Statistical Modeling of Sintered Density of Microwave Dielectric BiNbO$_4$ Ceramics

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Abstract

A statistical model to study the effect of four major processing variables; compaction pressure (P), wt% V$_2$O$_5$ 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:

$$D = 1.805898H^{0.0849705}W^{0.0122514}P^{0.1530576}T^{0.02512}$$

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 ($\varepsilon''$) and the quality factor ($Q_{\omega}$) were also measured. The $\varepsilon''$ demonstrated a close resemblance to the density profile of the samples studied, whereas, $Q_{\omega}$ values showed a slight deviation which was more dependent on quantity of V$_2$O$_5$ 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°C) sintering microwave dielectric ceramics (called as “Low-temperature cofiring – 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 ($\varepsilon''$) and quality value ($Q_{\omega}$) (inverse of loss tangent ($\tan\delta$)) 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$_2$O$_5$ or their mixtures, or B$_2$O$_3$ added in quantities ≤2 wt%) [8-12].

The response of $\varepsilon''$ and $Q_{\omega}$ 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$_2$O$_3$, ...
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 \( \varepsilon^\prime \) 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 experimental design used is a composite design [20]. A design with four factors at different levels is considered for experimentation. It consists of 2^4 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>
<thead>
<tr>
<th>Processing Variables, symbols and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variables</td>
</tr>
<tr>
<td>Compaction pressure (P)</td>
</tr>
<tr>
<td>Wt % ( V_2O_5 ) addition (W)</td>
</tr>
<tr>
<td>Sintering temperature (T)</td>
</tr>
<tr>
<td>Sintering time (H)</td>
</tr>
</tbody>
</table>

*Mean values are not considered in orthogonal array given in Table 2.*
**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>
<thead>
<tr>
<th>Processing variables &amp; possible Interactions with interactions¹</th>
<th>SS</th>
<th>df</th>
<th>$V_{factor}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1.05</td>
<td>1</td>
<td>1.05</td>
</tr>
<tr>
<td>W</td>
<td>0.298</td>
<td>1</td>
<td>0.298</td>
</tr>
<tr>
<td>T</td>
<td>8.332</td>
<td>1</td>
<td>8.332</td>
</tr>
<tr>
<td>H</td>
<td>0.294</td>
<td>1</td>
<td>0.294</td>
</tr>
<tr>
<td>PW</td>
<td>0.015</td>
<td>1</td>
<td>0.015</td>
</tr>
<tr>
<td>PT</td>
<td>0.631</td>
<td>1</td>
<td>0.631</td>
</tr>
<tr>
<td>PH</td>
<td>0.902</td>
<td>1</td>
<td>0.902</td>
</tr>
<tr>
<td>WT</td>
<td>0.031</td>
<td>1</td>
<td>0.031</td>
</tr>
<tr>
<td>WH</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>TH</td>
<td>0.409</td>
<td>1</td>
<td>0.409</td>
</tr>
<tr>
<td>PWT</td>
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<tr>
<td>PWH</td>
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<td>1</td>
<td>0.021</td>
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<tr>
<td>WTH</td>
<td>0.062</td>
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<td>0.062</td>
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<tr>
<td>PTH</td>
<td>0.001</td>
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<td>0.001</td>
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<tr>
<td>PWTH</td>
<td>1.233</td>
<td>1</td>
<td>1.233</td>
</tr>
</tbody>
</table>

³With 04 process variables there are only 11

The sum of 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).

$V_{factor} = SS_{factor} / df_{factor}$  

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.

$F = V_{factor}/V_{error}$

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/cm³) of BiNbO₃ ceramics and the investigated independent variables viz. compaction pressure (P in MPa), wt % V₂O₅ addition (W in grams), Sintering temperature (T in °C), and Sintering time (H in hours) can be represented by the following equation,

$Y = \beta_0 + \beta_1P + \beta_2W + \beta_3T + \beta_4H + \epsilon$

where, $Y$ is the sintered density, $P$, $W$, $T$, and $H$ are the process variables, $\beta_0$, $\beta_1$, $\beta_2$, $\beta_3$, and $\beta_4$ are the regression coefficients, and $\epsilon$ is the error term.

The final ANOVA table is as follows:

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Source</th>
<th>SS</th>
<th>df</th>
<th>$V_{factor}$</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.05</td>
<td>1</td>
<td>1.05</td>
<td>43.033</td>
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<tr>
<td>2</td>
<td>W</td>
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<td>1</td>
<td>0.298</td>
<td>12.213</td>
</tr>
<tr>
<td>3</td>
<td>T</td>
<td>8.332</td>
<td>1</td>
<td>8.332</td>
<td>341.475</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>0.294</td>
<td>1</td>
<td>0.294</td>
<td>12.049</td>
</tr>
<tr>
<td>5</td>
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<td>1</td>
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<td>25.861</td>
</tr>
<tr>
<td>6</td>
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<td>0.902</td>
<td>36.967</td>
</tr>
<tr>
<td>7</td>
<td>TH</td>
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<td>0.409</td>
<td>16.762</td>
</tr>
<tr>
<td>8</td>
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<td>1.233</td>
<td>1</td>
<td>1.233</td>
<td>50.533</td>
</tr>
</tbody>
</table>

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_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_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 = \frac{\Sigma X_i \log y_i}{\Sigma j^2} ..............................(7)
The equation (6) can be written as,
y' = y - e = a_0 X_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_4 X_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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sintered Density (y')</th>
<th>Logy'</th>
<th>X_1*Logy'</th>
<th>X_2*Logy'</th>
<th>X_3*Logy'</th>
<th>X_4*Logy'</th>
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</thead>
<tbody>
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<td>6.69</td>
<td>1.899866</td>
<td>1.899866</td>
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<tr>
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<td>1.893263</td>
<td>1.893263</td>
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</tr>
<tr>
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<td>1.858951</td>
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<tr>
<td>4</td>
<td>4.84</td>
<td>1.577328</td>
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<td>1.577328</td>
<td>1.577328</td>
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<tr>
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<td>6.73</td>
<td>1.906575</td>
<td>1.906575</td>
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<td>1.906575</td>
</tr>
<tr>
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<td>5.95</td>
<td>1.783727</td>
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<td>1.783727</td>
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<tr>
<td>7</td>
<td>5.58</td>
<td>1.718292</td>
<td>1.718292</td>
<td>1.718292</td>
<td>1.718292</td>
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<tr>
<td>8</td>
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</tr>
<tr>
<td>9</td>
<td>6.63</td>
<td>1.892057</td>
<td>1.892057</td>
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</tr>
<tr>
<td>10</td>
<td>6.54</td>
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<tr>
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<tr>
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<tr>
<td>15</td>
<td>4.97</td>
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<td>1.602413</td>
<td>1.602413</td>
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</tr>
<tr>
<td>16</td>
<td>4.11</td>
<td>1.412449</td>
<td>1.412449</td>
<td>1.412449</td>
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<td>1.412449</td>
</tr>
</tbody>
</table>

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, 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).

\[ \frac{\partial D}{\partial \phi} = \frac{\partial D}{\partial P} \times \frac{\partial P}{\partial \phi} + \frac{\partial D}{\partial W} \times \frac{\partial W}{\partial \phi} + \frac{\partial D}{\partial T} \times \frac{\partial T}{\partial \phi} + \frac{\partial D}{\partial H} \times \frac{\partial H}{\partial \phi} \]

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 ~ 690°C) to flow and addition of higher V_2O_5 content (W > 1 %) 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).
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, 
\[ \log D = \log Z + 0.049701 \log P + 0.022514 \log W + 0.130327 \log T + 0.02512 \log H \]  
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, 
\[ D = 1.805898 P^{0.049701} W^{0.022514} T^{0.130327} \]  
Similarly, for 22 observations considering mean values, the model becomes, 
\[ D = 1.873219 P^{0.049701} W^{0.022514} T^{0.130327} \]  
(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, 
\[ \Delta D/D = (0.049701 (\Delta P/P) + 0.022514 (\Delta W/W) + 0.130327 (\Delta T/T) + 0.02512 (\Delta H/H) \]  
Where, \( \Delta P/P \) – error due to variation in compaction pressure, \( \Delta W/W \) – error due to variation in wt\% V\textsubscript{2}O\textsubscript{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\textsubscript{4}. Assuming 10% variation in each variable, the percentage error in sintered density output is given by, 
\[ \Delta D/D = (0.049701 + 0.022514 + 0.130327 + 0.02512) \times 0.1 = 0.02277 \]  
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\textsubscript{2}O\textsubscript{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\textsubscript{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\textsubscript{4} ceramics.

Table 7- Comparison of experimental results under different processing conditions with model values for verification tests
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 V₂O₅ 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 BiNbO₄ ceramics with P = 200 MPa and H = 4 h (a) 0.5 wt% V₂O₅ sintered at 960°C, with 1 wt% V₂O₅ 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 BiNbO₄ ceramics with processing conditions of 200 MPa, 1 wt% V₂O₅ content, 4 h sintering time and sintered at (a) 920°C, (b) 940°C, (c) 960°C and (d) 980°C respectively and (e) shows SEM image of BiNbO₄ sample under similarly processed sample with 0.5 wt% V₂O₅ addition, sintered at 960°C, 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 920°C to 960°C. The grain size is increasing from ~ 3 - 4 microns to ~ 5 - 7 microns with the rise in temperature from 920°C to 980°C. Nearly uniform grain growth and fine size of grains for BiNbO₄ ceramics is observed up to 960°C (Fig. 4 (d)). Further, the density appears to improve with increase in V₂O₅ content from 0.5 to 1 wt % (comparing Fig. 4 (e) with Fig. 4 (c) - both samples sintered at 960°C, 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 BiNbO₄ ceramics as discussed in next section (section 3.7). The study of 16 observations gives appreciable R² value of 0.96, whereas, for 22 observations the R² value drops to 0.89 (see Fig. 2).

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′ and Q/f show variation identical to the sintered density [6, 10, 12, 13-16]. Interestingly, it is observed that ε′ closely resemble the density profiles, whereas, Q/f show a slight departure from the density profile for all the samples studied. ε′ increases from ~ 23.8 at a sintered density of ~ 4.89 gm/cm³ to ~ 39.0 at sintered density of ~ 6.69 gm/cm³. In general for the range of experimental parameters studied it appears that, lower compaction pressures, lower wt % V₂O₅ addition, intermediate sintering temperature and time gives higher Q/f values. The Q/f values are getting most adversely affected by increase in amount of V₂O₅ addition. As the
amount of V<sub>2</sub>O<sub>5</sub> addition is increased from 0.25 to 1.5 wt % (with all other parameters constant), the Q<sub>rel</sub> 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') and quality factor (Q<sub>rel</sub>) values.](image)

4. Conclusions:

A reliable mathematical model for estimating the sintered density of BiNbO<sub>4</sub> ceramic compacts from the four important processing variables viz. compaction pressure, wt % V<sub>2</sub>O<sub>5</sub> 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,

\[ D = 1.805898 \times 10^{-3} \times \text{F}_{V_2O_5}^{-0.089701} \times \text{W}_{V_2O_5}^{0.02514} \times \text{T}_{V_2O_5}^{-0.130327} \times \text{H}_{V_2O_5}^{0.02512} \]

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

\[ D = 1.873219 \times 10^{-3} \times \text{F}_{V_2O_5}^{-0.089701} \times \text{W}_{V_2O_5}^{0.02514} \times \text{T}_{V_2O_5}^{-0.130327} \times \text{H}_{V_2O_5}^{0.02512} \]

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 0.02777 % variation in the sintered density, which is insignificant. Decrease of R<sup>2</sup> 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<sub>4</sub> 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<sub>rel</sub> values.

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References