Experimental Measurement and Investigation on the Feasibility of Improvement of Physical and Dielectric Properties of Barium Titanate

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Abstract
Recent research has examined the improvement of physical and dielectric properties of BaTiO$_3$ ceramic material by the small addition of excess TiO$_2$ or BaCO$_3$. The prepared samples sintered at different temperatures and varying soaking time. The results show that increasing the sintering temperature within (1350 °C) and soaking time within (10 hrs) gives better electrical and physical properties, which indicate that the reaction is complete at higher temperature and periods.

Keywords: Barium Titanate; Soaking Time; Sintering Temperature; Dielectric Properties

Introduction
The inorganic compound Barium titanate (BaTiO$_3$) is transparent as larger crystals and white powder with piezoelectric properties, photorefractive effect and a ferroelectric ceramic material. It is used in electromechanical transducers, nonlinear optics and capacitors.

Piezoelectricity is one property of a group of dielectric materials called ferroelectrics. These materials are characterised by a domain structure that can be modified by an electric field. The piezoelectric effect manifests as a spontaneous potential difference across the opposite faces of a volume of material when under an applied stress. This potential is proportional directly to the mechanical stress applied to it. The inverse is also true, i.e., electric field implementation causes strain in a volume of piezoelectric material [1].

The first piezoelectric material discovered was Calcium Titanate, which has the perovskite structure. A traditional commercial example is Barium titanate, which is commonly used in capacitors and transducers due to its high permittivity [2]. The reaction between BaCO$_3$ and TiO$_2$ proceeds via several intermediate stages of which formation of BaTiO$_4$ is the most distinct. The grain size of BaTiO$_3$ ceramic is controlled by inhibition the grain growth by using an excess amount of TiO$_2$ as a second phase which behaves as inhibitor [3].

By adjusting the Ba/Ti ratio it can be obtain the stoichiometric powders, in the powder excess Barium incorporation when higher Ba/Ti ratio [4]. With range of
 stoichiometry 0.995 - 1.00, optimum electric properties and sintering behavior are expected obtained [5].

In hybrid vehicles, electric ships and pulse power systems used widely energy storage capacitors. Because of applications of electronic systems are lighter demand and smaller, the desired for each capacitor high-energy density, when dielectric constant increase for a linear dielectric, the stored energy density was improves linearly, while electric field develops quadratically. Therefore, a strong interest has created by the drive toward device miniaturization with high dielectric breakdown strength (BDS) in ferroelectric glass–ceramic materials. Glass–ceramics are an almost zero porosity and crystallization possess a uniformity of microstructure and fabricated through controlled nucleation, which supply singular characteristic for capacitor applications at high-energy density. In contrast to the processed ferroelectric ceramics (the conventional powder) [6-9].

Little alteration in porosity, grain size, composition, etc., can considerably alter dielectric materials physical properties. These influences are the ultimate significance for ferroelectric glass–ceramics capacitor applications. Even in the situation of exceedingly investigated Tungsten–Bronze glass–ceramics and perovskite such as strontium bariumniobate (SBN) and barium titanate (BT) these influences away from purified, and strong study efforts are yet underway in order to discovery relationships between dielectric properties, the microstructure (grain morphology, grain size, etc.) and composition. This paper concentrate on tailoring the BaO–TiO₂–Al₂O₃–SiO₂ composition of glass by means of change the ratio of Ba/Ti in order to investigate its effect on the crystalline phases, microstructure, and hence the resulting glass–ceramics dielectric properties. Microstructure development, phase developments, detailed thermal analysis, dielectric constant and dielectric BDS, loss spectra were calculated as a function of the ratio of Ba/Ti. The relationship between the dielectric properties and microstructure was correlated [10-12].

Synthesize Barium titanate by heating barium carbonate and titanium dioxide. These reactions occur by means of sintering of liquid phase. Barium titanate Single crystals can be created from molten potassium fluoride at around 1100°C. Barium titanate indissoluble in alkalis and water. It is whilst, soluble in various acids such as hydrofluoric acid, hydrochloric acid and sulfuric acid. The compound can melt totally in concentrated sulfuric acid and hydrofluoric acid. Barium titanate is obtainable in crystal forms or powder high have a perovskite constructing, solid Barium titanate structure may alter with temperature. Five different phases can exist, from high temperature to low temperature. Hexagonal, cubic, orthorhombic, rhombohedral and tetragonal. Ferroelectric characteristic are present by all the phases excluding the cubic phase. Octahedral TiO₆ centers are the cubic phase which realizes Ti vertices and a cube with Ti-O-Ti edges [13-28].

Experimental Work

Barium Titanate (BaTiO₃) is white to grey powder in color and its structure is perovskite. In numerous acids is soluble including hydrochloric, sulfuric and hydrofluoric acids. In alkalis and water its insoluble, an electrical insulator in the pure form. However it becomes semiconducting when doped with little amounts of metals, most notably samarium, neodymium, yttrium, scandium etc [8].

A semiconductor shows positive temperature of resistivity co-efficient (PTCR) properties in the form of polycrystalline. At Curie temperature an raise in resistivity will show various orders of extent, and can controlled by the dopant. Barium titanate Curie temperature suffers change from tetrahedral to cubic phase. Barium titanate monocular crystals show resistivity temperature co-efficient negative (NTCR) properties. it show properties of ferroelectric and is photorefractive material excellent [12].

The piezoceramic material Barium Titanate (BaTiO₃) was prepared by reacting a suitable grade of BaCO₃ with TiO₂. These raw materials are weighed out in four different ratio's (1.03/1, 1/1, 1/1.03, 1/1.003) according to the stoichiometric equation below:

$$\text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2$$  (1)

For each run the raw materials mixed and milled in an agate ball mill for 8 hrs and then calcined the result powder at 1200°C for 8 hrs.

The calcined powder milled and sieved in an 38 μm sieve, then weighed a proper amount and press it after mixing with PVA binder, in a rod with 1 cm diameter using 2.5 ton load. These samples at various temperatures (1200, 1300, 1350)°C then sintered in air for different periods (2, 4, 6, 8, 10) hrs. The bulk density measured and the true porosity is calculated by the relation:
The true density for BaTiO$_3$ is 6.02 g/cm$^3$. [5]

The relative dielectric constant (K) is measured by using LCR meter for the electroded samples:

$$K = \frac{c \cdot d}{\varepsilon_0 \cdot A}$$

Where

c: capacitance of the prepared samples (Farad).
d: thickness of the sample (m).
$\varepsilon_0$: permittivity of vacuum = $8.85 \times 10^{-12}$ C$^2$/N.m$^2$.
$A$: cross-sectional area of samples (m).

Results and Discussion

Bulk Density

Results shows that the sintering temperature and soaking time has a remarkable influence on the bulk density of the prepared BaTiO$_3$ for the two Ba/Ti ratio’s as shown in Figures 1 & 3. Above 1300 $^\circ$C sintering causes discontinuous grain growth by increased diffusion in the liquid phase. A number of different compounds are possible with either excess of TiO$_2$ or BaCO$_3$. Under the condition of excess titania, a liquid phase is formed to enhance sintering and this has been reported experimentally in figures 1 & 3 [3].

True Porosity

Porosity for the sintered BaTiO$_3$ with different sintering temperature and soaking time for the two cases of Ba/Ti (0.997, 1.03), was calculated in the percentage law using true density of BaTiO$_3$ equal to 6.02 gm/cm$^3$. The percentage true porosity as a function of soaking time is shown in Figures 2 & 4.

Figure 1: Bulk density of BaTiO$_3$ samples sintered at different temperatures with Ba/Ti = 0.997.
Figure 2: Percentage True porosity of BaTiO$_3$ samples sintered at different temperatures with Ba/Ti = 0.997.

Figure 3: Bulk density of BaTiO$_3$ samples sintered at different temperatures with Ba/Ti = 1.03.
Dielectric Constant

Dielectric constant of BaTiO$_3$ is extremely sensitive to Ba / Ti ratio, and also to the sintering temperature and soaking period as shown in Figures 5 & 6, in which the dielectric constant increased as the sintering temperature increased, it reaches a maximum value at 1350°C at (8-10) hrs, and it differs slightly after this temperature.
The temperature at which the spontaneous polarisation disappears is called the Curie temperature, $T_C$. Above 120°C, barium titanate has a cubic structure. This means it is centro-symmetric and possesses no spontaneous dipole. With no dipole the material behaves like a simple dielectric, giving a linear polarisation. $T_C$ for barium titanate is 120°C.

Below 120°C, it changes to a tetragonal phase, with an accompanying movement of the atoms. The movement of Ti atoms inside the $O_6$ octahedra may be considered to be significantly responsible for the dipole moment.

Cooling through 120 °C causes the cubic phase of barium titanate to transform to a tetragonal phase with the lengthening of the lattice parameter. The dipole moment may be considered to arise primarily due to the movement of Ti atoms with respect to the O atoms in the same plane, but the movement of the other O atoms (i.e. those O atoms above and below Ti atoms) and the Ba atoms is also relevant.

**Conclusions**

Sintering below 1350°C is advised to prevent production of reaction phases. However, high temperature is required to improve the sintered density by thermal activation. The physical and dielectric properties influence by the Ba / Ti ratio, sintering temperature and the soaking time. Increasing TiO$_2$ in a small proportion effect largely the physical and dielectric properties of the resulted piece. Increasing BaCO$_3$ in a quantity larger than that of TiO$_2$ also effect the physical and dielectric properties of BaTiO$_3$. But the small addition of TiO$_2$ effect is more effective than that of larger amount of BaCO$_3$.

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