Effects of Niobium Doping on Microstructure of BaTiO$_3$ Based Ceramics

A. N. Ahmed, H. M. M. A. Rashed

Abstract— Being an electroceramic barium titanate has dielectric, photorefractive and piezoelectric properties which can be modified if it is doped with donor ions such as Nb^{5+} . In addition to that controlling sintering parameters in an optimized condition can remarkably improve microstructure of the ceramics which directly influences the electrical properties. In this work, based on the formula BaTi$_{1-x}$Nb$_x$O$_3$; x=0.004, 0.008, 0.016, Nb doped BaTiO$_3$ was prepared through the process of calcination. Consistency of calculated and experimental values of constituents was checked by XRF. XRD data confirmed the formation of perovskite Nb doped BaTiO$_3$ structures. Above 90% of theoretical density was achieved for samples having different doping level and different sintering temperature ranged from 1425 to 1475 °C. Consistency of the particle size distribution of raw materials and product has also been observed after particle size analysis. Grain growth behavior was also observed when microstructures were studied by scanning electron microscope SEM. Furthermore, in order to generate the significance of variables, a statistical modeling by ANOVA, analysis of variance has been performed on different sintering parameters and frequencies for some particular set of data. Stronger effects of sintering temperature, Nb concentration and frequencies have been found on density, grain size and dielectric constant respectively.

Index Terms— Barium Titanate (BaTiO$_3$), Calcination, Niobium (Nb), Sintering, Scanning electron microscopy (SEM), X-ray diffraction (XRD), Analysis of variance (ANOVA).

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1 INTRODUCTION

FOR its ferroelectric properties barium titanate is used extensively as dielectric materials in capacitors. Due to its perovskite crystal structure containing Ti^{4+} at the octahedral position of the lattice with O^{2-} in the surrounding positions having Ba^{2+} ions at the corners of the lattice, polarization occurs in the crystal structure when it is subjected under an electric field. The octahedral Ti^{4+} can shift into six possible sites in the lattice due its small size compared to the octahedral hole, resulting spontaneous polarization. This type of phenomena leads to the formation of permanent dipole when BaTiO$_3$ is cooled below the Curie temperature 120°C, where crystal structure of the same transforms from cubic to tetragonal [1].

Properties of BaTiO$_3$ can be modified if it is doped with donor atoms such as niobium (Nb) replacing the octahedral Ti^{4+} ion. Due to the sluggish nature of diffusion of Nb at high temperature, an attempt has been made to incorporate Nb in the octahedral site of BaTiO$_3$ through the process of calcination. Nb doped perovskite BaTiO$_3$ was prepared with BaCO$_3$, TiO$_2$ and Nb$_2$O$_5$. Particle size distribution, phase formations, microstructure development with different sintering parameters were observed along with statistical modeling on sintering conditions, microstructural features and dielectric constant.

2 EXPERIMENTAL

2.1 Material Processing and Characterization

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On the basis of the formula BaTi$_{1-x}$Nb$_x$O$_3$; x=0.004, 0.008 and 0.016, Nb doped BaTiO$_3$ was prepared by weighing BaCO$_3$, TiO$_2$ and Nb$_2$O$_5$ in electronic balance followed by ball milling in yttria stabilized zirconia ball with a milling media of acetone for 18 hours. After drying, the milled powders were calcined at 1300 °C for 2 hours in order to form the BaTi$_{1-x}$Nb$_x$O$_3$ perovskite. After post calcination milling for 6 hours, mixtures were dried, PVA binder was added and finally pressed into pellets. Green pellets were dried and then sintered from 1425 to 1475 °C for 2 hours with an intermediate heating at 500 °C in order to remove the PVA binder. From the X-ray diffraction (XRD) data, perovskite formation was ensured by Bruker D8 Advance diffractometer with Cu$_{k\alpha}$ λ=1.5406 Å. XRF analysis was done by Lab Center, XRF 1800, Shimadzu. Particle size analysis was done by using a laser based particle size analyzer (model microtrac-S3500). Microstructures of the samples were observed with a Philips Scanning Electron Microscope (SEM). Density was measured with precision electronic balance and slide calipers.

2.2 ANOVA Modeling and Pareto Charts

Analysis of variance or ANOVA requires two sets of variables and a measured property on which the significance of variables can be studied. In this work, significance of Nb doping level and sintering temperature was studied on grain size and density respectively. In addition to that, holding hour and frequencies' effects on dielectric constant of a particular composition was also observed. If 'A' and 'B' are the two variables with their high and low levels + and - and the measured property is 'Y' Then AB which is the interaction of A and B must be determined. The basic calculation of ANOVA modeling has been shown in Table 1 as an example.
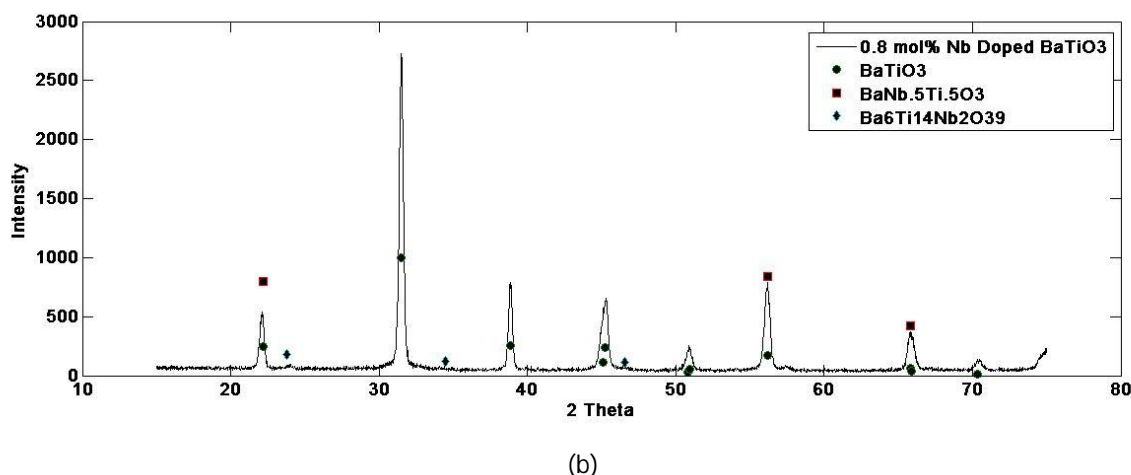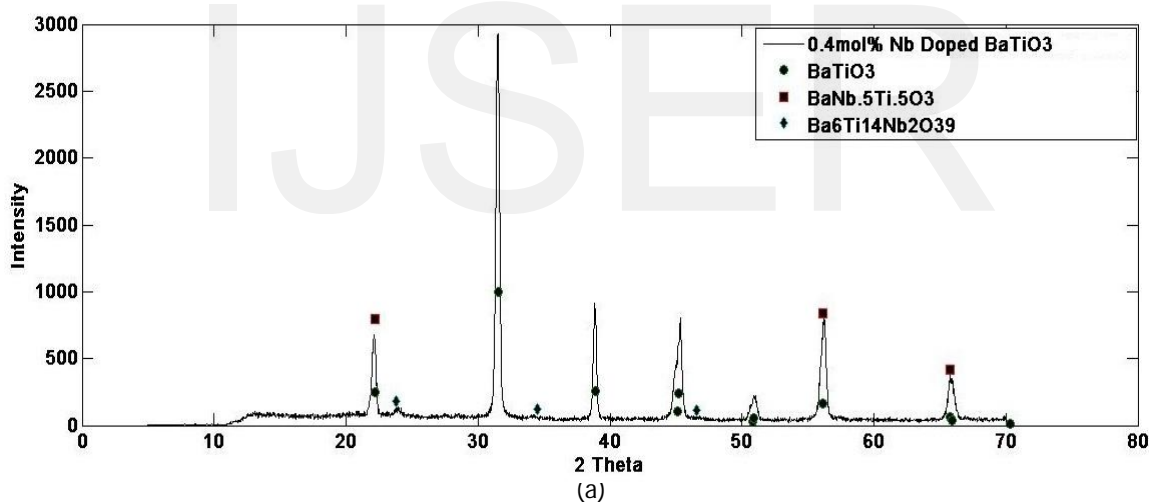
TABLE 1
CALCULATION OF ANOVA MODELING

%Nb (A)	Temperature °C (B)	A	B	AB
0.4	1425	-	-	+
0.4	1450	-	+	-
0.8	1425	+	-	-
0.8	1450	+	+	+

Significance of variables on measured properties can be projected via Pareto charts, where individual as well as collective effect of variables A, B or AB on property Y can be shown. This can be constructed by multiplying the average value of Y with corresponding sign of A, B and AB, followed by determining Δ by summing up the values. Finally charts are constructed by ranking the Δ/2 values. ANOVA is not a technique of testing the difference between two sample variances but it is a technique in order to test the significance of differences among the sample means [2].

3 RESULTS AND DISCUSSIONS

Initially perovskite Nb doped $BaTiO_3$ formation was confirmed with the XRD data Fig. 1. For different doping level x=0.004, 0.008 and 0.016, $BaTi_{1-x}Nb_xO_3$ formation was ensured as the standard $BaTiO_3$ having perovskite structure indicated by solid circle marks in Fig. 1, nearly superimposed on the peaks generated by the samples. Moreover, positions indicated by solid square correspond to the phase of $BaNb_5Ti_5O_3$ [3] has also been observed, which states the substitution of Ti ions by Nb ions in the octahedral sites. Additional phases indicated by solid diamond have also been found as $Ba_6Ti_{14}Nb_2O_{39}$ [4]. Since Nb content is very low, the peak height of secondary phase is too low to observe. Furthermore, with the XRF data shown in Table 2, consistency of calculated and experimental achievement was checked for sample containing 0.4 mol% Nb. In particle size analysis, the data has been shown in Fig. 2 where size of particles with their percentage has been plotted. Form fig. 2-a, small range distribution with lower particle size was observed for $BaCO_3$ whereas, larger size and distribution was observed for TiO_2 and Nb_2O_5 respectively fig. 2-b and c. But after calcinations, different size distribution of Nb doped $BaTiO_3$ has been observed due to reactions for all three doping level showing same trend of curve producing wider size-range of particles fig. 2-d, e and f. As doping level of Nb is low, the effect of doping on particle size and distribution is difficult to understand.
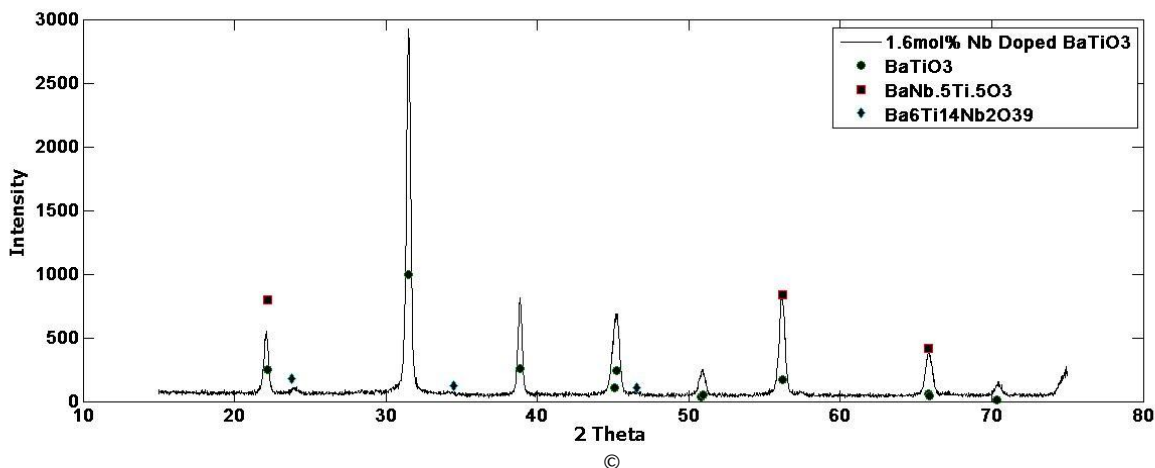

(a)

(b)

Fig.1. XRD patterns showing standards and other phases (a) 0.4mol% (b) 0.8mol% and (c) 1.6 mol% Nb

TABLE 2

XRF OF 0.4 MOL% NIOBIUM DOPED SAMPLE SINTERED AT 1475°C

Calculated Weight Percent Initially Added	Weight Percent After Sintering by XRF
$BaCO_3$ 55.276	BaO 61.9858
TiO_2 28.679	TiO_2 36.874
Nb_2O_5 .19166	NbO 0.2576

In table 3, the density data of the samples have been tabulated. In each case more than 90% of the theoretical density has been achieved. High density materials with finer grain size are always preferable for better dielectric properties.

In Fig. 3 micrographs of the samples have been shown, in which Fig. 3-a,b and c represent the samples containing 0.4 mol% Nb; d,e and f 0.8mol% Nb and g, h and i 1.6 mol% Nb. Sintering temperatures of the samples have been marked on the micrographs. From Fig. 3, existence of porosity has been found indicated by arrow for sample (a) sintered at 1425°C containing 0.4 mol% Nb. Minimum porosity was observed for figs. 3(d-f) comparing with others. Distinct and developed grain with little porosity was observed for samples containing 0.4 mol% Nb, Fig. 3(a-c). An increase in holding time during sintering may be required to remove the remaining pores.

In Figs. 3 (d–f), finer grains with low porosity are evident. In Figs. 3 (g–i), structure with some coarse grains (indicated by arrow in Fig. 3-i) and porosities can be found which may not the optimum microstructure required for better dielectric properties. It is therefore essential to give more energy to remove the pores in terms of holding time or sintering temperature. In this scenario, the issue of fine-grain microstructure may need to be compromised. Second stage sintering can be a solution in this situation so that shorter holding at higher temperature and longer holding at lower temperature can restrict the grain growth with minimum porosity.

Six transport mechanisms that may occur during sintering: surface diffusion, volume diffusion, evaporation-condensation, grain boundary diffusion, volume diffusion and plastic flow [5]. Transport of material is required into the pores in order to remove the pores. It is the dominating mechanism or combination of mechanisms corresponding to the sintering parameter and doping agent that decide the amount and size of pore. On the other hand, driving force for densification that acts during sintering is the reduction of excess surface free energy of the particles and it may be reduced by reducing the total surface area with increasing average size of the particle thus grain coarsening [6]. The dominant phenomena between these matter transport and grain coarsening decides the final microstructure of ceramics.

TABLE 3

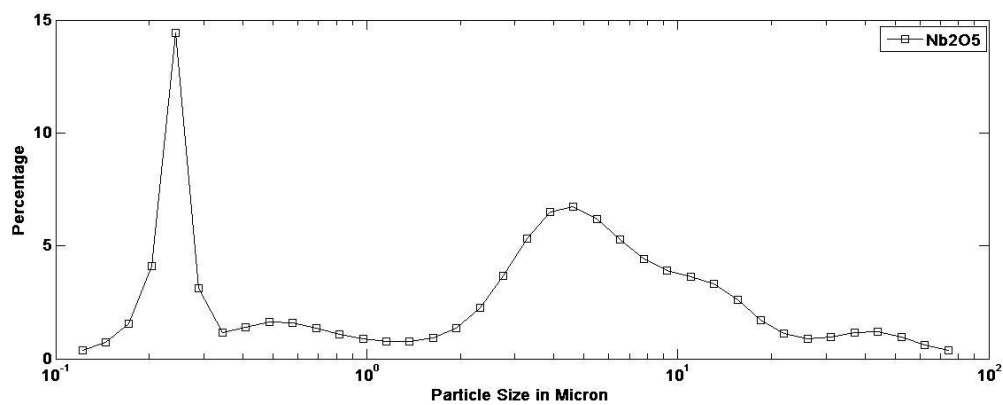DENSITY DATA OF NIOBIUM DOPED BARIUM TITANATE

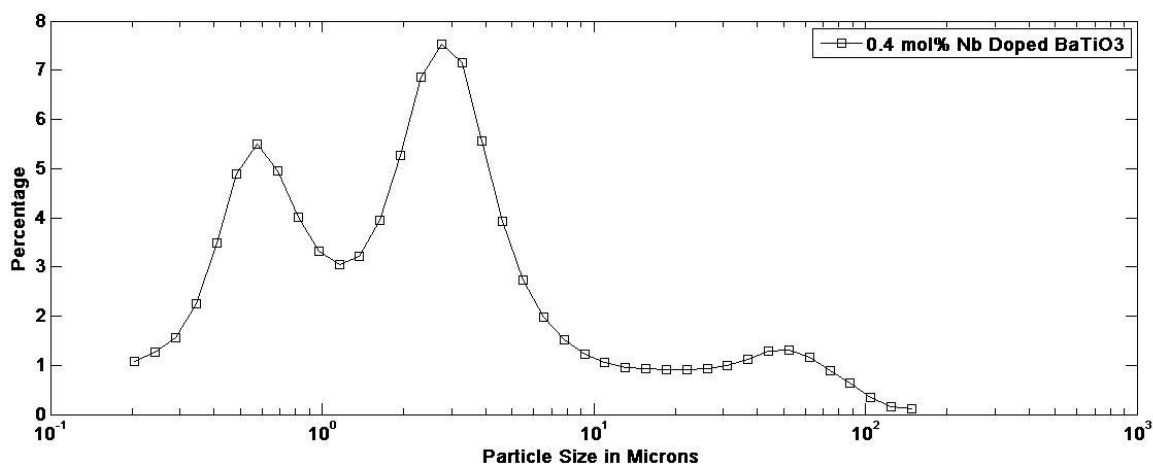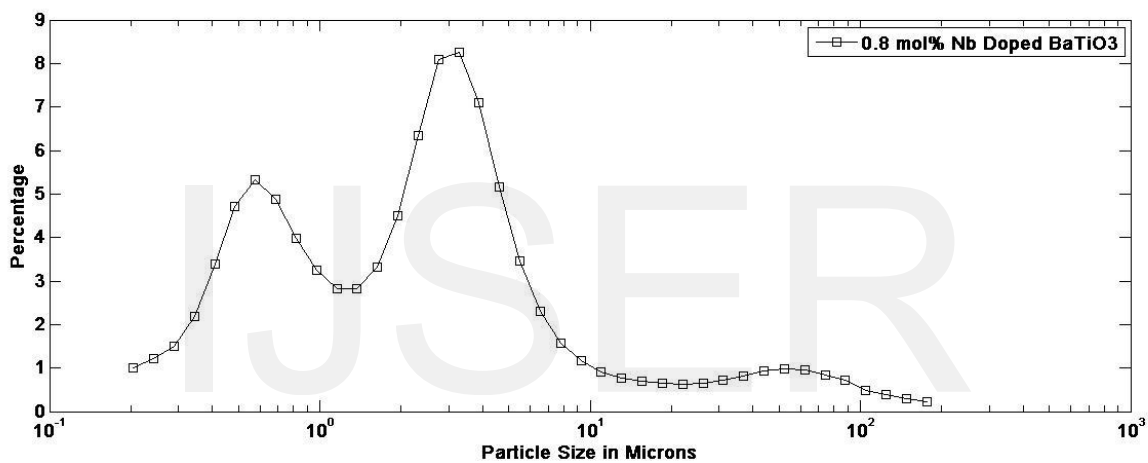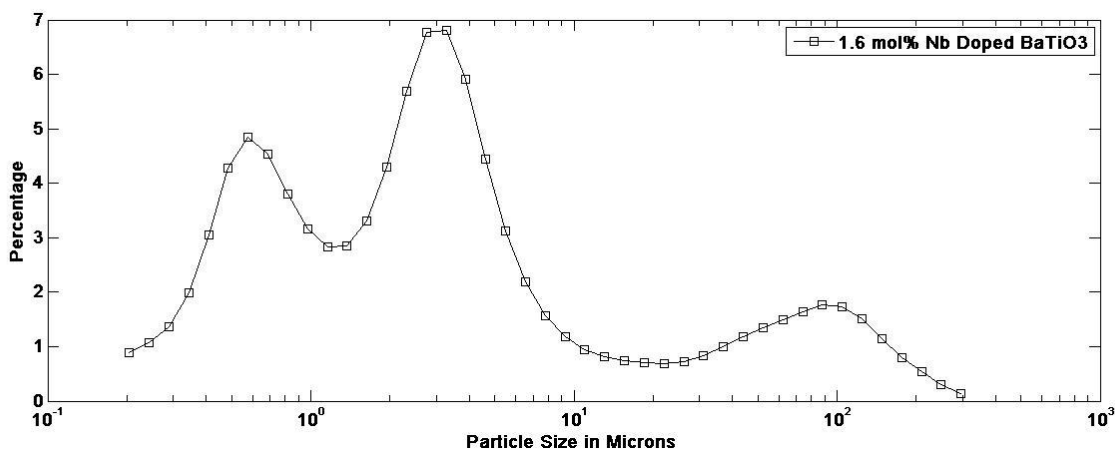| Nb mol%	Sintering Temperature °C	Density gm/cc	% Theoretical Density Achieved
0.4	1475	5.83±0.06	96.63±1.01
0.8	1475	5.95±0.01	98.49±0.17
1.6	1475	5.83±0.11	96.19±1.87
0.4	1450	5.91±0.12	97.97±1.78
0.8	1450	5.67±0.06	93.94±0.98
1.6	1450	5.73±0.06	94.57±0.99
0.4	1425	5.95±0.06	98.72±1.03
0.8	1425	5.99±0.02	99.15±0.25
1.6	1425	5.51±0.04	90.91±0.66

(a)

(b)

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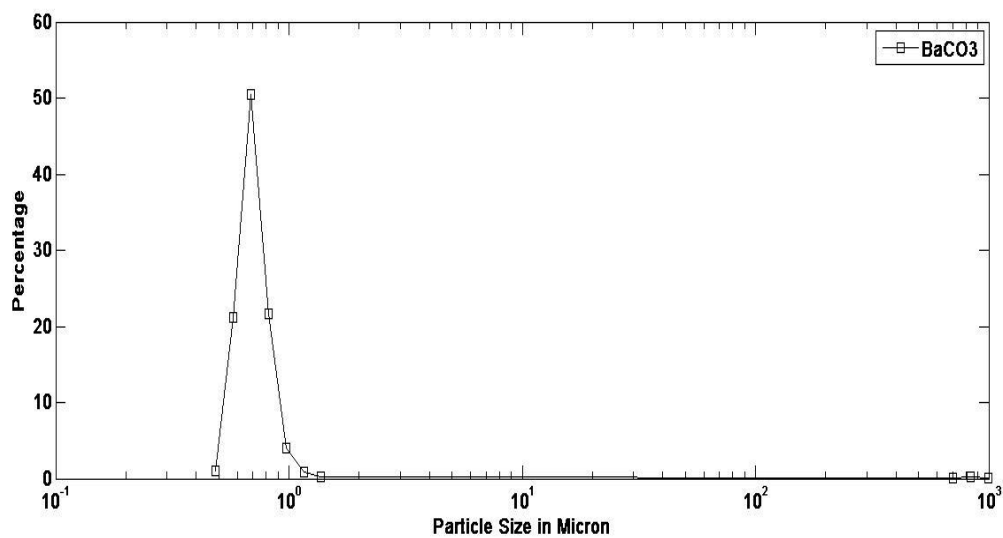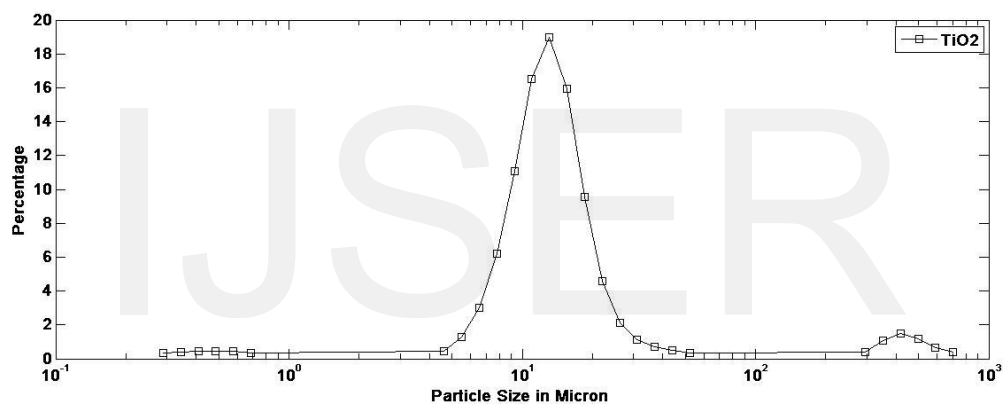
(d)

(e)

(f)

Fig. 2. Particle size analysis of (a) BaCO$_3$ (b) TiO$_2$ (c) Nb$_2$O$_5$ (d) 0.4 (e) 0.8 and (f) 1.6 mol% Nb doped BaTiO$_3$
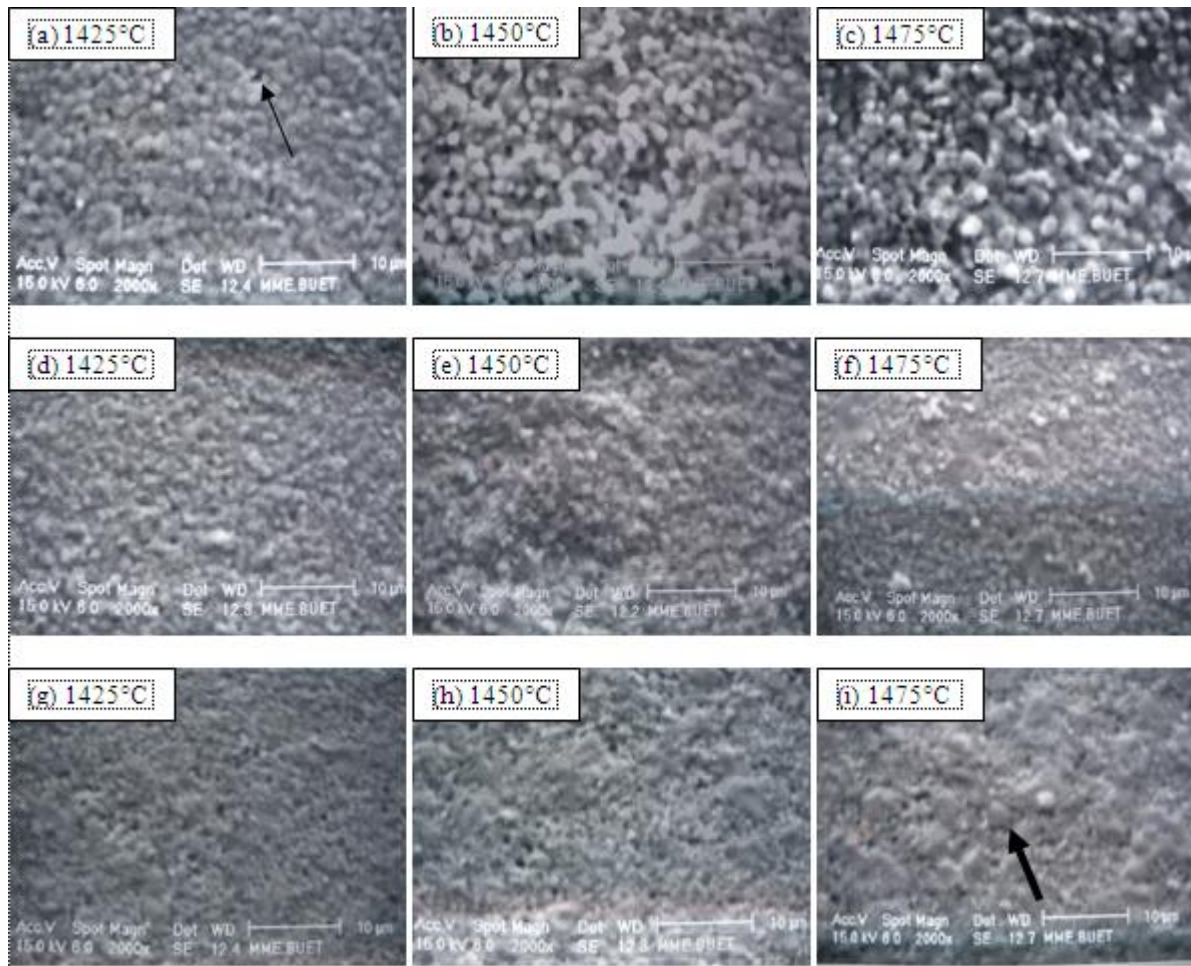
Fig. 3. SEM micrograph of $BaTi_{1-x}Nb_xO_3$ samples with different sintering temperature and doping level (a, b, c) 0.4 mol% Nb, (d, e, f) 0.8 mol% Nb and (g, h, i) 1.6 mol% Nb

As the sintering range is narrow, only 50 °C starting from 1425 to 1475 °C, the effect of temperature on grain size is not so significant for 0.4 and 0.8 mol% Nb concentration, but for 1.6 mol% Nb, increasing number of coarse grains have been observed with increasing sintering temperatures which has been indicated by arrow in Fig. 3-i. Higher temperature and higher Nb content may cause the grain growth of the samples. Grain growth due to higher Nb content has also been reported earlier [3].

Following the procedure in 2.2 for ANOVA, the first Pareto chart was developed for different Nb concentration taking as variable 'A' and different sintering temperature as variable 'B' and their significance on density in gm/cc, Fig. 4. The corresponding data set is given on Table 4. From the output of Fig. 4, it can be said that temperature has much more stronger effects on sample density than the combined effect of both temperature and Nb concentration. Moreover, the effect of Nb concentration alone on density has been found least than the others. It is the column with larger value in Pareto charts, that has more significance than the others. In addition to that, $\Delta/2$ values from Table. 4 calculated as ahown in experimental section, indicate that all the $\Delta/2$ values are negetive for A, B and AB which states that, increasing Nb content as well sintering temperature individually or combinedly will reduce the density of Nb doped $BaTiO_3$. Higher sintering tempeaure may cause the entrapment of pores inside the grain during faster grain growth thus reducing density.
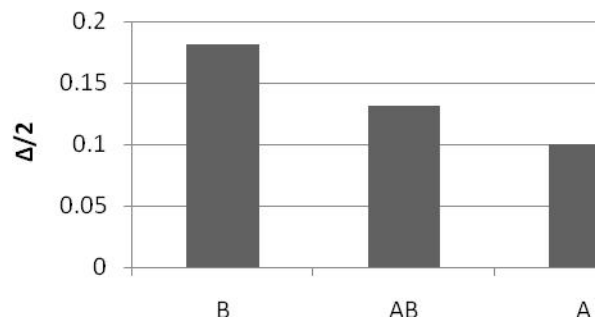

Fig. 4. Pareto chart for density A=Nb concentration in mol%, B=Sintering temperature in degree celsius.

Moreover, increasing Nb content may produce microstructure associated with porosity which may be another reason for reducing density and this type of phenomena has also been reported earlier [4].

TABLE 4

PARETO CHART DATA FOR DENSITY

Run	%Nb (A)	Temperature °C (B)	A	B	AB
1	0.4	1425	-	-	+
2	0.4	1450	-	+	-
3	0.8	1425	+	-	-
4	0.8	1450	+	+	+
		Δ/2	-0.1	-0.1815	-0.1315

The next modeling was executed in order to identify the significance of Nb concentration (C) and sintering temperature (D) on grainsize measured in µm of the sintered samples. From the Pareto chart it is evident that Nb concentration has stronger effect on grain size than sintering temperature in region of 1425-1450°C. Combined effect of C and D has been found minimum in this case Fig. 5. From the Δ/2 values of Table. 5, it can be said that negetive value of C reduces grain size with increasing Nb content which has also been reported in [7,8], whereas positive value of D or sintering temperature increases grain size which is common phenomena and reported in early literatures [9]. Increasing both C and D simultanously reduces grain size as CD has negetive Δ/2 . From the microstrctures of the sintered sample a better interpretation of this modeling can be made, Fig. 3.
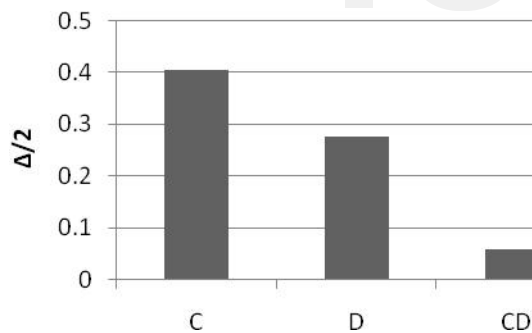

Fig. 5. Pareto chart for grain size C=Nb concentration in mol%, D=Sintering temperature in degree celsius.

TABLE 5

PARETO CHART DATA FOR GRAIN SIZE

Run	%Nb (C)	Temperature °C (D)	C	D	CD
1	0.4	1425	-	-	+
2	0.4	1450	-	+	-
3	0.8	1425	+	-	-
4	0.8	1450	+	+	+
		Δ/2	-0.4025	0.2758333	-0.0575

The final pareto chart was developed considering holding time during sintering 'E' and applied frequency to the sintered final product as 'F' to understand their significance on dielectric constant for the samples containing 0.4mol% Nb sintered at 1450°C Fig. 6. It is the applied frequency that affects mostly the dielectric constant value than the others. From Table 6 it is cleared that sufficient time must given to the samples during sintering in order to increase the dielectric constant of the materials as the Δ/2 values for E is positive , because porosity in materials can lower the dielectric constant of the and sufficient time is required to remove the pores. But Δ/2 values for F or frequency is negetive which indicates increasing frequency will reduce the dielectric constant of the materials. This results as the mechanisms of polarization in dielectric materials; electronic, ionic, interfacial and dipolar start to deactivate with increasing frequencies [5].
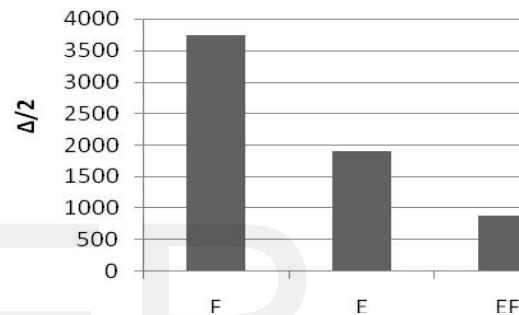

Fig. 6. Pareto chart for dielectric constant k, E=Holding time in hour, F=Applied frequency in kHz.

TABLE 6

PARETO CHART DATA FOR DIELECTRIC CONSTANT.

Run	Holding hr (E)	Frequency kHz (F)	E	F	EF
1	0	0.1	-	-	+
2	0	1	-	+	-
3	1	0.1	+	-	-
4	1	1	+	+	+
		Δ/2	1908.6	-3739.09	-874.83

4 CONCLUSION

With the presence of minor secondary phases, successful formation of perovskite $BaTi_{1-x}Nb_xO_3$ was observed when powders were calcined at 1300°C. Bimodal distribution of particle size of the calcined product has been observed for all three doping level resulting from the particle size distribution of the reactant powders. Over 90 percent of theoretical density was achieved for all of the samples with fine grain and low porosity content for 0.8 mol% Nb, higher porosity for 0.4 mol% Nb. Coarse as well as fine grained structure was observed for 1.6 mol% Nb.

For ANOVA modeling significant parameters have been identified in order to find the dominating processing variables. Nb content has been found dominating for grain size over sintering temperature whereas opposite effects have been observed for density. Applied frequency has been found dominating over sintering holding time for dielectric constant of the material as dielectric constant is directly related to polarization mechanism which is controlled by applied frequencies.

ACKNOWLEDGEMENT

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