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ANOVA modeling on sintering parameters and frequencies, affecting microstructure and dielectric constant of Nb doped $BaTiO_3$

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Abstract

Properties of barium titanate ($BaTiO_3$) which is used as a dielectric material can be engineered if it is doped with metal ions such as niobium, tantalum, zirconium etc. Moreover both sintering temperature and doping level have significant effects on grain size as well as density which directly affect the dielectric constant of the material. In this work in order to generate the significance of variables a statistical modeling by ANOVA, analysis of variance has been performed on sintering parameters and frequencies effecting microstructure and dielectric constant of Nb doped $BaTiO_3$ having a formula of $BaTi_{1-x}Nb_xO_3$; x= 0.004, 0.008. After processing and characterization of the prepared material, it was evident that sintering temperature has stronger effect than doping level of Nb in determining the density of niobium doped $BaTiO_3$ whereas Nb concentration has stronger effect in determining the grain size over sintering temperature which was clearly established in ANOVA. Furthermore, effect of frequencies in determining dielectric constant of $BaTiO_3$ was strongly observed when it was modelled with holding time during sintering.

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Keywords: ANOVA; Pareto Charts; X-ray Diffraction; Scanning Electron Microscopy (SEM); Barium Titanate ($BaTiO_3$); Niobium (Nb)

1. Introduction

Barium titanate is basically used as dielectric material in capacitors. Dielectric material is an insulating material which can be polarized by the application of an electric field. In dielectric material when an electric field is applied slight shift of charge from their equilibrium lattice position results dielectric polarization. Four mechanisms can jointly or individually work in producing dielectric polarization; electronic, ionic, interfacial and dipolar [1].

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Dielectric properties of barium titanate can be engineered if it is doped with donor dopants such as niobium, tantalum, zirconia etc. Moreover sintering parameters such as heating rate, holding time, sintering temperature also have significant effects in determining the microstructure which directly affects the dielectric properties of materials.

In addition to that, applied frequency also has significant effects in triggering the polarization mechanism for which dielectric constant changes as increasing frequencies cause polarization mechanisms to deactivate [1]. Numbers of variables are responsible in determining the ultimate dielectric properties of materials. As a result ANOVA modeling was performed in order to identify the role and significance of variables on properties of dielectric materials. ANOVA is defined as analysis of variance used in analyzing experimental data. The determination of significance of the factors on the dependent variables in other words properties can be analyzed by ANOVA. ANOVA is a presentable part of factorial design which consists of a set of a variable. For a level two design, levels or variables are denoted as high or low and responses represent the properties at those conditions. Another presentable part of factorial design is called Pareto charts, where graphical representation of high and low variables on the properties is projected. 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].

2. Experimental

2.1. Material Processing and Characterization

According to the $BaTi_{1-x}Nb_xO_3$; x= 0.004, 0.008 formula, samples were prepared starting with $BaCO_3$, TiO_2 and Nb_2O_5. After weighing in high precision electronic balance, powders were ball milled for 18 hours with acetone and yittria stabilized zirconia ball. Powders were then dried and calcined at 1300°C followed by milling again in the similar way for 6 hours. After calcination, formation of Nb doped barium titanate was ensured with X-ray diffraction with Bruker D8 Advance diffractometer with $Cu_{k\alpha}$ λ=1.5406 Å radiation**.** Milled powders were dried again and PVA (polyvinyl alchohol) binder was added. Then powders were pressed into pellets, dried and sintered from 1425-1450°C. From SEM (scanning electron microscopy) micrograph, grain size of the samples were measured using image analysis, density was measured with high precision balance and slide calipers and finally dielectric properties were measured with impedance analyzer.

2.2. ANOVA Modeling and Pareto Charts

Modeling with ANOVA and producing Pareto charts require variables and properties for which the variables' significance can be studied. In this work, significance of Nb concentration and sintering temperature on density, Nb concentration and temperature on grain size and finally sintering holding time and applied frequencies on dielectric constant have been studied. If 'A' and 'B' are considered two variables with their high and low levels + and - and the measured property is 'Y', then first of all, interaction of A and B which is AB, must be determined. The basic calculation of ANOVA was followed in the following way for one set of experiment as shown in the Table 1.

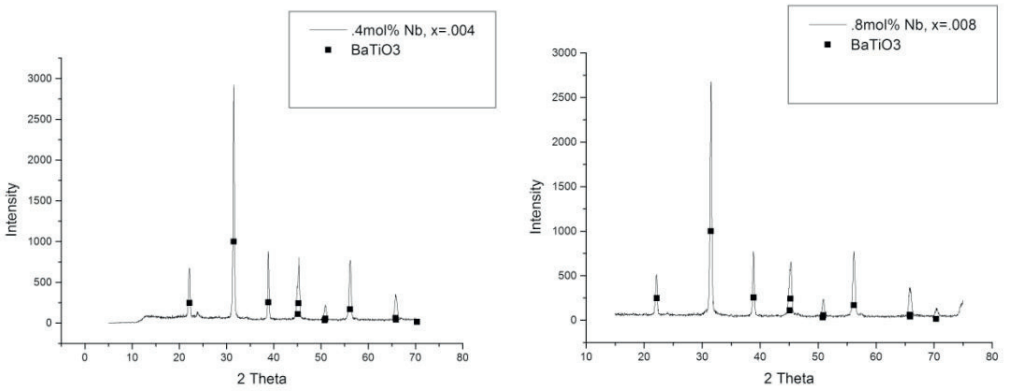
Table 1. Calculation of ANOVA modeling .

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

Pareto charts can be constructed projecting the significance of variable A, B or collective effect of AB on property. This can be determined by multiplying the average value of property (Y) with corresponding sign of A, B and AB and calculating Δ by summing up the values. Final Pareto chart is constructed on the ranking of Δ/2 values.

3. Results and Discussions

Nb doped barium titanate was prepared by calcinations. After calcinations formation of Nb doped barium titanate having perovskite crystal structure was ensured by comparing experimental data with standard $BaTiO_3$ pattern Fig. 1



(a) (b)

Fig. 1. XRD patterns of Nb doped $BaTiO_3$ (a) 0.4mol% Nb ; (b) 0.8mol% Nb.

From Fig. 1, it is evident that, formation of our desired product was confirmed on which this modeling was performed.

Following the procedure stated in experimental section for ANOVA, Pareto chart was developed initially for different Nb concentration taking as variable ‘A’ and different sintering temperature as variable ‘B’ and their significance on density in gm/cc, Fig. 2. The corresponding data set is given on Table 2.

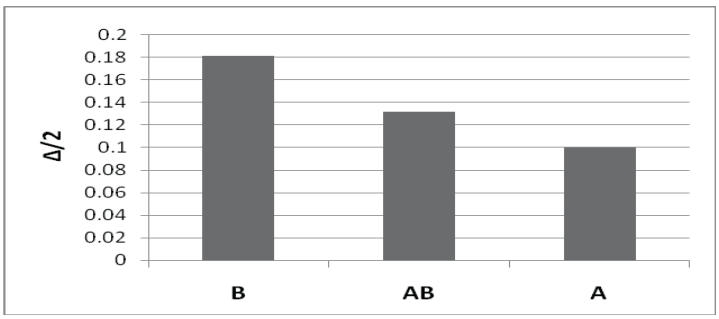


Fig. 2. Pareto chart for density A=Nb concentration in mol%, B=Sintering temperature in degree celceus.

Table 2. Pareto chart data for density in gm/cc.

		Temperature °C			
Run	%Nb (A)	(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

From the output of Fig. 2, 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 only Nb concentration on density has been found least than the others. It is the column with larger value, that has more significant effect than the others. In addition to that, Δ/2 values from Table. 2 calculated as ahown in experimental, indicates that all the Δ/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 temperaure may cause the entrapment of pores inside the grain during faster grain growth thus reducing density. 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].

The next modeling was executed in order to identify the significance 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. 3. From the Δ/2 values of Table. 3, it can be said that negetive value of C reduces grain size with increasing Nb content which has also been reported in [4,5], whereas positive value of D or sintering temperature increases grain size which is common phenomena and reported in early literatures [6]. 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. 4.

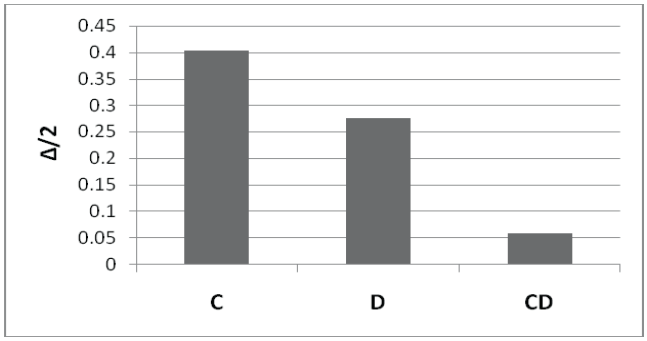


Fig. 3. Pareto chart for grain size C=Nb concentration in mol%, D=Sintering temperature in degree celceus.

Table 3. Pareto chart data for grain size in μm.

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. It is the applied frequency that affects mostly the dielectric constant value than the others. From Table 4 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 [1].

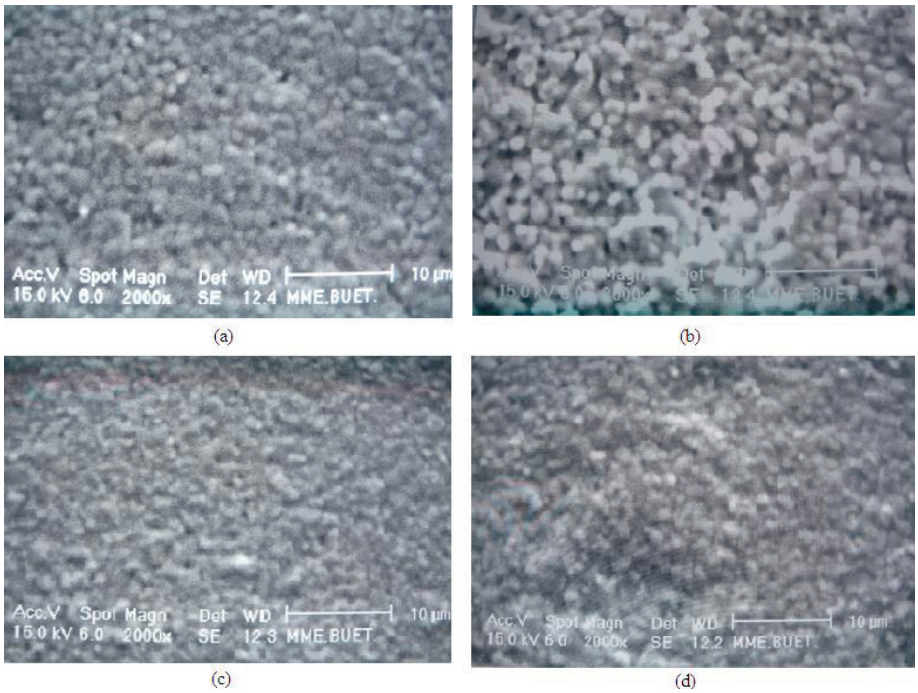


Fig. 4. SEM micrographs showing 0.4 mol% Nb sintered at (a) 1425°C (b)1450°C and 0.8mol% Nb sintered at (c) 1425°C and (d) 1450°C.

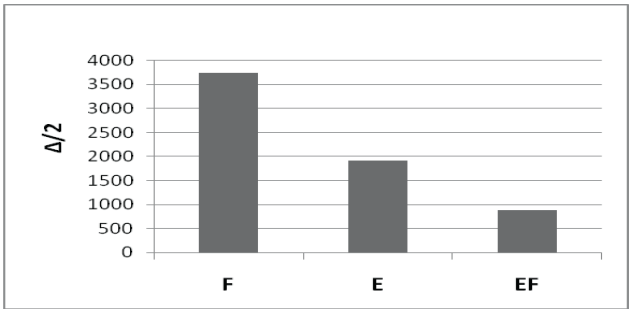


Fig. 5. Pareto chart for dielectric constant k, E=Holding time in hour, F=Applied ferency in kHz.

Table 4. 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	-3739.09167	-874.8317

4. Conclusion

Properties of dielectric materials can be improved by improving the grain size, density with appropriate applied frequency and this improvement can be achieved if important processing variables can be identified so that process parameter can be controlled in a narrow range of option rather than wider range. Sintering temperature has been found dominating over Nb content on density whereas reverse effect has been observed on grain size. Applied frequency has been found dominating over sintering holding time on dielectric constant as frequency controls the mechanism of polarization which directly affects the dielectric constant of material. Consistency of modeling has also been observed with some early literature as well.

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