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Investigation into the Effect of Reagent Choice on the Dielectric Properties of the Ferroelectric Oxides $Ba(MTa)_{0.05}Ti_{0.9}O_3$ (where M=Sc, Er, Ho or Y)

by Virginia Lea Miller and Steven C. Tidrow

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14. ABSTRACT

This report investigates the effects of reagent choice on the physical properties of ferroelectric oxides of the composition Ba(MTa)0.05Ti0.9O3 (M=Sc, Er, Ho or V). These materials are of particular interest because they possess relatively low to medium dielectric constants and improved tunabilities. In this project, samples of $Ba(MTa)_{0.05}Ti_{0.9}O_3$ (M=Sc, Er, Ho or Y) were prepared using two different synthetic methods. The first method consisted of heating a stoichiometric mixture of binary carbonates and oxides in air at 1500 °C for 25 hours. In the second synthetic method, $Ba(MTa)_{0.05}Ti_{0.9}O_3$ was prepared using the same reaction conditions as the first method, but stoichiometric mixtures of $BaTiO_3$ and Ba_2MTaO_6 (M= Sc, Er, Ho or Y) were used as the reagents. The goal of this project was to determine if using $BaTiO_3$ and Ba_2MTaO_6 as reagents in the synthesis of $Ba(MTa)_{0.05}Ti_{0.9}O_3$, rather than binary oxides and carbonates, would alter and possibly improve the material's dielectric properties. The results indicated that the choice of reagents had a noticeable effect on the dielectric properties. Materials prepared using $BaTiO_3$ and Ba_2MTaO_6 had larger dielectric constants and were more temperature sensitive than the materials prepared using binary carbonates and oxides.

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1. Introduction

Currently, there is interest in using ferroelectric materials in electric field tunable RF devices (*1,2*). The use of ferroelectrics in RF phase shifters has the potential to meet the low-loss, low-cost requirements of microwave phase-arrays. These ferroelectric phase shifters are based on the change in the effective electric length of the device due to a change in the materials permittivity induced by applying an electric field. However, one of the issues affecting the development of these phase shifters is the need for materials that possess a relatively low permittivity, high tunability and low microwave losses over a fairly large temperature and frequency range.

Ferroelectric oxide materials with the perovskite structure are currently being studied for use in microwave phase shifters (*3,4*). Materials for use in the design of these phase shifters must have a small dielectric constant, be highly tunable and exhibit low microwave losses over the temperature and frequency ranges of interest for military applications. A variety of methods have been used to synthesize ferroelectric oxide materials for use in phase shifters. For example, by preparing a composite of $BaTiO_3$ and MgO, one can reduce the permittivity and loss tangent without destroying the tunability of the material at room temperature (*5*). Another method involves doping perovskite oxides with small amounts of Al_2O_3 (~1 %) in an attempt to increase tenability (*6*). Research conducted in the RF Electronics Division at the U.S. Army Research Laboratory (ARL) has shown that “dilute” binary charge-balanced substitutions of 3^+ and 5^+ ions into the B-site of $Ba_{1-x}Sr_xTiO_3$ have produced materials with relatively low to medium dielectric constants (which were also temperature-insensitive) and improved tunabilities (*7 through 12*). These results could not be obtained from non-charge balanced substitution on the B-site of $Ba_{1-x}Sr_xTiO_3$ or from substitution of Ti with other 4+ ions such as Sn^{4+}, Zr^{4+}, Ge^{4+} (*13*).

The materials prepared at ARL can be described by the formula $Ba_{1-x}Sr_x(MM')_yTi_{1-y}O_3$ where M and M' are two different transitions metals with an average charge of 4^+. All of these compounds were found to crystallize with the perovskite structure. The perovskite crystal structure, ABX_3, is one of the most commonly encountered structures in solid-state chemistry. It consists of corner sharing BX_6 octahedra with the A cations located in the 12-fold coordination site between these octahedra. Many ternary compounds, especially oxides, form a simple perovskite structure. However, more complicated variations, such as mixing of atoms on the B site ($ABB'X_3$) or vacancies on the X site (ABX_{3-y}) are also found to occur. This structure is extremely flexible and it can accommodate almost all of the elements in the periodic table. Because of this flexibility, perovskites are numerous in nature and exhibit a wide range of physical properties such as ferroelectricity, ferromagnetism, piezoelectricity, high temperature superconductivity and giant magnetoresistance. In fact, most of the technologically important ferroelectric materials are ceramic oxides with the perovskite structure (*14*).

The ferroelectric materials prepared at ARL are unique in that they possess relatively low dielectric constants and improved tunabilities. Moreover, the dielectric constants of these materials are fairly temperature insensitive over the range –55 °C to 120 °C. Many of these materials are of the composition $Ba_{1-x}Sr_x(MM')_{0.05}Ti_{0.9}O_3$ where x ranges from 0 to 0.6, M is a transition metal with a charge of 3+ and M' is a transition metal with a charge of 5+. $BaTiO_3$ is a common perovskite ferroelectric that exhibits a sharp increase in its dielectric constant at the Curie temperature (~130 °C) (*15*). The substitution of Sr^{+2} for Ba^{2+} results in a decrease in the Curie temperature from ~130° C for x=O to ~–165 °C for x=1 (*15*). The substitution of M^{3+} and M'^{5+} cations for Ti^{4+} results in materials with relatively low, temperature-insensitive dielectric constants. The explanation for why these materials exhibit improved dielectric properties may lie in that fact that they contain two different transition metals (M^{3+} and M'^{5+}) with of an average charge of 4+. These charges maybe be randomly distributed through the structure, or they may join together to create dipole-like pairs of ($M^{3+}M'^{5+}$). Previous in-house calculations have indicated that the presence of these dipole-like pairs in $BaTiO_3$ can cause a "flattening" of the dielectric constant, resulting in a material with relatively temperature insensitive dielectric properties.

In this report, the effect of reagent choice on the dielectric properties of select materials is investigated. The ferroelectric oxides, $Ba(MTa)_{0.05}Ti_{0.9}O_3$ (where M=Sc, Er, Ho or Y) are prepared using two different synthetic methods. The first method utilizes a conventional solid state chemistry technique to synthesize the material. This method consists of heating a stoichiometric mixture of $BaCO_3$, M_2O_3 (where M=Sc, Er, Ho or Y), $Ta_20_5$and TiO_2 in air at elevated temperatures. This technique was previously used at ARL to produce materials with relatively low to medium dielectric constants and improved tunabilities. In this scenario, the B-site cations (M^{3+}, Ta^{5+}, and Ti^{4+}) are completely randomized in the starting mixture. In order for the dipole-pairs (M^{3+}, Ta^{5+}) to form, the M^{3+} and Ta^{5+} cations must diffuse through material to find each other and eventually "pair up". In the second synthetic method, $Ba(MTa)_{0.05}Ti_{0.9}O_3$, is prepared using the same reaction conditions as the first method, but stoichiometric mixtures of $BaTiO_3$ and Ba_2MTaO_6 (where M=Sc, Er, Ho or Y) are used as the reagents (instead of binary oxides or carbonates). Both $BaTiO_3$ and Ba_2MTaO_6 have the perovskite structure. Ba_2MTaO_6 is a double perovskite in which the M^{3+} and Ta^{5+} cations both occupy the B-site. In the material Ba_2MTaO_6, the dipole pairs of (M^{3+}, Ta^{5+}) are already situated very close to one another in the crystal lattice. As this material reacts with $BaTiO_3$, it is very likely that the (M^{3+}, Ta^{5+}) dipole-pairs will diffuse into the $BaTiO_3$ lattice as one unit. This would eliminate the need for the individual cations to diffuse through the lattice in an attempt to locate one another and then form a dipole-pair. The goal of this project was to determine if using $BaTiO_3$ and Ba_2MTaO_6 as reagents in the synthesis of $Ba(MTa)_{0.05}Ti_{0.9}O_3$, rather than binary oxides and carbonates, would result in a material with an identical chemical composition, but improved dielectric properties.

2. Materials Preparation of $Ba(MTa)_{0.05}Ti_{0.9}O_3$ where M = Sc, Er, Ho or Y

Method 1. The above samples were prepared in bulk polycrystalline form by mixing together stoichiometric amounts of $BaCO_3$, M_2O_3 (M=Sc, Er, Ho or Y), Ta_2O_5 and TiO_2. The purity of all reagents was 99.9% or better. This mixture was pressed into a pellet and placed on sacrificial powder of the same composition on platinum foil on an alumina slab. The pellet was then calcined in air at 1100 °C for 8 hours. The heating rate was 3 °C/min and the sample was allowed to cool in the furnace. This step was necessary to convert the binary carbonates to binary oxides. This was followed by grinding, isostatically repressing the pellet 45 Kpsi and heating the pellet in air at 1500 °C for 25 hours (final sintering temperature). The heating rate was 3 °C/min and the sample was allowed to cool in the furnace.

Method 2. This method consisted of the following three steps:

1) A bulk polycrystalline sample of $BaTiO_3$ was prepared by mixing together stoichiometric amounts of $BaCO_3$ and TiO_2. The purity of all reagents was 99.9% or better. This mixture was pressed into a pellet and placed on sacrificial powder of the same composition on platinum foil on an alumina slab. The pellet was then calcined in air at 1100 °C for 8 hours. The heating rate was 3 °C/min and the sample was allowed to cool in the furnace. This was followed by grinding, repressing the pellet and heating in air at 1200 °C for 10 hours. The heating rate was 3 °C/min and the sample was allowed to cool in the furnace.

2) A bulk polycrystalline sample of Ba_2MTaO_6 (where M = Sc, Er, Ho or Y) was prepared by mixing together stoichiometric amounts of $BaCO_3$, M_2O_3 and TiO_2. The purity of all reagents was 99.9% or better. This mixture was pressed into a pellet and placed on sacrificial powder of the same composition on platinum foil on an alumina slab. The pellets were then calcined in air at 1100 °C for 8 hours. The heating rate was 3 °C/min and the sample was allowed to cool in the furnace. This was followed by grinding, repressing the pellet and heating in air at 1500 °C for 72 hours. The heating rate was 3 °C/min and the sample was allowed to cool in the furnace.

3) A polycrystalline sample of $Ba(MTa)_{0.05}Ti_{0.9}O_3$ (where M = Sc, Er, Ho or Y) was then prepared by combining stoichiometric amounts of the previously prepared $BaTiO_3$ and Ba_2MTaO_6. The resulting mixture was isostatically pressed to 45 Kpsi and placed on sacrificial powder of the same composition on Pt foil on an alumina slab. The sample was then heated at 1500 °C for 25 hours (final sintering temperature). The heating rate was 3 °C/min and the sample was allowed to cool in the furnace (same reaction conditions as described in Method 1).

3. X-ray Diffraction Analysis

Phase purity was determined by powder X-ray diffraction using a Bruker 1/4 Circle Chi Platform System with GADDS Area Detector Diffractometer. Diffraction patterns were collected at room temperature using CuKα radiation. Scans were run between 5 and 100° 2θ. The lattice constants were calculated using the following method:

In a cubic system

$$\frac{\Delta d}{d} = \frac{\Delta a}{a} = \frac{a - a_o}{a_o} = K[(\cos^2\theta / \sin\theta) + (\cos^2\theta / \theta)]$$

where *d* is the interplanar spacing, *a* is the calculated unit cell parameter, a_o is the true value of the cell parameter and K is a constant. The term in the brackets is called the Nelson-Riley Function and the value of a_o can be found by plotting *a* against this function, which approaches zero as θ approaches 90 °C. The value of *a* in a cubic system can be calculated using the following equation:

$$a^2 = d^2 (h^2 + k^2 + l^2)$$

where h, k and I are the Miller indices corresponding to each value of *d.*

4. Capacitance Measurements

Measurements of the dielectric constant versus temperature and frequency were made for each of the samples prepared by the methods described above. E-beam evaporation techniques were used to deposit metal contacts on circular samples of ~10.5 mm diameter and 0.5 mm thickness to form a parallel plate capacitor. The contacts were composed of layers of 250Å Ti, 1500Å Au, 3000Å Ag, 1500Å Au in that order. The small-signal capacitance was measured by an impedance bridge in the temperature range $-55 \leq T \leq 120$ °C and the frequency range $0 \leq f \leq 1 \times 10^6$ Hz at 5 values of bias voltage across the capacitors from 0 to 500V. The bias voltages needed for the measurement were provided by a Bertan 205B high-voltage D.C. power supply.

5. Results and Discussion

$Ba(ScTa)_{0.05}Ti_{0.9}O_3$

The sample prepared using Method 1 was a tan color after the final sinter. X-ray diffraction revealed the resulting sample to be single phase and to have a cubic unit cell. The lattice constant, *a,* was derived from the X-ray diffraction peaks using the method of Cullity and was calculated to be ~4.008Å. The sample prepared using Method 2 had a dark tan color after the final sinter. Its X-ray diffraction pattern could be also be indexed using a cubic unit cell. The lattice constant, *a,* was calculated to be ~4.009Å. Figure 1 is a comparison of X-ray diffraction patterns of the $Ba(ScTa)_{0.05}Ti_{0.9}O_3$ samples prepared using the two different synthetic methods. Both samples have extremely similar lattice parameters indicating that they have the same chemical composition.

Although both samples appear to be identical in chemical composition, their physical properties are very different. The dielectric constant of each sample was measured as a function of temperature and frequency. Figure 2 is a comparison of the dielectric constant versus temperature and frequency at zero applied electric field (E=O) for the two different samples and figure 3 is a comparison of the percent tuning versus temperature and frequency. The dielectric constant of the sample prepared using Method 1 is relatively temperature insensitive and has a value of ~1000 over the entire measured temperature range. At temperatures greater than 0 °C, the dielectric constant increases as the frequency decreases. The tuning is about 10% over the measured temperature range. For the sample prepared using Method 2, the plot of dielectric constant versus temperature shows a broad peak that reaches a maximum dielectric constant of ~12000 at –20 °C. The dielectric constant then decreases rapidly to ~1000 at 120 °C. The tuning shows immense variation with temperature, ranging from ~100% at –20 °C to less than 10% at 120 °C. The tuning drops to less than 20% at ~60 °C. There is no change in the dielectric constant or percent tuning with frequency.

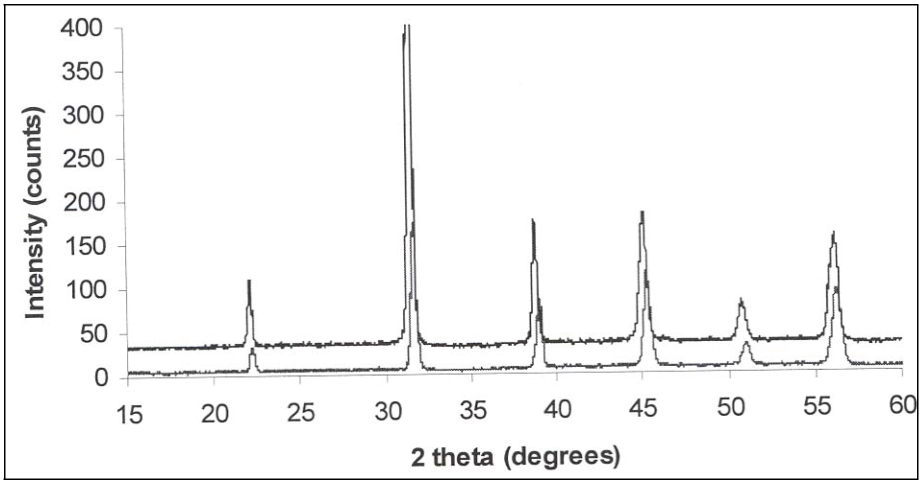


Figure 1. Comparison of the X-ray diffraction patterns of the $Ba(ScTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods. The red line corresponds to the sample prepared using Method 1 and the blue line corresponds to the sample prepared using Method 2.

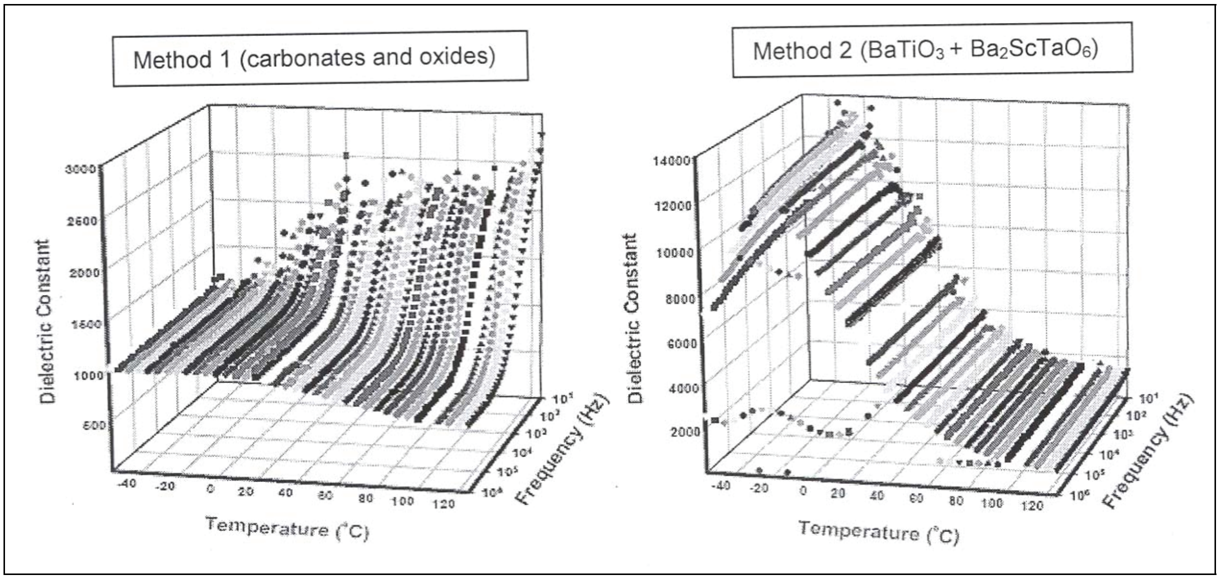


Figure 2. Comparison of the dielectric constant versus temperature and frequency at E=O for the $Ba(ScTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.

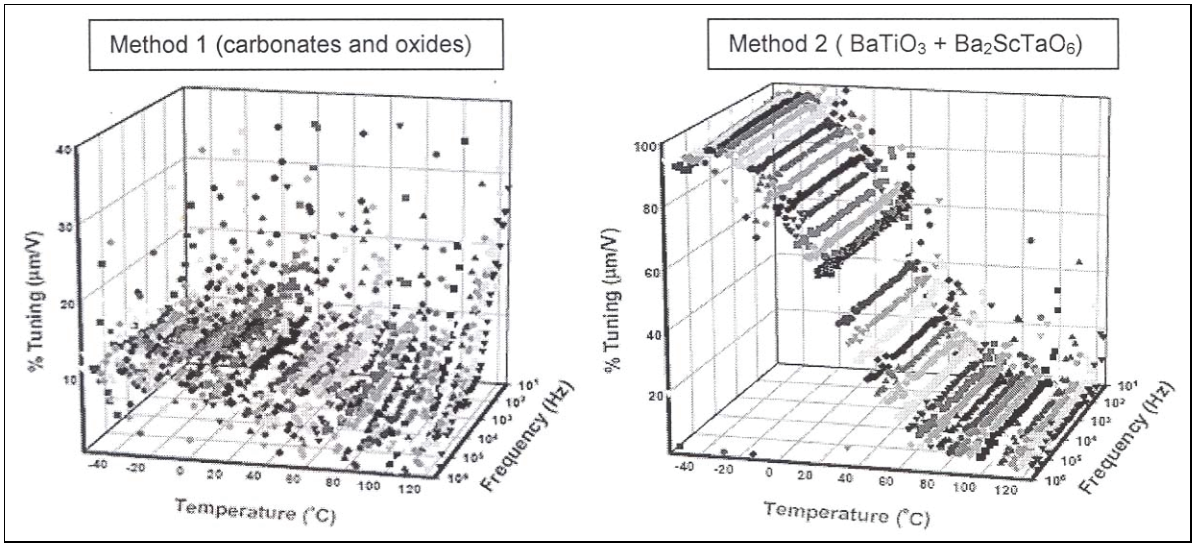


Figure 3. Comparison of the percent tuning versus temperature and frequency for the $Ba(ScTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.

$Ba(ErTa)_{0.05}Ti_{0.9}O_3$

The sample prepared using Method 1 was a tan color after the final sinter. X-ray diffraction revealed the resulting sample to be single phase and to have a cubic unit cell. The lattice constant, *a*, was derived from the X-ray diffraction peaks using the method of Cullity and was calculated to be ~4.023Å. The sample prepared using Method 2 had a very dark tan color after the final sinter. Its X-ray diffraction pattern could also be indexed using a cubic unit cell. The lattice constant, *a*, was calculated to be ~4.027Å. Figure 4 is a comparison of X-ray diffraction patterns of the $Ba(ErTa)_{0.05}Ti_{0.9}O_3$ samples prepared using the two different synthetic methods.

Both samples have very similar lattice parameters indicating that they have the same chemical composition.

The dielectric constant of each sample was measured as a function of temperature and frequency. figure 5 is a comparison of the dielectric constant versus temperature and frequency at E=0 for the two different samples and figure 6 is a comparison of the percent tuning versus temperature and frequency. The dielectric constant of the sample prepared using Method 1 varies from ~3000 at temperatures less than 20 °C to ~1000 at 120 °C over the measured temperature range and at all frequencies. The tuning ranges from 40% at temperatures less than 20 °C to less than 10% at 120 °C. For the sample prepared using Method 2, the plot of dielectric constant versus temperature shows a well-defined peak that reaches a maximum dielectric constant of ~10000 at –20 °C. The dielectric constant then decreases rapidly to ~2000 at 120 °C. The tuning varies from ~60% at temperatures less than –20 °C to ~20% at temperatures greater than 20 °C. The tuning also begins to increase slightly at 120 °C. There is no change in the dielectric constant or percent tuning with frequency.

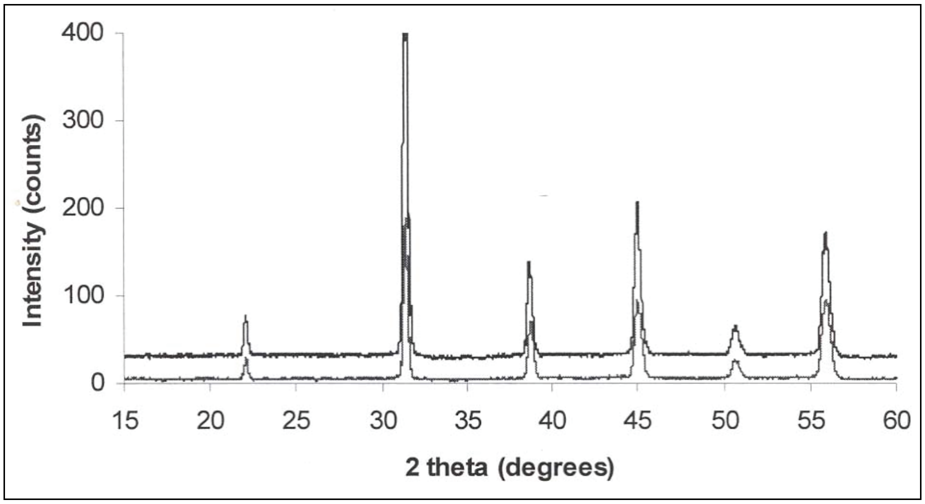


Figure 4. Comparison of the X-ray diffraction patterns of the two Ba(ErTa)$_{0.05}$Ti$_{0.9}$O$_3$ samples prepared using different synthetic methods. The red line corresponds to the sample prepared using Method 1 and the blue line corresponds to the sample prepared using Method

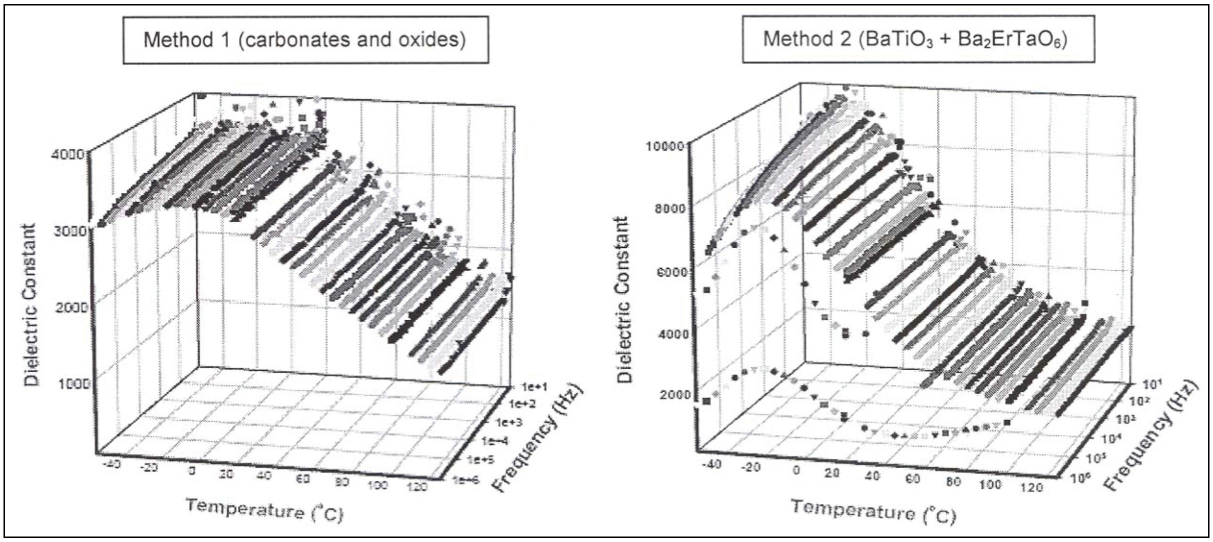


Figure 5. Comparison of the dielectric constant versus temperature and frequency at E=O for the $Ba(ErTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.

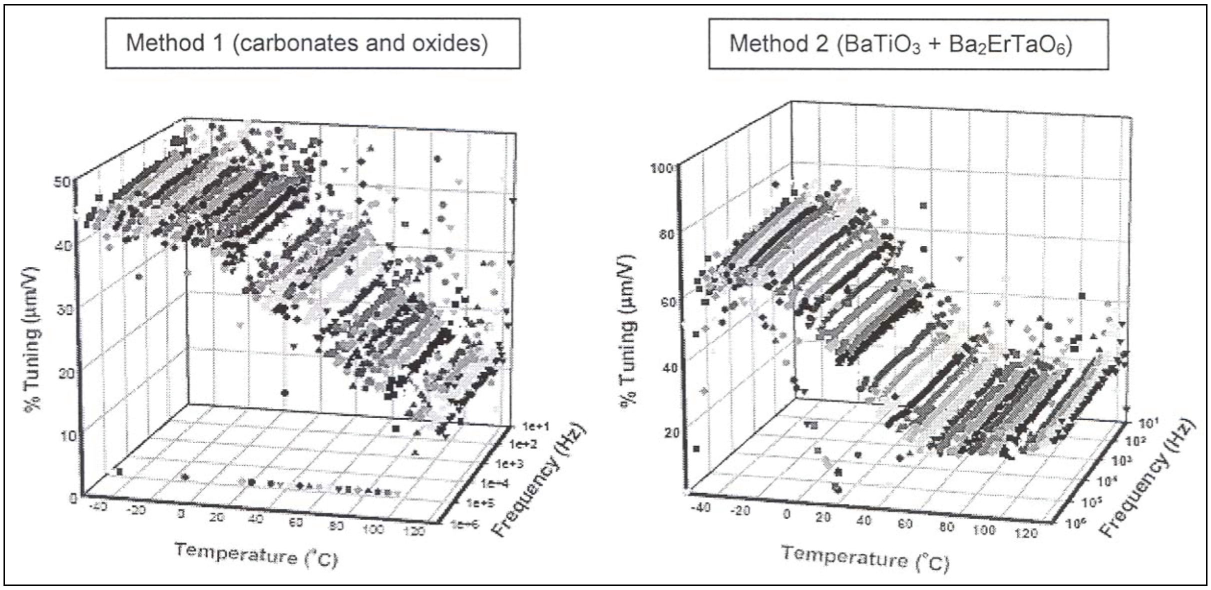


Figure 6. Comparison of the percent tuning versus temperature and frequency for the $Ba(ErTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.

$Ba(HoTa)_{0.05}Ti_{0.9}O_3$

The sample prepared using Method 1 was a dark brown color after the final sinter. X-ray diffraction revealed the resulting sample to be single phase and to have a cubic unit cell. The lattice constant, *a*, was derived from the X-ray diffraction peaks using the method of Cullity and was calculated to be ~4.025Å. The theoretical density of $Ba(HoTa)_{0.05}Ti_{0.9}O_3$ was calculated to be 6.26 g/cm^3. The actual density was determined to be 5.59 g/cm^3. The sample prepared using Method 2 had a very dark tan color after the final sinter. Its X-ray diffraction pattern could be indexed using a cubic unit cell. The lattice constant, *a*, was calculated to be ~4.028Å. Figure 7 is a comparison of X-ray diffraction patterns of the $Ba(ErTa)_{0.05}Ti_{0.9}O_3$ samples prepared using the two different synthetic methods. Both samples have very similar lattice parameters indicating that they have the same chemical composition.

The dielectric constant of each sample was measured as a function of temperature and frequency. Figure 8 is a comparison of the dielectric constant versus temperature and frequency at E=O for the two different samples and figure 9 is a comparison of the percent tuning versus temperature and frequency. The dielectric constant of the sample prepared using Method 1 varies from ~5000 to ~2000 over the measured temperature range and at all frequencies and the tuning ranges from 40% to 20%. There is no change in percent tuning with frequency. For the sample prepared using Method 2, the dielectric constant is around 8000 at –40 °C and then steadily decreases down to ~2000 as the temperature increases to 120 °C. The tuning ranges from ~60% at temperatures less than –20 °C to ~10-15% at temperatures above 20 °C. There is no change in the dielectric constant or tuning with frequency.

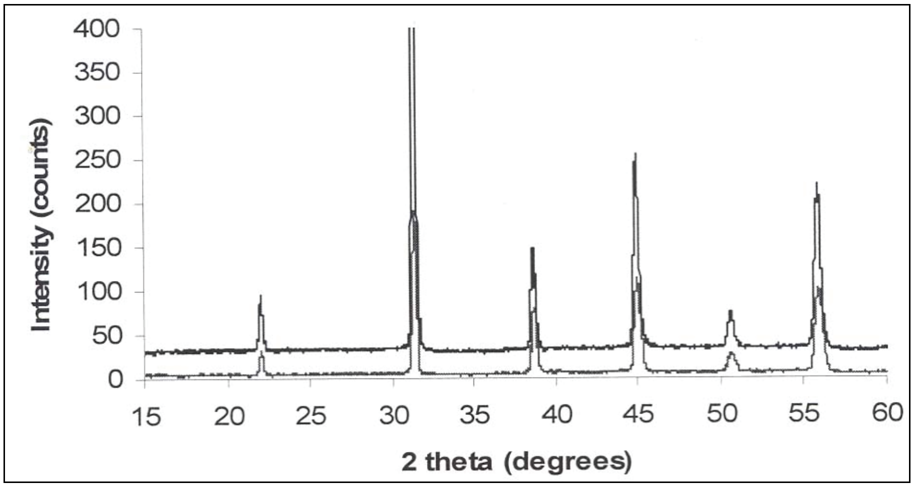


Figure 7. Comparison of the X-ray diffraction patterns of the $Ba(HoTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods. The red line corresponds to the sample prepared using Method 1 and the blue line corresponds to the sample prepared using Method 2.

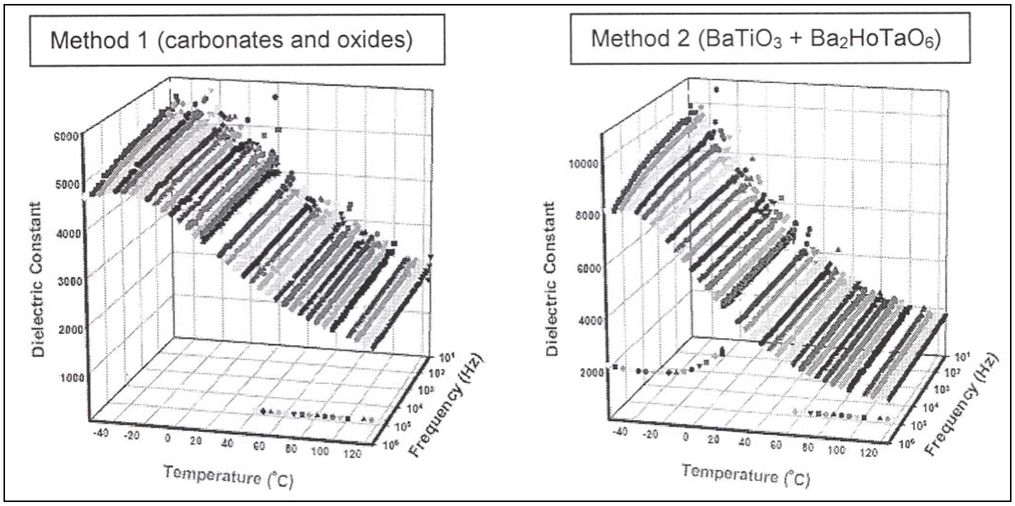


Figure 8. Comparison of the dielectric constant versus temperature and frequency at E=O for the $Ba(HoTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.

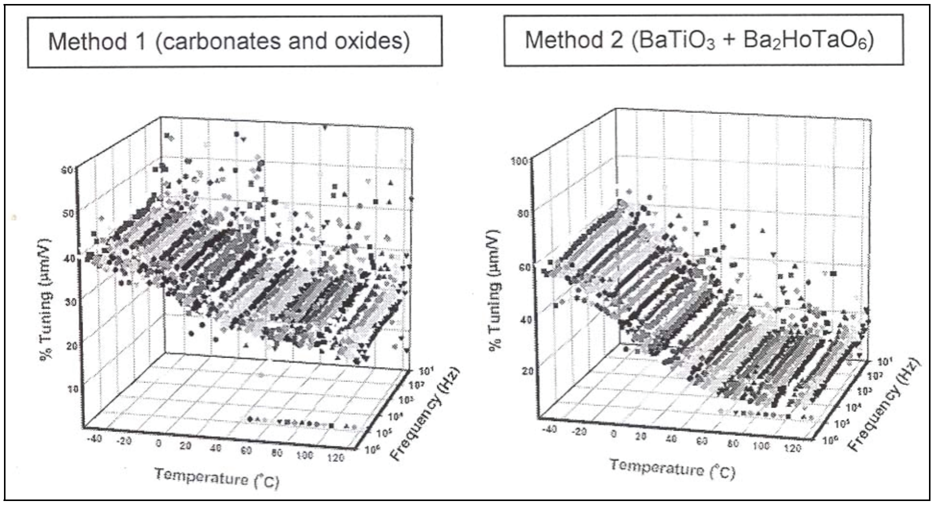


Figure 9. Comparison of the percent tuning versus temperature and frequency for the $Ba(HoTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.

$Ba(YTa)_{0.05}Ti_{0.9}O_3$

The sample prepared using Method 1 was a dark brown color after the final sinter. X-ray diffraction revealed the resulting sample to be single phase and to have a cubic unit cell. The lattice constant, *a*, was derived from the X-ray diffraction peaks using the method of Cullity and was calculated to be ~4.023Å. The X-ray diffraction peaks were very sharp and well defined. The theoretical density of $Ba(YTa)_{0.05}Ti_{0.9}O_3$ was calculated to be 6.17 g/cm^3. The actual density was determined to be 5.38 g/cm^3. The sample prepared using Method 2 had a very dark tan color after the final sinter. Its X-ray diffraction pattern could be indexed using a cubic unit cell. The lattice constant, *a*, was calculated to be ~4.029Å. Figure 10 is a comparison of X-ray diffraction patterns of the $Ba(ErTa)_{0.05}Ti_{0.9}O_3$ samples prepared using the two different synthetic methods.

Both samples have very similar lattice parameters indicating that they have the same chemical composition.

The dielectric constant of each sample was measured as a function of temperature and frequency. Figure 11 is a comparison of the dielectric constant versus temperature and frequency at E=O for the two different samples and figure 12 is a comparison of the percent tuning versus temperature and frequency. The dielectric constant of the sample prepared using Method 1 varies from ~4500 to ~2000 over the measured temperature range and at all frequencies. The tuning ranges from 40% to 20%. There is no change in percent tuning with frequency. For the sample prepared using Method 2, the plot of dielectric constant versus temperature shows a broad peak that reaches a maximum dielectric constant of ~8000 at –30 °C. The dielectric constant than decreases to ~2000 as the temperature is increased. The tuning varies from ~50% (at temperatures less than 0 °C) down to less than 20% at 40-50 °C and then increases slightly to ~30% as the temperature continues to increase. There is no change in the dielectric constant or tuning with frequency.

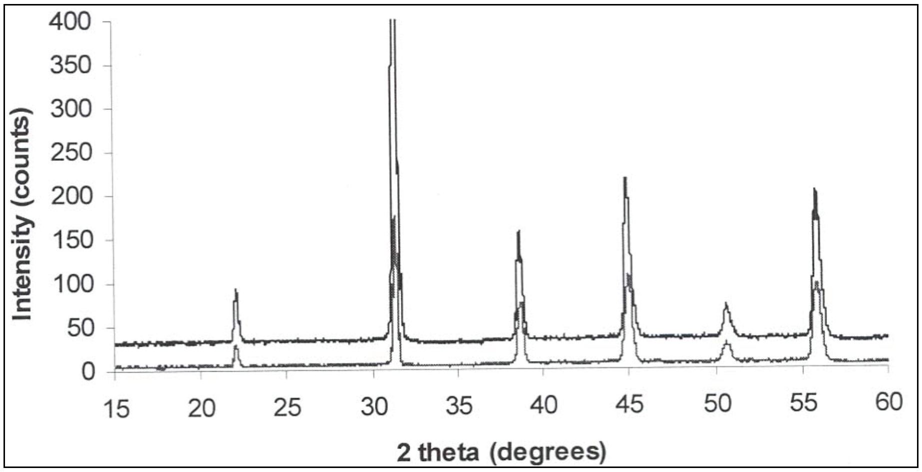
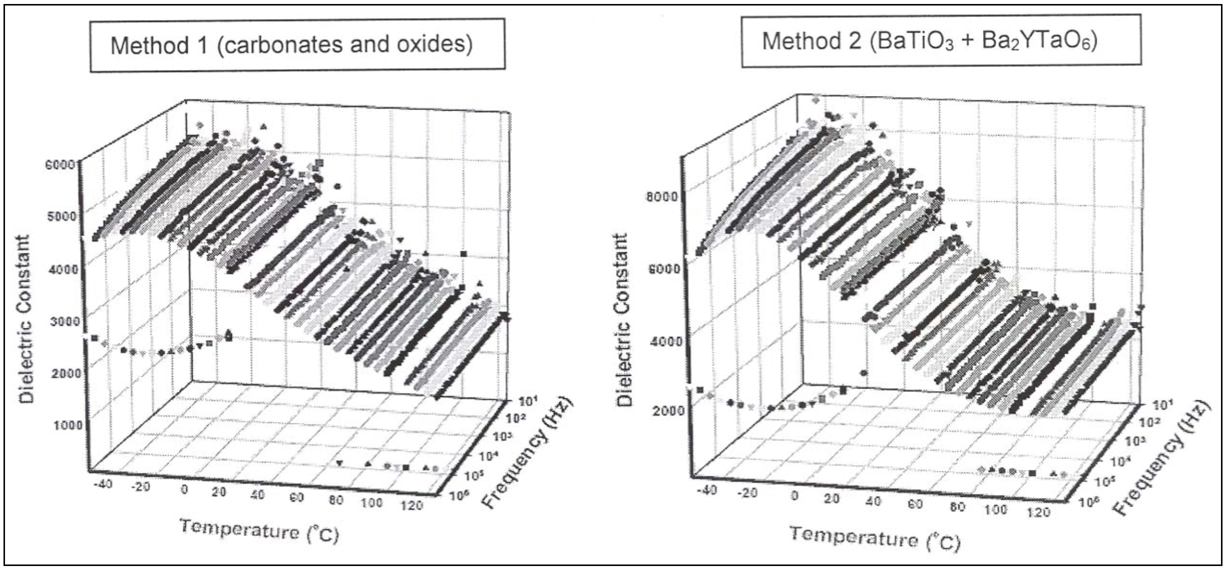
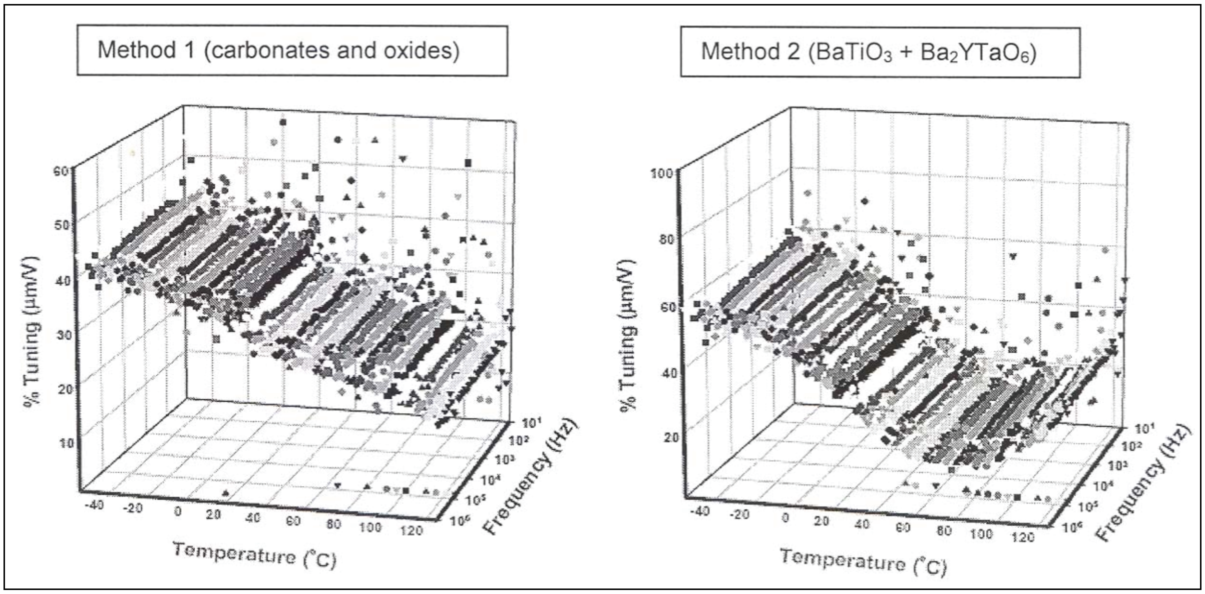


Figure 10. Comparison of the X-ray diffraction patterns of the two $Ba(YTa)_{0.05}Ti_{0.9}O_3$ samples prepared using different synthetic methods. The red line corresponds to the sample prepared using Method 1 and the blue line corresponds to the sample prepared using Method 2.


Method 1 (carbonates and oxides)

Method 2 ($BaTiO_3 + Ba_2YTaO_6$)

Figure 11. Comparison of the dielectric constant versus temperature and frequency for the $Ba(YTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.


Method 1 (carbonates and oxides)

Method 2 ($BaTiO_3 + Ba_2YTaO_6$)

Figure 12. Comparison of the percent tuning versus temperature and frequency for the $Ba(YTa)_{0.05}Ti_{0.9}O_3$ samples prepared using two different synthetic methods.

Discussion

As is illustrated in figures 2 and 3, the dielectric properties of $Ba(ScTa)_{0.05}Ti_{0.9}O_3$ vared greatly depending on whether the reagents were binary carbonates and oxides, or $BaTiO_3$ and Ba_2ScTaO_6. Using the conventional technique of heating binary carbonates and oxides yielded a material with a relatively low, temperature-insensitive dielectric constant and low tunability. When $BaTiO_3$ and Ba_2ScTaO_6 were used as reagents, the resulting material had a dielectric constant that was much higher and exhibited greater temperature sensitivity. The percent tuning of this sample was also very temperature dependant and varied greatly as the temperature increases from –55 °C to 120 °C. Similar results were obtained for $Ba(ErTa)_{0.05}Ti_{0.9}O_3$ (see figures 5 and 6) For this compound, the sample prepared using $BaTiO_3$ and Ba_2ErTaO_6 exhibited much larger dielectric constants over the entire measured temperature range. This sample also showed less temperature-insensitivity than the sample prepared using binary carbonates and oxides as the starting materials. And although this sample exhibited a higher percent tuning at lower temperatures, it greatly decreased in value as the temperature reached 60 °C. At temperature above 60 °C, the tuning of both sample was extremely similar. The $Ba(HoTa)_{0.05}Ti_{0.9}O_3$ and $Ba(YTa)_{0.05}Ti_{0.9}O_3$ samples also exhibited different dielectric properties depending on whether the reagents were binary carbonates and oxides or $BaTiO_3$ and Ba_2HoTaO_6 (Ba_2YTaO_6) (see figure 8, 9, 11, and 12). The plots of dielectric constant versus temperature and frequency for the two $Ba(HoTa)_{0.05}Ti_{0.9}O_3$ samples were very similar in shape (see figure 8). The only difference was that the sample prepared from $BaTiO_3$ and Ba_2HoTaO_6 had a slightly higher dielectric constant (as was the case with the Sc and Er samples). Similarily, the dielectric constant of the $Ba(YTa)_{0.05}Ti_{0.9}O_3$ sample prepared from $BaTiO_3$ and Ba_2YTaO_6 had a larger value and was more temperature sensitive than the sample prepared form the binary carbonates and oxides (see figure 11). Overall, the shape of the plot of these two samples was very similar, unlike that of the Sc and Er samples.

Although all samples are believed to contain (M^{3+}, Ta^{5+}) dipole-pairs, it is very possible that the samples prepared using $BaTiO_3$ and Ba_2MTaO_6 have a higher concentration of these dipole-pairs, which results in larger dielectric constants and great temperature sensitivity. Samples prepared using binary carbonates and oxides also contain (M^{3+}, Ta^{5+}) dipole-pairs, but these materials may also have a large percentage of M^{3+} and Ta^{5+} cations that are individually situated throughout the lattice. This may be a result of the fact that when binary carbonates and oxides are used as reagent, the cations must diffuse through the structure to find one another and "pair up". This diffusion process may limit the number of (M^{3+}, Ta^{5+}) dipole-pairs that form, which may lead to low to medium dielectric constants and temperature insensitivity. In the situation in which $BaTiO_3$ and Ba_2MTaO_6 are used as reagents, the dipole pairs are already formed in Ba_2MTaO_6 and it is very possible that when this compounds reacts with $BaTiO_3$, the (M^{3+}, Ta^{5+}) dipole-pairs remain in tact and diffuse through the structure as a unit. This may results in higher dielectric constants and less temperature insensitivity. Additional x-ray and neutron diffraction studies are necessary to determine the amount of cations that form dipole-pairs and the amount of cations which are individually scattered throughout the structure. Moreover, SEM and TEM studies should be performed to determine if the grain size varies between samples, which may be a factor in explaining the difference in dielectric properties.

6. Conclusions

Materials of the composition $Ba(MTa)_{0.05}Ti_{0.9}O_3$ where M= Sc, Er, Ho or Y were prepared using two separate methods. The methods differed in the choice of reagents used in the synthesis of these compounds. In the first method, a sample of $Ba(MTa)_{0.05}Ti_{0.9}O_3$ where M= Sc, Er, Ho or Y was prepared using binary carbonates and oxides as reagents. In the second method, a sample of the same composition was prepared using $BaTiO_3$ and Ba_2MTaO_6 (where M=Sc, Er, Ho or Y) as reagents. The choice of reagent was found to have a noticeable effect on the dielectric properties. In all cases, using $BaTiO_3$ and Ba_2MTaO_6 as reagents resulted in materials with larger dielectric constants and greater temperature sensitivity. The percent tuning of these samples was higher, but it was also very temperature sensitive. It is postulated that during the reaction process, the (M^{3+}, Ta^{5+}) dipole-pairs in Ba_2MTaO_6 diffuse through the $BaTiO_3$ lattice as one unit. This results in a large number of dipole-like pairs, which may be partly responsible for the increase in the dielectric constant and decrease in the temperature insensitivity of the material.

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7. References

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1. Rao, J.B.L.; et al. *Mat. Res. Soc. Symp. Proc.* **2002**, *720*, H5.2.1.
2. Tidrow, S. C.; et al. *Integrated Ferroelectrics* **2000**, *28* (1-4), 15t.
3. Babbitt, R.; et al. *Microwave Journal* **1992**, *63*.
4. Babbitt, R.; et al. *Integrated Ferroelectrics* **1995**, *8* (1-2), 65.
5. Sengupta, L. C.; et al. *IEEE Trans. Ultrasonics, Ferroelectrics and Freq. Control* **1997**, *44*, 792.
6. Wu, L.; et aI., *J Mater. Sci.* **2000**, *35*, 5945.
7. Tidrow, S. C.; et al. *Mat. Res. Soc. Symp. Proc.* **2004**, *784*, C8.20.1.
8. Potrepka, D.; et al. *Mat. Res. Soc. Symp. Proc.* **2002**, *720*, H5.5.1.
9. Potrepka, D. M.; et al. *Integrated Ferroelectrics* **2002**, *42*, 97.
10. U.S. Patent 6,818,144, 16 November 2004.
11. U.S. Patent 7,087,186,8 August 2006.
12. U.S. Patent 6,875,369 Bl, 5 April 2005.
13. Potrepka, D.; et al. *Mat. Res. Soc. Symp. Proc.*, 656E, 2001, DD5.9.t.
14. Van Aken, B.; et al. *Nature Materials* **2004**, *3*, 164.
15. West, A. R. *Basic Solid State Chemistry;* John Wiley & Sons, Ltd., 1999.

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