Microstructure Development of Zirconia Doped Barium Titanate Nano Ceramics

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Abstract

Usually when barium titanate ceramics are doped with zirconium, substitution of titanium ions by zirconium ions is expected, which significantly alters the dielectric properties. However, a very small addition of zirconia up to 2% was studied here. In case of such small addition rather than any substitution of ions at the octahedral sites, zirconia stays close to grain boundaries of barium titanate hence disrupting the growth of the grains of base material. It results in the formation of a core-shell structure where the core is pure BaTiO₃ and shell is ZrO₂. Such structural modification induced by ZrO₂ resist the transformation from cubic to tetragonal formation and results in superior dielectric properties along with very low losses. Here the effect of zirconia on disrupting the grain growth was studied. The procedure did not follow the conventional calcination-sintering route. Sintering temperature was varied over a wide range and density was found to increase with increasing sintering temperature. Domain structures were revealed in the fine-grained ceramics.

Keywords: Barium titanate, zirconia, processing, fine grain

1. INTRODUCTION

Barium titanate is one of the most important dielectric materials for the electronic devices. Barium titanate (BT) has become increasingly important in the electro-ceramic industry, because of its ferroelectric properties. The dielectric properties of BaTiO₃ have been shown to be very grain size dependent. Fine grain BaTiO₃ exhibits permittivity of 3500 to 4000 at room temperature \(^{1-5}\) and values approaching 6000 has been reported. Kinoshinto and Yamaji\(^6\) showed as the grain size decreases, the permittivity of the material increases.

For high dielectric properties dense fine-grained microstructure is essential. This is achieved by isovalent or aliovalent cations substitution into the perovskite lattice. In small concentrations, substitution of NiO, ZrO₂, Dy₂O₃ and Nb₂O₅\(^7-9\) found to act as grain growth inhibitors. Below 1300°C\(^{10}\), ZrO₂ is found at the grain boundary as discreet particles(~3µm). Zirconia has been shown by Brajer\(^{11}\) and Kulscar\(^{12}\) to increase the orthorhombic-tetragonal transition temperature in BaTiO₃. Maurice\(^13\) was able to prepare dense ceramic bodies from oxalate-derived barium titanate which showed a flattened dielectric response to ZrO₂ additions ≤2.0 wt%. This behavior was attributed to ZrO₂ particles accumulation at the grain boundaries and to suppression of grain growth in sintered barium titanate. Armstrong and Buchanan further determined that ZrO₂ resided permanently at the grain boundaries below 1320°C. In these doped ceramics core-shell grains are formed, characterized by a core of pure barium titanate surrounded by a Zr-modified material as described by rawal\(^10\). Convergent-beam diffraction analysis showed the shell to be tetragonal, but highly strained, with expanded lattice parameters corresponding to a cell volume increase ≈4%. The resultant compressive stress on the core produced a more pseudocubic structure overall\(^10\).

The objective of this investigation was to examine the effects of small additions of ZrO₂ on the microstructure, dielectric properties, and, in particular, the densification and grain size of BaTiO₃. Unstabilizerd ZrO₂ was dope
under sintering condition where solid solubility was not fully achieved to ensure the grain-boundary residence of the additives.

2. EXPERIMENTAL PROCEDURE

(1) Powder Processing and Compaction

ZrO₂ doped barium titanate was prepared by direct mixing of barium titanate and zirconia. Hence no intermediate calcinations stage is bothered. One and two percent ZrO₂ was doped. 99.99% pure barium titanate nano powder – 100 nm and 99.99% pure Zirconium oxide nano powder – 30/60 nm were the starting materials. 25g batches were placed in a 250 ml polypropylene pot 1/3 full of cylindrical yttria stabilized zirconia ball (with rounded ends). The balls were of two types based on their size. One size was 3 mm and other was 5 mm. The balls and pots were cleaned ultrasonically to remove slightest of dust which may show up as impurity in the final structure with resultant harmful properties. The balls stay at the bottom and powders stay on balls. Then acetone was added to sufficient quantity which acted as the milling media. After that, the mouth of pot was closed tightly and then shaken to mix the ingredients. Then powders were milled for 16 to 20 hours in order to mix all the zirconia with barium titanate. After milling the powders containing acetone were separated from the balls very carefully. Then the powders were dried; for quick drying powders were kept at 100 C for 2 to 3 hours.

Before final pressing the powders were kept at 100 ⁰C for 30 to 60 minutes to make sure that all the acetone and moisture were completely removed. Binder was mixed in proper amount. Binder, poly vinyl alcohol was available in the form of powders. 10 grams of powders were taken into a bicker to which about 110 ml of distilled water was added. Then the mixture was put onto burner which heated the bicker up to 100 C temperatures. Afterwards, the powders were taken for pressing. The pressing die had a diameter of 13 mm. At each pressing 1.5 grams of powder was pressed into a disc of about 2 mm thickness. The applied pressure on this occasion was about 300 MPa corresponding to approximately 4.062 tons of load. After pressing the discs were kept at 110 C for about 3 hours to remove any moisture present within the discs.

(2) Sintering

A number of cycles are applied to compacts of various compositions which vary sintering temperature and soaking time. Single stage sintering technique was used in the experiments. Sintering temperatures were 1220⁰C, 1240⁰C and 1260⁰C. Each time varying the holding time 2, 3 and 4 hour at the sintering temperature. The dwell time at the primary stages were for the removal of binder. Usually binders’ boiling point is 300 ⁰C. Hence holding at 550 C was well enough to get the binder off of the disc. Up to this point the heating rate was low to avoid cracking during binder removal. Depending upon the composition and the samples’ tendency to warp during sinter the heating rate was changed at each stage.

(3) Property Measurement

Percent Theoretical Density

After sintering ends sample’s dimensions were measured e.g. thickness and diameter using a micrometer. Then the sample was weighed using electrostatic balance. From these data densities were calculated. These resultant densities were then compared to the theoretical densities and were expressed in terms of percent theoretical density achieved. Theoretical densities are listed below for the tested compositions.
Table 1. Theoretical densities of different composition

<table>
<thead>
<tr>
<th>Material</th>
<th>Theoretical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO3 doped with 1% zirconia</td>
<td>6.016 gm/cc</td>
</tr>
<tr>
<td>BaTiO3 doped with 2% zirconia</td>
<td>6.013 gm/cc</td>
</tr>
</tbody>
</table>

Microstructure Analysis

Since the sintered samples were meant to be watched under a scanning electron microscope (SEM) which was a very powerful tool, no further preparation of samples were needed for this step. Since ceramic sample is not conductive the samples needed to be made conductive by applying a gold coating by sputtering technique. The thin gold coating caused the electron to interact with the samples’ inner atomic shells.

3. RESULTS AND DISCUSSION

For both 1% and 2% doped BaTiO₃ density and grain size was found to increase with increasing temperature and sintering time (Figure 1 - Figure 4). Sintering temperature were 1220°C, 1240°C and 1260°C.

Density achieved for 1% Zirconia doped Barium titanate was found always to be higher than that of 2% doped barium titanate for the same sintering cycle (Figure 5). It was because higher sintering temperature was required for higher content of Zirconia.

Grain size was much smaller in 2% Zirconia doped than that was in 1% Zirconia doped BaTiO₃ for the same sintering cycle (Figure 6).

Figure 1: Sintering time Vs. % Theoretical density for 1% Zirconia doped BaTiO₃

Figure 2: Sintering time Vs. % Theoretical density for 2% Zirconia doped BaTiO₃
Figure 3: Sintering time Vs. Grain size for 1% Zirconia doped BaTiO$_3$

Figure 4: Sintering time Vs. Grain size for 2% Zirconia doped BaTiO$_3$

Figure 5: Sintering time Vs. % Theoretical density for both 1% & 2% Zirconia doped BaTiO$_3$
Density achieved in doped barium titanate, both 1% and 2% sintered at 1220°C for 2 hr was unsatisfactory. When sintered at the same temperature for 3 hr and 4 hr density did not increase too much. Rather grains were coarsened. At lower temperature grains found elongated. Domain structure appears clearly with increasing sintering time.

When sintering temperature was increased above 1220°C, even for 2 hr sintering period, better density was achieved with relatively finer grain size compared to that found for sintering at lower temperature for prolong sintering duration (Figure 7 – Figure 8). Grains were less elongated in samples sintered at higher temperature.

Figure 6: Sintering time Vs. Grain size for both 1% & 2% Zirconia doped BaTiO3

Figure 7: 1% ZrO2 doped BaTiO3 (a) sintered at 1220°C for 2 hr. 78.42% theoretical density was achieved with grain size 6.13 µm (b) sintered at 1220°C for 4 hr. 81.41% theoretical density was achieved with grain size 7.83 µm (c) sintered at 1240°C for 2 hr. 81.59% theoretical density was achieved with grain size 6.54 µm
Figure 8: 2% ZrO₂ doped BaTiO₃ (a) sintered at 1220°C for 2 hr. 72.13% theoretical density was achieved with grain size 3.31 µm (b) sintered at 1220°C for 4 hr. 76.27% theoretical density was achieved with grain size 4.31 µm (c) sintered at 1240°C for 2 hr. 77.62% theoretical density was achieved with grain size 3.79µm

Thus effect of sintering temperature was found to be more on densification than the effect of sintering time, which indicated that sintering temperature was not sufficient. Rather prolong sintering time lead to excessive grain growth. So sintering at rather higher temperature for shorter sintering duration was studied later on. Better results were achieved in following sintering cycles.

Table 2: Sintering schedule

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Temperature(°C)</th>
<th>Holding time at sintering temperature(hr)</th>
<th>%Theoretical density achieved</th>
<th>Grain size(µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% ZrO₂ doped BaTiO₃</td>
<td>1280</td>
<td>5</td>
<td>78.5</td>
<td>10.56</td>
</tr>
<tr>
<td>2% ZrO₂ doped BaTiO₃</td>
<td>1280</td>
<td>5</td>
<td>76</td>
<td>5.23</td>
</tr>
<tr>
<td>1% ZrO₂ doped BaTiO₃</td>
<td>1300</td>
<td>5</td>
<td>80</td>
<td>11.89</td>
</tr>
<tr>
<td>2% ZrO₂ doped BaTiO₃</td>
<td>1300</td>
<td>5</td>
<td>79</td>
<td>5.99</td>
</tr>
<tr>
<td>1% ZrO₂ doped BaTiO₃</td>
<td>1320</td>
<td>5</td>
<td>86</td>
<td>12.11</td>
</tr>
<tr>
<td>2% ZrO₂ doped BaTiO₃</td>
<td>1320</td>
<td>5</td>
<td>85</td>
<td>6.13</td>
</tr>
<tr>
<td>1% ZrO₂ doped BaTiO₃</td>
<td>1320</td>
<td>2.5</td>
<td>89</td>
<td>11.23</td>
</tr>
<tr>
<td>2% ZrO₂ doped BaTiO₃</td>
<td>1320</td>
<td>2.5</td>
<td>88</td>
<td>4.98</td>
</tr>
</tbody>
</table>
At higher sintering temperature density was increased. When sintering time was decreased at higher temperature higher densification with relatively smaller grain size was achieved. At 1320°C for 2.5 hr holding time 89% theoretical density was achieved with grain size 11.13 µm in 1% ZrO2 doped BaTiO3 (Figure 9) and 88% theoretical density was achieved with grain size 4.98 µm in 2% ZrO2 doped BaTiO3.(Figure 10).

4. CONCLUSION

Small addition of unstabilized ZrO2 to BaTiO3 was found to result in grain growth inhibition. The added ZrO2 was resident at the grain boundary. Maximum density was attained for sintering at 1320°C for 2.5 hr. But grain size was not fine enough. The study suggested shorter holding period at sintering temperature to achieve fine grain size at 1320°C and above temperature.

5. REFERENCES