The Dependence of Dielectric Properties on Composition Variation in
$\text{Ba}_{0.6}\text{Sr}_{0.4}(\text{YTa})_y\text{Ti}_{1.2y}\text{O}_3$

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ABSTRACT

$\text{Ba}_{0.6}\text{Sr}_{0.4}(\text{YTa})_y\text{Ti}_{1.2y}\text{O}_3$ has been shown to have properties which are promising for 
tunable applications requiring low dielectric constant [1]. $\text{Ba}_{0.6}\text{Sr}_{0.4}(\text{YTa})_y\text{Ti}_{1.2y}\text{O}_3$ with $y \leq 0.10$
has been synthesized and well-characterized using x-ray diffraction, EDAX, and Raman 
Spectroscopy. The dependence of the dielectric properties on concentration, $y$, of Y and Ta are 
discussed along with implications for improved performance in device applications.

INTRODUCTION

It has been shown that binary charge-balanced substitutions of 3+ and 5+ ions into the B site (for Ti$^{4+}$) in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) lead to changes in the characteristics of the ferroelectric 
(FE) transition, Curie Temperature ($T_c$), and tunability of the dielectric constant that do not occur 
for non-charge-compensated doping of BST or for 4+ substitutions into the Ti$^{4+}$ site [1,2]. The 
binary charge-balanced substitution of 3+ and 5+ ions for Ti lead to greater applicability of the 
FE technology due to broader temperature ranges of operation which include the U. S. Military 
Specification temperature range (mil spec). Such behavior is consistent with device 
requirements as discussed in References [3,4] where tunability is of major importance but losses 
are of less importance. For certain choices of charge-balanced substitution of 3+ and 5+ ions, $T_c$
shifts dramatically by as much as $-60^\circ$C or more accompanied by a significant broadening of the 
FE transition. The behavior of the tunability in such cases is similar to that of the dielectric 
constant, reflecting the broadening and shifting of the difference between the dielectric constant 
at zero electric field and the dielectric constant tuned by the application of a DC electric field. 
This paper focuses on research investigations which seek to characterize, in more detail, the 
compositional dependence of the dielectric properties due to simultaneous variation of the Y and 
Ta content in the Ti site. Results of effects of sintering temperature ($T_s$) on selected charge-
balanced substitutions, $y$, are presented and discussed. The character of the synthesized material 
has been studied using x-ray diffraction, Raman spectroscopy, density, and SEM measurements. 
Electrical properties were obtained through studies of the temperature dependence of the 
capacitance. The lattice constant, grain size, dielectric constant, tunability, and an electric-field-
and temperature-dependent figure of merit (FOM) were studied to determine the effects of the Y 
and Ta concentration variation and changes in $T_s$.

EXPERIMENTAL DETAILS

Compositions of $\text{Ba}_{0.6}\text{Sr}_{0.4}(\text{YTa})_y\text{Ti}_{1.2y}\text{O}_3$ with $y \leq 0.10$ were prepared by mixing BaCO$_3$, 
SrCO$_3$, Y$_2$O$_3$, Ta$_2$O$_5$, and TiO$_2$ in stoichiometric proportions. The samples were then ground and 
pressed into pellets which were calcined at 1100 $^\circ$C for 8 hours. Next the samples were reground
and pressed at 50 kpsi, then sintered between 1450 °C and 1600 °C. There were particular samples with \( y = 0.03 \) and 0.05, which were separated into two parts of equal mass prior to sintering. One portion of each composition was then sintered at a temperature of \( T_s = 1550 \) °C and the other was sintered at 1600 °C. After sintering, a portion of each synthesized sample was cut away and ground and polished. Volume densities were obtained on a microbalance, \( \theta-2 \theta \) x-ray diffraction scans and diffraction ring graphs were obtained using Cu K\( \alpha_1 \) radiation, and Raman spectroscopy was performed. For each sample, contacts were then deposited to form a parallel plate capacitor, and capacitance was measured at a sampling frequency of 1 MHz with applied DC electric fields in the range \( 0 \leq E \leq 1 \text{ V/}\mu\text{m} \) and the temperature varied over \(-75 \leq T \leq 100 \) °C using an environmental chamber. Selected samples were fractured and the grain structure was studied using SEM. Nominal grain sizes were estimated for samples with different \( y \).

RESULTS

The ratio of the volume density to the theoretical value (in percent) was found to drop from \(-95 \% \) for \( y = 0 \) to \(-60 \% \) for \( y > 0.03 \). Theoretical densities were estimated using the lattice constants obtained by x-ray diffraction measurements. For samples with \( y = 0.03 \) and 0.05 that were sintered at 1450 - 1600 °C, \( T_s \) was found to have a modest effect on density, with the density increasing up to 10% with increases over this temperature range. The x-ray diffraction scans show that the samples are single phase and cubic up to \( y = 0.08 \). At \( y = 0.10 \) a peak due to second phase appears at \( d = 3.06502 \) Å and splitting is observed in the major peaks that are significantly above the noise levels indicating deviation from the cubic structure. For \( y = 0.05 \), spots associated with the beginnings of grain size enhancement or grain growth ordering in the samples were more enhanced in the x-ray diffraction rings for samples sintered at 1600 °C than at 1550 °C. Spots indicative of grain growth were seen in the rings for the \( y = 0.03 \) sample sintered at 1550 °C. In addition, for \( T_s = 1600 \) °C compared to \( T_s = 1450 \) °C, the lattice constant is smaller by a significant amount (0.005 Å) for \( y = 0.03 \), but by an insignificant amount (< 0.003 Å) for \( y = 0.05 \). This may be an indication of ordering [5]. There was no evidence of superlattice peaks in the x-ray diffraction scans. Further evidence of the nature of the lattice was obtained from the Raman studies. For \( y \leq 0.05 \), the 306 cm\(^{-1} \) position associated with the E(TO\(_2\)) Raman line in BaTiO\(_3\) was monitored. The absence of an E(TO\(_2\)) peak was observed on a linear scale. This is consistent with the expected behavior for Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\), \( x \geq 0.32 \) [6]. However, on a log scale, there appears a shallow bump at \(-306 \text{ cm}^{-1} \) for each sample in the range \( 0.01 < y < 0.05 \) (Figure 1) which may be evidence of the onset, with YTa concentration, of the noncubic phase observed in the 0-20 diffraction scan for the \( y = 0.10 \) phase.

Nominal grain sizes estimated from the SEM studies of samples are shown in Figure 2 for \( T_s \) and \( y \) values. The grain size drops by an order of magnitude from \(-30 \mu\text{m} \) for \( y = 0 \) (BST) to \(-1 \mu\text{m} \) for \( y = 0.01 \). Grain-like features are observed for \( 0.04 \leq y \leq 0.10 \) at low \( T_s \) (1450 °C - 1500 °C) but do not appear to be well-defined. In all samples with \( y > 0 \), the porosity of the samples due to Ostwald ripening [7] can be observed and volume densities are \(-65 \% \) compared to \(-93 \% \) for \( y = 0 \). For \( y = 0.03 \) and 0.05, at the more elevated \( T_s \) values of 1550 °C and 1600 °C, distinct cubic grain features are clearly seen in the cleaved sections and at the walls of the porous regions. For an increase in \( T_s \) from 1550 °C to 1600 °C, the grain size is estimated to double, from 1 \( \mu\text{m} \) to 2 \( \mu\text{m} \) for both the \( y = 0.03 \) and the \( y = 0.05 \) samples.

The dielectric constant (real relative permittivity, \( \varepsilon \)) plotted versus temperature (Figure 3) is consistent with similar plots for the general case of simultaneous substitution of 3+ and 5+
ions for Ti as reported in References [1,2]. In that work, $T_c$ shifted to lower temperature, the FE transition broadened and the magnitude of $\varepsilon$ was markedly reduced for small concentrations ($y = 0.03$) for many such ion pairs. In comparison, substitutions of 4+ ions for Ti do not shift the $T_c$ of BST very much but can broaden the FE transition and reduce $\varepsilon$ [2,8]. The behavior of $T_c$ with concentration of Y and Ta is plotted in Figure 4 (in analogy to similar plots for BST [8]) and that of the peak value of the dielectric constant $\varepsilon(T)$, in Figure 5. For Figure 5, the values of $\varepsilon(T)$ for $y = 0.08$ and 0.10 are obtained by a graphical extrapolation of Fig. 4 and of $\varepsilon(T)$ below the minimum measurement temperature, $-75 \degree C$, of the environmental chamber. For the device applications that these studies are relevant to, temperature-insensitive materials over the mil spec range are desired so that the device can operate without the added burden of refrigeration or heating and to eliminate sensitivity to sudden temperature spikes or fluctuations. The material must also be highly-tunable [4]. Therefore, a figure of merit (FOM) was developed for the perovskites studied which is given by the expression,

$$FOM = \frac{\Delta \varepsilon / \Delta E}{\Delta \varepsilon / \Delta T}$$

Figure 6 shows the tunability plots for $y \leq 0.10$ and their respective values of the FOM evaluated.
at the maximum dielectric constant measured. This FOM is largest at the intermediate concentration of \( y = 0.05 \). More importantly, the FE transition and tunability broaden as \( y \) increases, and the FOM approaches a constant value over a larger portion of the mil spec range.

Figure 7 shows \( \varepsilon \) plotted versus temperature for \( y = 0.03 \) and 0.05 and \( T_c = 1550 \, ^\circ\text{C} \) and 1600 \( ^\circ\text{C} \). Figure 8 shows the corresponding tunability plots and their FOM values. Recall that, in Figure 2, increased concentrations, \( y \), of Y and Ta reduce the grain size for low \( T_c \) (\( \leq 1550 \, ^\circ\text{C} \)), but this can be reversed somewhat with increase in \( T_c \), with very little measured change in density. Spots, which are an indication of grain growth, begin to occur in the area detector images obtained from x-ray diffraction at 1550 \( ^\circ\text{C} \) and 1600 \( ^\circ\text{C} \). Also for increase in \( T_c \) from 1550 \( ^\circ\text{C} \) to 1600 \( ^\circ\text{C} \), grain size increases and grains become more faceted, as observed in the SEM micrographs, plus the FE transition is sharpened. Since grain size increases were observed for both decreased \( y \) and increased \( T_c \), one may thus wish to see if grain size changes are the sole cause of the changes in the ferroelectric nature of the BST as Y and Ta are added while maintaining charge balance. However, when grain size is increased due to increase in \( T_c \), not all the electrical characteristics are reversed relative to those due to decrease in \( y \). \( T_c \) shifts to a lower temperature with both increased \( y \) and increased \( T_c \). So the changes in the grain size that occur for changes in \( y \) due to increased but charge-balanced additions of Y and Ta to BST do not appear to be the sole cause of changes in the nature of the ferroelectric transition away from that of BST as \( y \) increases. A study of the dielectric constant and tunability for the \( y = 0.03 \) sample in

Figure 4. Ferroelectric Transition Temperature, \( T_c \), vs YTa content, \( y \).

Figure 5. Dielectric constant at the critical temperature, \( \varepsilon(T_c) \), vs YTa content, \( y \).

Figure 6. Percent tunability / Electric Field and figure of merit for \( y \leq 0.10 \).
Figures 7 and 8 further shows that $e(T)$ at the higher $T_s = 1600 \, ^\circ C$, relative to that at the lower $T_s = 1550 \, ^\circ C$, is sharper and higher in magnitude at or near the perceived $T_c$ as though returning to a state more like that of BST, except shifted to a lower $T_c$. The $y = 0.05$ sample appears to have the same trend, although $T_c$ is below the range of measurement. The FOM although lower by about 30% for the $T_s = 1550 \, ^\circ C$ samples applies over a broader temperature range than the FOM for $T_s = 1600 \, ^\circ C$. Room-temperature losses at 1 kHz for the various $y$ and $T_s$ are given in Table I. It of note that for the samples with $T_s = 1600 \, ^\circ C$, even though the measurements are made well above $T_c$, in the paraelectric (PE) regime, the losses are larger, by a factor of ten, than those for samples sintered at 1550 °C. This implies a resistance of FE domains to respond to external fields in the samples sintered at $T_s = 1600 \, ^\circ C$ compared to those sintered at 1500 °C.

The shift in the $T_c$ as a result of the introduction of $Y^{3+}$-Ta$^{5+}$ pairs in the B site of BST (which does not occur for 4+ ion substitutions) suggests an array of dipole pairs distributed throughout the PE/FE domains in which the FE long range order is modified in such a way that $T_c$ is shifted to a lower temperature compared to the unsubstituted BST. This modification occurs in coincidence with a reduction of grain size that correlates with the broadening of the FE transition. The sharpening of the FE transition, observed for $y = 0.03$ when $T_s$ is increased from 1550 °C to 1600 °C, also correlates with increase in grain size. The fact that $T_c$ shifts to a lower temperature and losses increase at room temperature (well above $T_c$), at $y = 0.03$ for $T_s$ increased from 1550 °C to 1600 °C, suggests a difference in the nature of the relationship between the $Y^{3+}$-Ta$^{5+}$ pairs and the FE/PE environments in these two samples. More studies are needed.

Theoretical studies of how $T_c$ is affected by the competition between short range dipole forces and the long range order of ferroelectricity in a dense frozen dipolar system have been carried

### Table I

<table>
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<th>$T_s$ (°C)</th>
<th>$D$</th>
<th>$Q$</th>
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out by Klapp and Patey [9]. A number of other papers discuss dipolar effects in ferroelectrics (see for example References [10-13]) and the shift in $\epsilon(T_c)$ of Fig. 5 is modeled in [13], but there is no theoretical discussion of small percentages of $3^+$ and $5^+$ ions in charge-balanced substitution for the majority $4^+$ ions (which in our case is $\text{Ti}^{4+}$) in the B site of perovskites, which predict the observed $T_c$ shifts.

**CONCLUSIONS**

Tunability, characterized by FOM, is the key parameter in frequency-agile device studies at ARL [4]. A study has been made to better understand the effects of concentration, $\gamma$, and sinter temperature, $T_s$, on tunability, $T_c$, in charge-balanced, $3^+$ and $5^+$ substitutions for Ti in BST. For $T_s \leq 1550 \, ^\circ\text{C}$, increases in $\gamma$ cause $T_c$ to decrease and the FE transition to broaden, leading to a reduction and less variation in dielectric constant, improvement in FOM over the mil spec range as $\epsilon(T)$ and tunability broaden, and decrease in grain size. An increase in $T_s$, from 1550 $\, ^\circ\text{C}$ to 1600 $\, ^\circ\text{C}$, also causes $T_c$ to decrease. However, the FE transition sharpens, $\epsilon(T_c)$ increases, tunability increases near $T_c$ (but FOM decreases away from $T_c$), grain size increases, and $Q$ is reduced. For device applications, the improved FOM over the mil spec range, due to charge-balanced substitutions with $T_s \leq 1550 \, ^\circ\text{C}$, small grain size, and broad FE transition, is preferred.

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**REFERENCES**