Characterization of the electrical and dielectric properties of barium titanate doped with Holmium oxide and manganese oxide and sintered microwave.

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Abstract

Barium titanate is one of the most important piezoelectric materials used in microelectronic devices such as ultrasonic devices, sensors, transducers, etc. This is due to the high dielectric constant and low dielectric losses of this material. These types of materials have a perovskite crystal system. In this study, barium titanate was synthesized by wet chemistry and its powder doped by holmium oxide and manganese oxide. The effects of these additives on the secondary phases formed, shape, and morphology of particles and dielectric properties of the samples are discussed.

The microstructure of the samples was investigated by field emission scanning electron microscopy (FESEM). X-ray diffraction analysis was used to investigate the formation of phases. The surface of the specimens was gold-coated to measure their dielectric properties by precision LCR meter. The dielectric properties depend on the frequency and sintering method and the frequency variations affect the dielectric constant and dielectric losses. Microwave samples had better dielectric properties than microwave samples, and the particle shapes differed in the two sintering methods. This is due to differences in the heating mechanism.

Keywords: piezoelectric materials, Dielectric properties, Microwave sintering, secondary phases

Introduction

Piezoelectric materials are one of the most important materials used in electronic devices that generate electricity by applying pressure and change the orientation of the dipole by applying electrical current in one or more dimensions (1,2). These materials have a perovskite crystalline system and have a general chemical formula ABO_3 (2-5,9). The addition of impurities in the crystalline system of these materials affects the electrical and dielectric properties of these materials and effectively modifies some dielectric properties including their dielectric constant (5,6,12). Also the type of heating process in the calcination and sintering step is effective on particle shape, density, dielectric properties, etc (11,16,18). The simultaneous doping of holmium and manganese significantly changed the dielectric properties, secondary phase formation, and abnormal grain growth (1,11,22).

In this study, barium titanate was prepared by wet chemistry method, simultaneous doped via Ho-Mn, sintering by microwave and electrical furnace, and study on the effect of these impurities on microstructure and dielectric properties.

Experimental

Barium titanate was prepared by wet chemistry method. In this method used precursor of Barium chloride dehydrate ($BaCl_2.2H_2O$, Merck purity>99%), Titanium (Ⅳ) chloride ($TiCl_4$, Merck purity>99%) and Sodium hydroxide (NaOH, Scharlau purity>99%) and Barium titanate were co-doped with Holmium (Ⅲ) Oxide (Ho_2O_3, Aldrich purity>99%), Manganese (Ⅳ) Oxide (MnO_2, Dae jung purity>99%). Initially an aqueous solution (1M) of $BaCl_2.2H_2o$ was prepared by distilled water and in another eruption, $TiCl_4$ was added into distilled water at 5°C under stirring. The prepared barium chloride solution was slowly added to titanium chloride and severely swirled for an hour. The prepared solution was added to the 6M solution of NaOH (sodium hydroxide) heated at 90°C for sedimentation. Prepared sedimentation separated by centrifuge at 4000rpm for 11min then washed four times by distilled water and was dried into the oven at 120°C for 12h (19). The dried powder was grounded into the mortar with a pestle to earn uniform size particles. Powder After synthesizing, Ho_2O_3 and MnO_2 were added into BT powder. Lastly powders were mixed in a mortar with pestle and grounded manually to achieve suitable distribution of dopant (7,12,20). According to the general formula ($Ba_{1-2x}Ho_{2x}Ti_{1-x}Mn_xO_3$), the content of additives Ho_2O_3 and MnO_2 is x=0.04. Doped samples x=0.04 was named BTM4 and BTM (without dopant) for microwave sintering and BTF4 and BTF (undoped) for furnace samples. After mixing, the powder was pressed into pellets to 10mm diameter and 1mm thickness with the cold isostatic press and 6.9MPa pressure (7,13).

All of the pellets were pre-sintered for 2h at 700°C with a heating rate of 10 °C/min into the electrical furnace (20). thereafter pellets were sintered into microwave crater for 30 minutes (BTM, BTM4) and the electric furnace for 3 hours with a 10°C/min heating rate (BTF, BTF4) and at both methods temperature of sintering is T_S=1100°C. Then pellets were cooling into the microwave crater and furnace chamber. The crystal structure and chemical formula of phases were carried out with XRD diffract meter (Bruker D8, Cu Kα, (λ=1.54060Å), step time=1s, step size=0.06) at room temperature (20). Microstructure and morphology of calcinated and sintered samples were observed by field emission scanning electron microscope (FE-SEM) (MIRA TESCAN LMU, Czech Republic). The pellets were coated with gold to create both surfaces conductively and measured the dielectric properties. Capacitance and loss tangent (dissipation factor) of pellets was measured by precision LCR meter (model 8110 G, Gwinstek) at a frequency range of 20Hz-1MHz (12,13,20). The dielectric constant was calculated based on the following equation (1) and t, c, A, ε_0, and ε_r parameters respectively are thickness, capacitance, surface area, distributed capacitance of the vacuum, and dielectric constant of pellets. Vacuum permittivity or distributed capacitance of the vacuum has a value of 8.8541×10^{-12} $F.m^{-1}$ (20).

1. $\varepsilon_r = \frac{C.t}{\varepsilon_0.A}$

Results and Discussion

1. 1. X-ray Diffraction Patterns of Simultaneous Dope Ho-Mn Characterization

Diagram of the X-ray diffraction patterns of barium titanate powder added to Holmium (HO) and Manganese (Mn) are shown in Figure 1. With adding Ho-Mn dopant in pure powder (BT), peaks of phases in small quantities were shifted to a low angle and the lattice parameter was increasing that's issues were affirmed at XRD pattern of all powders. As shown in the diagram, the secondary phases are formed by adding impurities to the powder. These secondary phases are the pyrochlore phase ($HO_2Ti_2O_7$) and $HOTiO_3$, which have ionic conducting properties, have a complex crystal lattice, and generally have the chemical formula $A_2B_2O_7$. Manganese doesn't produce any secondary phases during the addition process, but holmium produces two secondary phases with ionic conductivity properties. In the doped powder (BT4), the peaks of the secondary phases $HO_2Ti_2O_7$ and $HoTiO_3$ are created, which have the same intensity, which can be due to the uniformity of these phases in the microstructure. Both of these secondary phases have negative and positive effects on the dielectric properties of the samples due to their ion conductivity. that these issues it has been explained in 1. 2 and 1. 3 sections(12).

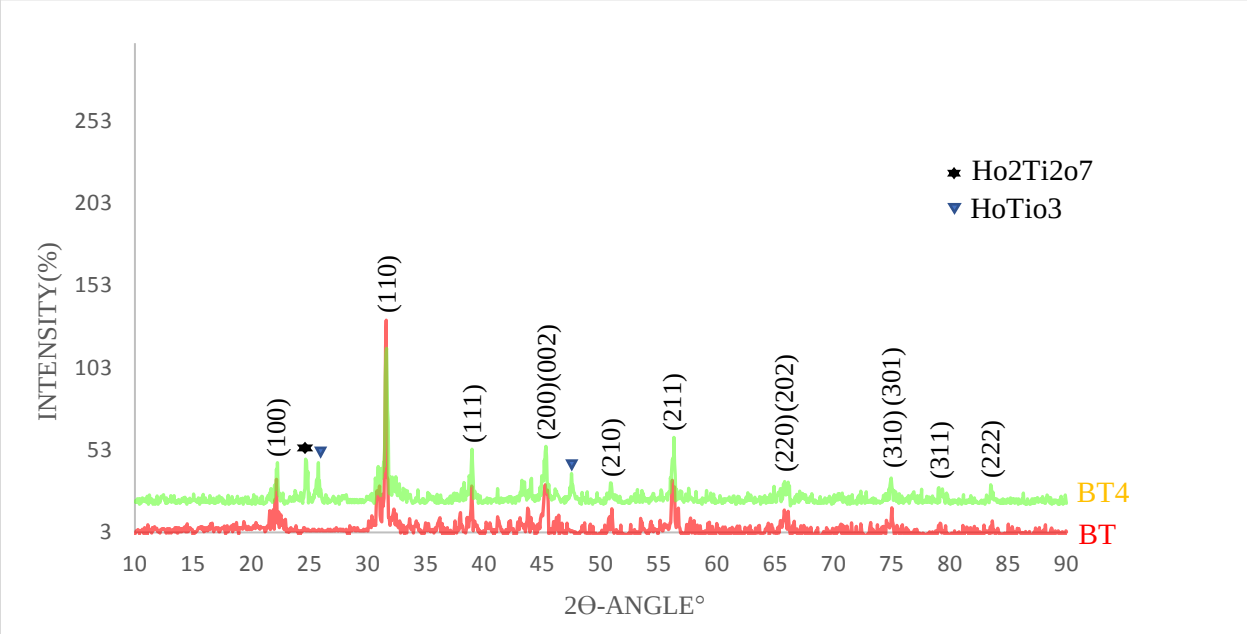
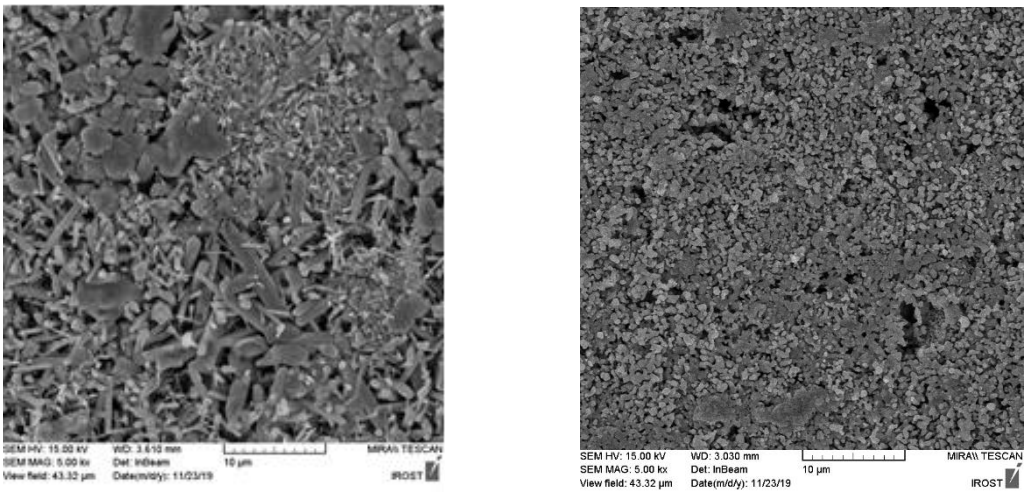


Fig. 1. XRD profile of pure Barium titanate (BT) powder and Simultaneous doped BT with HO-Mn.

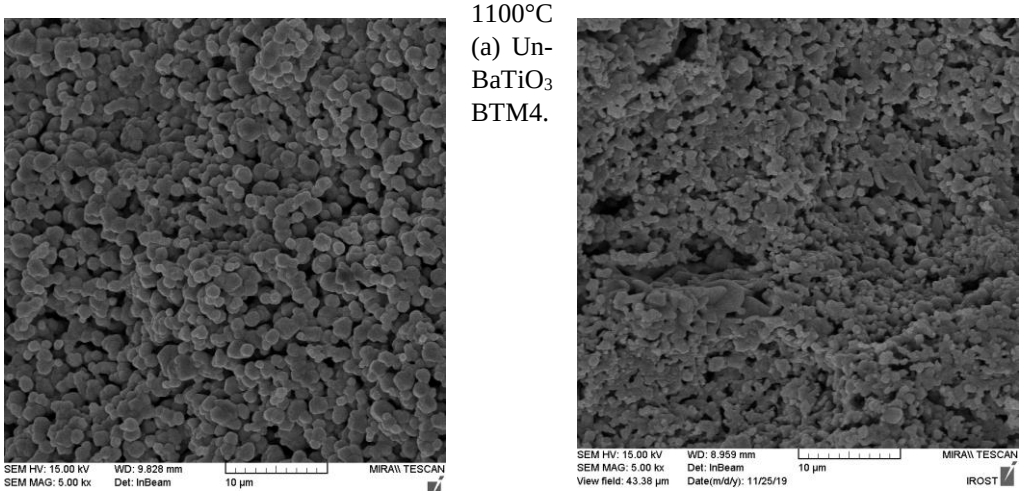
1. 2. Characterization of shape, morphology, and microstructures of Simultaneous doped samples

FE-SEM microscopic images of doped and sintered samples by a domestic microwave and sintered conventionally by an induction furnace are shown in Figures 2 and Fig. 3.



(a) (b)

Fig. 2. FE-SEM image of samples was Simultaneously doped by Ho-Mn and sintered by a domestic microwave at 1100°C for 30min. (a) Un-doped $BaTiO_3$ (b) BTM4.



(e) (f)

Fig. 3. FE-SEM image of samples was Simultaneously doped by Ho-Mn and sintered by induction furnace at 1100°C for 3h. (a) Un-doped BaTiO3 (b) BTF4.

FE-SEM microscopic images of un-doped microwave sintered samples in Figure 3 show that the grains have sharp corners and generally the grains are rectangular cubes (Fig. 2 (a)) but the shape and morphology of the un-doped sintered samples in the induction furnace are different compared to the microwave samples, the furnace samples being spherical in morphology and shape and having curved corners this issue was approved at Fig. 3 (e) (1,19,12). The difference in the type of heating in the sintering process is strongly influenced on the shape of particles and grains samples, such that in the microwave heating method the samples are heated by electromagnetic waves but in the conventional method (furnace), samples are heated by the molybdenum elements ($MoSi_2$) (19). Furnace samples are heated by different heat transfer mechanisms such as convection, conduction, and radiation (17). On the other hand, the slope of heat transfer in the microwave samples is from the brain to the surface of the sample but in the furnace samples the slope is the heat transfer from the surface to the brain sample (17). It has been found that with increasing sintering time grains size was increased. The furnace samples have been sintered for a longer time than the microwave samples, and it's clear in the images that the furnace samples had larger grain sizes than the furnace samples which this issue was reported at other places. With adding dopant in the pure powder of BT, the grain size of sintered pallets was noticeably decreased in both the sintering method hence this matter was more obvious in microwave and furnace samples (Fig. 2 (b), Fig. 3 (f)). Also Secondary phases with coarse grains were observed with the addition of impurities and on the other hand these secondary phases had better distribution in microwave samples compared to the furnace samples (1,4,11,12). Via adding dopant content sinterability was decreased because the melting point of holmium oxide (2415°C) is higher than the melting point of Barium titanate (1625°C) which its increasing sintering temperature of Simultaneous doped Barium titanate. In micrometer-scale porosity on the surface of all sintered samples was observed (5).

1.3. Dielectric properties characterization

1. 3. 1 Dielectric constant characterization

The dielectric constant versus frequency diagrams for the samples is obtained by calculating the capacitance of the samples at the frequency range 20Hz-1MHz by LCR-meter these diagrams of samples were displayed respectively in Fig. 4 and Fig. 5 (4,12). As observed, the dielectric constant of the samples changes with frequency changes, so the dielectric constant depends on the frequency (4,12,13,20). The dielectric constant of barium titanate doped depends on the polarization and the time required for the dipole orientation and also increases the dielectric constant of these materials by increasing the dipole orientation speed and decreasing the dipole orientation time (relaxation time) (13,14,20,23). With rising the frequency and in low oscillation times fewer dipoles was oriented so by enhancement of frequency, dipoles orientations were decreased thus via increasing frequency dielectric constant (ε_r) was decreased which this subject was approved at both diagram for all sample (Fig. 4 and Fig. 5) (4,12,13,20). Samples with higher dielectric constant have lower relaxation time, which means that the dipoles are oriented less, resulting in higher dielectric constant at higher frequencies this is true in the furnace samples

diagrams. Doped furnace sample (BTF4) have lower relaxation time and higher dipole orientation than the un-doped sample (BTF), this is meaning that adding these impurities reduces relaxation time and increases the dipoles orientation speeds, hence sample BTF4 has higher dielectric constant than BTF this issue which is acknowledged at Fig. 5 (25). In microwave samples it is observed that that doped sample (BTM4) has a higher dielectric constant in high frequency than the pure sample (BTM), which means that the doped sample has a lower relaxation time than the pure sample (25).

But with increasing frequency, we have seen a significant decrease in the dielectric constant of the doped sample, which can be due to the non-uniform distribution of secondary phases in the microstructure but this issue was not observed in furnace samples because the furnace samples had a uniform distribution of secondary phases in microstructure (25).

By comparing the dielectric constants of the samples, we found that the microwave samples have higher dielectric constants than the furnace samples, which could be due to the type of heating process and their effects on the microstructural and crystalline properties such as the distribution of secondary phases, grain size and tetragonality ratio (4,18). Electromagnetic waves are strongly effective on the tetragonal ratio so that with increasing sintering time in microwave heating this ratio increases. On the other hand, this ratio was effective on dielectric constant, and with the increase in this ratio, dielectric constant decreased. Thus, the microwave samples have a higher tetragonal ratio than the furnace samples and, consequently, the microwave samples have a higher dielectric constant than the furnace samples which this issue is confirmed in Fig. 4 and Fig. 5 (3,5,7).

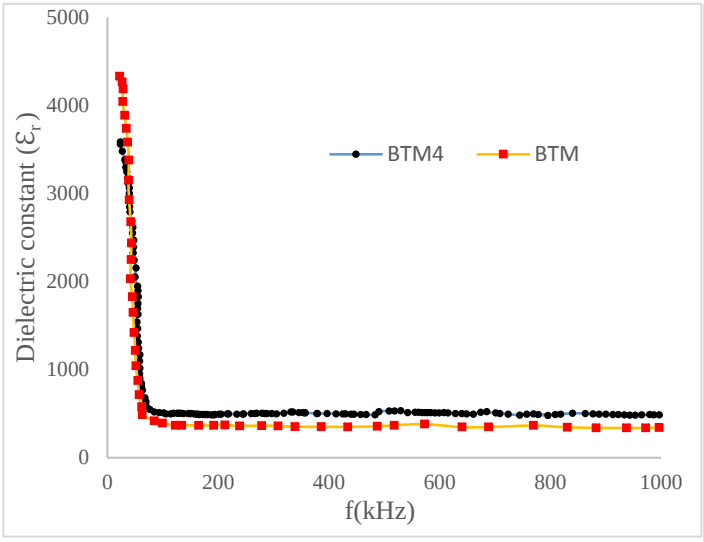


Fig. 4. Shows the diagram of dielectric constant versus frequency of the sintered samples by domestic microwave.

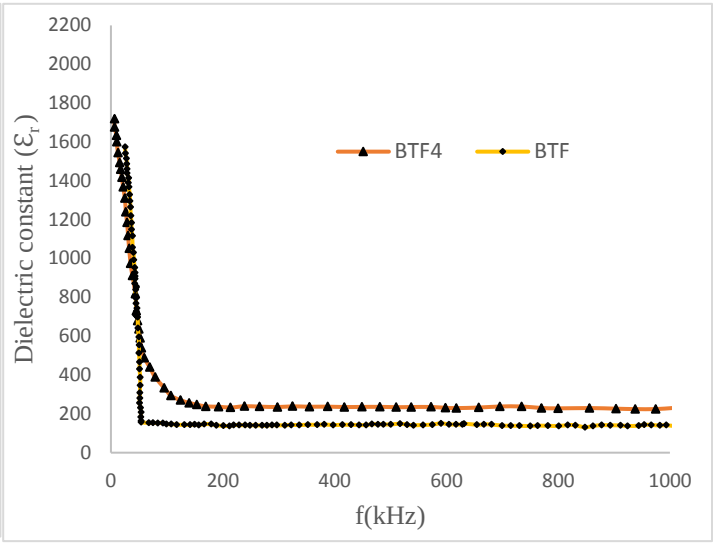


Fig. 5. Shows the diagram of dielectric constant versus frequency of the sintered samples by induction furnace with 10 °C.min^{-1} heating rate.

1. 3. 2 Dielectric loss (dissipation factor) characterization

Fig. 6 and Fig. 7 respectively shows a dielectric loss (tanδ) based on frequency for all sintered samples in domestic microwave and induction furnace. Dielectric loss is the result of dividing the dielectric loss factor (ε´´) into the dielectric constant (ε_r) (24,26).

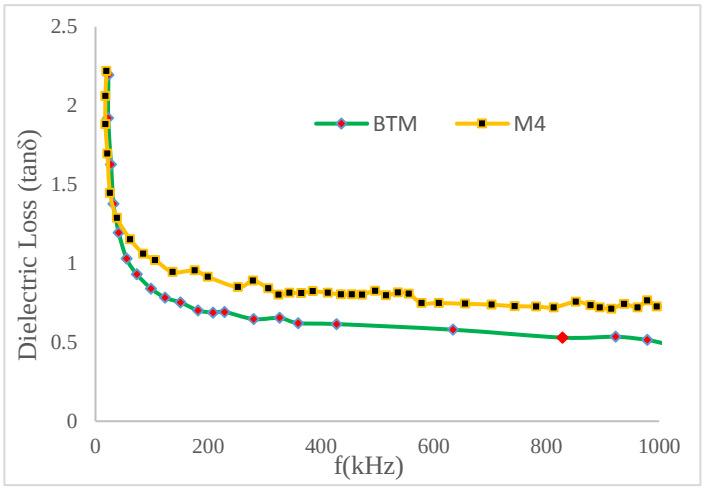


Fig.6. Shows diagram of dielectric loss versus frequency for sintered pellets within microwave.

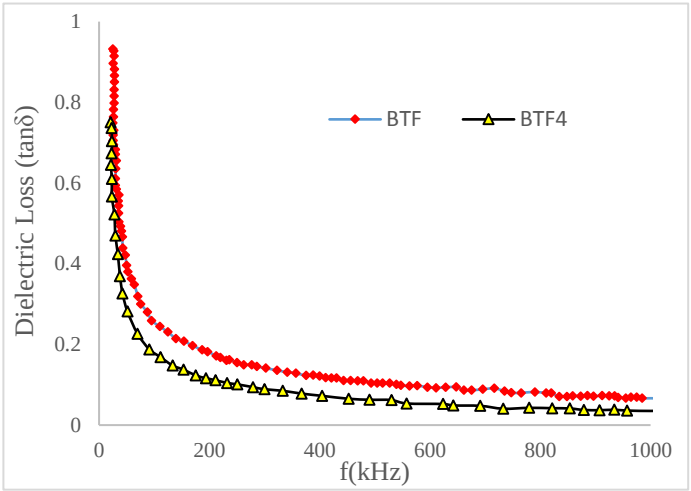


Fig. 7. Shows diagram of dielectric loss versus frequency for sintered pellets within furnace with 10 °C.min^{-1} heating rate.

Dielectric loss is the loss of dielectric power, which means that when a dielectric material is impacted by an electric field it loses dielectric energy as heat energy (13,20,26). As observed, as the frequency increases, dielectric losses decrease, which may be due to the complex physical microstructural reactions within the samples. These complex physical reactions depend on various factors such as insulation, moisture content, sintering process, applied voltage, and sample density (25).

Also, other factors such as the distribution of phases, cracks, and pores in the sample, have a significant effect on the amount of dielectric loss (tanδ) (25,26). The doped sample (BTF4) has the lowest amount of dielectric loss compared to the pure sample (BTF). Also, in the microwave samples, BTM and BTM4, have the lowest amount of dielectric loss, respectively (12). Microwave samples have higher dielectric loss than furnace samples, which can depend on various factors as the second phase distribution, the length of the time of sintering, and sample density (26). Furnace samples were sintered for a longer time than microwave samples, as a result, in higher density furnace samples and less microstructural micro-cracks than microwave samples (20).

On the other hand, the distribution of secondary phases in the microstructure is effective on dielectric loss. Samples with more uniform secondary phase distributions have a lower dielectric loss (20,25). As a result, furnace samples with suitable secondary phase distribution have lower dielectric loss than microwave samples. Therefore, furnace samples have less porosity, lower dielectric loss, and a much better dielectric loss compared to microwave samples (12,25). All the issues were confirmed in Fig.6 and Fig. 7.

Conclusion

This paper discusses the effect of additives Holmium and Mn on the microstructural and electrical and dielectric properties of barium titanate synthesized by wet chemistry. In this study, using microwave heating reduced the time and energy required to sinter the samples and improved some dielectric properties. However, some properties such as dielectric loss and sample density were negatively affected, and the samples sintered by the furnace had a lower dielectric loss and higher density than microwave samples. Also, the microwave waves have a positive effect on increasing the tetragonality ratio and subsequently on the dielectric constant of these materials. On the other hand low sintering time caused to samples had more porosity and micro-cracks and it has negative effects on the dielectric loss (tanδ). Also, adding dopants such as holmium (Ⅲ) oxide and manganese (Ⅳ) oxide is effective on microstructure and dielectric properties. Also, these additives are affected by the formation of condensed secondary phase and increase sintering temperature. However, choosing the optimal sintering time for microwave samples can harm the electrical and dielectric properties and density of the samples and their shape and morphology. In all samples with increasing frequency tanδ and ε_r were decreased and these items respectively depended on the time of dipoles orientation and complex physical process in dielectric samples.

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