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STRUCTURAL CHARACTERISTICS & DIELECTRIC PROPERTIES OF TANTALUM OXIDE DOPED BARIUM TITANATE BASED MATERIALS

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Resume

In this research, the causal relationship between the dielectric properties and the structural characteristics of 0.5 & 1.0 mole % Ta_2O_5 doped $BaTiO_3$ based ceramic materials were investigated under different sintering conditions. Dielectric properties and microstructure of $BaTio_3$ ceramics were significantly influenced by the addition of a small amount of Ta_2O_5. Dielectric properties were investigated by measuring the dielectric constant (k) as a function of temperature and frequency. Percent theoretical density (%TD) above 90 % was achieved for 0.5 and 1.0 mole %Ta_2O_5 doped $BaTiO_3$. It was observed that the grain size decreased markedly above a doping concentration of 0.5 mole % Ta_2O_5. Although fine grain size down to 200 - 300 nm was attained, grain sizes in the range of 1-1.8μm showed the most alluring properties. The fine-grain quality and high density of the Ta_2O_5 doped $BaTiO_3$ ceramic resulted in tenfold increase of dielectric constant. Stable value of dielectric constant as high as 13000 - 14000 was found in the temperature range of 55 to 80 °C, for 1.0 mole % Ta_2O_5 doped samples with corresponding shift of Curie point to ~82 °C. Experiments divulged that incorporation of a proper content of Ta_2O_5 in $BaTiO_3$ could control the grain growth, shift the Curie temperature and hence significantly improve the dielectric property of the $BaTiO_3$ ceramics.

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1. Introduction

Ferroelectric materials, particularly-polycrystalline ceramics, have attracted considerable interest for applications in a variety of fields; such as high dielectric constant capacitors, piezoelectric transducers, actuators, ferroelectric random access memories, electro-optic devices etc. Barium titanate ($BaTiO_3$) is the first ferroelectric ceramics and a good candidate for a variety of applications due to its excellent dielectric, ferroelectric and piezoelectric properties. It is extensively used in high dielectric constant capacitors, MLCC and energy storage devices. $BaTiO_3$ having the perovskite structure with tetragonal symmetry at room temperature, possesses a relatively high dielectric constant (~1500 - 2000).

Despite the advantage offered by the $BaTiO_3$ ceramic regarding small sized capacitors, their use is limited by a number of operating variables. The electric field strength and the operating temperatures are strong determinants of dielectric constants. Grain size has a significant effect on dielectric property of $BaTiO_3$ ceramics. Fine-grained $BaTiO_3$ with an average grain size of ~1μm exhibits dielectric constant of 3000 - 4000 at room temperature [1-5] and values as high as 6000 have also been reported [6]. According to Kinoshinto and Yamaji, as the grain size decreases the dielectric constant of the material increases and a general broadening of the transition peak results [7]. Moreover Martirena and Burfoot suggested that the room temperature

dielectric constant of $BaTiO_3$ should significantly increase when the peak of the transition region is suppressed [8]. Grain size of $BatiO_3$ can be markedly modified by altering the sintering conditions. Dielectric constant also vary significantly depending on the presence and distribution of impurity, stress imposed by surrounding grains, presence of second phase particle, condition of the material at the start of manufacturing, procedure of manufacturing and various processing variables.

The dependence on temperature along with other properties can be appreciably modified by forming solid solutions or doping the base perovskite with a range of compositions. Recent research and development works involve development of $BaTiO_3$ based ceramics with high dielectric properties using various doping elements of different concentrations [9-16], i.e. the effect of Cerium doping on microstructure and dielectric properties of $BaTiO_3$ has previously been investigated [17]. Moreover, the effect of Ta_2O_5 (Tantalum Oxide) doping in $BaTiO_3$ceramic materials has shown promising dielectric properties. In addition, Yoeng Jung Kim et al. [18] have suggested that Ta^{5+} inhibits grain growth and when added in small amountspromote densification.

The objective of this investigation was to examine the effects of small additions of Ta_2O_5 on the microstructure and dielectric properties of pure $BaTiO_3$; and furthermore to establish a proper structure-property relationship.

2. Experimental Procedure

The starting materials of making Tantalum doped Barium Titanate were $BaTiO_3$ (size =100 nm) and Ta_2O_5 powders [Manufacturer: INFRAMAT (USA); Purity better than 99 %].Ta_2O_5 was doped at two different percentage viz. 0.5 and 1.0 mole %. The powders were milled in the pot mill containing Yttria stabilizedzirconia balls for 16-20 hours, while a sufficient amount of acetone was added as the milling media. PVA was added as a binder following the drying process. Stirring for at least 30 - 40 minutes was carried out to make homogenous binder distribution in the mix. The mix was dried and pressed into disc shaped samples under 2 tons of load. Next, the samples were soaked for binder removal and different sintering cycles were performed. Microstructure and fracture surface of sintered pellets were examined by a Scanning Electron Microscope (SEM). Temperature dependence of the dielectric constant was measured at four different frequencies i. e. 10,50,100 and 500 kHz at a heating rate of 4^oC/min.

3. Results and Discussion

Numerical data of percent theoretical density (%TD) and grain size of 0.5 and 1.0 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1250, 1275 and 1300 °C for zero minute with a sintering rate of 5 °C/min are tabulated in Table 1.

Table 1

Percent theoretical density (%TD) and grain size of sintered Ta_2O_5 doped $BaTiO_3$ samples

Sl. No.	Sintering Rate (°C/min)	Maximum Sintering Temp. (°C)	Holding Time (min)	Cooling Rate (°C/min)	Doping mole%	% TD	GrainSize (μm)
1	5	1250	0	3	0.5	95.45	0.18- 0.30
					1.0	91.25	0.18- 0.30
2	5	1275	0	3	0.5	97.00	0.358
					1.0	92.65	0.255
3	5	1300	0	3	0.5	97.66	1.60
					1.0	96.44	0.295

The sintering cycle with a sintering rate of 5 °C/min yielded better densification for both doping mole % with optimum density and grain size for 0.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for zero minutes. The average grain size of the samples sintered at 1250 °C were in the range 0.18- 0.25µm for both 0.5 and 1.0 doping mole %, which as a result of being too fine, had an adverse effect on the dielectric properties. Grain size of samples sintered at 1275 °C and 1300 °C were relatively coarser with satisfactory densification. The microstructures of these samples sintered at 1275 °C and 1300 °C for zero minutes are shown in Fig. 1.

Less porous and dense micrographs were obtained for all the samples sintered at 5 °C/min. The time provided for sintering was sufficient as slower sintering rate of 5 °C/min provided longer sintering time. Though optimum density and grain size were attained for 0.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for zero minutes, but for doping 1.0 mole % Ta_2O_5 the grain size reduced prominently (< 0.5 µm)

for sintering rate of 5 °C/min.

These results are also commensurate with the findings of M.N. Rahman and R.Manalert [20] as they describe the effect of penta-valence donor cations on microstructure of $BatiO_3$ through defect structure. They reported that for the penta-valance donor cations, the boundary mobility initially increases with cation concentration but then decreases markedly above a doping threshold of 0.3- 0.5 mole %, which is commensurate with our results. This factor significantly controls the microstructure of Ta_2O_5 doped $BaTiO_3$. Since Ta^{5+} ion has a valence state (+5) different than that of Ba^{2+} or Ti^{4+} ions (+2 and +4 respectively), substitution with Ta^{5+} ions cause charge imbalance which leads to charge compensation requiring the production of electrons, electron holes, or vacancies. Donor cations of higher valence than the host cation leads to a dramatic change in the behavior of $BaTiO_3$. This phenomenon is sometimes referred to as the "doping anomaly" or "grain size anomaly" [18,19,20].
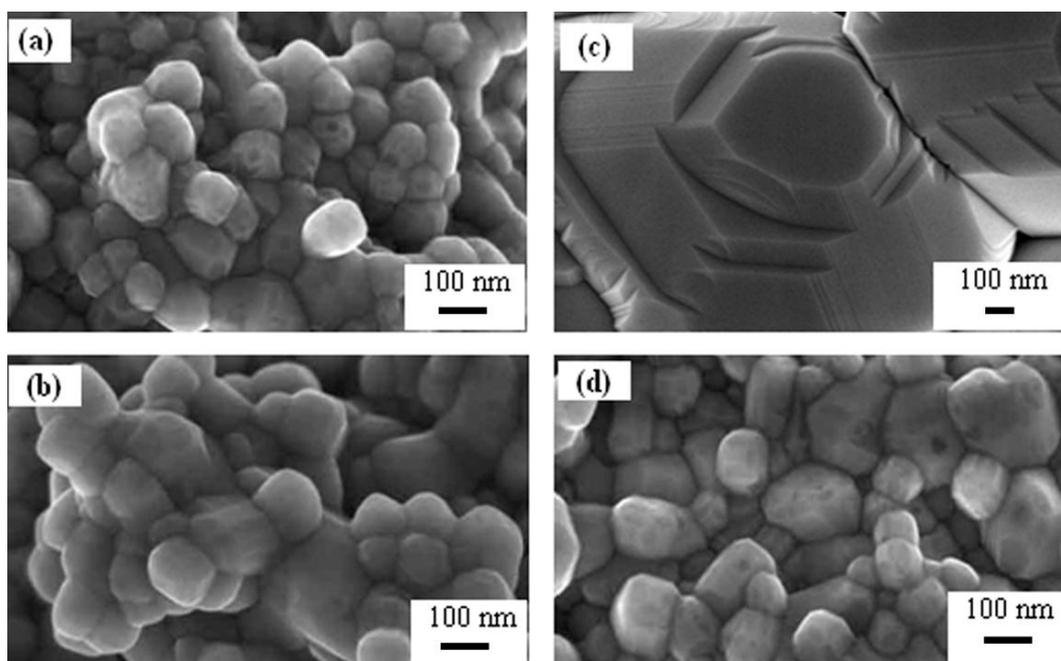
(a) Avg. Grain Size = 0.358 µm; % TD = 97, (b) Avg. Grain Size = 0.255 µm; % TD = 92.65
(c) Avg. Grain Size = 1.6 µm; % TD = 97.66, (d) Avg. Grain Size = 0.295 µm; % TD = 96.44

Fig. 1. SEM micrograph of (a) 0.5 mole % and (b) 1.0 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1275 °C for 0 minute and (c) 0.5 mole % and (d)1.0 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 0 minute

Below the doping threshold, a possible defect reaction for the incorporation of Ta^{5+} into $BaTiO_3$ can be written in the Kroger-Vink notation as: [20]

$$4BaO + Ta_2O_5 \rightarrow 4Ba_{Ba}{}^X + 4Ta_{Ti} + \\ + 12O_o{}^X + O_2 + 4e^- \qquad (1)$$
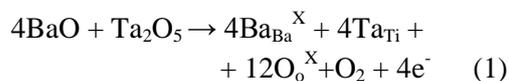
Above the doping threshold, assuming that ionic compensation occurs by the formation of Ti vacancies, a possible defect reaction is: [20]

$$4BaO + 2Ta_2O_5 + BaTiO_3 \rightarrow 5Ba_{Ba}{}^X \\ + 4Ta_{Ti} + 15O_o{}^X + TiO_2 + V_{Ti} \qquad (2)$$
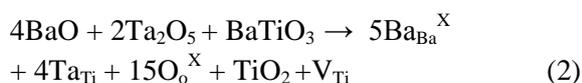
Above the threshold, the accumulation of Ti vacancies in the space charge may be associated with a depletion of oxygen vacancies. Because of their relatively large size, the diffusivity of oxygen ions across the grain boundary is expected to be slow. The low diffusivity of oxygen ions across the grain boundary provides a possible mechanism for the significant reduction in grain boundary mobility, which yields finer grain. Such grain growth inhibiting mechanism has also been evident in the study of $BaTiO_3$ doped simultaneously with calcium (Ca^{2+}) and tantalum (Ta^{5+})ions [19, 20]. In this study, replacement of V_{Ti} with Ca^{2+} was found to negate the grain growth inhibiting effect of Ta^{5+}.

The effect of excess doping mole % of Ta_2O_5 above the threshold on microstructure of $BaTiO_3$ can also be described by using another perspective other than through the defect structure. Excess doping mole % of penta-valence donor cations above the threshold is found to restrict grain growth by pinning effect [18]. Our results are in accordant with this finding also.

In our research, above the threshold value of 0.5 mole % doping, the grain size reduced prominently (<0.5µm) for sintering rate of 5 °C/min which can be attributed to the pinning effect of excessive Ta_2O_5 doping above the threshold value [18, 20]. A high concentration of Ta^{5+}ions at or near grain boundaries restricted grain growth during sintering and promoted the formation of $BaTiO_3$ with fine grains. Such small grain size has an adverse effect on dielectric properties.

No or insignificant energy is needed for the dopant to concentrate at the grain boundaries. However, the energy needed to incorporate a dopant ion into an individual lattice site in complex oxides is related to distortions, i.e. difference in ionic radii, and the formation of compensating defects during the incorporation of aliovalent ions that have different valence states [18]. Thus, more energy was required in our research for diffusion of the dopants to move inwards from the grain boundary and reduce the pinning effect. The required energy was provided by means of increasing the holding time to 240 minutes at the maximum sintering temperature of 1300 °C for both dopant
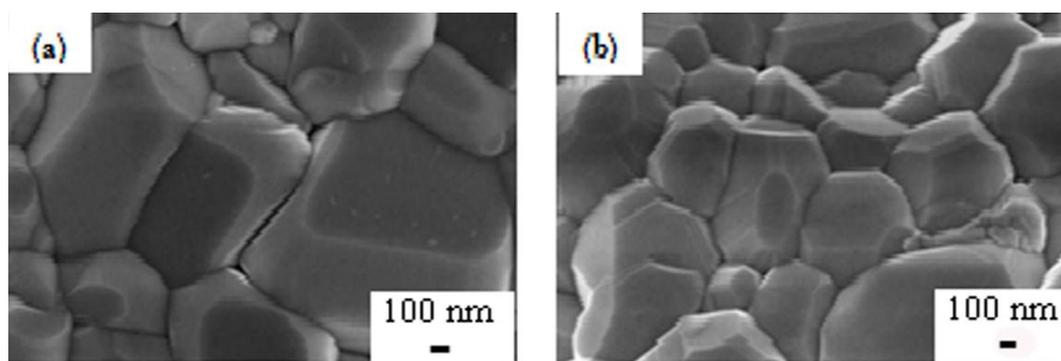
(a) Avg. Grain Size = 1.8 µm; % TD = 91, (b) Avg. Grain Size = 1.375 µm; % TD = 90

Fig. 2. SEM micrograph of a) 0.5 mol% & b) 1.0 mol% Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 240 min.

concentrations. To control abnormal grain growth, sintering rate was increased to 15 °C/min and the cooling rate was also modified (Table 2). The grain size obtained by this modified sintering parameters caused significant increase in dielectric properties as shown in the later section.The microstructures of 0.5 and 1.0 mole % Ta_2O_5 doped $BaTiO_3$ sintered under this modified condition is shown in Fig. 2.

This time, the average grain size of the doped samples was about 1– 2 μm which is a favorable condition for obtaining good dielectric properties. However, increasing the holding time to 240 minutes was also incorporated, along with a certain decrease in densification which can be attributed to the uniform distribution of almost similar sized grains, that too of moderately large size. This can be included here that, bimodal distribution of grains is more favorable for high density [16].

However, the consequences of the modified sintering cycle can be explained from the XRD patterns shown below. Fig. 3 shows the XRD plots for (a) pure Barium Titanate powder (b) 0.5mole %Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 0 min at sintering rate 15 °C/min (c) 1.0 mole %Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 240 min at sintering rate15 °C/min.

The XRD plot shows that the twin peaks in $BaTiO_3$ powder do not appear in the plots for 0.5 and 1.0 mole % Ta_2O_5 doped $BaTiO_3$ samples sintered at 1300 °C for 240 minutes. This is an indication of reduced tetragonality and

it suggests that the structure may retain the cubic phase to a greater degree than it usually does. This fits the dielectric constant results shown
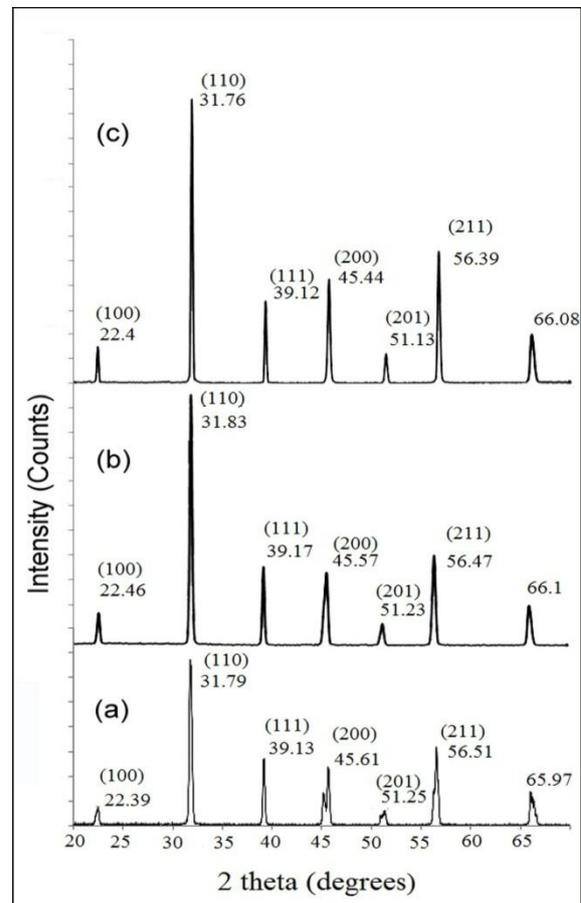
Fig. 3.XRD plots for (a) pure Barium Titanate powder (b) 0.5 mole %Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 0 min at sintering rate 15 °C/min (c) 1.0 mole %Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 240 min at sintering rate 15 °C/min

in Fig. 5 in the next section where the Curie temperature marking the cubic to tetragonal transition was found at 110 °C for 0.5 mole % and 80 °C for 1.0 mole % Ta_2O_5 doped $BaTiO_3$ samples which is at 120- 130 °C in general. The

Table 2

Percent theoretical density (%TD) and grain size obtained for the modified sintering cycle

Sintering Rate (°C/min)	Maximum Sintering Temp. (°C)	Holding Time (min)	Cooling Rate (°C/min)	Doping mole %	% TD	Grain Size (μm)
15	1300	240	10 °C/min up to 1000°C and then 5 °C/min up to end temperature	0.5	91	1.8
15	1300	240	10 °C/min up to 1000°C and then 5 °C/min up to end temperature	1.0	90	1.375

disappearance of twin peaks also means that samples have had changes in 'c' and 'a' lattice parameters. Also no trace of second phase was appeared in the plot of sintered samples. The microstructure of these samples in Fig.2 showed the grains to be much larger than samples sintered under the previous condition at 5°C/min. All these means that under the modified cycle the powder has Ta^{5+} well diffused into the crystal structure of $BaTiO_3$ and almost no Ta^{5+} was left at the grain boundaries to resist grain growth by pinning effect, as expected from our results listed in Table 2.

3.1 Dielectric Property Measurement

0.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 0 min at sintering rate 5 °C/min and 1 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1300 °C for 240 min at sintering rate 15 °C/min showed satisfactory dielectric constant along with desired densification and grain size (Table 3).

Fig. 3 illustrates that sintering at 1300 °C for 240 min at a sintering rate of 15 °C/min resulted in an abrupt rise in dielectric constant for 1.0 mole % Ta_2O_5 doped $BaTiO_3$ which was due to attainment of favorable grain size and densification. However, a slight declivity in dielectric constant was observed for 0.5 mole % Ta_2O_5 doped $BaTiO_3$ when the holding time was increased to 240 min at 1300 °C. Sintering at 1300 °C for 240 min at sintering rate 15 °C/min caused only a slight increase in grain size, from 1.6 to 1.8μm, together with marked attenuation of densification for 0.5 mole % Ta_2O_5 doped $BaTiO_3$ as reported in Table 3. Hence, for 0.5 mole % Ta_2O_5 doped $BaTiO_3$ the maximum

dielectric constant, together with approbative grain size and densification was obtained when sintered at 1300 °C for 0 min at sintering rate 5 °C/min.

The pinning effect or influence on defect structure of doping mole % was found to effect grain size; grain size effect dielectric properties. So pinning effect or influence on defect structure of dopants has obvious effect on dielectric properties. Average grain size around 1 μm normally provides a good condition for dielectric properties for doped $BaTiO_3$. In this research, grain sizes in the range of 1- 1.4 μm showed high values of dielectric constant, while further increase in grain size deteriorated its property. Variation of Dielectric Constant (k) with temperature for 0.5 and 1 mole % Ta_2O_5 doped $BaTiO_3$ that have a maximum dielectric constant is shown in Fig. 5. The best stable value of dielectric constant as a function of temperature was obtained in the range 13000-14000 for 1.0 mole % Ta_2O_5 doped $BaTiO_3$ as shown in Fig.5(b). Curie point (Tc) normally occurs at 120 °C for pure $BaTiO_3$ It is evident from Fig. 5 that the curie point was shifted to about 110 °C for 0.5 mole % Ta_2O_5 doped $BaTiO_3$; and to about 80 °C for 1 mole % Ta_2O_5 doped $BaTiO_3$. This shift of Curie Temperature has already been explained using XRD patterns.Suppression of the peak at Curie temperature is also apparent from the figure. According to the literature [21,22, 23], a decrease in dielectric constant with an increase of frequency for a particular temperature is also ostensible from the figure. This effect of frequency is shown more prominently in Fig.6 for both doping mole %.

Table 3

% Theoretical density (%TD), grain size and dielectric constant of sample sintered at optimum sintering cycles

Sl, No.	Sintering Rate (°C/min)	Maximum Sintering Temp. (°C)	Holding Time (min)	Cooling Rate (°C/min)	Doping mole %	% TD	Grain Size (μm)	Dielectric Constant(k) Value (room temp.)
1	5	1300	0	3	0.5	97.66	1.6	14600
2	5	1300	0	3	1.0	96.44	.358	1900-2000
3	15	1300	240	10 °C/min up to 1000°C and then 5 °C/min up to end temperature	0.5	90	1.8	14000
4	15	1300	240		1.0	91	1.375	17000
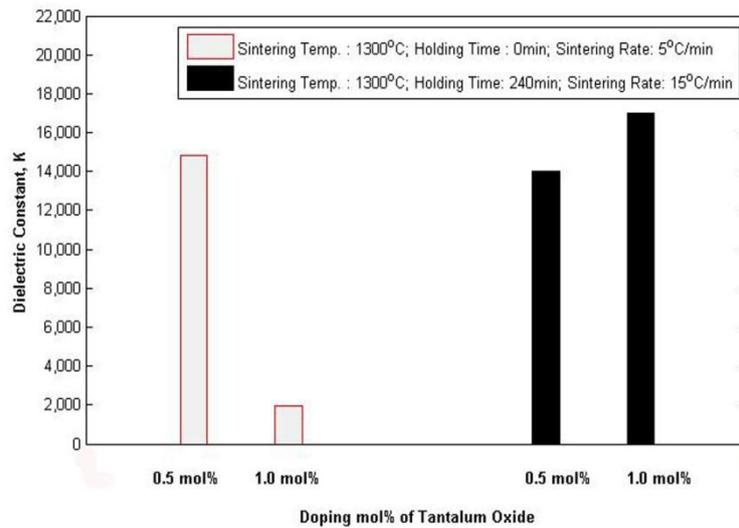
Fig.4 Dielectric constant of samples sintered at optimum sintering cycles
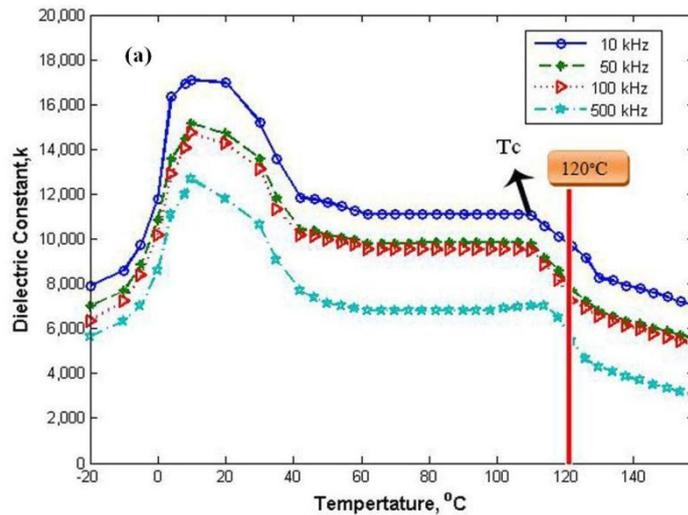
a) for 0.5mole. % Ta$_2$O$_5$ doped BaTiO$_3$ sintered at 1300°C for 0 min at sintering rate 15°C/min
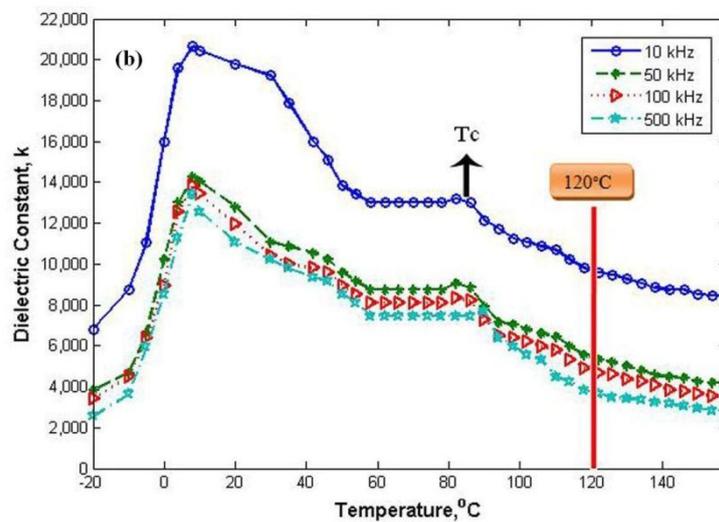
b) for 1.0mole. % Ta$_2$O$_5$ doped BaTiO$_3$ sintered at 1300°C for 240 min at sintering rate15°C/min

Fig. 5 Variation of "k" with temperature (full colour version available online)
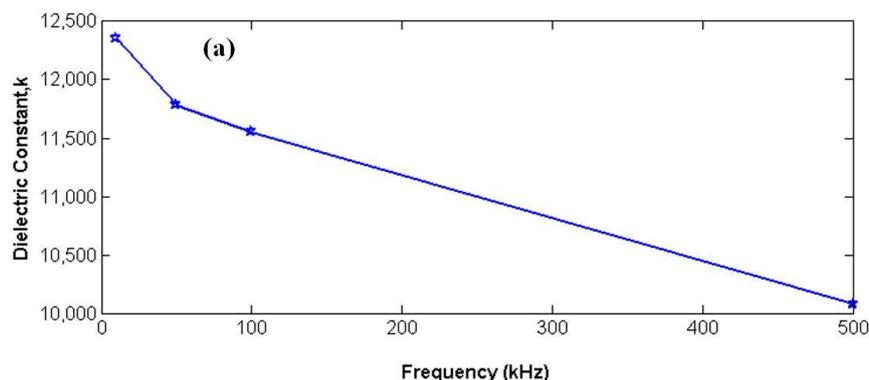
a) for 0.5mole. % Ta_2O_5 doped $BaTiO_3$ sintered at 1300°C for 0 min at sintering rate of 10°C/min
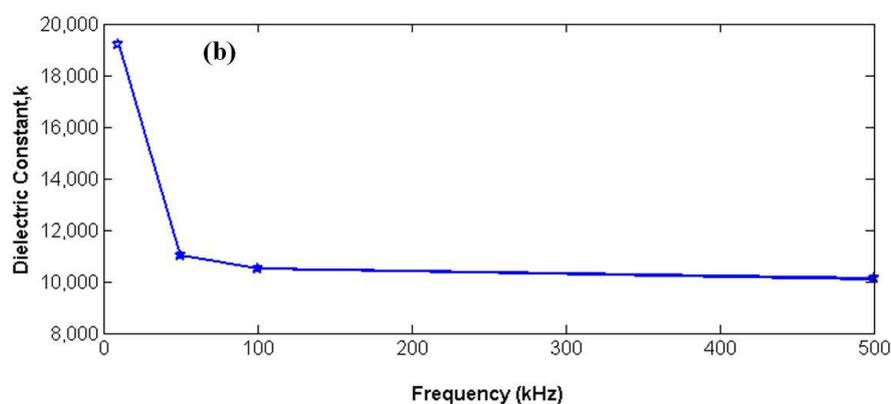
b) for1.0mole. % Ta_2O_5 doped $BaTiO_3$ sintered at 1300°C for 240 min at sintering rate15°C/min

Fig. 6 Variation of "k" with frequency at room temperature

4. Conclusions

- Doped tantalum oxide acted as a strong peak suppressor and shifted the Curie point to a lower temperature.
- Alluring value of dielectric constant was obtained when average grain size of the Ta_2O_5 doped $BaTiO_3$ were in the range of 1 - 1.8 µm and the best stable value as a function of temperature was obtained in the range of 13000- 14000 for 1.0 mole % Ta_2O_5 doped $BaTiO_3$ having an average grain size of 1.375µm.
- For a particular temperature, the value of dielectric constant was found to decrease with an increase of the applied frequency.

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