International Journal of Automotive and Mechanical Engineering (IJAME)
ISSN: 2229-8649 (Print); ISSN: 2180-1606 (Online); Volume 7, pp. 840-849, January-June 2013

DOI: http://dx.doi.org/10.15282/ijame.7.2012.4.0069

EFFECT OF Ta_2O_5 DOPING ON THE MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF $BaTiO_3$ BASED CERAMICS

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ABSTRACT

The main focus of the research was to correlate composition and sintering parameters with the microstructure and dielectric properties of Ta_2O_5 doped $BaTiO_3$ ceramics. The samples were sintered using both single and two-stage sintering techniques. Thereafter SEM and XRD techniques were used to examine the structure of the samples with a particular focus on the incorporation of Ta^{5+} ions into the $BaTiO_3$ crystal lattice. The SEM analysis focused on measuring the grain size and investigating the grain size distribution of the sintered samples. Finally, the dielectric properties were analysed and the relationship between the properties and structure of the doped $BaTiO_3$ was established. From the research it can be stated that two-stage sintering yielded the best dielectric properties. The best stable value of the room temperature dielectric constant (k) of 19000 was obtained for the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sample sintered at 1320^0C for 0hrs and 1280^0C for 6hrs, due to the combination of a high percent theoretical density (%*TD*) and optimum grain size. At a temperature range of 30^0 to 60^0C, this combination of composition and sintering parameters yielded a dielectric constant in the range of 18000–19000.

Keywords: Barium titanate; tantalaum oxide; doping; ceramic; double-stage sintering.

INTRODUCTION

$BaTiO_3$, a ferroelectric ceramic material, has attracted considerable interest for application in a variety of fields, such as capacitors, transducers, actuators, electro-optic devices. There are several reasons for its extensive practical application. Firstly because it is chemically and mechanically very stable; secondly it exhibits ferroelectric properties at and above room temperature, and finally because it can be easily prepared and used in the form of ceramic polycrystalline samples. However, pure $BaTiO_3$ with an average grain size of around 1μm exhibits a dielectric constant of 3000–5000 at room temperature (Amarande et al., 2007; Arlt et al., 1985; Sivakumar et al., 2011; Jingkun et al., 1999). Dielectric constants as high as 5800 have also been reported (Amarande et al., 2007). For pure $BaTiO_3$, the dielectric constant value increases with a decrease in grain size and a general broadening of the transition peak results (Kinoshinta and Yamaji, 1976). Moreover, the suppression of the transition peak significantly increases the room temperature dielectric constant of pure $BaTiO_3$ (Burfoot and Martirena, 1974). Despite all these findings, the industrial application of pure $BaTiO_3$ is still somewhat limited due to its low dielectric properties.

In order to use $BaTiO_3$ on an industrial scale, $BaTiO_3$ has been doped with several dopants like MgO, ZrO_2, Nd_2O_3, Ta_2O_5, Nb_2O_5, and many more to control its grain size

and to improve its dielectric properties (Armstrong et al., 1989; Kelvin et al., 2010; Chan et al., 1986; Chao et al., 2008; Hwang et al., 2000; Kelvin et al., 2010; Mastelaro et al., 2004). Among these dopants, pentavalent oxides such as Ta_2O_5, Nb_2O_5 have a strong influence on the dielectric properties of $BaTiO_3$. They influence the dielectric properties of pure $BaTiO_3$ by controlling the grain size, improving the density and shifting the Curie temperature. Under optimum sintering conditions and doping levels, the dielectric properties of pure $BaTiO_3$ can be significantly enhanced with Ta_2O_5, Nb_2O_5 (Ahn et al., 2009). Judging the potential of pentavalent oxides used as dopants, the current study extensively examined the effects of Ta_2O_5 doping on the microstructure and dielectric properties of $BaTiO_3$ ceramics. The ultimate aim of the study was to develop an environmentally-friendly ceramic capacitor for electronic industries.

EXPERIMENTAL

Reagent-grade nano-sized oxide powder of $BaTiO_3$ with a purity better than 99% was used as the starting raw materials. The powder was doped with Ta_2O_5 at concentrations ranging from 0.5–1.5 mole %. Both powders were mixed and milled for 18–20 hrs. Following that, the powders were dried and a binder PVA was added. Then the powders were pressed into pellets, approximately 5 mm thick and 12 mm in diameter, at a pressure of around 150MPa using a hydraulic press (Figure 1(a)). Subsequently, the pressed samples were sintered in a high temperature furnace (Figure 1(b)). For a particular sintering cycle, the samples were at first heated to 550^0C for one hour to remove the binder and were then heated to the desired sintering temperature. Single stage sintering was carried out in the range of 1250–1300^0C for two hours. Whereas, two-stage sintering was carried out by keeping the 1st stage sintering condition fixed at 1320^0C for zero hours and only varying the holding time during 2nd stage sintering from 4–6 hrs at a constant temperature of 1280^0C. After sintering, X-ray diffraction (XRD) was performed in order to determine the percent theoretical density (%*TD*), phase and structural analysis. Moreover, micro-structural analysis was performed using a field emission scanning electron microscope (FESEM) (Figure 2(a)), and the temperature dependence of the dielectric constant (k) was measured at various frequencies (10 to 500 kHz) at a heating rate of 4^oC/min using an Impedance analyser (Figure 2(b)).

(a) (b)

Figure 1. Experimental setup for sample preparation: (a) Hydraulic press for pelletizing; (b) High temperature furnace for sintering.

(a) (b)

Figure 2. Experimental setup for characterisation and dielectric property measurement: (a) FE-SEM for microstructural analysis; (b) Impedance analyser for dielectric property measurement.

RESULTS AND DISCUSSION

Numerical data on the effect of single stage sintering on the percent theoretical density (*%TD*), grain size and dielectric constant (*k*) of Ta_2O_5 doped $BaTiO_3$ samples are tabulated in Table 1. Table 1 shows that for a particular mole % of Ta_2O_5 doping, the percent theoretical density of the Ta_2O_5 doped $BaTiO_3$ samples increased with increasing temperature. However, at a certain temperature, an increase in the Ta_2O_5 mole % resulted in a lowering of percent theoretical density of the samples.

Table 1. Percent theoretical density (*%TD*), grain size and dielectric constant (*k*) of single stage sintered Ta_2O_5 doped $BaTiO_3$ samples

SI No:	Sintering rate (^{0}C/min)	Sintering temperature (^{0}C)	Holding time (Hours)	Cooling rate (^{0}C/min)	Doping mole %	%TD	Grain size (µm)	Dielectric constant (k) at room temperature
1	5	1250	2hrs	3	0.5	91.7	0.30	1700–2000
2	5	1250	2hrs	3	1.0	90.5	0.28	1700–2000
3	5	1250	2hrs	3	1.5	88.0	0.25	1700–2000
4	5	1275	2hrs	3	0.5	92.0	0.35	1700–2000
5	5	1275	2hrs	3	1.0	91.6	0.30	1700–2000
6	5	1275	2hrs	3	1.5	90.0	0.26	1700–2000
7	5	1300	2hrs	3	0.5	93.0	1.10	13000
8	5	1300	2hrs	3	1.0	92.0	0.40	1700–2000
9	5	1300	2hrs	3	1.5	91.5	0.38	1700–2000

It is also observed from Table 1 that for all Ta_2O_5 doped $BaTiO_3$ samples sintered within the temperature range of 1250–1275^{0}C, 2hrs of holding time proved to be insufficient, resulting in samples with a fine grain size. Due to their fine grain size, all these samples exhibited a poor dielectric constant in spite of having a high percent theoretical density. However, at 1300^{0}C the 2hrs of the holding time proved to be sufficient for the 0.5 mole % Ta_2O_5 doped $BaTiO_3$ sample. As a result, the sample exhibited a high percent theoretical density, satisfactory grain size, and moderate dielectric constant. For 1.0–1.5 mole % Ta_2O_5 doped $BaTiO_3$ samples, the holding time again proved to be inadequate and resulted in samples of fine grain size. As a consequence, these samples again presented a poor dielectric constant. All these results are consistent with the findings of Manalert and Rahaman (1998), who concluded that the amount of pentavalent oxide dopants controls the microstructure of Ta_2O_5 doped $BaTiO_3$ samples. For the penta-valance donor cations, the grain boundary mobility initially increases with cation concentration but then decreases significantly above a doping threshold of 0·3–0·5 mole %. Generally dopants need very low to almost no energy to concentrate at the grain boundaries. However, energy is required to incorporate a dopant ion into an individual lattice site in complex oxides. The amount of energy required is related to the distortions, i.e. difference in ionic radii, and the formation of compensating defects during the incorporation of aliovalent ions that have different valence states (Ahn et al., 2009). Thus, more energy was required in our research for the diffusion of the dopants to move inwards from the grain boundary into the lattice and to reduce the pinning effect. The required energy could have been supplied by increasing the holding time of the single stage sintering. But this route was associated with a high cost and would make the project less viable for industrial application. As a result, further research was focused on two-stage sintering. Numerical data of the effect of two-stage sintering on percent theoretical density (*%TD*), grain size and dielectric constant (*k*) of Ta_2O_5 doped $BaTiO_3$ samples are tabulated in Table 2.

Table 2. Percent theoretical density (*%TD*), grain size and dielectric constant (*k*) of two-stage sintered Ta_2O_5 doped $BaTiO_3$ samples.

SI No:	Sintering rate (^{0}C/min)	Sintering temperature and holding time (1st stage)	Sintering temperature and holding time (2nd stage)	Cooling rate (^{0}C/min)	Doping mole %	%TD	Grain size (μm)	Dielectric constant (k) at room temperature
1	5	1320^{0}C for 0 hrs	1280^{0}C for 4hrs	3	0.5	95.0	1.80	9500
2	5	1320^{0}C for 0 hrs	1280^{0}C for 4hrs	3	1.0	93.0	1.30	16500
3	5	1320^{0}C for 0 hrs	1280^{0}C for 4hrs	3	1.5	91.0	1.10	17900
4	5	1320^{0}C for 0 hrs	1280^{0}C for 6hrs	3	0.5	93.5	1.90	8900
5	5	1320^{0}C for 0 hrs	1280^{0}C for 6hrs	3	1.0	92.1	1.40	13700
6	5	1320^{0}C for 0 hrs	1280^{0}C for 6hrs	3	1.5	92.9	1.20	19000

Table 2 shows that for a 0.5 mole % Ta_2O_5 doped $BaTiO_3$ sample, 4hrs of holding time during 2nd stage sintering decreased the dielectric constant value due to an excessive increase in grain size. The high grain growth of the sample may have resulted from the complete diffusion of Ta_2O_5 into the bulk material. This phenomenon is clearly evident from the SEM micrograph of Figure 3(a), which shows no evidence of bimodal grain size distribution or the pinning effect. However, for a 1.0 mole % Ta_2O_5 doped $BaTiO_3$ sample, 4hrs of holding time produced controlled grain growth and increased the dielectric constant value to a moderate level, which is shown in the SEM micrograph of Figure 3(b). For the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sample, 4hrs of holding time might not have been sufficient for complete diffusion of the dopants into the lattice, and as a result there was evidence of the pinning effect. The SEM micrograph of Figure 3(c) clearly shows the presence of bimodal grain size distribution. However, the combination of a moderate percent theoretical density and suitable grain size of 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sample resulted in the best dielectric properties for 4hrs of holding time.

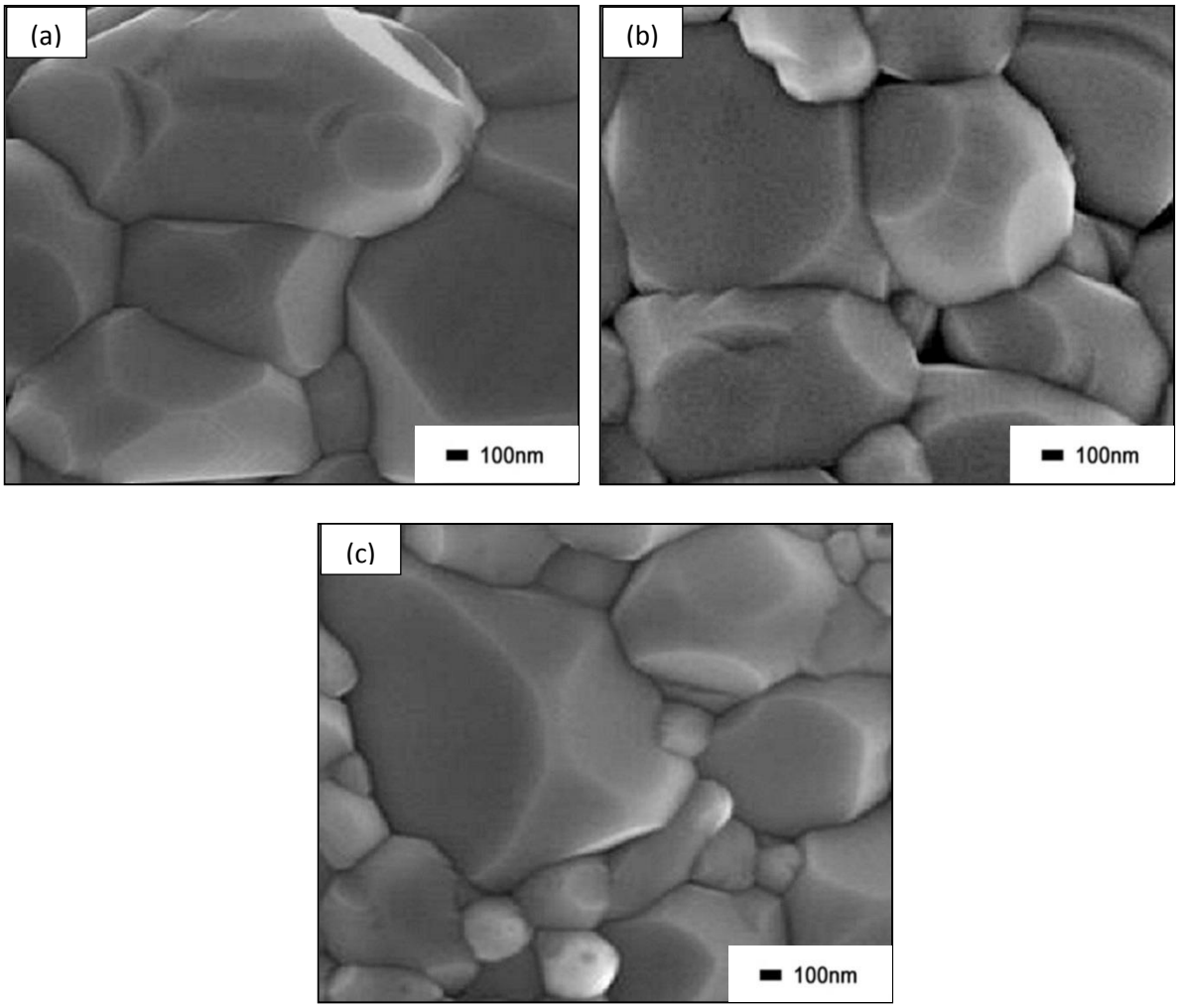

Figure 3. SEM micrographs (X 50,000) of: (a) 0.5 mole %; (b) 1.0 mole %; and (c) 1.5 mole % Ta_2O_5 doped $BaTiO_3$ samples sintered at 1320^0C (0 hrs) and 1280^0C (4 hrs).

Table 2 also shows that for 6 hrs of holding time, the 0.5 mole % Ta_2O_5 doped $BaTiO_3$ sample showed even more exaggerated grain growth in comparison to the sample sintered at 4hrs of holding time (Figure 4(a)). This excessive grain growth resulted in a decrease in percent theoretical density of the sample and also lowered its dielectric constant. However, under the same sintering conditions, the 1.0 mole % Ta_2O_5 doped $BaTiO_3$ sample showed controlled grain growth but larger than the sample sintered under previous sintering conditions (Figure 4(b)). For the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sample, even 6 hrs of holding time showed signs of the pinning effect. But the grain size of the sample was slightly higher than the sample sintered at 4hrs of holding time (Figure 4(c)). Due to the combination of high percent theoretical density and optimum grain size, the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sample exhibited the best dielectric properties for 6hrs of holding time.

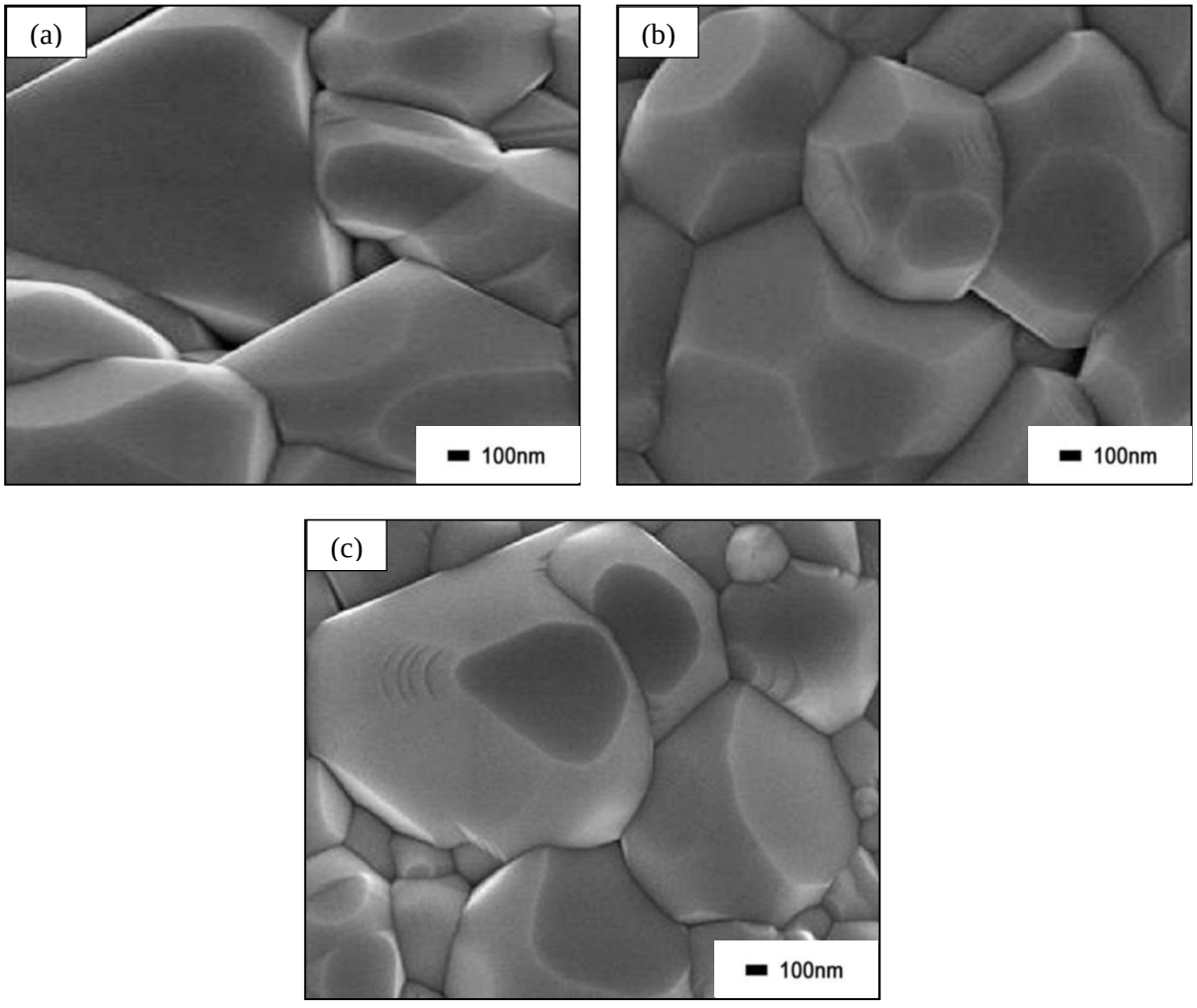

Figure 4. SEM micrographs (X 50,000) of: (a) 0.5 mole %; (b) 1.0 mole %; and (c) 1.5 mole % Ta_2O_5 doped $BaTiO_3$ samples sintered at 1320^0C (0hrs) and 1280^0C (6hrs).

The XRD patterns of Figure 5 indicate the formation of both tetragonal and cubic phases of $BaTiO_3$. The XRD pattern for the 0.5 mole % Ta_2O_5 doped $BaTiO_3$ sample sintered at 1320^0C for 0hrs and 1280^0C for 4hrs shows the presence of twin peaks

similar to pure $BaTiO_3$ powder (Figures 5(a) and 5(b)). So it can be concluded that for 0.5 mole % Ta_2O_5 doping, the $BaTiO_3$ retained the tetragonal perovskite structure. However, the XRD pattern for the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ samples sintered at 1320^0C for 0hrs and 1280^0C for 4hrs shows no evidence of twin peaks, which indicates that 1.5 mole % Ta_2O_5 reduced the tetragonality and stabilised the cubic phase of $BaTiO_3$ (Figure 5(c)). This phenomenon is also consistent in the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ samples sintered at 1320^0C for 0hrs and 1280^0C for 6hrs (Figure 5(d)). So it can be stated that 1.5 mole % Ta_2O_5 stabilised the cubic phase of $BaTiO_3$.

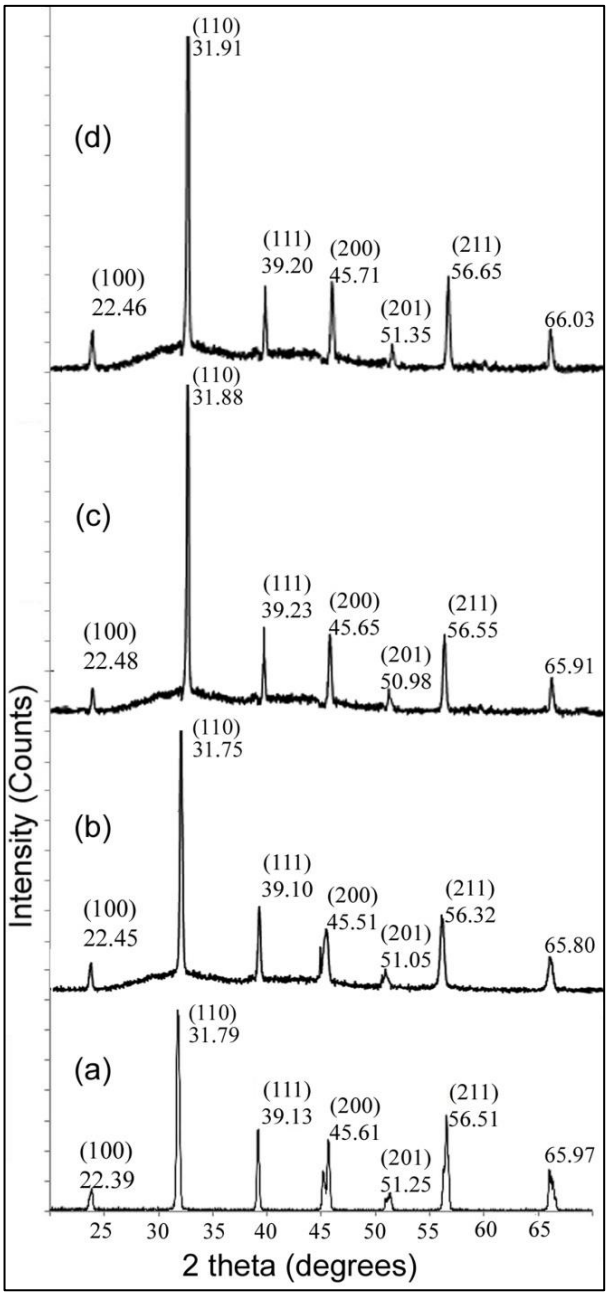

Figure 5. XRD plots for: (a) Pure Barium Titanate powder; (b) 0.5 mole %; and (c) 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1320^0C (0hrs) and 1280^0C (4hrs); and (d) 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1320^0C (0hrs) and 1280^0C (6hrs).

The findings from the XRD patterns are also consistent with the results of the temperature dependence of the dielectric constant (k). Although the Curie temperature (T_c) for pure $BaTiO_3$ is 120^0C, the Curie point of the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1320^0C for 0hrs and 1280^0C for 4hrs shifted to 84^0C (Figure 6), and the Curie point of the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1320^0C for 0hrs and 1280^0C for 6hrs shifted to 80^0C (Figure 7). According to theory, at a fixed temperature an increase in frequency results in a decrease in dielectric constant (Bowen et al., 1976; Carter and Norton, 2007; Richerson, 1992). This effect of tfrequency on the dielectric constant is clearly evident in Figure 8. The best stable value of dielectric constant as a function of temperature was obtained around 18000 for the 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sample sintered at 1320^0C for 0hrs and 1280^0C for 6hrs (Figure 7).

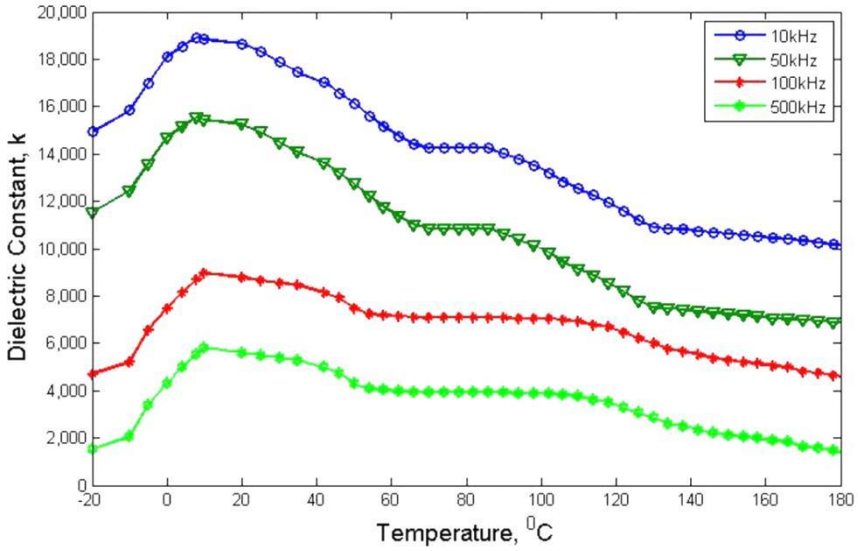

Figure 6. Variation in dielectric constant with temperature 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1320^0C (0 hrs) and 1280^0C (4 hrs).

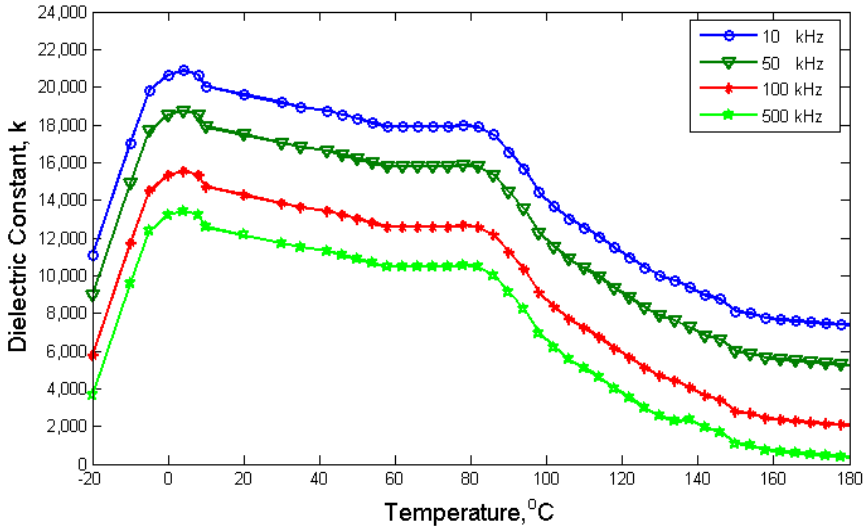

Figure 7. Variation in dielectric constant with temperature of 1.5 mole % Ta_2O_5 doped $BaTiO_3$ sintered at 1320^0C (0 hrs) and 1280^0C (6 hrs).

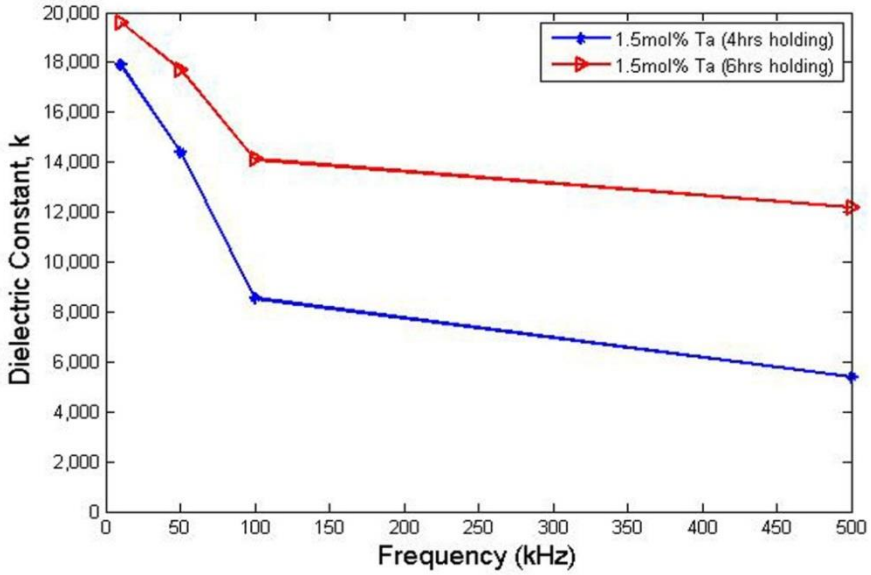

Figure 8. Room temperature dielectric constant of samples sintered at optimum sintering cycles.

CONCLUSION

An average grain size of around 1 µm normally provides a good condition for the dielectric properties of doped $BaTiO_3$. In this research, grain sizes in the range of 0.8–1.2 µm showed high values of dielectric constant, while a further increase in grain size deteriorated this property. It can also be concluded that up to 0.5 mole % Ta_2O_5 doping, $BaTiO_3$ retained its tetragonal perovskite structure. However, 1.5 mole % Ta_2O_5 stabilised the cubic phase of $BaTiO_3$ and shifted the Curie temperature towards room temperature.

ACKNOWLEDGEMENTS

The authors acknowledge Mr. Tan Teck Siong, JEOL Asia Pte Ltd for his assistance in the SEM analysis and BCSIR for their support in the XRD analysis.

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