Journal of ELECTRONIC MATERIALS, Vol. 36, No. 10, 2007
DOI: 10.1007/s11664-007-0271-9

Regular Issue Paper

Regression Analysis for Complex Doping of X8R Ceramics Based on Uniform Design

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Regression analysis based on uniform design was introduced as a new approach for designing $BaTiO_3$-based X8R ceramics. The amounts of Nb_2O_5, Nd_2O_3, $Zn_{0.8}Mg_{0.2}TiO_3$ (ZMT), and magnesium lithium borosilicate (MLBS) were the four investigated factors with respect to the dielectric constant at room temperature (ε) and temperature-capacitance characteristics (TCC) at 125°C ($TCC_{125°C}$) and $TCC_{150°C}$. Experiments were designed according to the uniform design with four factors for each at twelve levels. For each response, the second-order polynomial equations were obtained by multiple regression analysis. As a result, the empirical mathematical models could successfully predict the experimental results with very good accuracy. Finally, based on optimization strategy, we succeeded in producing lead-free X8R ceramics with various dielectric constants ranging from 1500 to 3300, which is promising for developing X8R MLCC with different capacities.

Key words: Dielectric properties, barium titanate, regression analysis, uniform design, X8R ceramics

INTRODUCTION

In recent years, multilayer ceramic capacitors (MLCC) have been applied to the electronic engine control (EEC) modules. These modules are subjected to high temperatures ranging from –20°C in winter to approximately 150°C in summer. Conventional ceramic compositions satisfying X7R characteristics ($\Delta C/C = \pm 15\%$ or less at –55°C to +125°C) cannot be employed in such electronic apparatus. Therefore, much attention has been paid to MLCC satisfying X8R specifications (–55°C to 150°C, $\Delta C/C_{25°C} = \pm 15\%$ or less).[1,2]

Tetragonal barium titanate ($BaTiO_3$, BT) is a well-known material for MLCC because of its high dielectric constant at room temperature. However, the permittivity of pure BT ceramics shows noticeable changes as the temperature changes, particularly when approaching the Curie temperature (T_c about 125°C). Thus, $BaTiO_3$ is modified with Nb_2O_5-Co_3O_4, Nb_2O_5-ZnO, Bi_2O_3-TiO_2, PbO-TiO_2, etc. to achieve high permittivity and smooth capacitance–temperature characteristics. It was suggested that the temperature-stable characteristics were attributed either to a fine-grained microstructure[3,4] or to the presence of core-shell grains. However, these $BaTiO_3$-based materials still suffer from significant limitations such as high sintering temperature (generally more than 1280°C), high dielectric loss, low resistivity, hazardous heavy metals, etc.[5] Accordingly, there is great demand to research an excellent system for X8R MLCC. In this study, microwave dielectric material $Zn_{0.8}Mg_{0.2}TiO_3$ (ZMT) obtained by the conventional solid-state reaction was added to $BaTiO_3$ to improve the temperature–capacitance characteristic. At the same time, magnesium lithium borosilicate glass (MLBS) synthesized by the Sol-Gel method was used as sintering aids.

In general, X8R compositions are optimized by varying the content of one experimental dopant while fixing the remaining dopants contents.

(Received January 31, 2007; accepted May 31, 2007;

Unfortunately, this process is time-consuming. Furthermore, the dielectric properties are possibly influenced by the interaction of different experimental dopants. Thus, experimental design-based approaches should be recommended for the optimization. But traditional designs such as factorial design or orthogonal array are impractical due to a large number of runs required to reach optimal results in our experiments. Hence, a type of design method called 'uniform design', proposed by Fang,[6,7] has been chosen for this study due to its advantages of space filling, robustness, multiple levels, and high manageability. Uniform design applies the experiments with many factors and levels. It is a space filling design and has a good robust performance because they spread the designs points uniformly in the design space. Regression analysis is used to derive a relationship that is believed to be uniformly applicable across the study area. In this paper, we examined the multiple regression relationships that existed in the independent variables (dosage of dopants) and the dependent variables (dielectric properties). An example with real data using regression analysis based on the uniform design is demonstrated.

In the present work, the objective was to obtain lead-free X8R materials with high performance by statistical evolution of experimental results. The experiments were carried out according to the uniform design, and MINITAB software was used for the regression analysis. The statistical calculation itself took only a few seconds.

EXPERIMENT

Preparation of ZMT

$Zn_{1-x}Mg_xTiO_3$ is a kind of useful microwave dielectric with low sintering temperature and promising microwave properties.[8] $ZnTiO_3$ has a perovskite-type oxide structure and could be a useful candidate for microwave materials. But the preparation of pure $ZnTiO_3$ from a mixture of ZnO and TiO_2 has not succeeded because the compound decomposes into Zn_2TiO_4 (cubic) and rutile at about 945°C is as follows[9,10]:

$$2ZnTiO_3(\text{hexagonal}) \xrightarrow{\geq 945^\circ C} Zn_2TiO_4(\text{cubic}) + TiO_2(\text{rutile})$$

$MgTiO_3$ can depress the above reaction and favor to form the hexagonal single-phase $Zn_{1-x}Mg_xTiO_3$ by a conventional solid-state reaction.[8] The characterization of $Zn_{1-x}Mg_xTiO_3$ was later clarified by Yee-Shin Chang.[11]

The $Zn_{0.8}Mg_{0.2}TiO_3$ composition used in our experiment was prepared using the conventional solid-state reaction, reagent-grade ZnO, rutile TiO_2, and MgO powders were used. After ball milling for 18 h, the mixed powders were sintered at 900°C for 2 h, and the resulting dopants were denoted as ZMT.

Preparation of MLBS

Analytical grade ethanol, ethyl silicate, nitric acid, polyethylene glycol 10,000, light magnesium carbonate, Li_2CO_3, and H_3BO_3 were used as the raw materials. First, light magnesium carbonate, Li_2CO_3 and a small amount of polyethylene glycol 10,000 were dissolved in HNO_3 solution; then the H_3BO_3 was dissolved in hot water (about 90°C) and mixed with the above solution to form an inorganic solution. Second, the ethanol and ethyl silicate were mixed together to form an organic solution. When the inorganic solution was heated to 90°C and became condensed, the organic solution was poured into it, and by vigorous and continuous stirring, a sol was achieved. The molar ratio of Mg, Li, B, and Si elements in the sol is 2:1:2:5. One day later, the transparent sol was transformed to a gel at 50°C. The gel was then poured in a glass dish and kept at 85°C for 5 days so as to get xerogels. The obtained xerogels were calcined at 800°C, and the resulting dopants were then denoted as MLBS.

Preparation of $BaTiO_3$ Ceramics

Hydrothermal fine-grained $BaTiO_3$ (0.4 μm) powders and Nb_2O_5, Nd_2O_3, ZMT, and sintering aid MLBS were used as the starting materials. The mixed powders were ball-milled in deionized water for 8 h. The prepared ceramic powders were granulated using 5 wt.% polyvinyl alcohol (PVA) solution and pressed to 10-mm-diameter and 1-mm-thick disks. The disks were finally fired at 1,200°C for 2 h in air.

After samples were fired at 800°C with Ag electrodes on both surfaces, the dielectric properties of samples were measured from –55°C to 150°C with an impedance analyzer LCR (HP4284A) at 1 KHz and 1 V rms. Insulation resistance was measured at room temperature on a megohmmeter (HM2672A) under 100 V DC.

RESULTS AND DISCUSSION

Experimental Results Based on Uniform Design

When the $BaTiO_3$ amount was equal to 100 g, there were four controllable variables to be considered: percentages of Nb_2O_5, Nd_2O_3, ZMT, and MLBS, denoted as X_1, X_2, X_3, and X_4, respectively. Experience showed that X_1, X_2, X_3, and X_4 in percentages should be within the following ranges:

$$\begin{aligned} 0.3 \leq X_1 \leq 4.7, \quad 0.05 \leq X_2 \leq 0.93, \\ 0.1 \leq X_3 \leq 3.4, \quad 0.05 \leq X_4 \leq 0.82 \end{aligned} \tag{1}$$

The present experiment was performed with 12 levels in X_1 to X_4. A comprehensive test for this setup requires performance of at least 12^4 = 20,736 times,

Table I. Experimental Data of X8R Ceramics Based on Uniform Design

						TCC/%				
Number	**Nb_2O_5/g**	**Nd_2O_3 /g**	**ZMT/g**	**MLBS /g**	**ε**	**−55°C**	**125°C**	**150°C**	**tgδ/%**	**ρ/10^{11} Ω · cm**
01	1.9	0.69	1	0.05	2804	−2.8	2.3	−12.8	0.88	3.2
02	1.5	0.13	0.1	0.54	3020	−9.3	7.6	−9.0	0.79	2.5
03	0.7	0.77	2.2	0.75	3514	−17.8	−17.1	−37.1	1.16	3.3
04	1.1	0.53	3.4	0.26	2955	−3.8	−31.4	−40.9	0.93	7.6
05	3.1	0.45	0.7	0.82	2492	−6.3	5.1	−6.2	0.63	12
06	2.3	0.93	2.8	0.47	1770	6.8	−5.8	−16.6	0.63	20
07	2.7	0.05	1.9	0.19	1952	−9.9	13.3	−4.4	0.73	15
08	4.7	0.61	1.6	0.61	1406	−4.5	1.8	−5.4	0.54	70
09	3.9	0.85	0.4	0.33	2685	−7.5	2.0	−17.7	0.94	1.2
10	4.3	0.37	2.5	0.12	1567	−6.9	7.4	−5.6	0.64	2.8
11	3.5	0.21	3.1	0.68	1485	−6.4	6.2	−7.1	0.58	3.5
12	0.3	0.29	1.3	0.4	3534	−22.5	16.2	−26.1	1.16	2.6

which is impractical to be actualized. The uniform design allows the maximum possible number of levels for every factor, and the number of levels can be equal to that of experiment runs. A uniform design U_{12} (12^{12}) with 12 runs was used. The setup and the observed response are shown in Table I. Figures 1 and 2 depict ε–T curves and $\Delta C/C_{25°C}$–T curves of all samples, respectively.

Regression Analysis

Since the TCC at the low-temperature side satisfied the X8R specification, the response functions, including dielectric constant at room temperature (ε), $TCC_{125°C}$, and $TCC_{150°C}$ need to be considered; these are denoted as Y_1, Y_2, and Y_3, respectively. These values were related to the coded variables calculated by the second-order polynomial in Eq. 2 as follows:

$$Y_k = A_0 + \sum_{i=1}^{4} A_i X_i + \sum_{i=1}^{4} A_{ii} X_i^2 + \sum_{i=1}^{4} \sum_{i<j} A_{ij} X_i X_j + \theta \tag{2}$$

where Y_k (k = 1, 2, 3) is the predicted response, A_0, A_i, A_{ii}, and A_{ij} are the regression coefficients, and X_i and X_j are the independent variables. A stepwise regression method in the software package MINITAB was used to fit the data for Y_1, Y_2, and Y_3 in Table I. The Student t-value and p-value could judge the significance of all terms in the polynomial statistically. The corresponding variables will be more significant if the absolute t-value becomes larger and the p-value becomes smaller.[12] The results are expressed in the form of Eq. 2 as presented in Table II.

The advantages or disadvantages of these models can be determined with the distribution of experimental values and comparison of the determination coefficient (R^2 > 80%). As shown in Table II, all of the regression coefficients (R^2) which described the prediction models were larger than 0.9, indicating that the model explained more than 90% of variability in responses, and the predicted model seemed to reasonably represent the observed values. Thus, the response was sufficiently explained by the model. A highly significant (p < 0.05) coefficient and F test for these models also indicated that the response could be estimated by these terms.

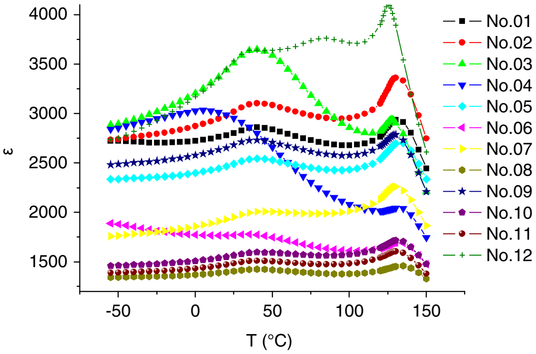


Fig. 1. ε–T curves of different ceramics.

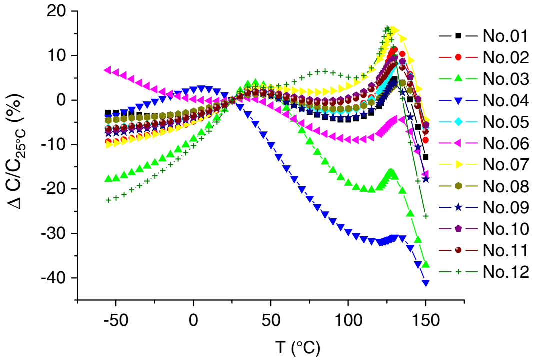


Fig. 2. $\Delta C/C_{25°C}$–T curves of different ceramics.

Table II. Regression Equations of Experimental Parameters

$\varepsilon(Y_1)$	$\varepsilon = 5817–1096X_1 – 1118X_3 – 4357X_4 + 119X_1X_1 + 317X_3X_3 + 2835X_4X_4 – 683X_2X_3 + 3797X_2X_4$	Eq. 3
	$S = 70.2 \quad R^2 = 99.8\% \quad F = 166.19 > F_{0.01}(8,3) = 27.49 \quad p = 0.001$	
$\mathrm{TCC}_{125°\mathrm{C}}(Y_2)$	$\mathrm{TCC}_{125°\mathrm{C}} = 32.8 – 8.11X_1 – 50.3X_2 – 1.68X_1X_1 – 4.82X_3X_3 + 16.9X_1X_2 + 5.86X_1X_3$	Eq. 4
	$S = 5.64 \quad R^2 = 91.8\% \quad F = 9.34 > F_{0.05}(6,5) = 5.0 \quad p = 0.013$	
$\mathrm{TCC}_{150°\mathrm{C}}(Y_3)$	$\mathrm{TCC}_{150°\mathrm{C}} = –24.1 + 13.0X_1 – 9.27X_2 – 2.54X_1X_1 – 3.11X_3X_3 + 3.24X_1X_3$	Eq. 5
	$S = 2.99 \quad R^2 = 97.0\% \quad F = 38.18 > F_{0.01}(5,6) = 8.8 \quad p = 0.0002$	

Discussion

It has been reported that temperature dependence of capacitance change at the high-temperature side will be shifted towards the negative direction as MLCC dielectric layers become thinner.[13] This phenomenon was called the 'clockwise effect'. Thus, the materials may not be suitable for MLCC application even though they can fit the EIA X8R specification in a thick-disc form if their $\mathrm{TCC}_{150°\mathrm{C}}$ values are close to −15%. So we must enhance the $\mathrm{TCC}_{150°\mathrm{C}}$ of BT ceramics to meet the required dielectric temperature characteristics of MLCC.

Using partial differentiation for Eq. 5, the predicted maximum of $\mathrm{TCC}_{150°\mathrm{C}}$ can be optimized as follows:

$$\frac{\partial Y_3}{\partial X_1} = 13.0 - 2.54 \times 2X_1 + 3.24X_3 = 0 \tag{6}$$

$$\frac{\partial Y_3}{\partial X_3} = 3.11 \times 2X_3 + 3.24X_1 = 0 \tag{7}$$

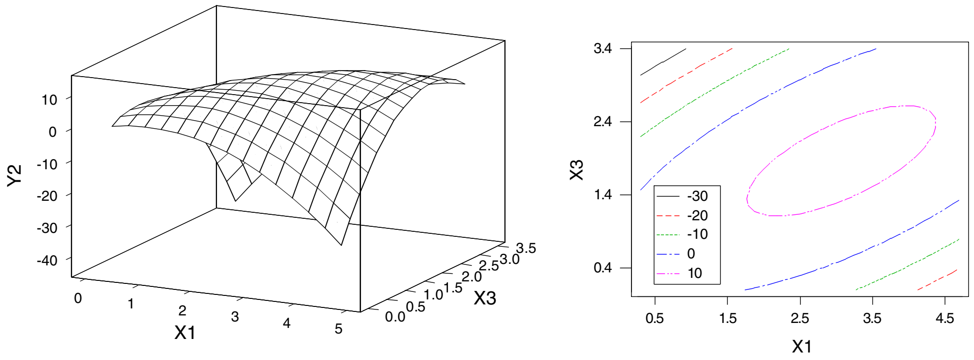
From the results of Eqs. 1, 5, 6, and 7, it could be deduced that the predicted $\mathrm{TCC}_{150°\mathrm{C}}$ could reach a maximum of 0.35 at:

$$X_1 = 3.83, \quad X_2 = 0.05, \quad X_3 = 2.00 \tag{8}$$

But we cannot choose the condition of Eq. 8 to optimize our dielectric materials because the remaining response functions of ε and $\mathrm{TCC}_{125°\mathrm{C}}$ also need to be considered to achieve desired properties.

The relationship between $\varepsilon(Y_1)$ and $\mathrm{Nb_2O_5}(X_1)$ derived from Eq. 3 shows that the value of dielectric constant at room temperature declined as the volume of $\mathrm{Nb_2O_5}$ increased in the range of 0∼4.6. This phenomenon was due to the increase of paraelectric phase in the so-called grain core and grain shell structures.[4] Therefore, the dosage of $\mathrm{Nb_2O_5}$ must be correct in order to get high-capacity ceramics.

The regression model of Eq. 4 allows prediction of the effects of the four parameters on the $\mathrm{TCC}_{125°\mathrm{C}}$. Two variables within the experimental range were depicted in three-dimensional surface plots while the other two variables were kept constant. Figure 3 shows 3D graphics and contour map of the effects of the two independent variables on the response function $\mathrm{TCC}_{125°\mathrm{C}}(Y_2)$, namely, the interaction effects of $\mathrm{Nb_2O_5}$ (X_1) and ZMT (X_3). The tortoise surfaces showed the dramatically complex interaction between X_1 and X_3. It is noted that we need more ZMT dopant to reach the maximum Y_2 when $\mathrm{Nb_2O_5}$ concentration increases. Therefore, it is



Hold values: x2: 0.49

Hold values: x2: 0.49

Fig. 3. Three-dimensional graphic surface and contour plots for the effects of X_1 and X_3 on Y_2.

Table III. X8R Ceramic Formulas Optimized by Regression Analysis

					Y_1		Y_2		Y_3	
Number	**X_1/g**	**X_2/g**	**X_3/g**	**X_4/g**	**TV**	**CI**	**TV**	**CI**	**TV**	**CI**
13	1.7	0.3	0.3	0.2	3399	(3232, 3564)	10.2	(1.3, 17.2)	−10.7	(−14.8, −6.9)
14	2.6	0.6	1.1	0.8	2626	(2433, 2817)	7.5	(−0.6, 15.4)	−7.5	(−11.7, −3.6)
15	2.4	0.4	1.0	0.4	2116	(1923, 2307)	9.0	(1.4, 16.5)	−6.6	(−10.5, −2.9)

TV theory value, *CI* confidence interval.

Table IV. Experimental Data of Optimized X8R Ceramic Formulas

						TCC/%				
Number	**Nb_2O_5/g**	**Nd_2O_3 /g**	**ZMT/g**	**MLBS/g**	**ε**	**–55°C**	**125°C**	**150°C**	**tgδ/%**	**$\rho/10^{11}\Omega\cdot$cm**
13	1.7	0.3	0.3	0.2	3366	−12.0	12.6	-9.8	0.98	2.5
14	2.6	0.6	1.1	0.8	2655	−8.9	8.3	−8.0	0.65	12
15	2.4	0.4	1.0	0.4	2104	−8.7	9.6	−7.1	0.73	5.6

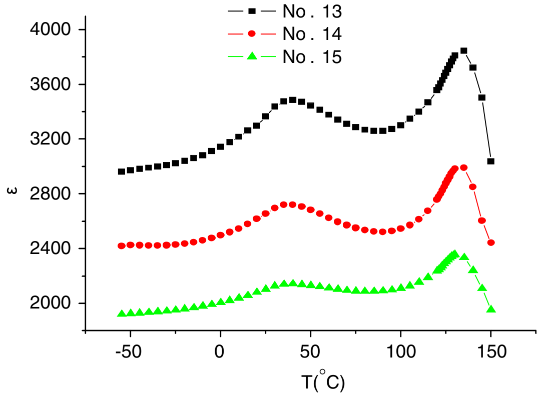


Fig. 4. ε–T curves of optimized X8R ceramics.

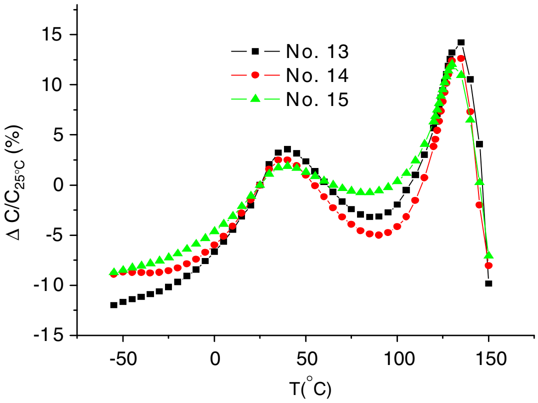


Fig. 5. $\Delta C/C_{25^\circ C}$–T curves of optimized X8R ceramics.

reasonable to conclude that greater Y_2 could be obtained when ZMT concentration is proportional to the dosage of Nb_2O_5.

Optimization

The regressed equations are convenient to derive the optimized process conditions for various response functions, here are the dielectric constants, $TCC_{125^\circ C}$ and $TCC_{150^\circ C}$. Based on the results discussed above, there are a number of combinations of variables that could give diverse levels of dielectric constant of X8R ceramics as shown in Table III. Table IV depicts the experimental data of the optimized composition. Figures 4 and 5 exhibit the dielectric temperature characteristics and temperature–capacitance change of optimized X8R materials, respectively.

It could be found from Tables III and IV that the predicted theory values and experimental results after optimization were in good agreement. The largest permittivity of X8R ceramics as shown in Table I before optimization was 3020 (No. 02). After optimization, the dielectric constant was raised up to 3366 (No. 13) in the composition of 100 g $BaTiO_3$, 1.7 g Nb_2O_5, 0.3 g Nd_2O_3, 0.3 g ZMT, and 0.2 g MLBS. Moreover, X8R dielectric composites with different dielectric constants were obtained to develop X8R MLCC with different capacities. The dielectric constants are close to 1500 (No. 08, No. 10, and No. 11), 2000 (No. 07 and No. 15), 2500 (No. 05 and No. 14), 3000 (No. 02), and 3300 (No. 13). It can be concluded that the regression analysis based on uniform design is an effective method to design $BaTiO_3$-based X8R ceramics.

CONCLUSIONS

The regression analysis method based on uniform design was successfully applied to develop $BaTiO_3$-based X8R ceramics. The dielectric constants, $TCC_{125^\circ C}$ and $TCC_{150^\circ C}$, can be improved by the results of uniform design, especially by the second-order polynomial models for various response functions. It has been found that the experimental results were in good agreement with the predicted values derived from regression equations. By using partial differentiation, surface/contour plots, and the established model, optimized proportion conditions were obtained at given ranges to achieve lead-free X8R ceramics with various dielectric constants ranging from 1500 to 3300. It is hoped that the regression analysis method based on uniform design conducted in this study shall be applied not only to the X8R ceramic optimization but also to other multi-doping material system optimizations.

ACKNOWLEDGEMENT

We acknowledge helpful discussions with Professor Wei He of the University of Electronic Science and Technology of China.

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