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Influence of Additive on the Microstructure and Properties of Multiferroic BaTiO₃

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Abstract

The work was done to understand the influence of additive (Nb_2O_5) on the properties of multiferroic $BaTiO_3$. Low diffusivity causes core-shell structure. Nanoparticles of $BaTiO_3$ were doped with different concentration of additives (0.22, 0.34 and 0.45 wt % Nb_2O_5). Both single and double stage sintering was done. For single stage, sintering, temperature was 1260°C, 1280°C and 1300°C respectively. While for double stage sintering, activation temperature was fixed at 1300°C. Final sintering temperature was varied to 1190°C, 1220°C and 1250°C. Double stage sintering gave better percent theoretical density (%TD) at lower temperature. Microstructural characterization was done using SEM. Grain size was measured. Dielectric property was measured using LCR meter. XRD and DTA were also done. XRD confirmed the diffusion of Nb^{5+}ions in BT lattice. While LCR meter and DTA revealed the shifting of Curie temperature (T_c) to lower temperature. Dielectric property was seen to increase and it became constant at higher frequency.

Keywords: Dopant, DTA, XRD, Percent theoretical density, Curie temperature, Grains.

1. Introduction

Dielectric characteristics of materials are of increasing importance as the field of solid state electronics continues to expand rapidly. This field is one in which limitations of available materials are frequently the bottleneck preventing improved designs. Also, the reliability of components is of great importance for many applications; the failure of one component can cause failure of an entire missile costing several millions of dollars, for example. At the same time there is an extensive effort to reduce the size and weight of all electronic devices. All these factors have led to an increasing interest in ceramic dielectric materials. A dielectric is a non-conducting substance, i.e. an insulator. Due to the distinctive structural characteristics ceramic materials are known for good insulators and therefore are referred to as dielectric materials [1, 2].

Among all the multi-ferroelectric materials, polycrystalline barium titanate (BaTiO₃) finds extensive application in the electronic industry as a dielectric in ceramic capacitors and, particularly in multilayer ceramic capacitors (MLCCs) due to its high relative dielectric constant (*k*=1500-2000) and low losses [3].

Recently, the possibility to achieve a large electro-strain effect in single crystal BaTiO₃ has been shown, and this may lead to a new generation of actuators. The continuous advance in microelectronics and communications is graduallyleading to the miniaturization of ferroelectric components and of MLCCs. The evolution of ceramic capacitors has continued in two directions: smaller-sized components and larger capacitance values. To be able to achieve high capacitance in a small volume, the dielectric layer thickness has to be reduced while increasing the total number of layers [4, 5].

Unmodified BaTiO₃ is not a good candidate for dielectric application because of its low capacitance value at and around room temperature. In addition, BaTiO₃ undergoes transformations in the crystalline phase with increasing temperature. The peak value of the capacitance (known as the Curie temperature) for unmodified BaTiO₃ is around 120°C. In order to utilize BaTiO₃ as a capacitor material, it is necessary to lower the Curie temperature and to stabilize the capacitance value with respect to changes in temperature [6].

Among the dopants that are used to modify the dielectric and semiconducting propertiesof BaTiO₃, niobium is the most useful donor dopant because it can be incorporatedin BaTiO₃ lattice as Nb^{5+} at Ti^{4+} sites. Depending on Nb concentration, BaTiO₃may exhibit semiconducting or insulating properties. It has been reported that if a dopingconcentration exceeds a certain limits (0.5 %) a dramatic decrease in grain size is occurred,thus leading

to the change from semiconducting $BaTiO_3$ to insulator. K. Kowalskiet all reported that up to 6 at% Nb^{5+} can be incorporated into $BaTiO_3$ latticeaccording to the formula $Ba[Ti_{(1-5x)}Nb_x]O_3$ [4, 7, 8].

Nb_2O_5 was one of the first dopants studied and has been used successfully for the last 30 to 40 years in $BaTiO_3$ based capacitor formulations. Niobium may be added to ceramic formulations in the form of compounds such as $NbCl_5$ and niobium oxalate, but the pentoxide (Nb_2O_5) is the preferred additive for general use [5].

The greatest advantage of Nb_2O_5 addition to multiferroic $BaTiO_3$ based formulations is that it is a powerful Curie temperature shifter. This property makes Nb_2O_5one of the most widely utilized dopants for air fired dielectric systems based on $BaTiO_3$. It is also a major constituent of Y5V relaxor dielectrics based on lead perovskite compounds. Nb_2O_5 is also useful as a grain growth inhibitor in ceramic capacitor formulations [3, 4].

2. Experimental Procedure

Conventional ceramic powder processing technique was used to prepare samples. Pure $BaTiO_3$ powder [60~100nm; Manufacturer: INFRAMAT (USA) purity: 99.99%] was doped with 0.22, 0.34 and 0.45wt% Nb_2O_5 [50~150nm; Manufacturer: INFRAMAT (USA) purity: 99.99%]. Raw materials were ball-milled in acetone media for 20 hours. After ball milling, the extracted wet powder was dried at 110ºC. PVA (Poly vinyl alcohol) was used as binding agent during compaction. Tablet shaped samples (pellets) were prepared using a uniaxial hydraulic or mechanical press machine.
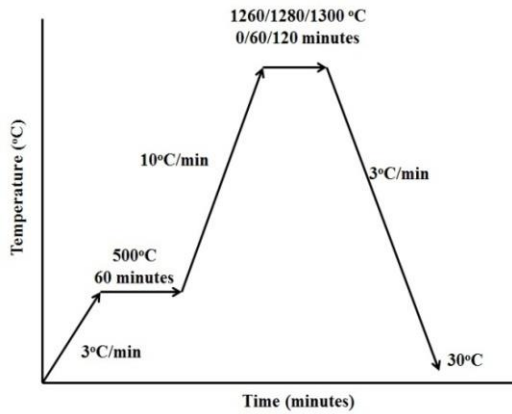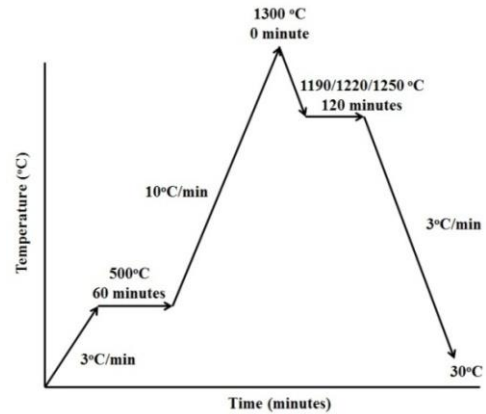

Fig. 1. Single Stage Sintering

Fig. 2. Double Stage Sintering

Both single and double stage sintering was done in a box type muffle furnace. Samples were sintered at definite temperature and soaking time with controlled heating and cooling rate. After sintering, percent theoretical density and grain size were measured. %TD was calculated by the following formula:

$$\%TD = \left(\frac{\text{Actual density}}{\text{Theoretical density}} \text{x} 100 \right) \%$$ (1)

Microstructures of the sintered ceramic samples were observed using a scanning electron microscope (SEM). Sintered samples were taken for XRD and DTA. Finally, the dielectric property was investigated using an impedance analyzer(LCR meter). Dielectric constant (k) was calculated by the following equation:

$$k = \frac{Cd}{\varepsilon_o A}$$ (2)

3. Results and Discussions

3.1 Percent Theoretical Density Measurement

3.1.1 Single Stage Sintering

Fig. 3-5 shows the variation of percent theoretical density (%TD) with increasing sintering temperature as well as soaking time for single stage sintered samples. Percent theoretical density increased up to 1280ºC with increasing soaking time. 1300ºC didn't give good result when soaking time was higher. High temperature along

with longer soaking period caused excessive grain growth. Samples doped with 0.22 and 0.34wt% Nb_2O_5 always gave higher %TD than samples of 0.45wt% Nb_2O_5.
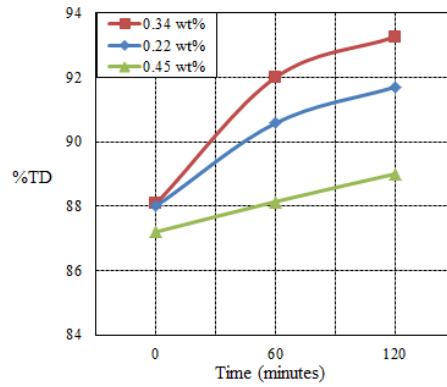

Fig. 3. Variation of %TD with soaking time (sintering temperature 1260°C)
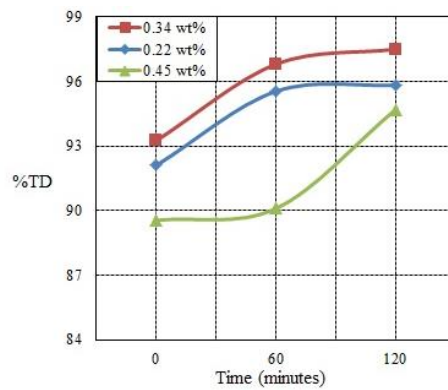

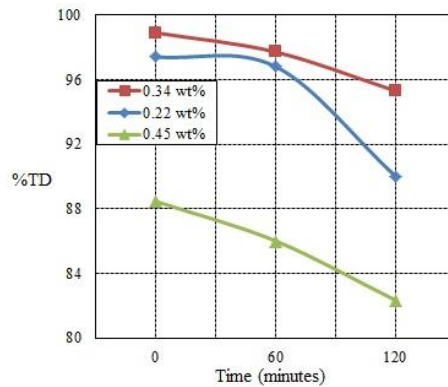**Fig. 4.** Variation of %TD with soaking time (sintering temperature 1280°C)

Fig. 5: Variation of %TD with soaking time (sintering temperature 1300°C)

3.1.2 Double Stage Sintering

In case of double stage sintering, there is an intermediate temperature zone known as activation temperature. At this temperature sample is taken without any holding time. Final sintering temperature is somewhat lower than the temperature usually seen in single stage sintering. Fig. 6 shows the effect of double stage sintering on %TD. Double stage sintered samples gave better result at lower sintering temperature than single stage sintered samples. But situation was same for 0.45wt% Nb_2O_5 doped samples.
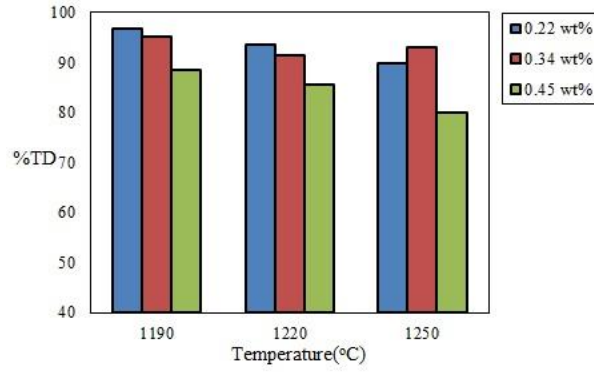
Fig. 6: Double stage sintering (120 minutes soaking)

3.2 XRD Analysis

XRD was done to ensure the diffusion of Nb^{+5} ions into the lattice of barium titanate. Fig. 7 shows the XRD pattern of 0.34wt% niobium oxide doped $BaTiO_3$ samples in different parameters. The peaks shifted in a regular fashion with increasing soaking time. Due to the higher ionic radius of Nb^{+5} than Ti^{+4}, the unit cells of the doped crystals was larger than the pure $BaTiO_3$ samples, resulted the shifting of the peak at higher angles.
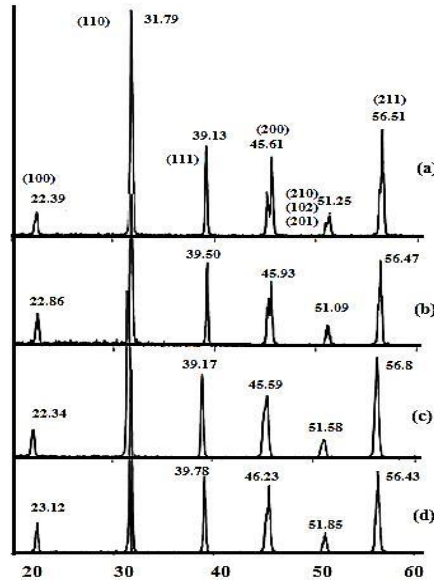
Fig. 7: XRD of (a) pure BT, 0.34wt% doped sintered at 1300ºC for (b) 0, (c) 60 & (d) 120 minutes

When Nb^{+5} entered in the crystal of barium titanate, it caused distortion of the structure. Hence, it changed theBragg's angle of many perfect planes of barium titanate. So rays were reflected from other angles and peak shifting occurred.Again, as the number of perfect planes had decreased, the total amount of rays reflecting from those planes also decreased. And hence, the peak height or the intensity of rays also decreased (Fig. 7).

3.3 DTA Analysis

Differential thermal analysis was done to ensure the shifting of Curie temperature. DTA curves showed (Fig. 8-10) the shifting of curie peak of barium titanate due to the presence of niobium as impurity. As the wt% of niobium oxide increased, the curie peak shifted to lower temperatures. It indicates the diffusion of Nb^{+5} in $BaTiO_3$ lattice. The peaks shifted to 72.7, 71.7 and 67.7ºC for 0.22, 0.34 and 0.45wt% niobium oxide doped samples respectively.
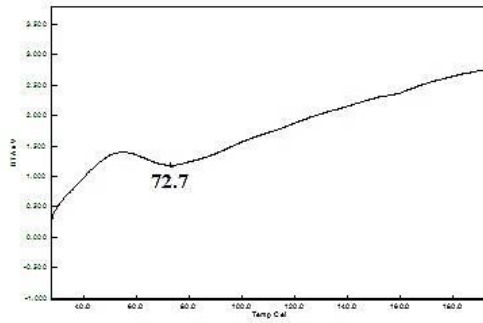
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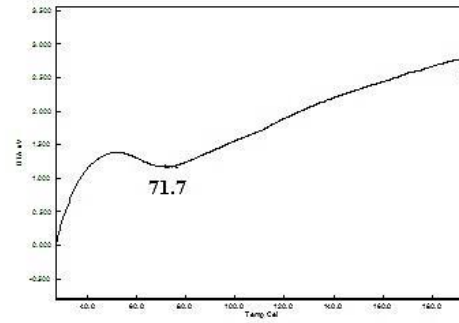**Fig. 8.** DTA curve of 0.22 wt% doped sample

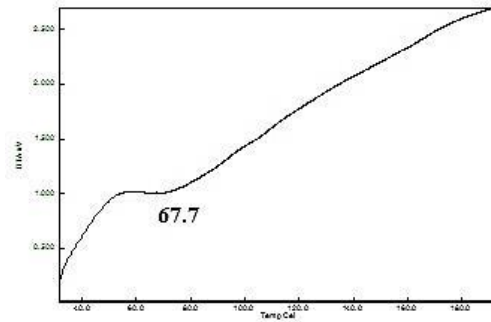**Fig. 9.** DTA curve of 0.34 wt% doped sample

Fig. 10. DTA curve of 0.45 wt% doped sample
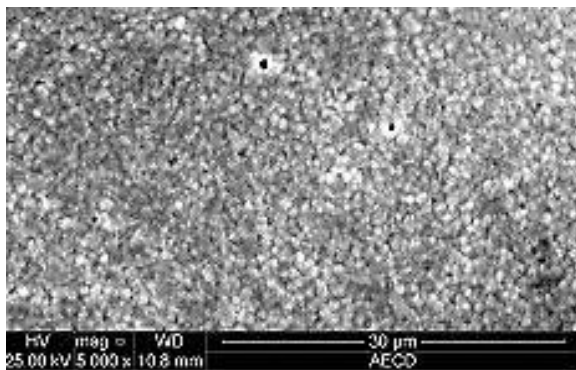
3.4 SEM Micrographs

Fig. 11. SEM micrographs of 0.22wt% samples
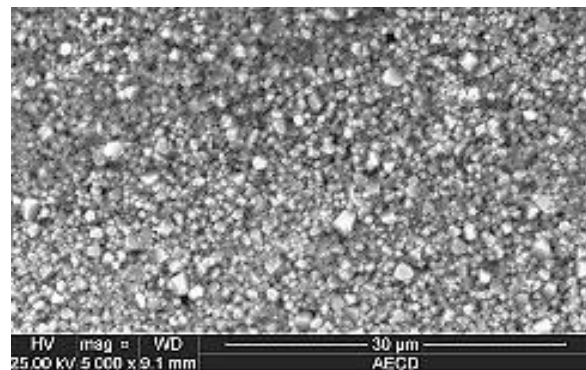(sintered at 1280°C soaked for 60 minutes)

Fig. 12. SEM micrographs of 0.22wt% samples
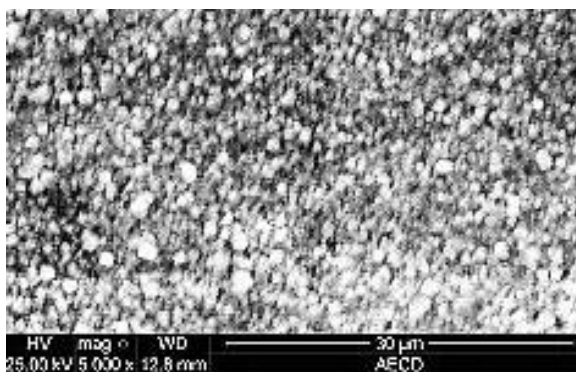(sintered at 1280°C soaked for 120 minutes)

Fig. 13. SEM micrographs of 0.34wt% samples
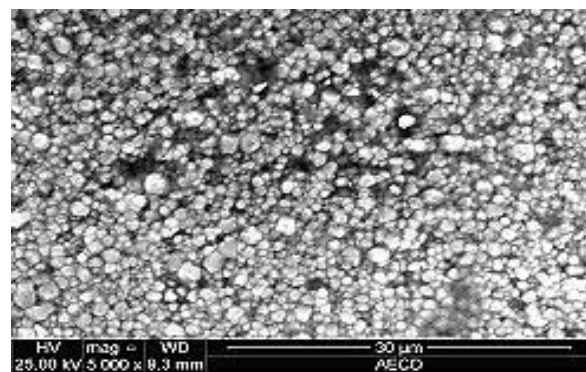(sintered at 1280°C soaked for 60 minutes)

Fig. 14. SEM micrographs of 0.34wt% samples
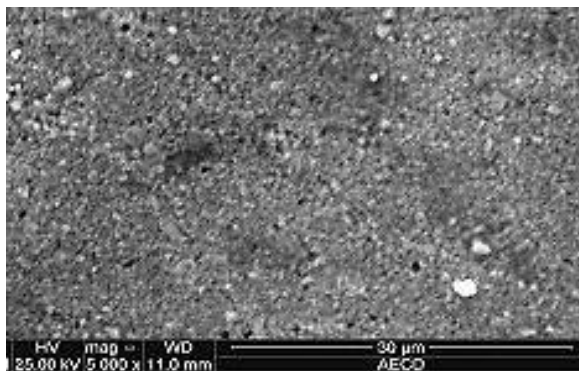(sintered at 1280°C soaked for 120 minutes)

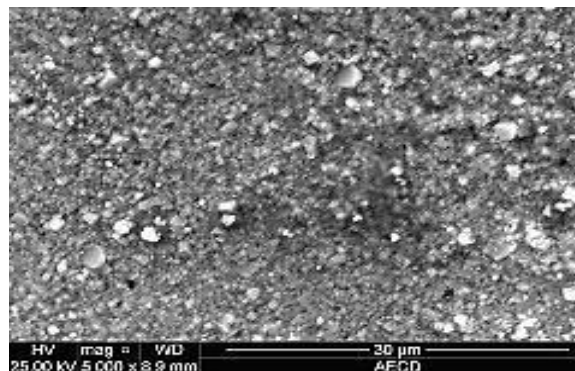| **Fig. 15.** SEM micrographs of 0.45wt% samples (sintered at 1280°C soaked for 60 minutes) | **Fig. 16.** SEM micrographs of 0.45wt% samples (sintered at 1280°C soaked for 120 minutes) |

The microstructure of sintered samples was observed by SEM. It was found that, 0.34 wt% niobium oxide doped samples always gave better microstructure with less porosity than other samples. For 0.22 wt% doped samples sintered at 1280°C, with increasing sintering time the grain size as well as density increased and percent porosity decreased (Fig. 11&12). Samples sintered with no soaking time, resulted porous microstructure as enough time was not provided for densification and grain growth. As the sintering time increased from 60 to 120 minutes, the effect of increasing time on grain size and density was not much significant for 0.22 wt% doped samples. In case of 0.34wt% niobium oxide doped barium titanate samples the effect of sintering time on microstructure was betterthan0.22 wt% niobium oxide doping (Fig. 13 & 14).

4. Conclusions

Addition of additives or dopants like niobium oxide had significant effect on microstructure. It gave excellent pinning which controlled the excessive grain growth. SEM showed that, with increasing the concentration of dopants, the pinning effect increased and thus the grain size decreased gradually. But some exception was present. XRD patterns revealed the diffusion of niobium ion in barium titanate crystal structure. Dielectric constant was seen to increase by the addition of niobium oxide in barium titanate. The ferro to para transition peak depressed and k value became constant at higher frequency. Curie temperature shifted to lower temperature with dopant concentration.

5. Acknowledgements

6. References

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