*Journal of Ceramic Processing Research. Vol. 12, No. 3, pp. 322~326 (2011)*

J O U R N A L O F
**Ceramic Processing Research**

# The dielectric and electrical properties of a X7R multilayer ceramic capacitor

**Hyun Duk Kim and Joon Tae Song***

*School of Information and Communication Engineering, Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-gu, Suwon, Geonggi-do, 440-746, Republic of Korea*

**The effects of the additive size and the sintering conditions on the electrical properties, especially in regards to the reliability, of a X7R type multilayer ceramic capacitor (MLCC) possessing a Ni internal electrode and thin layers were investigated. Using planetary and attrition milling (SC mill), we crushed the additive while utilizing an optimized solid loading. We achieved an average particle size of 500 nm using the pass crushing method of the high energy planetary and attrition milling according to the power intensity. In our results, we found a decrease in the permittivity of the multilayer ceramic capacitor as the average particle size of the additive decreased. However, the highly accelerated life testing (HALT) was improved. The dielectric permittivity and the insulation resistance (IR) increased as the additive amount of the MgO and glass increased. However, as the $Y_2O_3$ rate increased, these properties showed a decreasing trend. As the sintering temperature increased, the characteristics of the dissipation factor, insulation resistance, and the break down voltage (BDV) increased. In the aspect of the sintering conditions at ambient $H_2$, because a great quantity of $H_2$ was applied to the samples, the capacitance, dissipation on factor, insulation resistance, and break down voltage decreased. However, the samples' highly accelerated life testing properties were improved.**

**Keywords: MLCC, HALT, IR, BDV**

## Introduction

Recently, the X7R type (with a low dissipation factor of 2.5% or less and a temperature coefficient of capacitance (TCC) within the range of ± 15% between −55 and 125 °C) multilayer capacitor with a Ni internal electrode, based on $BaTiO_3$ (BT), has found applications in electronic equipment used for data processing, automotive applications, medical instrumentation, military systems, telecommunication equipment, and other applications. It is important to learn the dielectric properties and reliability for these multilayer ceramic capacitors in such applications [1-2]. In order to obtain these properties and the reliability, the dielectric materials must be fired in a low-oxygen partial pressure to prevent the Ni from oxidizing. Several studies have been made on additives, such as MgO and $MnO_2$, used to prevent the material from reducing and to control the temperature dependency of the dielectric constant [3]. Some studies have been conducted on the effect of rare-earth dopants that improve the multilayer ceramic capacitor lifetime [4-6]. In addition, many studies have been conducted on the effects of the manufacturing process variables that improve the multilayer ceramic capacitor lifetime [7]. However, little is known about the effect of the improvement of a multilayer ceramic capacitor's life time caused by the additive size. In our work, we studied the dielectric properties of the composites containing X7R type ceramics for Ni- multilayer ceramic capacitors. In this study, in one of the analysis methods, a mixture method was employed for the preparation of the multilayer ceramic capacitor where we fixed the quantity of the additives such as $Mn_3O_4$, $Cr_2O_3$, and $V_2O_5$ in the $BaTiO_3$ ($ABO_3$). The additive amount of the MgO, $Y_2O_3$, and glass were changed by 0.2-1 wt%, 0.3-1.5 wt%, and 0.5-2.5 wt%, respectively. Finally, we prepared an multilayer ceramic capacitor with a 3216 size at 2.2 μF and investigated the correlation of the reliability on the multilayer ceramic capacitor's life time by the additive size and sintering conditions.

*Corresponding author:
Tel : +82-31-290-7163
Fax: +82-31-290-7688
E-mail: vivacelove@skku.edu

## Experiment

We prepared fine barium titanate powders (400 nm, Sakai Chemical Company). These powders were then mixed with MgO (0.2-1 wt%), $Y_2O_3$ (0.3-1.5 wt%), glass(0.5-2.5 wt%), and some rare earth oxides resulting in X7R ceramics for the base metal electrode-multilayer ceramic capacitor. The additive that follows is classified by the bond strength. It was first treated with a planetary mill using $Y_2O_3$, and glass (5θ, zirconia ball) at 40 Hz for an 8 hour period, afterwards the mixture and the remaining powder were treated with an SC Mill (0.3θ, zirconia ball) at 2000 rpm. A scanning electron microscope (SEM) (the JEOL, JSM-840), the pore size distribution (PSD) (using a Horiba, LA-910), and a BET (using a micromeritics Tristar 3000/ flow prep 060) were used to analyze the slurry. The multilayer ceramic capacitor samples were prepared by the following procedure. The powders obtained and an appropriate organic binder were dispersed into the slurry. Green sheets with a thickness of 6.5 μm were then formed

by the so-called lip head method (casting machine, Hirano). After the Ni internal electrodes were printed on these green sheets, they were laminated and pressed into a bar with 151 dielectric layers and cut into pieces. After burning out the binder, they were fired at below 1280 °C. The sintering process was divided into three steps:(a) fired at 400 °C for 1 hour in a 99% $N_2$/1% $H_2$ atmosphere in order to remove the residual PVB, (b) fired at 1280 °C under a 97.5%$N_2$/2.5% $H_2$ atmosphere for 2 hours for the final sintering, and (c) annealed in a weak oxidizing atmosphere at 1000 °C. The surfaces of these samples were observed using a SEM (JEOL JSM840) with an EDS analysis. The temperature dependence of the dielectric constant was measured at temperatures ranging from –55 to 125 °C using a LCR meter (HP 4194) at 1 kHz and 1 Vrms. The dissipation factor was measured at room temperature using a LCR meter (HP 4278) at 1 kHz and 1 Vrms. The insulation resistance was measured at room temperature using a high resistance meter (HP 4349) at 16 V and a charging time of 60 seconds.

## Results and Discussions

### The composition test

In regards to the composition preparation of the X7R, we fixed the amount of $Mn_3O_4$, $Cr_2O_3$, and $V_2O_5$. The MgO, $Y_2O_3$, and Glass (Ba-Ca-Si) were controlled in a range of 0.2-1 wt%, 0.3-1.5 wt%, and 0.5-2.5 wt%, respectively, while measuring their dielectric properties. Table 1 presents the added amounts for the MgO, $Y_2O_3$, and glass. The dielectric properties for the compositions are shown in Table 2. The reliability figures with the additive crushing conditions are shown in Table 3. In our experimental results, we saw a decrease of the dielectric property as the average particle size of the additive decreased. However, the highly accelerated life testing was improved. Fig. 1 shows the variation of the dielectric characteristics according to the added amount. As the amounts of MgO and glass increased, the dielectric constant and insulation resistance increased. In contrast, as we increased the amount of $Y_2O_3$, the results showed trends of decreasing the dielectric constant and insulation resistance results. Because of these results, we assumed that an increase in the amount of MgO additive pushed up the sintering properties of the $BaTiO_3$. Additionally, the reduction of the particle size as well as the increase of the shell phase had an effect on the reduction [8]. In the case of increased $Y_2O_3$, it is very well known that it decreases the dielectric constant and the reliability [9]. We selected a composition condition for a response optimization using a minitab analysis tool that was based on our experimental results.

**Table 1** Compositions

| Disk | MgO | $Y_2O_3$ | Glass |
|---|---|---|---|
| | | wt% | |
| Disk 1 | 1.00 | 0.30 | 0.50 |
| Disk 2 | 0.20 | 1.50 | 0.50 |
| Disk 3 | 0.20 | 0.30 | 2.50 |
| Disk 4 | 0.47 | 0.70 | 1.17 |
| Disk 5 | 0.73 | 0.50 | 0.83 |
| Disk 6 | 0.33 | 1.10 | 0.83 |
| Disk 7 | 0.33 | 0.50 | 1.83 |

**Table 3.** The Reliability According to the Additive Crushing Conditions

| Additive Crushing conditions | | | |
|---|---|---|---|
| Degradation | Only S.C Milling | Individual Planatary Milling and S.C Milling (time) | Individual Planatary Milling and S.C Milling (pass) |
| 0/50 pcs | 10/50 pcs | 3/50 pcs | 0/50 pcs |

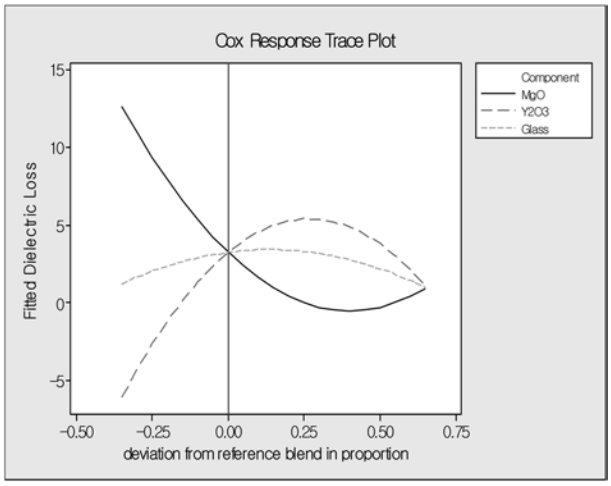
### The additive crushing

In order to observe the microstructure and particle size of each additive, a SEM was used. The results are shown in Fig. 2. In the SEM images, the MgO showed an average particle size of 400 to 500 nm; the $Y_2O_3$ additive had a uniform size of 200 to 300 nm. The $Mn_3O_4$ powder had a microstructure with sizes ranging from 100 to 200 nm. The $Cr_2O_3$ and the $V_2O_5$ showed an average particle size ranging from 500 to 800 nm. The glass powder had a large average particle size of 1-3 μm.

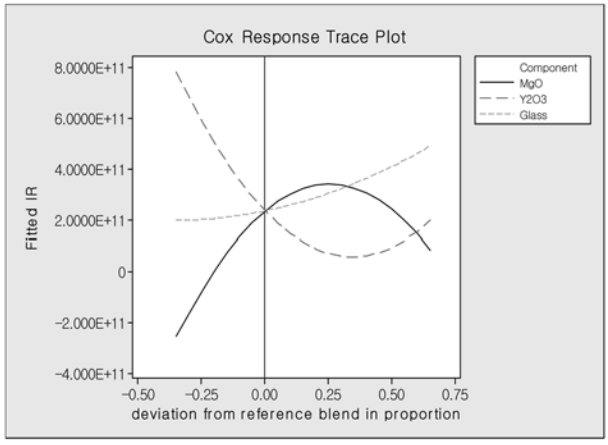
Fig. 3 illustrates the glass BET results from the planetary

**Table 2.** The Dielectric Properties with Compositions

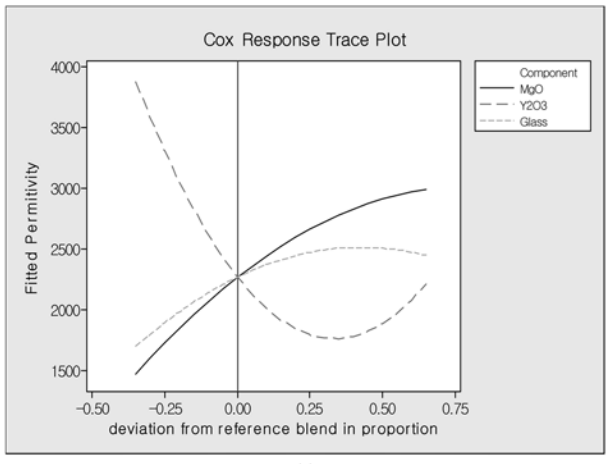
| Disk | Sintering conditions | Density [g/cm$^2$] | Capacitance [nF] | Dissipation factor [%] | Permittivity [$\varepsilon_r$] | IR | RC [ΩF] |
|---|---|---|---|---|---|---|---|
| Disk 1 | 1286 °C $N_2$:98.5% $H_2$:1.5% | 5.6306 | 2.3728 | 0.80 | 2986 | 7.4921E + 10 | 210 |
| Disk 2 | | 5.8275 | 1.7537 | 0.39 | 2249 | 2.2547E + 11 | 403 |
| Disk 3 | | 5.7316 | 1.8714 | 0.51 | 2428 | 5.1114E + 11 | 1056 |
| Disk 4 | | 5.7307 | 1.6566 | 0.41 | 2193 | 3.5001E + +11 | 510 |
| Disk 5 | | 5.6566 | 2.0454 | 0.88 | 2795 | 2.7770E + 11 | 647 |
| Disk 6 | | 5.1320 | 1.4247 | 6.58 | 1795 | 4.1278E + 09 | 5 |
| Disk 7 | | 5.7132 | 1.9791 | 4.35 | 2536 | 2.8229E + 11 | 624 |




(a)




(b)




(c)

**Fig. 1.** The dielectric properties of the composition tests.

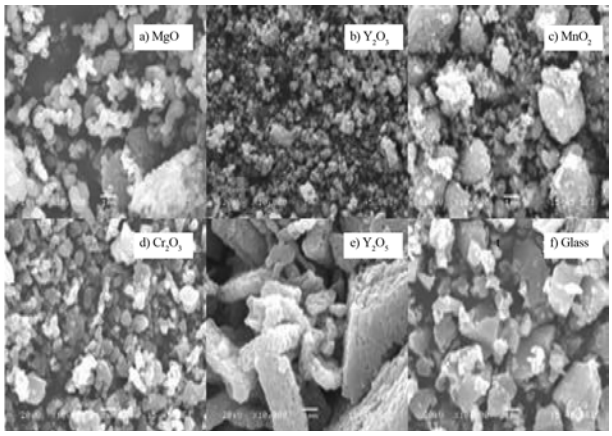



**Fig. 2.** SEM images of the microstructure and the particle size of each additive.

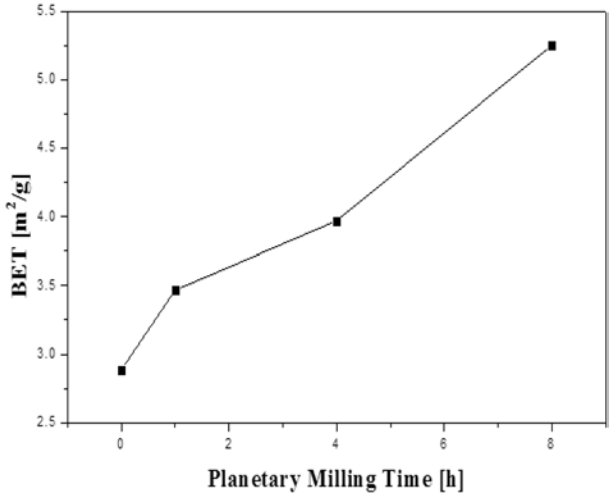



**Fig. 3.** The glass BET results obtained by the planetary milling method according to the time taken.

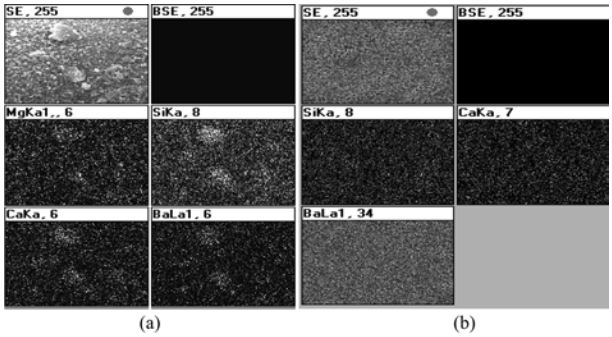



**Fig. 4.** a) SC Milling (time) only, and b) individual Planetary Milling and SC Milling (Pass).

milling method according to the time taken. When the sheet was fabricated using the pass planetary and attrition milling, the average size was observed to be small, as shown in Fig. 4. These particles confirmed that were crushed though the planetary milling of the glass powder. In addition, the added particle size needs to be of a similar size to that of the $BaTiO_3$ or smaller than $BaTiO_3$, due to the concentration of the electric field in the local area of the sheet.

Fig. 5 shows a comparison of the particle sizes for the three crushing methods. From our results, we obtained a particle size of approximately 500 nm and could confirm a good quality sheet though pass planetary and attrition milling after the individual crushing.

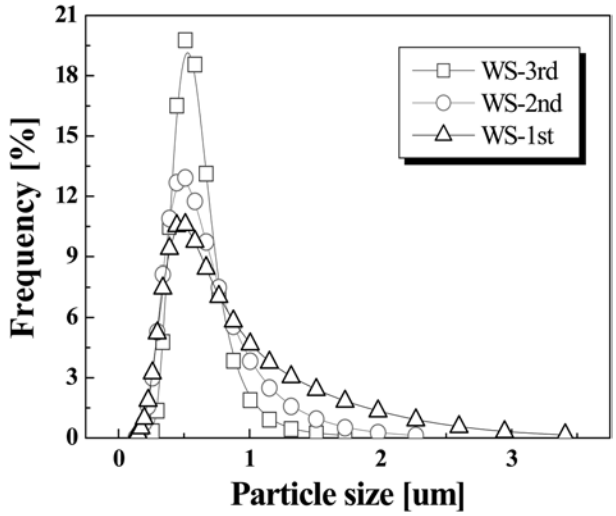



**Fig. 5.** A comparison of the particle sizes obtained by three types of crushing methods: WS-1st : SC Milling only, WS-2nd : Individual Planetary Milling and SC Milling(time), and WS-3rd : Individual Planetary Milling and SC Milling (pass).

## The sintering conditions

Table 4 presents the different sintering conditions for the multilayer ceramic capacitor.

Fig. 6 shows the dielectric properties of the multilayer ceramic capacitor with respect to the sintering temperature and atmosphere. As the sintering temperature increased, the dissipation factor, insulation resistance, and break down voltage increased. With respect to the sintering conditions at ambient $H_2$, because a great quantity of $H_2$ was applied to the samples the capacitance, dissipation factor, insulation resistance, and break down voltage decreased. However, the samples had improved highly accelerated life testing properties.

Fig. 7 shows the reliability with respect to the sintering temperature and atmosphere as the accelerated life testing was enhanced when reducing the atmosphere [10].

**Table 4.** The Different MLCC Sintering Conditions

| Experimental Conditions | | A | B | C | D |
|---|---|---|---|---|---|
| Sintering Temperature[°C] | | 1220 | 1250 | 1250 | 1284 |
| $H_2$ Amount [%] | First Zone [0-950 °C] | 1.0% | 1.0% | 1.0% | 1.0% |
| | Second Zone [950-1280 °C] | 1.5% | 1.5% | 1.5% | 1.5% |
| | Keep zone | 1.5% | 1.5% | 2.0% | 2.0% |
| Re-oxidation [at 1000 °C] | | 20 ppm | 20 ppm | 20 ppm | 20 ppm |

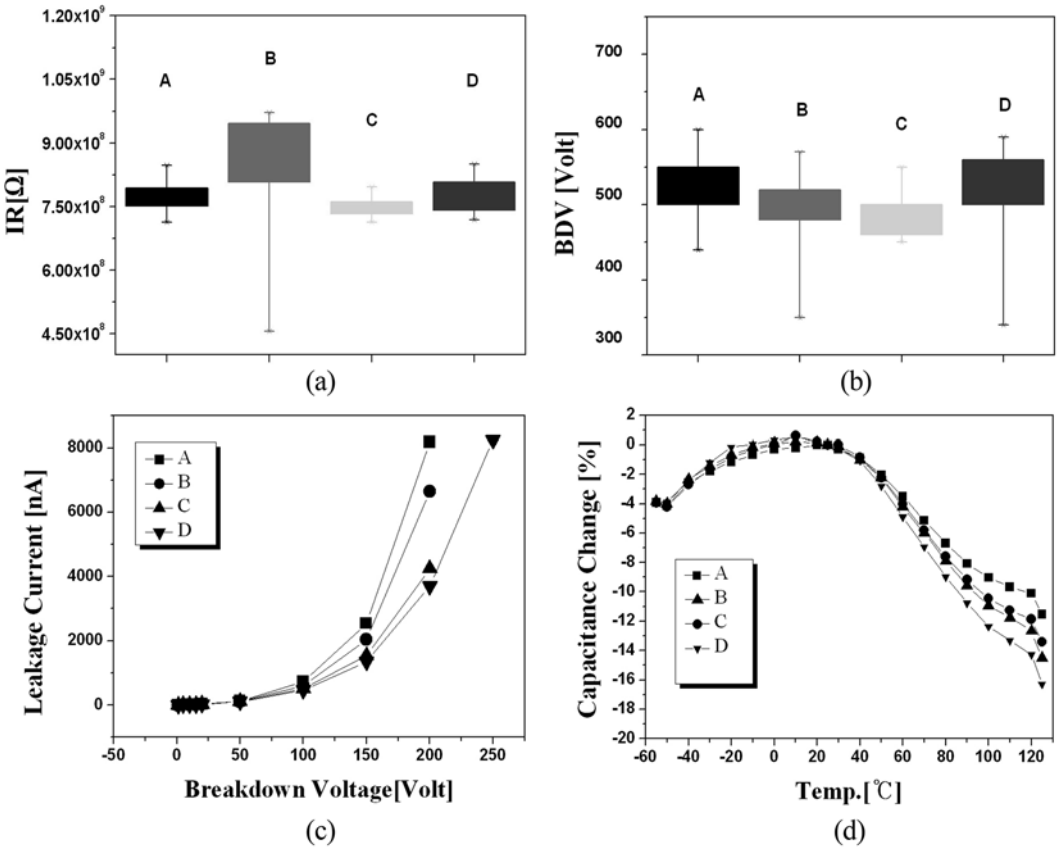



**Fig. 6.** The MLCC dielectric properties according to the sintering temperature and atmosphere a) IR b) BDV c) Leakage current d) Capacitance change.

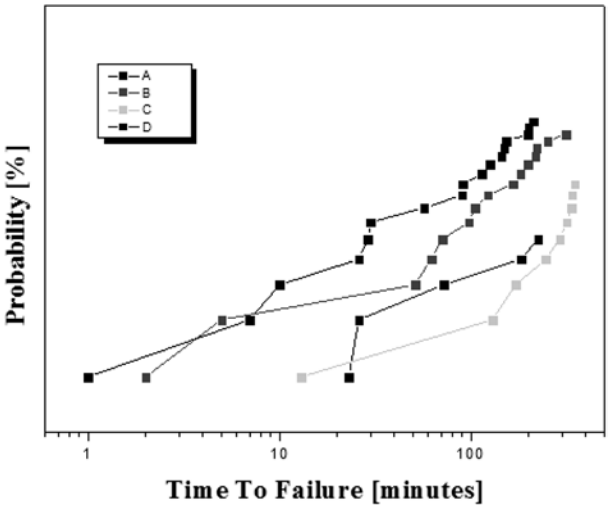



**Fig. 7.** The reliability according to the accelerated life testing regarding the sintering temperature and atmosphere.

## Conclusion

The effect of the additive size and sintering conditions on the dielectric properties, especially on the reliability, of an X7R multilayer ceramic capacitor with a Ni internal electrode and thin layers was investigated. Using planetary and attrition milling, we crushed the additives by utilizing an optimized solid loading and achieved an average particle size of 500 nm using the planetary and attrition milling pass crushing method according to the power intensity. During our experiments, we experienced a decrease in the dielectric properties as the average additive particle size was decreased. However, the high accelerated life tests were improved. We assume that the $BaTiO_3$ particles as well as the additive size were involved in the highly accelerated life testing improvement. With respect to the electrical characteristics, the dielectric constant and insulation resistance were increased as the added amount of MgO and glass increased. However, when the $Y_2O_3$ rate was increased, these properties showed a decreasing trend. As the sintering temperature increased, the dissipation factor, insulation resistance, and break down voltage increased. In the aspect of the sintering conditions at ambient $H_2$, because a great quantity of $H_2$ was applied to the samples, the insulation resistance, and the break down voltage decreased. However, the samples were improved in their highly accelerated life testing properties. In addition, at a 100% $N_2$ condition before the sintering, the sample that had a binder burn out at 700 °C was similar in its dielectric property when compared to the sample fabricated without the binder burn out. However, the reliability was improved. From these improved results, we deduce that when a lower oxygen partial pressure exists, the more the reliability was improved, because the oxygen vacancies were decreased by having hydrogen in the materials. In addition, the $N_2$ binder burn out resulted in an improvement of reliability resulting from the effect of removing the internal residual carbonate.

## References

1. S. Summita, M. Ikeda, Y. Nakano, K. Nishiyama and T. Nomura, J. Am. Ceram. Soc. 74, (1991) 2739-2746.
2. M. Shiojiri, T. Isshiki, H. Saijo, M. Tsujikura, A. Nakada, Y. Nakano, M. Ikeda and T. Nomura, Phys. Status Solid A 129 (1992) 353-362.
3. H. Saito, H. Chazono, H. Kishi and N. Yamaoka, Jpn. J. Appl. Phys. 30 (1999) 2307-2310.
4. H. Shizuno, S. Kusumi, H. Saito and H. Kishi, Jpn. J. Appl. Phys. 32 (1993) 4380-4383.
5. H. Kishi, N. Kohzu, J. Sugino, H. Ohsato, Y. Iguchi and T. Okuda, J. Eur. Ceram. Soc. 19 (1999) 1043-1046.
6. M. Youichi, K. Hiroshi , O. Kenji, I. Takanori and O. Hitoshi, J. Eur. Ceram. Soc 27 (2007) 4017-4020.
7. S. Summita, M. Ikeda, Y. Nakano, K. Nishiyama and T. Nomura, J. Am. Ceram. Soc. 74 (1991) 2739-2746.
8. H. Kishi, Y. Mizuno and H. Chazono, Jpn. J. Appl. Phys. 42 (2003) 1-15.
9. T. Nomura, N. Kawano, J. Yamamatsu, T. Arashi, Y. Nakano and A. Sato, Jpn. J. Appl. Phys. 34 (1995) 5389-5395.
10. G.Y. Yang, E.C. Dickey, C.A. Randall, D.E. Barber, P. Pinceloup, M.A. Henderson, R.A. Hill, J.J. Beeson and D. Skamser, Jpn, J. Appl. Phys. 96 (2004) 7492-7499.