

High Temperature Sodium Bismuth Titanate Capacitors – A New Product Realized

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ABSTRACT

This paper describes the development of a lead free, high temperature ceramic capacitor material having the base composition of $(\text{Na}_{0.5} \text{Bi}_{0.5}) \text{TiO}_3$. The goal is to modify this structure to create a material that has the relative permittivity of barium titanate with extended X7R-like properties to 250°C – an X14R. After an extensive compositional and theoretical modeling investigation a composition was selected and capacitors developed. The dielectric has a 1-kHz relative permittivity of ~1200 with $\pm 15\%$ variation from –25 to +250°C and $< 5\%$ loss from –55 to +250°C. These capacitors also have very low voltage coefficients, indeed they are positive at the low end of the temperature range, resulting in a combined T_C - V_C capacitance variation 0%/-25% of nominal from –55 to +200°C with applied voltage stress from 20 to 260 V/mil.

INTRODUCTION

This paper reports on a family of capacitor dielectrics based on sodium bismuth titanate (NBT) which is being developed to fill the need for MLCs with good temperature stability from –55°C to 300°C. NBT formulations can now achieve Y14R and X11E specifications and one has been introduced as “Type H” by Novacap in a multilayer capacitor (MLC) series with combined T_C - V_C capacitance variation $< +10\%$ /-25% from –55 to +200°C at operating voltages. Type H capacitors will be available in sizes from 0805 to 7565, and voltage ratings up to 1 kV.

The selection of a new material started with concepts derived from barium titanate, which has dominated ceramic capacitor production since the 1950s and will continue to do so in the predictable future. Barium titanate is limited for high temperature applications by a rapid drop in relative permittivity above its Curie temperature (T_C) at 130°C. Sodium bismuth titanate is a family of piezoelectric and dielectric materials that has recently received considerable attention. NBT was considered attractive as a high temperature dielectric because of its high temperature relative permittivity and multiple phase transitions at 220°C and 320°C to broaden the high temperature plateau of high relative permittivity [i]. The large temperature range of a stable relative permittivity is advantageous for use in the oil and natural gas industry for down-hole drilling instruments, automotive, aerospace and military applications directly on or near hot engine surfaces.

SELECTION OF DIELECTRIC

BARIUM TITANATE - Barium titanate differs from many other ceramic ferroelectrics in that it has three phase transitions (–90°C, 0°C, and 130°C) near the normal service temperature, –55°C to 125°C. It is these phase transitions that soften the structure and increase the relative permittivity. In addition to the softening at the ferroelectric-ferroelectric phase transitions it is well known that there is a significant increase in relative permittivity (K) with decreasing grain size.

Grain sizes under a few microns increase internal stress (reduce 90° domain walls) and increase κ down to about 0.7 microns. Once barium titanate is taken above the Curie temperature at 130°C, it is no longer ferroelectric. The stress enhancement and domain wall motion stop at T_C hence κ (and dielectric loss) rapidly decreases (Curie-Weiss Law) with increasing temperature [ii]

Years of experimentation have shown that the structure and useful phase transitions of BT can be altered with the substitution of +2 and +4 valence cations. These shifts are very pronounced for +2 ions such as Sr, Ca and Pb, however, the latter is the only isovalent substitution that can stabilize the Curie transition at higher temperatures.

Modern commercial barium titanate formulations have been refined for 50 years and are very temperature, voltage and time stable. Relative permittivity ranges from 1500 (very stable) to 12,000 (which has a narrow stability range just above room temperature). Figure 1 is a reasonable example of a formulation with X7R (-55°C, 125°C, +/-15%) characteristics (BX also includes DC bias) that is used in an avionics application. This type of ceramic is usually inhomogeneous with a low κ doped BT shell surrounding a nearly pure, high κ BT core. Remnants of T_C can be seen at 120°C.

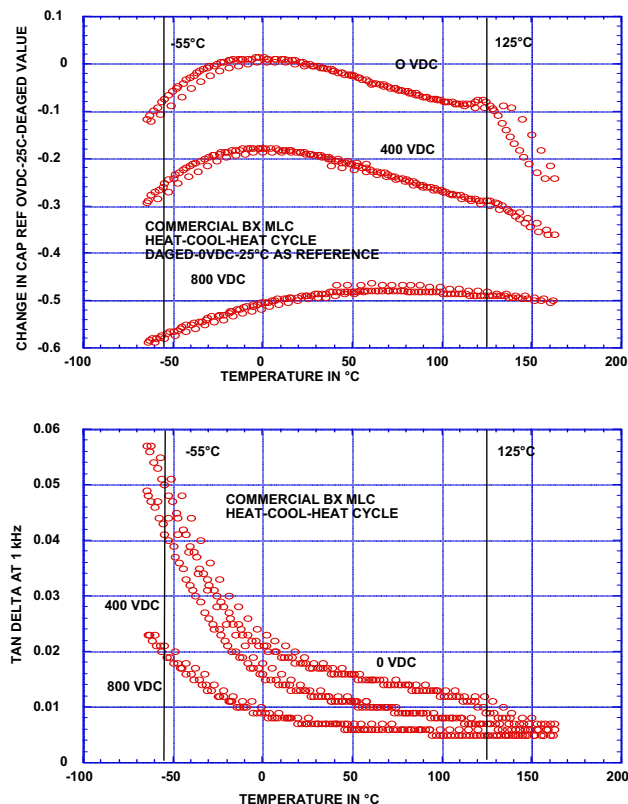


Figure 1: Capacitance and loss as a function of temperature and DC bias for a commercial X7R capacitor

SODIUM BISMUTH TITANATE - The sodium bismuth titanate (BNT) system is a relatively new family of dielectric materials that is being studied for its high

temperature dielectric constant and for its ability to achieve relatively high piezoelectric coefficients without the addition of lead [i]. BNT is a good candidate for future dielectric and piezoelectric materials for high temperature and wide temperature range uses for aerospace and military applications. Compositional additions are used to modify the phase transitions that occur within the BNT material at various temperatures. The dopants are selected to change specific characteristics of the phases such as dielectric constant, Curie temperature (T_C), or the number of phase transitions. The Curie temperature is the temperature where the dielectric constant of the material is the largest. This usually happens where there is a phase transition. By changing the phase transition temperatures and relative permittivity, a material can be modified to fit a wide variety of applications.

Barium titanate (BT) was used as a guide at the beginning of this project. Literature was searched looking for a κ greater than 1000 and phase transitions above 200°C. NBT was discovered in the piezoelectric literature with two strong phase transitions and a suggestion that there may be antiferroelectric activity that has been shown to be useful in lead lanthanum zirconate titanate (PLZT) under high DC bias.

Sodium bismuth titanate (NBT), like BT, is an ABO_3 distorted perovskite. NBT has a rhombohedral, $R3c$, crystal structure at room temperature [iii]. The standard ABO_3 perovskite formula for NBT is $(Na_{0.5} Bi_{0.5})TiO_3$. The $Na^{+1}-Bi^{+3}$ pair replaces two Ba^{+2} in the A-site and maintains charge neutrality without forming vacancies (which tend to lower resistivity). NBT has two main phase transitions, one from rhombohedral to tetragonal at 220°C, and the other from tetragonal (polar) to tetragonal (non-polar) at 320°C [1]. Control of phase transitions in ferroelectric materials is one of the primary tools used to tailor their properties for specific applications. Compositional additions to the NBT structure can be chosen to modify the phase transitions that occur within the material at various temperatures. Proper dielectric design requires dopants to be selected to change specific characteristics of the phases such as relative permittivity, Curie temperature, peak relative permittivity and number of phase transitions. Initial tactics were to find dopants that would raise κ and shift the 320°C transition to about 200°C while the 220°C transition needed to be brought down below room temperature to maintain high κ at -55°C.

DIELECTRIC DEVELOPMENT

Experimental and measurement procedures used in the development of NBT dielectrics have been described in previous papers [iii,iv,v]. Traditional ceramic oxide processing methods were used [iii], with the initial mixing conducted in denatured alcohol (95% ethanol, 5% water). Powders were calcined at 750°C for 12 h and sintering temperatures ranged from 1200-1300°C for 0.5-2 h. Batches ranged from 0.1 to 20kg. Composition

selection was guided by trends from the barium titanate literature outlined above and theoretical considerations described previously [iii].

DIELECTRIC PROPERTIES - The evolution of NBT formulations for high temperature capacitor applications is best described with respect to control of relative permittivity since this is the primary and most demanding goal. Initial work focused on aliovalent A-site dopants and is best understood with reference to Figures 2-4. The plots illustrate the increase in permittivity produced by polarizable ions like Pb^{+2} . In contrast with additions greater than 20% of low polarizability-small cations like Sr^{+2} there is a reduction in κ . Sr additions were the only dopant that followed this linear relation for additions greater than 20%. NBT-ST follows Vegard's Law for the dielectric peak, but probably has a morphotropic boundary around 30% after which peak κ drops. As seen in Figure 2, Pb has a limit at 17% where the rhombohedral phase is destabilized and a tetragonal phase dominates giving a very low κ as is found in PbTiO_3 . Pb at 15% demonstrates a near target response with two phase transitions raising and broadening the dielectric-temperature response.

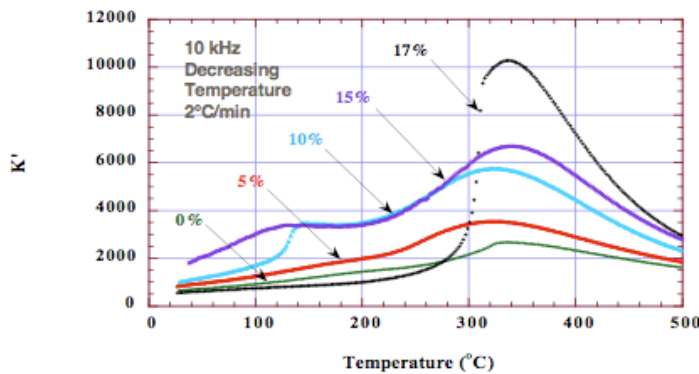


Figure 2: Shifting and broadening of NBT relative permittivity with Pb additions

Unfortunately the peaks in Pb doped NBT are too high in temperature and the dominant tetragonal phase breaks the trend at 17%. Ba additions function similarly to Pb, but go to a dominant tetragonal phase at about 10%.

The Sr modified NBT compositions shown in Figure 3 represent the broadest and most predictable compositional range found. Sr additions most closely matched Bond Valence predictions reported earlier [iii]. The shift in transition temperature with Sr follows a linear relationship as seen in the BaTiO_3 - SrTiO_3 system. Both systems are also similar with respect to increase in peak κ at moderate additions (contrast this to the decrease above 20% Sr discussed above). In BaTiO_3 this is attributed to the phase transition becoming more second order at intermediate compositions. As seen in Figure 5 Sr additions are useful for raising the κ below room temperature and thus flattening the permittivity across the entire temperature range.

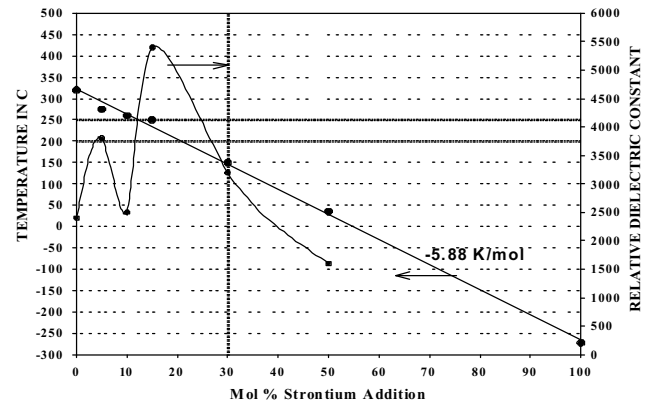
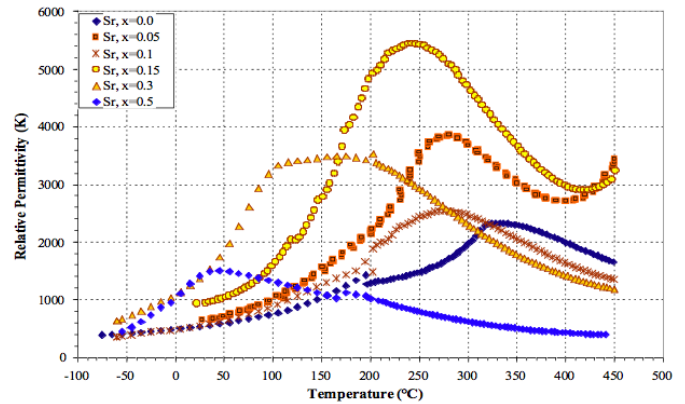


Figure 3: Shifting and broadening of NBT relative permittivity with Sr additions

The effect of Pb, Ba and Sr dopants in NBT is plotted in Figure 4. The principal difference between this and the well-known barium titanate dopant chart is in the limited solubility of Pb and Ba in the rhombohedral structure, which disappears at 17% and 10% respectively.

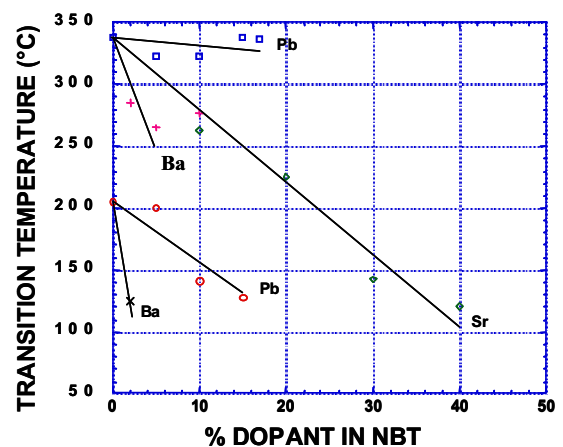


Figure 4: Phase stability of NBT as a function of Pb, Ba and Sr additions