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Effects of Y_2O_3 addition on electrical conductivity and dielectric properties of Ba-excess $BaTiO_3$

Jong Han Kim, Seok Hyun Yoon[1], Young Ho Han*

Department of Materials Engineering, Sungkyunkwan University, 300 Chunchun-dong,
Jangan-gu, Suwon 440-746, Republic of Korea

Abstract

When Y^{3+} ion was substituted for Ti or Ba sites, the electrical conductivity of Ba-excess $BaTiO_3$ showed an acceptor or a donor doped behavior, depending on the Ba/Ti ratio. When Y_2O_3 was added to Ba-excess $BaTiO_3$ ($Ba/(Ti + Y) = 1$), the solubility and the primary occupation site of Y^{3+} ions were estimated from the electrical conductivity behavior. Y_2O_3 addition to Ba-excess $BaTiO_3$ showed a donor-doped behavior at low levels of Y_2O_3 ($\leq$1.0 mol%) and an acceptor-doped behavior at higher levels (>1.0 mol%). Grain growth inhibition occurred at 1.0–1.25 mol% Y when the sample was fired at 1300 °C. Effects of Y_2O_3 addition on electrical conductivity and dielectric characteristics of Ba-excess $BaTiO_3$ were dependent on the site occupancy of Y^{3+} ion in $BaTiO_3$ lattice.

Keywords: $BaTiO_3$; Yttrium; Electrical conductivity; Defects; Dielectric properties

1. Introduction

Rare-earth oxide is an important additive for manufacturing multi-layer ceramic capacitors (MLCC) with base metal electrodes. Trivalent rare-earth cations can behave as an acceptor or a donor, depending on the site they occupy and the resulting electrical properties will depend strongly on the size of the impurity cation.[1–5] Lewis and Catlow calculated the solution energies of several trivalent cations for $BaTiO_3$ and the addition of Y_2O_3 to $BaTiO_3$ with TiO_2 excess led to a donor doped behavior and with BaO excess to an acceptor doped behavior.[6] There have been reported A-site and B-site models to explain the improvement in the life time of Y_2O_3 doped $BaTiO_3$.[7,8] It is thus necessary to understand the defect chemistry of Y-doped $BaTiO_3$ and define the role of Y_2O_3. The ionic radius of Y^{3+} ion (0.107 nm) is almost halfway between Ba^{2+} ion (0.161 nm) and Ti^{4+} (0.06 nm) ion. Thus, Y^{3+} could be accommodated on either cation site in $BaTiO_3$ lattice, depending on the Ba/Ti ratio.[9] The previous work by Lee and Smyth has shown that Y^{3+} acted as an acceptor in the presence of excess BaO, but as a donor in the presence of excess TiO_2.[10] The equilibrium electrical conductivity would elucidate the defect chemistry of doped $BaTiO_3$.

The incorporation reaction of Y_2O_3 into $BaTiO_3$ lattices at $Ba/Ti > 1$ can be written as follows[11]:

$$2BaO + Y_2O_3 \rightarrow 2Ba_{Ba} + 2Y'_{Ti} + 5O_O + V_O^{\bullet\bullet} \qquad (1)$$

The defect notation is that proposed by Kröger and Vink.[12] Y'_{Ti} is compensated by the corresponding number of oxygen vacancies.[13] The un-doped $BaTiO_3$ inherently includes ~100 ppm of oxygen vacancies due to the background acceptor impurities such as Na^+, K^+, Fe^{3+}, Mg^{2+} and Al^{3+}.[14,15] Therefore, the conductivity of un-doped $BaTiO_3$ indicates that it has acceptor impurity, a small amount of yttrium doped Ba-excess $BaTiO_3$ may represents acceptor behavior. However, recent results showed that Y^{3+} acts a donor character when Y_2O_3 is added to the stoichiometric $BaTiO_3$ ($Ba/Ti = 1$) and a transition from semiconductor to insulator occurs since Y^{3+} ions can be substituted for Ba and Ti sites in Ba-excess $BaTiO_3$.[16,17]

In this paper, the effect of yttrium addition on electrical conductivity and dielectric properties of Ba-excess $BaTiO_3$ ($Ba/(Ti + Y) = 1$) has been studied. The site occupancy of yttrium will be discussed in terms of microstructure, conductivity behavior, lattice parameter, and TCC (temperature coefficient of capacitance).

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* Corresponding author. Tel.: +82 31 290 7392; fax: +82 31 290 7410.
E-mail address: yhhan@skku.ac.kr (Y.H. Han).

[1] Present address: Samsung Electromechanics Co. Ltd., Suwon, Republic of Korea.

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2. Experimental procedure

Samples were prepared by a conventional ceramic processing with $BaTiO_3$ (Sakai BT04), $BaCO_3$ (Aldrich) and Y_2O_3 (NanoTek). Initial powders were weighed according to the composition $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ $(0 \leq x \leq 0.03)$ and mixed in a planetary mill with zirconia balls in deionized water and then dried. The dried powders were calcined at 1000 °C for 3 h and milled for 1 h in a polyethylene jar. The milled powders were dried, granulated with PVA binder and formed into disk and rectangular bar shapes under a uniaxial pressure of 150 MPa. The organic binder was burned out at 400 °C in air with a slow heating rate. These specimens were sintered at 1300 °C for 3 h in air. The conductivity was measured at 1100 °C using a four-point dc method. The desired oxygen partial pressure was obtained by means of N_2–O_2 and CO–CO_2. The oxygen activity was measured using a closed-end tube of stabilized zirconia. The microstructure was studied by SEM (Hitachi) and X-ray powder diffraction (XRD) analysis was used to identify the lattice constant change of the sample using Rigaku X-ray diffractometer. TCC (temperature coefficient of capacitance) was measured using the capacitance measurement system (Saunders & Associate) with an LCR meter (HP4284A) in the temperature range from −55 to 150 °C at 1 kHz and 1 V.

3. Results and discussion

Y_2O_3 doped $BaTiO_3$ was studied with nominal compositions $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ where $x = 0.002$, 0.005, 0.0075, 0.01, 0.0125, 0.015, 0.0175, 0.02 and 0.03; all these samples were sintered at 1300 °C for 3 h in air. Fig. 1 shows a microstructure development of Y_2O_3 doped $BaTiO_3$. An effective grain growth inhibition took place at the doping level of 1.0 mol% Y (Fig. 1(d)). This result is similar to the Ti-excess $BaTiO_3$ samples doped with donor oxides and the window of grain growth inhibition threshold (GGIT).[16–19] Suppressed microstructures are shown in Fig. 1(d) and (f). An abnormal of grain growth appeared in the sample doped with 2.0 mol% Y in Fig. 1(e). Fig. 2 shows the variations of grain size as a function of nominal yttrium contents (x) in the $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ samples. This may be explained by the electrical conductivity. When the low level of Y_2O_3 was added to the stoichiometric $BaTiO_3$, the conductivity profile showed a donor-doped bevavior.[11] This result implies that at lower levels of Y_2O_3 addition, Y^{3+} ions effectively incorporate into Ba sites instead of Ti sites.

Fig. 3 shows the electrical conductivity profiles measured as a function of oxygen partial pressure at 1100 °C for the samples of $BaTiO_3 + x(BaO + 0.5Y_2O_3)$. When 0.2–1.0 mol% Y ($x = 0.002$, 0.005, 0.01) was added to Ba-excess $BaTiO_3$, the conductivity

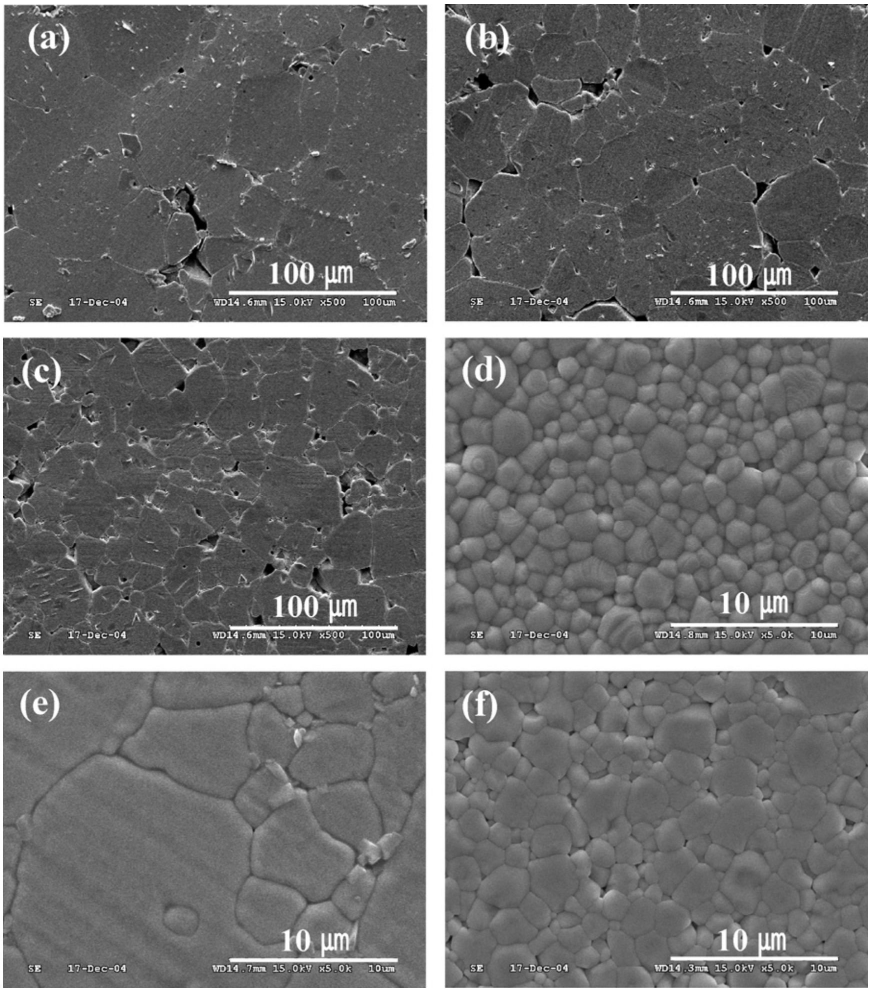

Fig. 1. SEM photomicrographs of $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ sintered at 1300 °C for 3 h: (a) $x = 0$, (b) $x = 0.002$, (c) $x = 0.005$, (d) $x = 0.01$, (e) $x = 0.02$, (f) $x = 0.03$.

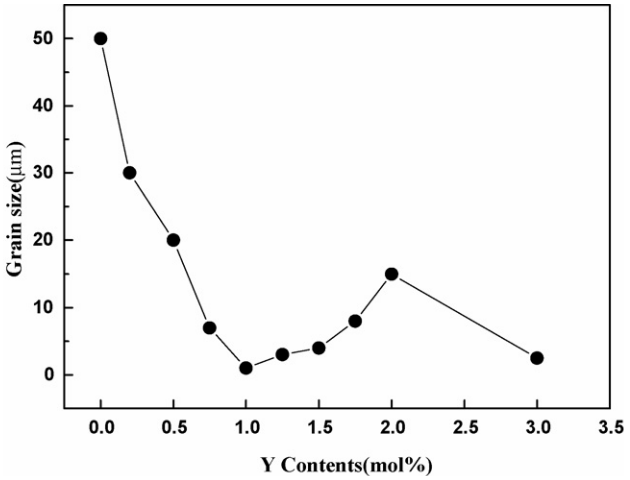

Fig. 2. Grain size as a function of nominal yttrium content (x) in $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ sintered at 1300 °C for 3 h.

profiles showed a donor doped behavior. When Y^{3+} ions are substituted for Ba sites as a donor, $Y_{Ba}^{\bullet}$ is compensated either by electrons or by cation vacancies. However, with 2.0 mol% Y ($x = 0.02$), the conductivity profile showed an acceptor doped behavior. When Y^{3+} was substituted for Ti sites as an acceptor, Y'_{Ti} is compensated by oxygen vacancies according to Eq. (1). Addition of yttrium as an acceptor also causes the conductivity minimum to be flattened.[13,20] The sample color changed from dark blue ($x = 0.002$, 0.005) to ivory hue as Y contents were increased to $x = 0.01$. The stoichiometric barium titanate is an insulator at room temperature. It becomes semiconducting when slightly doped with aliovalent ions such as trivalent cation donors. As the Y doping concentration exceeds a certain limit ($x = 0.005$), barium titanate changes into an insulator again because of the formation of ionic defects. Possible modes of incorporation reaction of Y^{3+} ions into Ba sites in $BaTiO_3$ are as follows:

$$Y_2O_3 + 2TiO_2 \rightarrow 2Y_{Ba}^{\bullet} + 2Ti_{Ti} + 6O_O + 1/2O_2 + 2e' \quad (2)$$

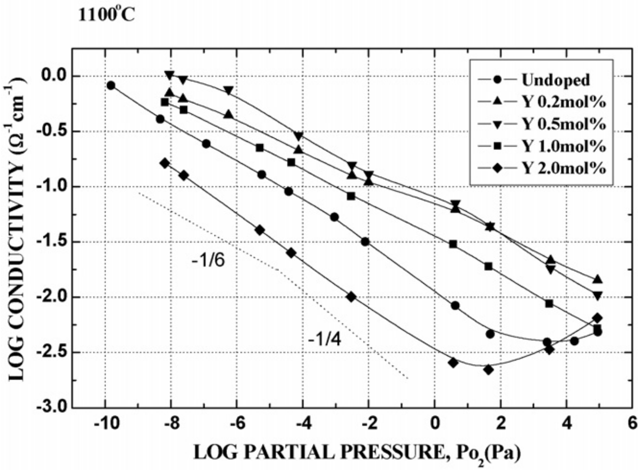

Fig. 3. Electrical conductivity at 1100 °C of $BaTiO_3$ doped with yttrium with $Ba/(Ti + Y) = 1.00$.

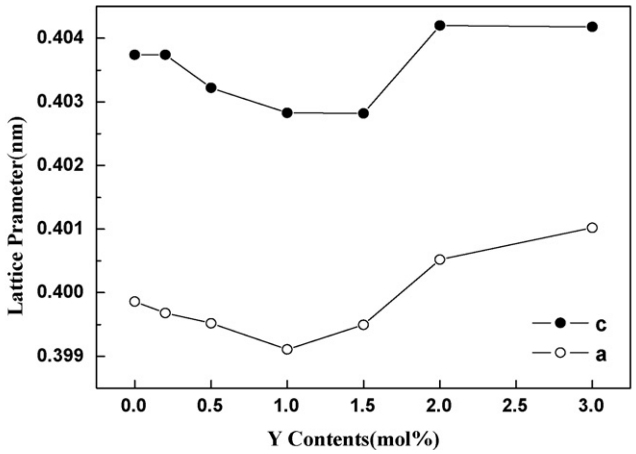

Fig. 4. Lattice parameter a and c as a function of nominal yttrium contents (x) in $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ samples.

$$3Y_2O_3 + 6TiO_2 \rightarrow 6Y_{Ba}^{\bullet} + 6Ti_{Ti} + V''_{Ba} + V''''_{Ti} + 21O_O \quad (3)$$

$Y_{Ba}^{\bullet}$ is compensated by the corresponding number of either electrons or cation vacancies as shown in Eqs. (2) and (3).[21–23] Thus, the electrical conductivity result indicates the preference of Y to Ba sites, which gave a donor doped behavior for the samples prepared by a conventional ceramic process. When 2.0 mol% Y was added, however, the Ba site could accept less Y than the Ti site, the net result exhibiting an acceptor doped behavior. Fig. 1 is consistent with the electrical conductivity shown in Fig. 3. The sample with small grain ($x = 0.01$) exhibits donor doped behavior, whereas the large grained microstructure ($x = 0.02$) is compatible with the acceptor doped behavior.

To the extent of XRD detection limit, none of second phases other than $BaTiO_3$ was detected in the compositions with $x \leq 0.03$. Fig. 4 shows the variations of lattice constants a and c as a function of nominal yttrium contents (x) in $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ samples. The solid solution energy of Y for the Ba site is similar to that for the Ti site.[6] Lattice parameters, a and c decrease with increasing x, for $x \leq 0.01$, whereas these increase with x, for $x > 0.01$. Since the size of the Y^{3+} ion (~0.107 nm) is almost intermediate between those Ba^{2+} ion (~0.161 nm) and Ti^{4+} ion (~0.06 nm), it seems likely that Y^{3+} ions would have an amphoteric behavior in $BaTiO_3$ sublattices. Thus, the lattice parameter may decrease with increasing the yttrium substitution for Ba sites ($Y_{Ba}^{\bullet}$), and increase with increasing the yttrium for Ti sites (Y'_{Ti}). The lattice parameter, a and c decreased gradually below 1.0 mol% Y, and then switched to increase at higher Y contents ($x > 0.01$ mol%). This result supports that below 1 mol% Y, Y^{3+} ions preferentially occupy Ba sites in $BaTiO_3 + x(BaO + 0.5Y_2O_3)$, regardless of excess BaO. This XRD data is compatible with the equilibrium electrical conductivity behavior shown in Fig. 3.

Fig. 5 shows the Curie temperature of $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ samples ($x = 0.00$, 0.01, 0.015, 0.02, 0.03). The Curie temperature decreases gradually with increasing Y contents up to 1.0 mol% and then with higher rates at $Y > 1.0$ mol%. The Curie point shifts to lower temperatures when the oxy-

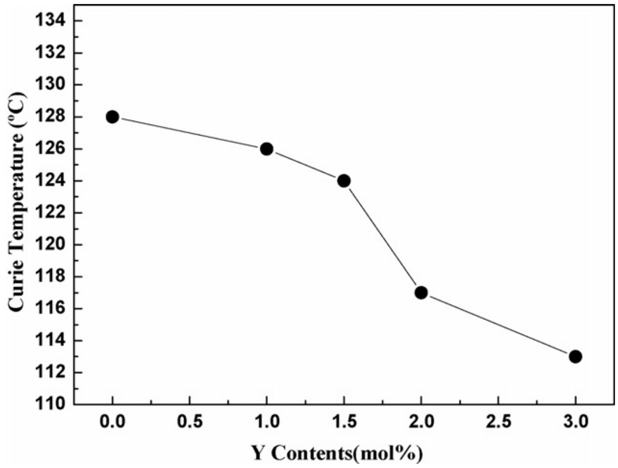

Fig. 5. Curie temperature variation of $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ (x = yttrium contents).

gen vacancy concentration is increased or the ions with smaller ionic radius replace the host ions.[24–28] The gradual decreases in Curie temperatures at lower levels of Y contents could be due to the Y substitution for Ba sites. The steeper Curie point suppression at >1.0 mol% Y may be attributed to the oxygen vacancy concentration as Y ions are incorporated into Ti sites according to Eq. (1). Thus, the TCC results are consistent with the equilibrium electrical conductivity behaviors shown in Fig. 3.

4. Conclusions

When Y_2O_3 was added to Ba-excess $BaTiO_3$ ($Ba/(Ti + Y) = 1$), the preferentially occupation site of Y^{3+} ions were estimated from microstructure developments, electrical conductivity behavior and XRD. The Y_2O_3 addition to the Ba-excess $BaTiO_3$ ($Ba/(Ti + Y) = 1$) lead to a donor-doped behavior at low level of Y_2O_3 ($\leq$1.0 mol%), an acceptor-doped behavior was observed at higher levels (>1.0 mol%). As Y contents were increased up to 1.0 mol%, the lattice parameter decreased gradually in $BaTiO_3 + x(BaO + 0.5Y_2O_3)$. However, the lattice parameters, a and c increased as Y contents were increased above 1.0 mol% Y. As long as Y contents were increased, the Curie temperature moved to lower temperatures. Y^{3+} ions preferentially occupy Ba sites in $BaTiO_3 + x(BaO + 0.5Y_2O_3)$ regardless of excess BaO and at >1.0 mol% Y, Y^{3+} ions are incorporated into Ti sites.

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References

1. Takada, K., Chang, E. and Smyth, D. M., Rare earth addition to $BaTiO_3$. *Adv. Ceram.*, 1986, **19**, 147–152.
2. Okino, Y., Shizuno, H., Kusumi, S. and Kishi, H., Dielectric properties of rare-earth-oxide-doped $BaTiO_3$ ceramics fired in reducing atmosphere. *Jpn. J. Appl. Phys.*, 1994, **33**, 5393–5396.
3. Kishi, H., Okino, Y., Honda, M., Iguchi, Y., Imaeda, M., Takahashi, Y. *et al.*, The effect of MgO and rare-earth oxide on formation behavior of core–shell structure in $BaTiO_3$. *Jpn. J. Appl. Phys.*, 1997, **36**, 5954–5957.
4. Mizuno, Y., Okino, Y., Chazono, H. and Kishi, H., Influence of the microstructure evolution on electrical properties of multiplayer capacitor with Ni electrode. *Jpn. J. Appl. Phys.*, 1998, **37**, 5227–5231.
5. Kishi, H., Kohzu, N., Sugino, J., Ohsato, H., Iguchi, Y. and Okuda, T., The effect of rare-earth (La, Sm, Dy, Ho and Er) and Mg on the microstructure in $BaTiO_3$. *J. Eur. Ceram. Soc.*, 1999, **19**, 1043–1046.
6. Lewis, G. V. and Catlow, C. R. A., Defect studies of doped and un-doped Barium titanate using computer simulation technique. *J. Phys. Chem. Solids*, 1986, **47**(1), 89–97.
7. Nakano, Y., Satoh, A., Hitomo, A. and Nomura, T., Microstructure and related phenomena of multilayer ceramic capacitors with Ni-electrode. *Ceram. Trans.*, 1993, **32**, 119–128.
8. Hitomi, A., Liu, X., Shrout, T. and Randall, C., In *Proceedings of the 8th US–Japan Seminar on Dielectric and Piezoelectric Ceramics*, 1997, p. 44.
9. Tsur, Y., Dunbar, T. D. and Randall, C. A., Crystal and defect chemistry of rare earth cations in $BaTiO_3$. *J. Electroceram.*, 2001, **7**, 25–34.
10. Lee, R. Y. and Smyth, D. M., Trivalent impurity behavior in $BaTiO_3$ and $SrTiO_3$. *Ceram. Bull.*, 1981, **60**(3), 401.
11. Jeong, J. H., Park, M. G. and Han, Y. H., Defect chemistry of Y-doped $BaTiO_3$. *J. Electroceram.*, 2004, **13**, 805–809.
12. Kröger, F. A. and Vink, H. J., *Solid State Physics*. Academic Press, New York, 1956, pp. 307.
13. Chan, N. H., Sharma, R. K. and Smyth, D. M., Non-stoichiometry in acceptor-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1982, **65**, 167–169.
14. Long, S. A. and Blumenthal, R. N., Ti-rich non-stoichiometric $BaTiO_3$. *J. Am. Ceram. Soc.*, 1971, **54**, 515–519.
15. Chan, N. H. and Smyth, D. M., Defect chemistry of $BaTiO_3$. *J. Electroceram.*, 1976, **123**, 1584.
16. Xue, L. A., Chen, Y. and Brook, J., The influence of ionic radii on the incorporation of trivalent dopants into $BaTiO_3$. *Mater. Sci. Eng.*, 1988, **B1**, 193–201.
17. Lin, M. H. and Lu, H. Y., Site-occupancy of yttrium as a dopant in BaO-excess $BaTiO_3$. *Mater. Sci. Eng.*, 2002, **A335**, 101–108.
18. Peng, C. J. and Lu, H. Y., Compensation effect in semiconducting Barium titanate. *J. Am. Ceram. Soc.*, 1988, **71**(1), C44.
19. Ting, C. J., Peng, C. J., Lu, H. Y. and Wu, S. T., Lanthanum–magnesium and lanthanum–manganese donor–acceptor-codoped semiconducting barium titanate. *J. Am. Ceram. Soc.*, 1990, **73**, 329–334.
20. Han, Y. H., Appleby, J. B. and Smyth, D. M., Calcium as an acceptor impurity in $BaTiO_3$. *J. Am. Ceram. Soc.*, 1987, **70**, 96–100.
21. Daniels, J. and Härdtl, K. H., Electrical conductivity at high temperatures of donor-doped barium titanate ceramics. *Philips Res. Rep.*, 1976, **31**, 489–504.
22. Chan, N. H. and Smyth, D. M., Defect chemistry of donor-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1984, **67**, 285–288.
23. Chan, H. M., Harmer, M. P. and Smyth, D. M., Compensating defects in highly donor-doped $BaTiO_3$. *J. Am. Ceram. Soc.*, 1986, **69**, 507–510.
24. Hennings, D. F. K. and Schreinemacher, H., Ca-acceptors in dielectric ceramics sintered in reducive atmospheres. *J. Eur. Ceram. Soc.*, 1995, **15**, 795.
25. Jing, Z., Ang, C., Yu, Z., Vilarinho, P. M. and Baptista, J. L., Dielectric properties of $Ba(Ti_{1-y}Y_y)O_3$ ceramics. *J. Appl. Phys.*, 1998, **84**, 983–986.
26. Nagai, T., Iijima, K., Hwang, H. J., Sando, M., Sakino, T. S and Nihara, K., Effect of MgO doping on the phase-transformations of $BaTiO_3$. *J. Am. Ceram. Soc.*, 2000, **83**, 107–112.
27. Hwang, J. H. and Han, Y. H., Dielectric properties of erbium doped barium titanate. *Jpn. J. Appl. Phys.*, 2001, **40**, 676–679.
28. Yang, W. C., Hu, C. T. and Lin, I. N., Effect of Y_2O_3/MgO co-doping on the electrical properties of base-metal-electroded $BaTiO_3$ materials. *J. Eur. Ceram. Soc.*, 2004, **24**, 1479–1483.