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Statistical Modeling of Sintered Density of Microwave Dielectric $BiNbO_4$ Ceramics

Swati Salunkhe[1], Rahul Dongre[2]

[1]Department of Mechanical Engineering, D.Y. Patil College of Engineering, Akurdi,Pune, Maharashtra, 411044,India.
[2]Department of Mechanical Engineering, D.Y. Patil College of Engineering, Akurdi,Pune, Maharashtra, 411044,India.

Abstract

A statistical model to study the effect of four major processing variables; compaction pressure (P), wt% V_2O_5 addition (W), sintering temperature(T) and sintering time (H) on the sintered density (D) of microwave dielectric $BiNbO_4$ ceramics was developed. The methods of analysis of variance (ANOVA) and multi-variable linear regression were used to develop the model. ANOVA demonstrated a significant effect of all the above variables on the sintered densities at 97.5% significance level. The sintering temperature was the most (~ 83.5 %) and sintering time was the least (~ 3%) significant variable contributing to the sintered density. The regression model developed was:

$$D = 1.805898\ P^{0.049701}\ W^{0.022514}\ T^{0.130327}\ H^{0.02512}$$

The error in the sintered density output was marginal (~ 0.02%) for even up to 10% variation in processing variables. The model when validated from experimentally determined densities, correlated well with error within 14%. The C-band microwave dielectric properties; dielectric constant (ε_r') and the quality factor ($Q_u.f$) were also measured. The ε_r' demonstrated a close resemblance to the density profile of the samples studied, whereas, $Q_u.f$ values showed a slight deviation which was more dependent on quantity of V_2O_5 added.

Key Words: $BiNbO_4$, Sintered density, Multi-variable linear regression, ANOVA.

1. Introduction

New dielectric materials are continuously being developed for applications such as microwave components for satellite and broadcasting equipments technology [1-4]. The passive integration in form of ceramic multicomponent modules (CMMs) or functional devices used therein requires low temperature (~ 900^0C) sintering microwave dielectric ceramics (called as "*Low-temperature cofiring ceramics – LTCCs'*) [1, 5, 6]. Bismuth-based dielectric ceramics ($BiNbO_4$) are used as candidate dielectrics for LTCCs due to advantages like low sintering temperatures (< 1000° C) and excellent dielectric properties [7]. Numerous citations in literature [6, 10, 12, 13-16] reveal that their microwave dielectric properties such as dielectric constant (ε_r') and quality value (Q_u) (inverse of loss tangent (tanδ)) strongly depend on the final sintered density of the components. Further, the sintered density is governed by the four important processing variables viz. compaction pressure, sintering temperature, sintering time and addition of sintering aids (low melting point compounds such as, CuO, V_2O_5 or their mixtures, or B_2O_3 added in quantities < 2 wt%) [8-12].

The response of ε_r' and Q_u to the process variables cannot be directly studies as at times there is no resonance (no response). In view of this, it is attempted here to develop a statistical model for the determination of the sintered density based on the four process variables as mentioned above and establish a correlation with the microwave dielectric properties. Almost all the published literature reports the effect of one or maximum two process variables at a time on sintered density. Nowhere the combined effect of more number of processing variables is reported. Hence, it generated our interest to explore, the individual (most and least significant process variables) and combined contribution (by developing a statistical model) of all the four main processing variables to the sintered density (viz. on microwave dielectric properties) of $BiNbO_4$ ceramics by Analysis of variance (ANOVA) and multi-variable linear regression analysis respectively. Statistical techniques like ANOVA are commonly employed in design of products and process and solution of problems in manufacturing engineering [17]. Similar attempt is made here to arrive at certain correlations providing valuable guidelines for the control of processing variables to improve the sintered density of $BiNbO_4$ ceramics. The experimentally observed densities are correlated with both the statistical studies (on the sintered densities) and measured microwave dielectric properties.

2. Experimental Work

2.1 Materials processing, characterization and properties measurements:

The general sequence of processing for all the samples included use of high-purity (≥ 99%) oxide powders of Bi_2O_3,

Nb_2O_5, and V_2O_5 (Central Drug house, New Delhi, India) as starting constituents. Proportionate amounts of starting materials of Bi_2O_3 and Nb_2O_5 were mixed according to the desired stoichiometry of $BiNbO_4$ ceramics and wet ground in methanol medium for 3 h to eliminate aggregates and reduce the particle size. These mixed powder after drying at 110ºC for 2 h, were initially solid state reacted at 860ºC for 3 h to get a nearly single (Columbite) phase structure. The powder XRD pattern of the reacted powder was recorded on PanAnalytical XPERT-PRO Diffractometer in 2θ range of 20^o to 70^o, using Cu Kα radiation, to check the phase formation. The phased powders were reground wet for 1 h and mixed with desired proportions of V_2O_5 as sintering aid and subsequently wet ground for another 3 h to achieve the fine grain size required for sintering. 3 wt% PVA solution in water was used as a binder. These powders were subjected to uniaxial compaction in a steel die to form green pellets of cylindrical shape. After careful debinding, sintering of the pellets was carried out at under ambient conditions. During both initial solid state reaction and sintering, small quantity of Bi_2O_3 was placed in separate crucible (for sacrificial action) and the samples were covered with alumina crucibles to prevent the Bi loss from the samples. XRD patterns of sintered pellets were again recorded to determine the crystal structure and identify the phases.

The main task of studying the effect of processing variables involved generation of a density profile for sintered density against each processing variable and was aimed at achieving maximum density in the sintered compacts. We need to begin at some starting point. Hence, on the basis of a number of initial representative tests conducted by varying the V_2O_5 content between 0.5 and 1 under sintering cycles of 900 - 980ºC for 2 - 6 h at compaction pressure of 100 MPa [8-12], an optimized condition 960ºC, 4 h sintering was arrived for 1 wt % V_2O_5 addition. This condition was subsequently used for studying the effect of process variables on the sintered density. Density profiles against each processing variable were accurately generated by varying one of the process variables at a time, while keeping the other three constant. The sequence and range of study was; (i) Compaction pressure (P) - six different compaction pressures from 50 MPa to 300 MPa with 50 MPa increment, (ii) Weight %V_2O_5 addition (W) – six different weight % of V_2O_5 from 0.25 to 1.5 wt% with 0.25 wt% increment, (iii) Sintering Temperature (T) – five different temperatures from 900 to 980ºC with 20^oC increment and (iv) Sintering Time (H) – five different time intervals from 2 to 6 h with 1h increment were used (see Fig. 1 (a) – (d)).

The bulk densities and apparent porosities of the sintered ceramics were measured by Archimedes method. Guidelines of the standard method of ASTM C 373 1988 (2006) were used. The microstructure investigation of polished and thermally etched surfaces of the sintered pellets was conducted using Hitachi S-3400N (Hitachi, Japan) low vacuum SEM. Dielectric Post (DP) resonator technique was employed for the microwave characterization of the ceramic samples. The sample under test was placed over a low loss support material and was enclosed in a microwave cylindrical cavity, which acted as a resonating structure. The TE_{011} mode was identified for each resonator. The measurements were done using Agilent 8722ES Vector Network Analyzer (VNA). The real part (ε_r') of relative permittivity was computed from the measured resonance frequency (f) of the resonator containing the sample under test. The loaded Q factor (Q_L) of the resonator was measured directly from the VNA and the unloaded Q factor (Q_u) was calculated using a computer program which took into account the cavity losses and coupling conditions [18, 19]. (The quality factor is usually reported as $Q_u.f$).

2.2 Design of Experiment for ANOVA and regression analysis

The experimental design used is a composite design [20]. A design with four factors at different levels is considered for experimentation. It consists of 2^{nd} test that is factorial design, used to find out the relation between the joint effect of four independent variables (compaction pressure, wt % V_2O_5 addition, sintering temperature and sintering time) and the sintered density as the dependent variable. The notations (often called as *geometric notations*) used in the experimental design for developing this model are "+" (High) "-" (Low), and "0" (Mean), as indicated in Table 1. Since there are four independent variables, the numbers of tests are determined as $2^4 = 16$, the details are given in Table 2.

Table 1 Processing variables, symbols and levels

Processing Variables (symbols)	Level		
	Low (-1)	Mean# (0)	High (+1)
Compaction pressure (P)	50	175	300
Wt % V_2O_5 addition (W)	0.25	0.875	1.5
Sintering temperature (T)	900	940	980
Sintering time (H)	2	4	6

#Mean values are not considered in orthogonal array given in Table 2

Table 2 - (2^4) Orthogonal Array of Experimental observations

Trial	P (MPa)	W (wt%)	T (°C)	H (h)	Level				Observed Density D (g/cm^3)
1	300	1.5	980	6	+1	+1	+1	+1	6.69
2	300	1.5	980	2	+1	+1	+1	-1	6.64
3	300	1.5	900	6	+1	+1	-1	+1	6.42
4	300	1.5	900	2	+1	+1	-1	-1	4.84
5	300	0.25	980	6	+1	-1	+1	+1	6.73
6	300	0.25	980	2	+1	-1	+1	-1	5.95
7	300	0.25	900	6	+1	-1	-1	+1	5.58
8	300	0.25	900	2	+1	-1	-1	-1	4.99

9	50	1.5	980	6	-1	+1	+1	+1	6.63
10	50	1.5	980	2	-1	+1	+1	-1	6.54
11	50	1.5	900	6	-1	+1	-1	+1	4.23
12	50	1.5	900	2	-1	+1	-1	-1	4.89
13	50	0.25	980	6	-1	-1	+1	+1	5.63
14	50	0.25	980	2	-1	-1	+1	-1	6.74
15	50	0.25	900	6	-1	-1	-1	+1	4.97
16	50	0.25	900	2	-1	-1	-1	-1	4.11
17*	**175**	**0.875**	**940**	**4**	**0**	**0**	**0**	**0**	**6.66**
18*	**175**	**0.875**	**940**	**4**	**0**	**0**	**0**	**0**	**6.74**
19*	**175**	**0.875**	**940**	**4**	**0**	**0**	**0**	**0**	**6.67**
20*	**175**	**0.875**	**940**	**4**	**0**	**0**	**0**	**0**	**6.66**
21*	**175**	**0.875**	**940**	**4**	**0**	**0**	**0**	**0**	**6.69**
22*	**175**	**0.875**	**940**	**4**	**0**	**0**	**0**	**0**	**6.69**

* Samples from trial 17-22 represents samples with mean processing conditions, which are added to study the effect of metallurgical variables with the help of R^2 value and are not a part of 2^4 Orthogonal array.

2.2.1 Analysis of variance (ANOVA)

Based on the four independent variables, a well-designed experiment consisting of 2^4 i.e. 16 observations is constructed (see Table 2). The analysis of variance (ANOVA) method used for analyzing experiments calculates correction factor (CF), sum of square for each factor (SS), sum of square total (SS_{total}), mean sum of square (MSS, also called a variance(V)), and degree of freedom (df). The degrees of freedom for factors (processing variable) are almost always one degree freedom less than the number of levels involved (see Table 3) [20, 21].

Table 3 - ANOVA Table with interactions

Processing variables & possible Interactions‡	SS	df	V_{factor}
P	1.05	1	1.05
W	0.298	1	0.298
T	8.332	1	8.332
H	0.294	1	0.294
PW	0.015	1	0.015
PT	0.631	1	0.631
PH	0.902	1	0.902
WT	0.031	1	0.031
WH	0	1	0
TH	0.409	1	0.409
PWT	0.041	1	0.041
PWH	0.021	1	0.021
WTH	0.062	1	0.062
PTH	0.001	1	0.001
PWTH	1.233	1	1.233

‡ With 04 process variables there are only 11 interactions possible, SS – Sum of squares, df – Degree of freedom, V_{factor} – Variance.

The sum of the squares (SS) calculated has one degree of freedom. To examine the interactions, the interaction table (Table 3) is formulated. For the 04 process variables studied, there are only 11 interactions possible for each trial. When the Sum of Square is divided by the degrees of freedom, we get a mean square, also called as variance (V) (from which the name of this method "Analysis of Variance (ANOVA)" is derived).

$V_{factor} = SS_{factor} / df_{factor}$ ……(1)

This V_{factor} calculated is indicated in Table 3. It is observed that, the values of V_{factor} vary from 0 to 8.332 which is a very wide range. Hence, to avoid tedious calculations, sources having small values of SS less than 0.294 are pooled together. These pooled figures are removed from their places on ANOVA table (Table 3) and a new V_{error} factor is created, which is recorded at the bottom of the final ANOVA table (Table 4). Our main aim in this method of analysis is to see if the signal created by the V_{factor} is stronger than the background noise (V_{error}). The F-test is used to compare the two variances.

$F = V_{factor}/V_{error}$ ……(2)

This F factor is included in the final ANOVA table (Table 4). The ANOVA method predicts the relative significance of each process variable and estimates the experimental errors. It also gives the percentage contribution of each variable and provides a better understanding of the relative effect of the different processing variables on the sintered density. Similar efforts have been reported elsewhere [17].

2.2.2 Formation of Multi-variable Linear Regression Model

The processing variables and the levels used in model formation are indicated in Table 1. The functional relationship between the sintered density (D in g/cm^3) of $BiNbO_4$ ceramics and the investigated independent variables viz. compaction pressure (P in MPa), wt % V_2O_5 addition (W in grams), Sintering temperature (T in ^oC), and Sintering time (H in hours) can be represented by the following equation,

Table 4 - Final ANOVA table

Sr. No.	Source	SS	df	V_{factor}	F
1	P	1.05	1	1.05	43.033
2	W	0.298	1	0.298	12.213
3	T	8.332	1	8.332	341.475
4	H	0.294	1	0.294	12.049
5	PT	0.631	1	0.631	25.861
6	PH	0.902	1	0.902	36.967
7	TH	0.409	1	0.409	16.762
8	PWTH	1.233	1	1.233	50.533
	Pooled Error	0.171	7	0.0244	

$D = f(P, W, T, H)$ ……(3)

Assuming an exponential relationship, equation (3) can be written as,
$D = Z P^k W^l T^m H^n$ ……(4)
Where Z is a constant of proportionality and k, l, m, n are the exponents.

Equation (4) may be written in logarithmic form as,
$\log D = \log Z + k \log P + l \log W + m \log T + N \log H$ ……(5)

The above equation (5) can be assumed to represent the following linear mathematical model,
$y = b_0 X_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4$ ……(6)
Where y is the true response of sintered density on a logarithmic scale, $X_0 = 1$ (a dummy variable), X_1, X_2, X_3, and X_4 are logarithmic transformations of compaction pressure, wt % V_2O_5 addition, sintering temperature and sintering time respectively, while, b_0, b_1, b_2, b_3 and b_4 are the variables to be estimated from the following equation (also see Table 5),
$b_i = \Sigma X_{ij} \times \log y_{ij} / \Sigma j^2$ ……..(7)

The equation (6) can be written as
$y' = y - e = a_0X_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4$.....(8)
where y' is the estimated response and y is the true response on a logarithmic scale, e is the experimental error and a_0, a_1, a_2, a_3 and a_4 values are estimates of the b_0, b_1, b_2, b_3, and b_4 variables respectively.

Table 5 - Calculations of Multiple Regression Analysis

Sr. No.	Sintered Density (y′)	Logy′	X_1*Logy′	X_2*Logy′	X_3*Logy′	X_4*Logy′
1	6.69	1.899866	1.899866	1.899866	1.899866	1.899866
2	6.64	1.893263	1.893263	1.893263	1.893263	-1.89326
3	6.42	1.858951	1.858951	1.858951	-1.85895	1.858951
4	4.84	1.577328	1.577328	1.577328	-1.57733	-1.57733
5	6.73	1.906575	1.906575	-1.90658	1.906575	1.906575
6	5.95	1.783727	1.783727	-1.78373	1.783727	-1.78373
7	5.58	1.718292	1.718292	-1.71829	-1.71829	1.718292
8	4.99	1.607235	1.607235	-1.60724	-1.60724	-1.60724
9	6.63	1.892057	-1.89206	1.892057	1.892057	1.892057
10	6.54	1.877937	-1.87794	1.877937	1.877937	-1.87794
11	4.23	1.441966	-1.44197	1.441966	-1.44197	1.441966
12	4.89	1.586374	-1.58637	1.586374	-1.58637	-1.58637
13	5.63	1.728465	-1.72846	-1.72846	1.728465	1.728465
14	6.74	1.908357	-1.90836	-1.90836	1.908357	-1.90836
15	4.97	1.602413	-1.60241	-1.60241	-1.60241	1.602413
16	4.11	1.412449	-1.41245	-1.41245	-1.41245	-1.41245
$\Sigma X_{ij} * \log y'_{ij}$			0.79522	0.360227	2.085238	0.401915
$\Sigma X_{ij} * \log y'_{ij} / \Sigma j^2$			0.049701	0.022514	0.130327	0.02512
			k	l	m	n

The following null hypothesis of equal means has been considered [21].
H_0 ($a_1 = a_2 = a_3 = a_4 = 0$) ……(9)
That is to say that, none of the factors viz. compaction pressure, wt. % V_2O_5 addition, sintering temperature and sintering time has a significant influence on the sintered density.

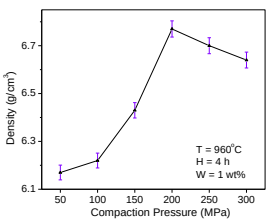
2.2.3 Sensitivity Analysis

The calculation of sintered density of $BiNbO_4$ ceramics is subject to certain error depending upon the error contribution in the measurement of the compaction pressure, wt % V_2O_5 addition, the sintering temperature and sintering time. Sensitivity analysis gives the variation (error) in the output response (yield) depending upon variation of individual operating parameters. The equation for sensitivity analysis is obtained by taking partial derivative with respective variables on both sides of equation (3).
$\partial D = \partial D/\partial P * \Delta P + \partial D/\partial W * \Delta W + \partial D/\partial T * \Delta T + \partial D/\partial H * \Delta H$ ……(10)

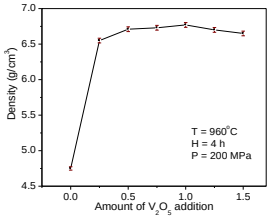
3. Results and Discussion

3.1 Effect of Processing Variable

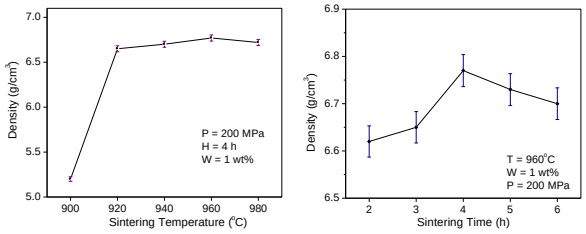
The individual effect of each process variable on sintered density was studied, while keeping the other three variables constant. From individual correlation of all these four processing variables to the sintered density of the ceramics, a general trend of increase in response on density till some threshold value followed by a subsequent drop as indicated in Figs. 1 (a) to (d) is observed. The occurrence of this typical phenomena can be ascribed to various reasons such as, particles getting very tightly bound and entangled within each other at excessively higher compaction pressures (P > 200 MPa) causing obstruction for liquid phase V_2O_5 (melting point of V_2O_5 is ~ 690ºC) to flow and addition of higher V_2O_5 content (W > 1 %) or over sintering temperature (T > 960°C) or over sintering time (H > 4h) causing abnormal grain growth (a diffusion controlled phenomena). The abnormal grain growth was clearly revealed in the SEM studies made, the details being discussed in section 3.6 of this article.
This study meant that there is no linear relationship evident for ceramics under consideration. Thus, it gets reflected as drop in R^2 value from 0.96 (for 16 number of observations) to 0.89 (for 22 observations with mean values taken for regression analysis) associated with deviation from linearity (see Fig. 2).



(a)



(b)



(c) (d)

Fig. 1 - Density of $BiNbO_4$ sintered ceramics as a function of (a) compaction pressure, (b) wt % V_2O_5 addition, (c) sintering temperature and (d) sintering time.

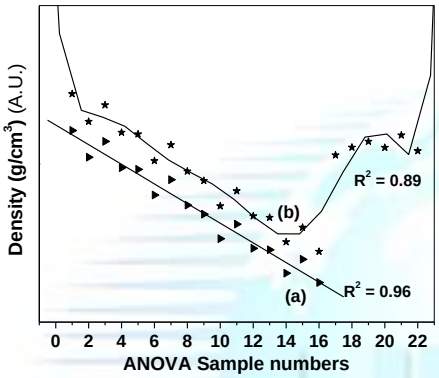


Fig. 2 - R^2 values for (a) 16 samples and (b) 22 samples after polynomial fitting of data

3.2 Analysis of variance (ANOVA)

Considering F distribution Table with 1, 7 DOF F97.5 value is 8.0727, i.e. with 97.5 % level of significance [20, 21], it is found that all F values in Table 4 are greater than 8.0727. From the above ANOVA analysis, the Null Hypothesis of equal means (equation (9)) is rejected for our samples. Hence, it is concluded that, all of the process variables viz. compaction pressure, wt % V_2O_5 addition, sintering temperature and sintering time have significant effect on the sintered density on 97.5% significance level. Table 6 illustrates the results of the analysis of variance depicting the effect of contributing factors on the sintered density. These factors can be placed in their order of deceasing magnitudes (of contribution) i.e. sintering temperature (~ 83.54 %), compaction pressure (~ 10.53 %), wt % V_2O_5 addition (~ 2.99 %), and sintering time (~ 2.95 %).

Table 6 - Percentage contribution of each variable affecting the sintered density

Parameter	Level		df	SS	% contri-bution
	(High)	(Low)			
P	5.98	5.47	1	1.05	10.53
W	5.86	5.59	1	0.298	2.99
T	6.44	5.00	1	8.332	83.54
H	5.86	5.59	1	0.294	2.95
			4	9.974	100

3.3 Multi-variable Linear Regression Method

The values of k, l, m, and n as calculated from the regression calculations are shown in Table 5. For finding value of constant Z, the values from our observation Table 2 are submitted in equation (6) and it becomes,

$\log D = \log Z + 0.049701 \log P + 0.022514 \log W + 0.130327 \log T + 0.02512 \log H$ ……..(11)

From the above equation (11), the average value of Z determined is 1.805898, the experimental error as found out from equation (8) is e = 0.011316 and corresponding regression coefficient is $R^2 = 0.96$ as shown in Fig. 2.

For 16 observations without considering mean values, the model becomes,

$D = 1.805898\ P^{0.049701}\ W^{0.022514}\ T^{0.130327}\ H^{0.02512}$ …… (12)

Similarly, for 22 observations considering mean values, the model becomes,

$D = 1.873219\ P^{0.049701}\ W^{0.022514}\ T^{0.130327}\ H^{0.02512}$ …….... (13)

(The values of exponents k, l, m & n is remaining same for both 16 & 22 variables)

3.4 Sensitivity Analysis

From equation (12) we get error due to variation in sintered density as,

$\Delta D/D = (0.049701\ (\Delta P/P) + 0.022514\ ((\Delta W/W) + 0.130327\ (\Delta T/T) + 0.02512\ (\Delta T/T)$ ..... (14)

Where,

$\Delta P/P$ – error due to variation in compaction pressure,
$\Delta W/W$ – error due to variation in wt% V_2O_5 addition,
$\Delta T/T$ – error due to variation in sintering temperature
$\Delta H/H$ – error due to variation in sintering time.

Equation (14) gives the Sensitivity Analysis of sintered density of $BiNbO_4$. Assuming 10% variation in each variable, the percentage error in sintered density output is given by,

$\Delta D/D = (0.049701 + 0.022514 + 0.130327 + 0.02512) \times 0.1 = 0.02277$ …….. (15)

Thus for 10% variation, percentage variation in sintered density is 0.02277, which is seen to be insignificant contribution to the sintered density as compared to individual contribution made by each of the factors viz. compaction pressure, wt% V_2O_5 addition, sintering temperature and sintering time.

3.5 Verification

Table 7 indicates the comparison between the foreseen values by the model developed in equation (12) and the experimental results of the sintered density of $BiNbO_4$ ceramics. The obtained results show the error to be within 14%. Equation (12) is thus considered a feasible and an effective way for the evaluation of the sintered density of $BiNbO_4$ ceramics.

Table 7- Comparison of experimental results under different processing conditions with model values for verification tests

D - Sintered density of $BiNbO_4$ ceramics.

3.6 Structure - properties correlation

Although the processing was done at temperatures < 1020°C, powder XRD record on a few representative sintered samples was taken to check occurrence of triclinic phase, if any, due to V_2O_5 added [6] (see Fig. 3). All the samples revealed a monophasic structure. All the peaks could satisfactorily be indexed to orthorhombic crystal structure (JCPDF File No. 820348). No secondary phase and/or triclinic phases were observed.

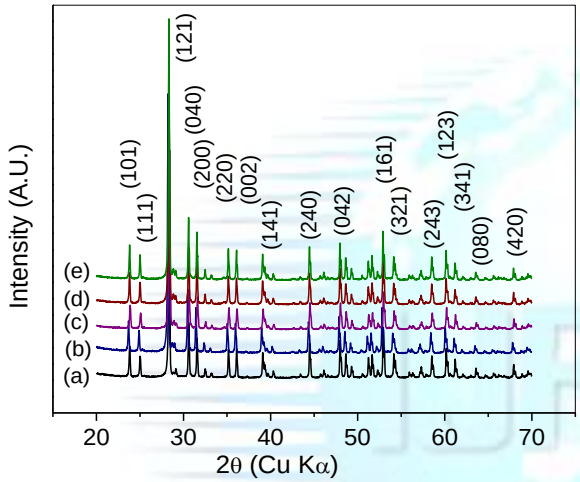


Fig. 3 - Powder XRD patterns of $BiNbO_4$ ceramics with P = 200 MPa and H = 4 h (a) 0.5 wt% V_2O_5 sintered at 960°C, with 1 wt% V_2O_5 addition sintered at (b) 920°C, (c) 940°C, (d) 960°C and (e) 980°C.

Fig. 4 (a) to (d) shows the SEM images of the $BiNbO_4$ ceramics with processing conditions of 200 MPa, 1 wt% V_2O_5 content, 4 h sintering time and sintered at (a) 920ºC, (b) 940ºC, (c) 960ºC (d) 980ºC respectively and (e) shows SEM image of $BiNbO_4$ sample under similarly processed sample with 0.5 wt% V_2O_5 addition, sintered at 960ºC, 4 h. In Fig. 4 (a) - (d), it is observed that the porosity in the sintered samples is decreasing (contributing to increase in sintered density) with increase in sintering temperature from 920ºC to 960ºC. The grain size is increasing from ~ 3 - 4 microns to ~ 5 - 7 microns with the rise in temperature from 920ºC to 980ºC. Nearly uniform grain growth and fine size of grains for $BiNbO_4$ ceramics is observed up to 960°C (Fig. 4 (a) - (c)). Abnormal grain growth is clearly observed with further increase of temperature to 980°C (Fig. 4 (d)). Further, the density appears to improve with increase in V_2O_5 content from 0.5 to 1 wt % (comparing Fig. 4 (e) with Fig. 4 (c) - both samples sintered at 960ºC, 4h).

For the sintered samples studied, though a marginal change is seen in most of the values of sintered density in the experimental range studied, it is quite significant to cause variation in dielectric properties of the $BiNbO_4$ ceramics as discussed in next section (section 3.7). The study of 16 observations gives appreciable R^2 value of 0.96, whereas, for 22 observations the R^2 value drops to 0.89 (see Fig. 2). It implies that the abnormal grain growth as observed at higher sintering temperatures has contributed to drop in R^2 value. The grain growth parameter is not considered in formulation of the present model.

Test No.	Processing conditions				D (gm/cm^3)		
	P (MPa)	W (wt %)	T (ºC)	H (h)	Experi-mental values	Model values Eq^n (13)	Error (%)
1	200	1	960	4	6.77	5.95	13.7
2	175	0.875	940	4	6.66	5.88	13.3
3	200	1	920	4	6.59	5.92	11.4

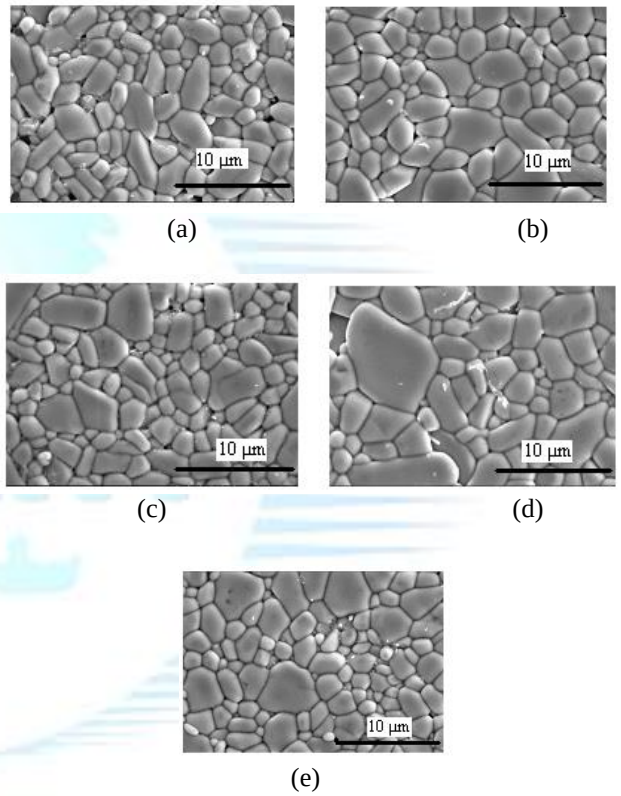


Fig. 4 - SEM micrographs of $BiNbO_4$ ceramics processed at 200 MPa, 1 wt% V_2O_5 addition, 4 h sintering time and sintered at (a) 920ºC, (b) 940ºC, (c) 960ºC (d) 980ºC and (e) 200 MPa, 0.5 wt% V_2O_5 addition and sintered at 960ºC, 4 h.

3.7 Microwave dielectric properties

Dielectric measurements on all 22 samples shown in Table 2 in the microwave frequency range ~ 5 - 6 GHz are compiled in Fig. 5. It is a general convention that, both the microwave dielectric properties ε_r' and $Q.f$ show variation identical to the sintered density [6, 10, 12, 13-16]. Interestingly, it is observed that ε_r' closely resemble the density profiles, whereas, $Q_u.f$ show a slight departure from the density profile for all the samples studied. ε_r' increases from ~ 23.8 at a sintered density of ~ 4.89 gm/cm^3 to ~ 39.0 at sintered density of ~ 6.69 gm/cm^3. In general for the range of experimental parameters studied it appears that, lower compaction pressures, lower wt % V_2O_5 addition, intermediate sintering temperature and time gives higher $Q_u.f$ values. The $Q_u.f$ values are getting most adversely affected by increase in amount of V_2O_5 addition. As the

amount of V_2O_5 addition is increased from 0.25 to 1.5 wt % (with all other parameters constant), the $Q_u.f$ value has decreased from ~ 2935 to ~ 408, which is quite a significant drop.

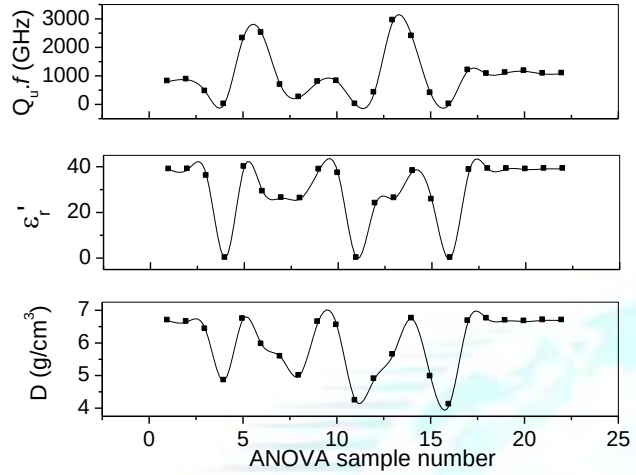


Fig. 5 - Correlation of density (D) profile of 22 number of ANOVA samples with dielectric constant (ε_r') and quality factor ($Q_u.f$) values.

4. Conclusions:

A reliable mathematical model for estimating the sintered density of $BiNbO_4$ ceramic compacts from the four important processing variables viz. compaction pressure, wt % V_2O_5 addition, sintering temperature and sintering time has been developed and validated from experimentally determined sintered densities. ANOVA results show that, all the processing variables have a significant effect on the sintered density at 97.5 % significance level with sintering temperature as the most significant and sintering time as the least significant parameter. The regression model developed for 16 observations (without considering mean values) is,

$$D = 1.805898\ P^{0.049701}\ W^{0.022514}\ T^{0.130327}\ H^{0.02512}$$

Whereas, for 22 observations (with consideration of the mean values) it is,

$$D = 1.873219\ P^{0.049701}\ W^{0.022514}\ T^{0.130327}\ H^{0.02512}$$

Experimentally determined density is found to correlate well with model density (error within 14%). The sensitivity analysis reveals that for 10% variation in processing variables, there is 0.02277 % variation in the sintered density, which is insignificant. Decrease of R^2 values from 0.96 for 16 observations to 0.89 for 22 observations associated with change of model from linear variation to polynomial variation correlates well with the abnormal grain growth (metallurgical phenomena) observed at higher temperatures in the microstructures of sintered $BiNbO_4$ ceramic compacts. The model developed is found more suitable up to the maximum sintered density achieved. Microwave dielectric measurements show that the dielectric constant more closely resembles the density profile than $Q_u.f$ values.

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