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Modeling of room temperature resistivity and grain size for polycrystalline $(Ba_{0.8-x}Sr_{0.2})Y_xTiO_3$ by response surface method

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The effect of yttrium content and heat-treatment processes on the room temperature resistivity and grain size of polycrystalline $(Ba_{0.8-x}Sr_{0.2})Y_xTiO_3$ ceramics has been systematically studied using response surface method. The yttrium content, sintering temperature and cooling rate were taken as experimental factors. The modeling equations for the room temperature resistivity and grain size were obtained by using three experimental factors and measured values of the room temperature resistivity and grain size. The yttrium content has larger effect than other experimental factors on the room temperature resistivity and grain size. The validity of polynomial equations was confirmed by comparing the predicted values with those obtained from additional experiments.

1. Introduction

$BaTiO_3$ ceramics having the properties of positive temperature coefficient of resistivity (PTCR) have been widely investigated owing to their ferroelectric and dielectric properties. Nevertheless, the factors related to PTCR properties are still of great concern, because the PTCR properties can be controlled by various factors such as dopant concentration, sintering temperature, sintering time and cooling rate, etc. [1]. These factors are further found to cause the change of the PTCR properties of $BaTiO_3$ ceramics through the variation of the room temperature resistivity and microstructure.

In particular, the main factors which influence the room temperature resistivity of $BaTiO_3$ ceramics were found to be dopant concentration [2], sintering temperature [3] and cooling rate [4]. However, it is difficult to know the relative importance of each factor, which contributes to lowering the room temperature resistivity. Consequently, selecting the condition for optimum of the room temperature resistivity is complex. The most general approaches for optimization of the process conditions are commonly based on simple univariate optimization process, e.g., an examination of the room temperature resistivity according to the variation of a single factor. However, such an univariate optimization would not be effective in some cases, therefore a multivariate simultaneous approach is desirable [5, 6]. The response surface method (RSM) is one of choices for the systematic optimization, but has not used except in a few related works such as the optimization of supercritical fluid extraction [7] and modeling of high pressure chemical vapor deposited blanket tungsten [8] and GaAs etching using ion beams [9].

In this study, RSM has been applied to the simultaneous optimization of the room temperature resistivity and grain size for $(Ba_{0.8-x}Sr_{0.2})Y_xTiO_3$ ceramics. The yttrium content, sintering temperature and cooling rate were chosen as experimental factors, because these factors can largely influence the room temperature resistivity and grain size. The modeling equations of the room temperature resistivity and grain size for polycrystalline $(Ba_{0.8-x}Sr_{0.2})Y_xTiO_3$ ceramics were obtained and validated.

2. Experimental

The $(Ba_{0.8-x}Sr_{0.2})Y_xTiO_3$ ceramics were obtained by calcination of yttrium doped barium strontium titanyl oxalates ($(Ba_{0.8-x}Sr_{0.2})Y_xTiO(C_2O_4)_2 \cdot 4H_2O$), which were prepared by an oxalate coprecipitation method as described in a previous paper [10]. In brief, an aqueous solution of oxalic acid and nitrate solutions of barium, strontium, yttrium and titanium were used as starting materials. A titanyl oxalate solution was prepared by adding a titanyl nitrate solution slowly to the solution of oxalic acid. The pH of titanyl oxalate solution was adjusted to 4.5 by addition of aqueous ammonium hydroxide. The titanyl oxalate solution was instantaneously added to the mixed solution of barium, strontium and yttrium and then stirred at 1200 rpm for 3 h. The quantity of oxalic acid was 20% in excess over the stoichiometric amount required to

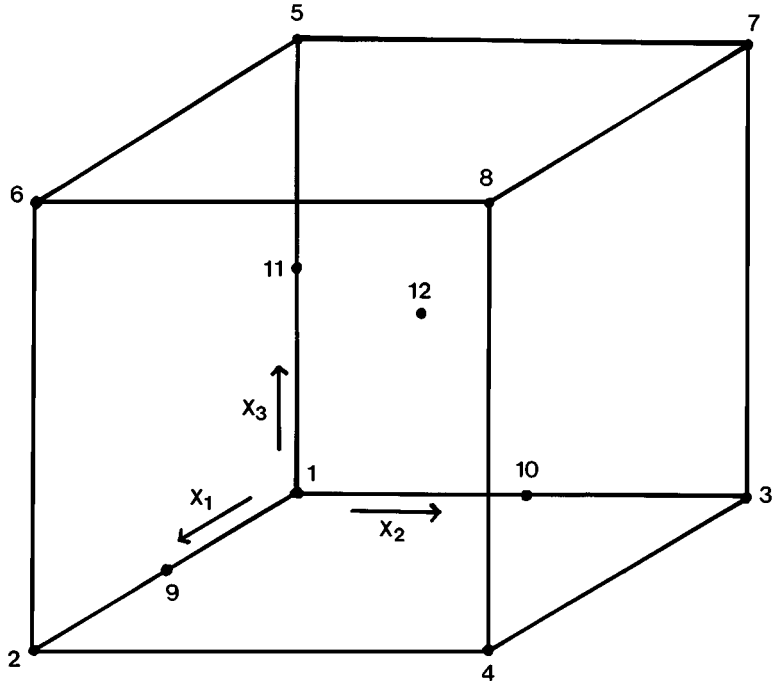

Figure 1 A schematic diagram of twelve experimental points on a cube.

produce oxalate precipitates. The oxalate precipitates were filtered and washed with chilled water and finally with acetone. The precipitates were dried at 100 °C for 12 h and then calcined at 900 °C for 2 h in air to produce $(Ba_{0.8-x}Sr_{0.2})Y_xTiO_3$ powders. The ratios of (barium + yttrium)/titanium and strontium/titanium were adjusted to 0.8 and 0.2, respectively. The yttrium content was chosen as 0.1, 0.3 and 0.5 mol %. The dried powders were pressed into disks and the green bodies sintered at temperatures of 1375, 1400 and 1425 °C. The cooling rate was also chosen as 1.0, 2.5 and 4.0 °C/min. The disks were coated with nickel paste and the resistance of each sample at room temperature was measured with a digital multimeter. The room temperature resistivity was calculated from the measured resistance and area and thickness of the disk. The microstructure of each sample was observed with an optical microscope and the grain size was measured by the linear intercept method [11].

The cubic diagram for experimental design is shown in Fig. 1. The three axes of the cube, X_1, X_2 and X_3, represent the yttrium content, sintering temperature and cooling rate, respectively. Twelve experiments as shown in Fig. 1 were selected to be the conditions that correspond to the eight apex points of the cube, three midpoints on the axes and the cube center.

TABLE I Actual and coded experimental factors

Factor		Actual values (coded values) (0)	(0.5)	(1.0)
Yttrium content (mol %)	X_1	0.1	0.3	0.5
Sintering temperature (°C)	X_2	1375	1400	1425
Cooling rate (°C/min)	X_3	1.0	2.5	4.0

TABLE II Twelve experimental conditions coded and measured values of room temperature resistivity and grain size

Experimental No.	X_1	X_2	X_3	Room temperature resistivity log ρ (Ω·cm)	Grain size (μm)
1	0	0	0	4.4	6.3
2	1	0	0	8.8	3.0
3	0	1	0	3.2	8.3
4	1	1	0	7.5	4.0
5	0	0	1	3.0	5.8
6	1	0	1	7.7	2.7
7	0	1	1	2.4	6.5
8	1	1	1	4.1	3.1
9	0.5	0	0	3.5	6.0
10	0	0.5	0	3.4	7.3
11	0	0	0.5	3.1	6.0
12	0.5	0.5	0.5	2.7	6.0

3. Results and discussion

It is convenient to deal not with the actual values but with coded values instead. The ranges for the actual and coded values of X_1, X_2 and X_3 are indicated in Table I. The measured values of the room temperature resistivity and grain size obtained from twelve experiments coded are listed in Table II. The modeling procedure adopted in this study was a modified scheme of the procedure for the optimization of supercritical fluid extraction [7]. The general form for such a model is given by Equation 1.

$$Z = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_2 + b_5X_2X_3 + b_6X_1X_3 + b_7X_1^2 + b_8X_2^2 + b_9X_3^2 + b_{10}X_1X_2X_3 \quad (1)$$

where, Z is predicted response values such as room temperature resistivity or grain size. The X_1, X_2 and X_3 are the coded values of the three experimental factors such

TABLE III Coefficients of modeling equations for room temperature resistivity and grain size

Coefficient	Room temperature resistivity	Grain size
b_0	4.03	6.35
b_1	−5.75	1.85
b_2	−0.53	1.65
b_3	−1.77	−0.95
b_4	−0.23	−0.95
b_5	0.25	−1.23
b_6	0.10	0.18
b_7	10.4	−5.18
b_8	−0.45	0.27
b_9	0.92	0.43
b_{10}	−2.73	0.58
R^2	0.97	0.99

R^2 are multiple correlation coefficients of modeling equations.

as the yttrium content, sintering temperature and cooling rate. The polynomial coefficients, $b_0, b_1, \ldots, b_9$ and b_{10}, were obtained from the coded experimental factors and the measured values of the room temperature resistivity and grain size obtained from twelve experiments. The calculated coefficients of modeling equations for the room temperature resistivity and grain size are listed in Table III. Since the multiple correlation coefficient R^2 was moderately high as 0.97 and 0.99 (1.0 is the best possible) for the room temperature resistivity and grain size, respectively. The models for the room temperature resistivity and grain size are considered to be accurate representations of the measured values.

3.1. Room temperature resistivity

In the coefficients of polynomial equation for the room temperature resistivity, the coefficient of X_1 is larger than that of X_2 and X_3. Therefore, the yttrium content (X_1) had larger effect than other experimental factors on the room temperature resistivity. The contribution of X_1 to the room temperature resistivity was considered by changing of the X_2 and X_3 values stepwise from 0 to 1. A minimum room temperature resistivity appeared at X_1 from 0.28 to 0.40. The room temperature resistivity decreased as the yttrium content increased to 0.21 mol % (X_1 of 0.28). Whereas the room temperature resistivity increased with versus the yttrium content above 0.26 mol % (X_1 of 0.40). These results are close to those reported by Chen and Smyth [12]. They suggested that donor dopants such as yttrium or lanthanum contributed to the transition from an electron compensation to a vacancy compensation at minimum room temperature resistivity. Our results indicate that the electron compensation is predominant when the yttrium content is below 0.21 mol % (X_1 of 0.28), whereas the vacancy compensation is predominant above the yttrium content of 0.26 mol % (X_1 of 0.40).

In case of X_2 (sintering temperature) and X_3 (cooling rate), the room temperature resistivity decreased smoothly with increasing of X_2 and X_3. The results concerning the variation of the room temperature resistivity versus sintering temperature agree with the results by Cheng *et al.* [13], who reported that the room temperature resistivity of $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics decreased with increasing the sintering temperature. Chen and Tseng [4] reported the effect of the cooling rate on the room temperature resistivity of lanthanum doped $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics. They observed that the faster the cooling rate, the lower the room temperature resistivity is, in agreement with our results obtained by response surface method.

Fig. 2 shows the contour map which indicates the effects of the yttrium content and cooling rate on the

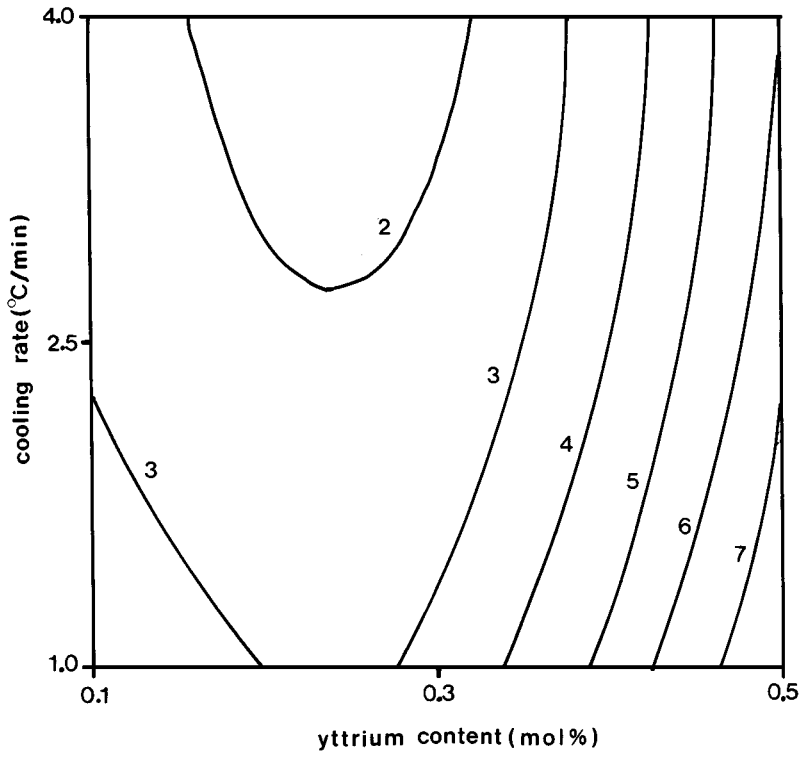

Figure 2 A contour map of room temperature resistivity at sintering temperature of 1400 °C.

room temperature resistivity after sintering at 1400 °C (X_2 of 0.50). As the yttrium content X_1 increased to 0.24 mol %, the room temperature resistivity decreased. A minimum of the room temperature resistivity appeared at the yttrium content of 0.24 mol % (X_1 of 0.34), and the room temperature resistivity increased with the yttrium content. The interval of the room temperature resistivity in the yttrium content of 0.30–0.50 mol % (X_1 range of 0.5–1.0) is narrower than that in the yttrium content of 0.10–0.30 mol % (X_1 range of 0.0–0.50) as shown in the contour map of Fig. 2. This means that the yttrium content (X_1) in the range of 0.30–0.50 mol % is much sensitive to the room temperature resistivity.

3.2. Grain size

The coefficient of X_1 in the polynomial equation for the grain size as listed in Table III is also larger than those of X_2 and X_3. This implies that the effect of the yttrium content on the grain size is greater than any other experimental factors, sintering temperature and cooling rate. The grain size had a large value at the yttrium content of 0.22 mol % (X_1 of 0.30) and rapidly decreased as the yttrium content increase beyond 0.30. This result is close to the variation reported by Daniel [14], who suggested that the grain growth inhibited by the donor ions at the grain boundaries during the sintering process. The X_2 (sintering temperature) and X_3 (cooling rate) affected the grain size inversely, that is, the grain size increased smoothly when the sintering temperature increased and when the cooling rate decreased in the range investigated.

The contour map for the grain size is plotted versus variations of the yttrium content and of the cooling rate at the sintering temperature of 1400 °C (X_2 of 0.50) as shown in Fig. 3. The grain size was almost uniform in the yttrium content from 0 to 0.22 mol % (X_1 from 0 to 0.30), and decreased rapidly with increasing the yttrium content. The values of the grain size in the range of the yttrium content from 0.30 to 0.50 mol % had a narrow interval like the room temperature resistivity. The room temperature resistivity increased and the grain size decreased for a same cooling rate above the yttrium content of 0.24 mol % (X_1 of 0.34) as shown in Figs 2 and 3. This implies that the grain size decreases as the yttrium content increases due to grain growth inhibition [15, 16] above the yttrium content of 0.24 mol %.

TABLE IV Comparison of measured and predicted values of room temperature resistivity and grain size

Experimental No.	Yttrium content (mol %)	Sintering temperature (°C)	Cooling rate (°C/min)	Room temperature resistivity log ρ (Ω·cm)		Grain size (μm)	
				Measured	Predicted	Measured	Predicted
a	0.3	1400	1.0	3.2	3.3	6.5	6.6
b	0.5	1400	1.0	8.0	8.2	3.7	3.4
c	0.1	1400	4.0	2.7	2.9	7.6	6.2
d	0.3	1400	4.0	2.4	1.9	6.0	5.7
e	0.5	1400	4.0	5.3	5.9	3.4	2.9

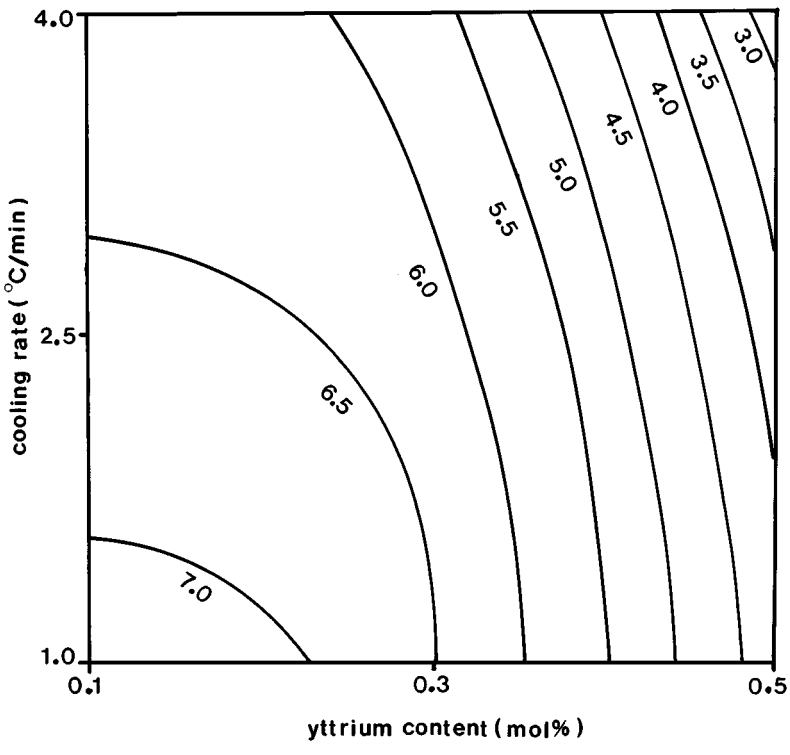

Figure 3 A contour map of grain size at sintering temperature of 1400 °C.

Five experiments were randomly selected to confirm the validity of polynomial equations for the room temperature resistivity and grain size. The measured and predicted values of the room temperature resistivity and grain size were measured by experiments and predicted from the polynomial equations, respectively. Reasonably good agreement (within $\pm 10\%$) was obtained between the measured and predicted values as listed in Table IV.

4. Conclusion

Modeling of room temperature resistivity and of grain size of polycrystalline $(Ba_{0.8-x}Sr_{0.2})Y_xTiO_3$ ceramics was investigated by response surface method. The yttrium content, sintering temperature and cooling rate were used as experimental factors. After comparison of the coefficients of the polynomial equations obtained, it is found that the yttrium content has larger effect than other experimental factors on the room temperature resistivity and grain size. The validity of the polynomial equations for the room temperature resistivity and grain size was confirmed by good agreement between the measured and predicted values.

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References

1. M. DROFENIK, A. POPOVIČ and D. KOLAR, *Ceram. Bull.* **63** (1984) 702.
2. P. BLANCHART, J. F. BAUMARD and P. ABELARD, *J. Amer. Ceram. Soc.* **75** (1992) 1068.
3. B. S. CHIOU, C. M. KOH and J. G. DUH, *J. Mater. Sci.* **22** (1987) 3893.
4. H. P. CHEN and T. Y. TSENG, *J. Mater. Sci. Lett.* **8** (1989) 1483.
5. D. L. MASSART, B. G. M. VANDEGINSTE, S. N. DEMING, Y. MICHOTTE and L. KAUFMAN, "Chemometrics: A Text Book" (Elsevier Science, New York, 1988) p. 255.
6. H. E. HILL and J. W. PRANE, "Applied Techniques in Statistics for Selected Industries" (John Wiley & Sons, New York, 1984) p. 369.
7. K. LI, C. P. ONG and S. F. T. LI, *J. Chromato. Sci.* **32** (1994) 53.
8. T. E. CLARK, M. CHANG and C. LEUNG, *J. Vac. Sci. Technol.* **B9** (1991) 1478.
9. J. M. VILLALVILLA, C. SANTOS and J. A. VALLES-ABARCA, *Vacuum* **47** (1996) 39.
10. T. NOH, S. KIM and C. LEE, *Bull. Kor. Chem. Soc.* **16** (1995) 1180.
11. L. H. VAN VLACK, "Elements of Materials Science and Engineering," 6th ed. (Addison-Wesley, New York, 1989) p. 218.
12. N. H. CHEN and D. M. SMYTH, *J. Amer. Ceram. Soc.* **67** (1984) 285.
13. H. F. CHENG, T. F. LIN, C. T. HU and I. N. LIN, *ibid.* **76** (1993) 827.
14. J. DANIEL, *Philips Res. Rep.* **31** (1976) 544.
15. K. H. YOON and K. B. PARK, *J. Appl. Phys.* **64** (1990) 2189.
16. H. NEMOTO and I. ODA, *J. Amer. Ceram. Soc.* **63** (1980) 398.

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