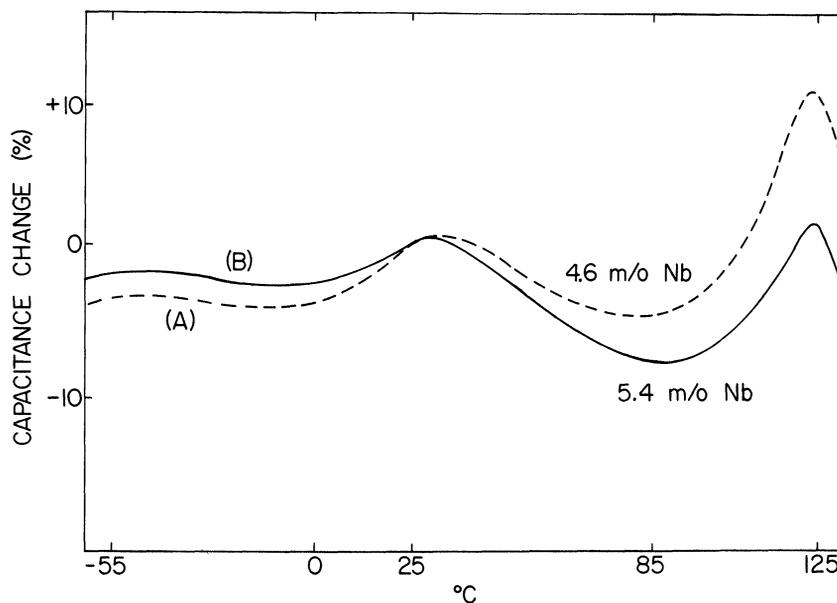


FIGURE 8 Temperature-stable dielectrics with higher Nb content (as shown) and 0.8 m/o Mg sintered at 1400°C for (A) 2 h, (B) 1.5 h.

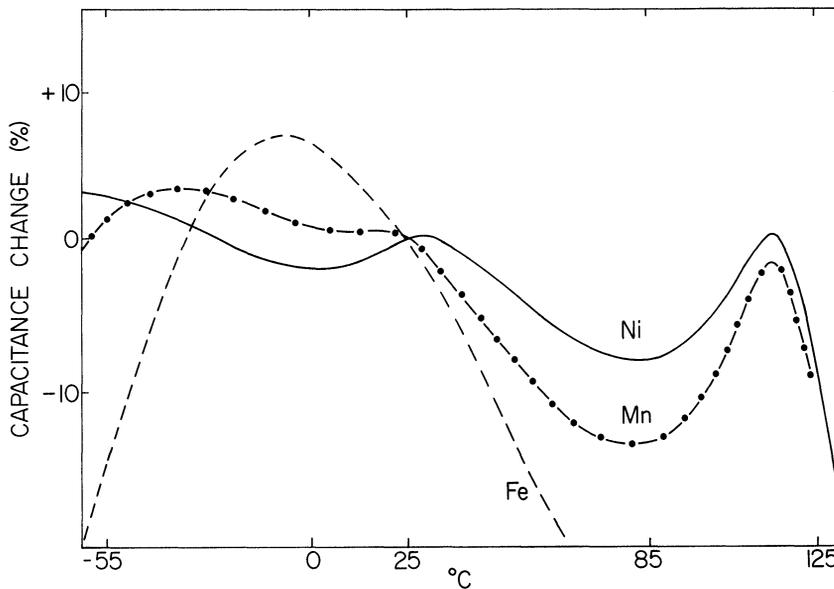
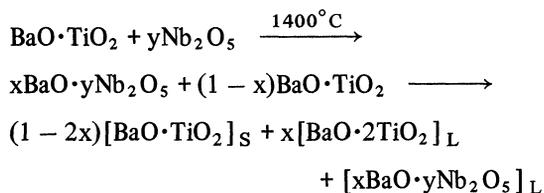


FIGURE 9 Influence of 0.8 mol % Ni, Mn or Fe on the permittivity-temperature characteristic of barium titanate with 3.8 m/o Nb (plus 0.6 m/o TiO_2) sintered 5 h. at 1400°C .

phase, form during sintering, possibly as follows:



Melting below 1400°C occurs over a wide composition range in the $\text{BaO}-\text{Nb}_2\text{O}_5$ system and the liquidus is near 1300° for x/y approximately equal to $1/3$ to $3/5$.¹³ In this range, for example, the amount of dititanate phase might be 0.5 to 0.9 mol % for a niobium addition of 3 mol %. Consequently, small additions of BaO or CaO together with the niobium would be expected to reduce the amount of dititanate phase but not the amount of low melting niobate phase. Since little grain growth was observed during sintering, solution of the niobium probably occurred by a dissolution-precipitation reaction, at least when no modifying additives were present.

In some studies of the influence of niobium on the properties of barium titanate, barium was added with the niobium as $\text{Ba}_{0.5}\text{NbO}_3$ in an attempt to balance the stoichiometry.^{1,2} It is generally accepted that Nb^{5+} substitutes for Ti^{4+} in barium titanate with the charge difference being compensated by one barium vacancy for every two niobium ions; this applies except for very low Nb levels (e.g. $\leq 0.1\%$ Nb) when

each Nb ion is compensated by one Ti^{3+} ion, resulting in a semiconducting ceramic.¹⁴ It seems most likely, however, that in materials of the type discussed here, the major role of any barium addition is in its influence on the sintering characteristics and, in turn, its effect on the rate at which an equilibrium distribution of the niobium is reached.

The fact that oxides of Co, Mg, Ni or Mn retarded the sintering of the barium titanate when niobium was present was unexpected since these additives in small amounts often improve densification in barium titanate ceramics, as do oxides of iron or chromium.^{5,15} It is possible, therefore, that in the presence of niobium the result of these oxide additives is equivalent to having added part of the niobium as $\text{Me}^{2+}\text{Nb}_2\text{O}_6$ in the case of Co, Mg, Ni, and Mn, or as $\text{Me}^{3+}\text{NbO}_4$ in the case of Fe or Cr. Niobates of Co, Ni and Mn are known to form high permittivity solid solutions with barium titanate,¹⁶ and magnesium niobate probably does also. Although it has been suggested that in solid solutions of these transition metal niobates with barium titanate, the transition metal ions occupy Ba sites,¹⁶ it is possible that solution of niobium in barium titanate is made easier by the simultaneous inclusion of Me ions on Ti sites. Thus divalent ions would be twice as effective as trivalent ions in compensating the excess charge of the niobium ions,¹⁴ and could explain why the divalent metal oxide additions had more influence on the permittivity-temperature characteristics. Similar

considerations could apply to additions of Na^{7-9} , or $\text{Li}^{8,10}$ for which the niobium charge is most likely compensated on a one to one basis, as for the trivalent ions, but by singly charged alkali metal ions on barium sites.

The retarding effect on densification of the modifying oxides could have resulted simply from a reduction in the amount of sintering phase, either because of initial formation of niobates that are more refractory than barium niobate, or by encouraging solid solution of the niobium in the barium titanate. If solid solution is concentrated in the "skins" of the grains then permittivity-temperature characteristics of the type observed can be expected.

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