Journal of Ceramic Processing Research. Vol. 16, No. 5, pp. 495~498 (2015)

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

Electrical properties of Dy-doped $BaTiO_3$-based Ceramics for MLCC

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To understand the contribution of rare earth additive material (Dy_2O_3) in $BaTiO_3$-MgO-Mn_3O_4-$BaCO_3$-SiO_2-xwt%Dy_2O_3-based (hereafter BT-based) ceramics ($0.3 \leq \times \leq 1.2$) for multilayer ceramic capacitors (hereafter MLCC) prepared using BT-based powder and their properties were investigated electrical and structural properties. The BT grain size and dielectric constant of Dy-doped samples was found to increase with increasing Dy_2O_3 content. In particular, the 0.6 wt%Dy_2O_3 doped sample shows high resistance capacitance (RC) values of 2500 Ω · F, dielectric constant of 3600, dielectric loss of 1.4%, stable temperature coefficient of capacitance (TCC). These results indicate that 0.6 wt%Dy_2O_3 doped BT-based ceramic is a promising candidate material for superior X5R type MLCC.

Key words: Dy_2O_3, $BaTiO_3$-based,TCC, X5R type, MLCC.

Introduction

Multilayer ceramic capacitors (MLCCs) are widely used in the electronic industry for smart phone, automotive applications and other applications [1, 2]. There has been a continuous scaling down of both the dielectric and electrode layer thickness for high volumetric capacitance [3-5]. The $BaTiO_3$ based ceramics with Ni internal electrodes must be cofired under highly reducing atmospheres to prevent Ni oxidation. The co-firing of $BaTiO_3$ oxide and Ni metal requires a reducing atmosphere, and thus oxygen vacancies (V_O) are generated in $BaTiO_3$ insulating layers. It was shown that V_O in $BaTiO_3$ layers spoils the insulating reliability of MLCC, i.e., V_O migrates the vicinity of electrodes under direct-current electric field, and then it finally results in a short circuit. The temperature stability of capacitance can be created by control of the so-called core shell structure. The core shell structures are the coexistence of ferroelectric structure of tetragonal $BaTiO_3$ and ferroelectric region by a solid solution of rare oxides in $BaTiO_3$. In a previous study, It was suggested that the substitution of rare earth elements into the shell phase of the $BaTiO_3$-MgO-R_2O_3(such as Dy, Ho, Er, Y) base system changed from Ba-site (act as a donor) to Ti-site s(act as an acceptor) occupation, rare earth elements were effected forming core-shell microstructures and high insulation resistance and improved temperature characteristics and reliability [6]. In general, the sintering condition such as soak time and temperature, atmosphere are of significance for the microstructure of $BaTiO_3$, the physical and chemical properties of starting materials could also have an effected MLCC, especially to the tiny amount of additives. For example, the additives, such as rare earth oxide, influenced the formation of the core shell structure and dielectric properties. This paper describes the effect of the dielectric properties of BT-based ceramics with various amount of Dy_2O_3.

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Experiments

Conventional mixed oxide processing was used to prepare the BT-based ceramics with different Dy_2O_3 (X = 0.3. 0.6, 0.9, 1.2 mol%) contents. $BaTiO_3$ powder (Kyriz, Japan) with a particle size of 200 nm was used as the raw material. The BaTiO3 powder and additives such as MgO (Kojundo chemical, Japan), $BaCO_3$(Sakai, Japan), Dy_2O_3 (Rhodia, China), SiO_2 (Kojundo chemical, Japan) and Mn_3O_4 (Kojundo chemical, Japan), were ball-milled in ethanol with zirconia balls for 24 h and then granulated with polyvinyl alcohol as a binder. The granulation was then pressed into ceramic disks, 16 mm in diameter, at 1,500 kg/cm^2. The green disks were sintered at the optimum sintering temperatures of 1200-1280 °C for 2 hours in a reducing atmosphere. The BT-based powders with organic binder system and methylethly-ketone (MEK) and toluene as solvent were cast into green sheet by doctor blade. After printing the nickel sheets as internal electrode, MLCC was laminated, pressed, and then cut into small green chips. The green chips were held at 260 oC for 40 h in an air atmosphere to burn out the binder and then sintered at 1230 °C for 2 h. After grinding the sintered chips in a barrel, MLCCs

were terminated with Cu electrode paste. Then, Ni and Sn were electroplated in regular sequence to the end terminals. The microstructure of sintered MLCC samples was characterized by scanning electron microscopy (SEM, S-4700, Hitachi, Japan). The x-ray diffraction (XRD) patterns were measured on Rigaku Corporation, Rigaku Model SmartLab installed at the Hanyang Center for Research Facilities (Seoul) at Hanyang University. The TCC curves and capacitances were determined using HP 4284A precision LCR meter (HP, USA) at test voltage of 1 V and a frequency of 1 kHz. Capacitance measurements were taken in the temperature range from −55 °C to 125 °C placing the MLCCs in a temperature chamber (S&A Inc., USA). The insulation resistance was measured using high resistance meter (HP 4329).

The high temperature insulation resistance of MLCC was performed using HP4329 at 125 °C under stepwise boosting voltage from 1 Vr ~ 7.5 Vr (1 Vr = 35 V).

Results and Discussion

Fig. 1 shows the dielectric constant and loss of BT based ceramics as a function of Dy_2O_3 content and sintering temperature. The dielectric properties of Dy doped BT-based MLCC tend to depend on the sintering temperature and Dy doping amount. The dielectric properties were enhanced as the amount of Dy doping and sintering temperature increases. The sintering temperature can be deduced to be related to the particle growth of the BT-based ceramic. Also Dy doping amount can be caused by solubility which affects oxygen vacancies. Y. Sakabe *et al*. [100] reported that Dy ion occupied shell regions and grain boundaries. This result can reduce oxygen vacancies which is a major factor of reducing the electrical properties and reliability of MLCC.

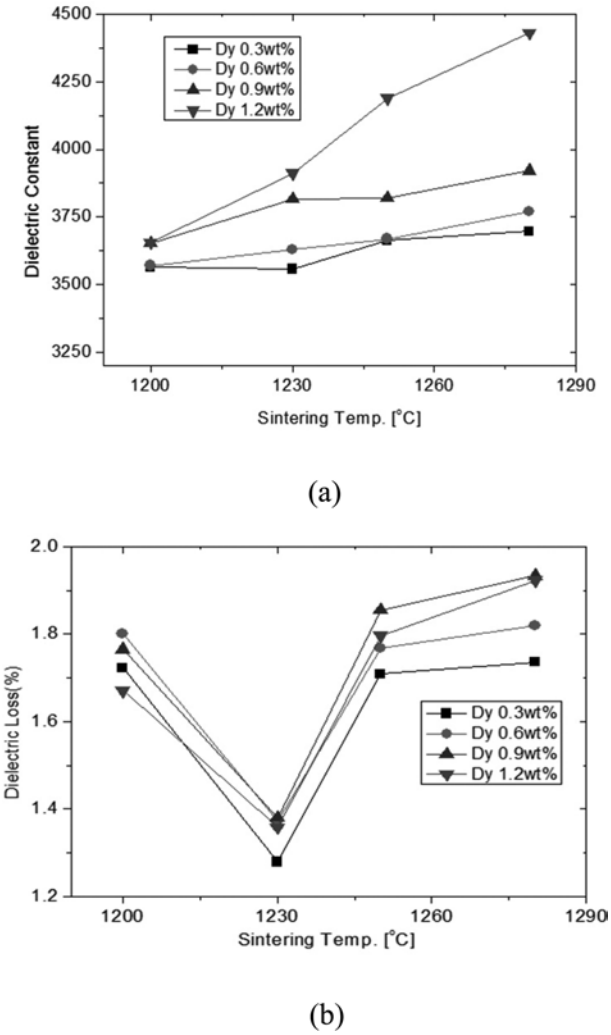

Fig. 1. Dielectric constant (a) and loss (b) of BT-based ceramics as a function of Dy_2O_3 contents and sintering temperatures.

Fig. 2 shows the changes in RC value (Insulation resistance x Capacitance) of BT-based ceramics as a function of Dy_2O_3 content and sintering temperature. All samples regardless of Dy_2O_3 content show similar behavior. The RC value rapidly increases with sintering temperature below 1230 °C. However, RC value generally decreased above 1230 °C. This can be

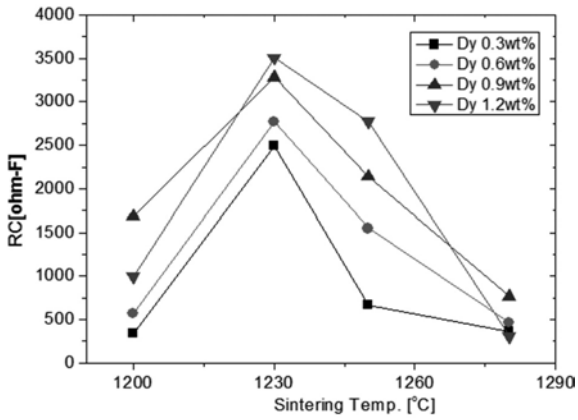

Fig. 2. Time constants of BT-based ceramics as a function of Dy_2O_3 content and sintering temperature.

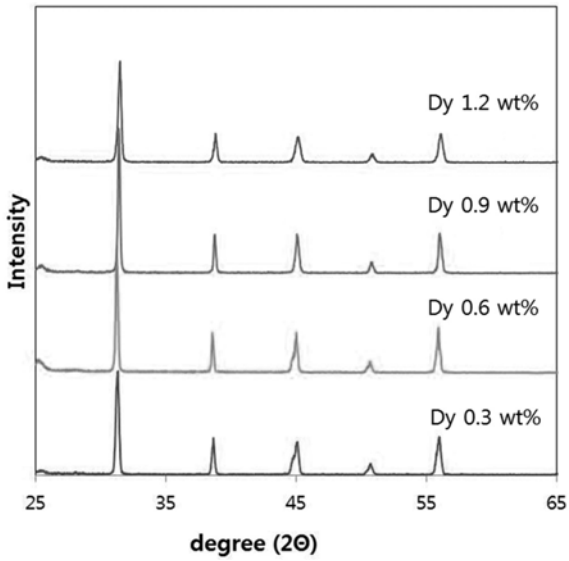

Fig. 3. XRD patterns of different Dy doped BT-based ceramics

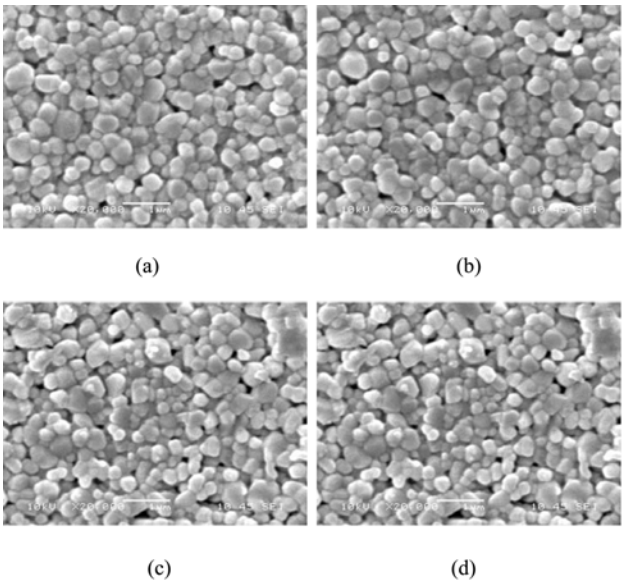

Fig. 4. SEM images of different Dy doped BT-based ceramics (a) 0.3 wt% (b) 0.6 wt% (c) 0.9 wt% (d) 1.2 wt%.

explained by normal or abnormal grain growth of BT-based ceramics that are associated with core-shell structure [6]. An abnormal grain growth reduces the insulation resistance factor which is related leakage current of MLCC. Therefore, we can consider an optimal sintering temperature of 1230 ºC owing to high RC value.

Fig. 3 shows the XRD patterns of BT-based ceramics as a function of Dy_2O_3 contents sintered at 1,230 ºC for 2 hours. All the samples show the typical XRD patterns of perovskite structure and there is no second phase. The (110) peak of sample is almost same position regardless of Dy_2O_3 contents. This indicated that Dy ion (R = 1.03 Å) can be selectively substituted both Ba-site (R = 1.42 Å) and Ti-site (R = 0.61 Å) [3]. This phenomenon leads superior reliability as well as electrical properties of the MLCC. Fig. 4 shows the microstructure of BT-based ceramics with different Dy_2O_3 content. Regardless of the amount Dy contents, grain growth of BT-based ceramics show similar behavior. As compared to the raw grain size (200 nm), the slight grain growth with average grain size of 300 nm is occurred. The Dy plays important role in inhibiting grain growth by two reasons. First, Dy existing in the grain boundary delays the necking between BT grains. The second reason for the delay of sintering process is an energy consumption which is associated with doping Dy into BT structure. This small grain size enables the lamellation of dielectric sheets which is one of the most important factors for high capacity and reliability MLCC.

Fig. 5(a) shows the temperature coefficient of capacitance (TCC) of different Dy doped BT-based ceramics sintered at 1230 ºC. The temperature stability of different Dy doped BT-based ceramics

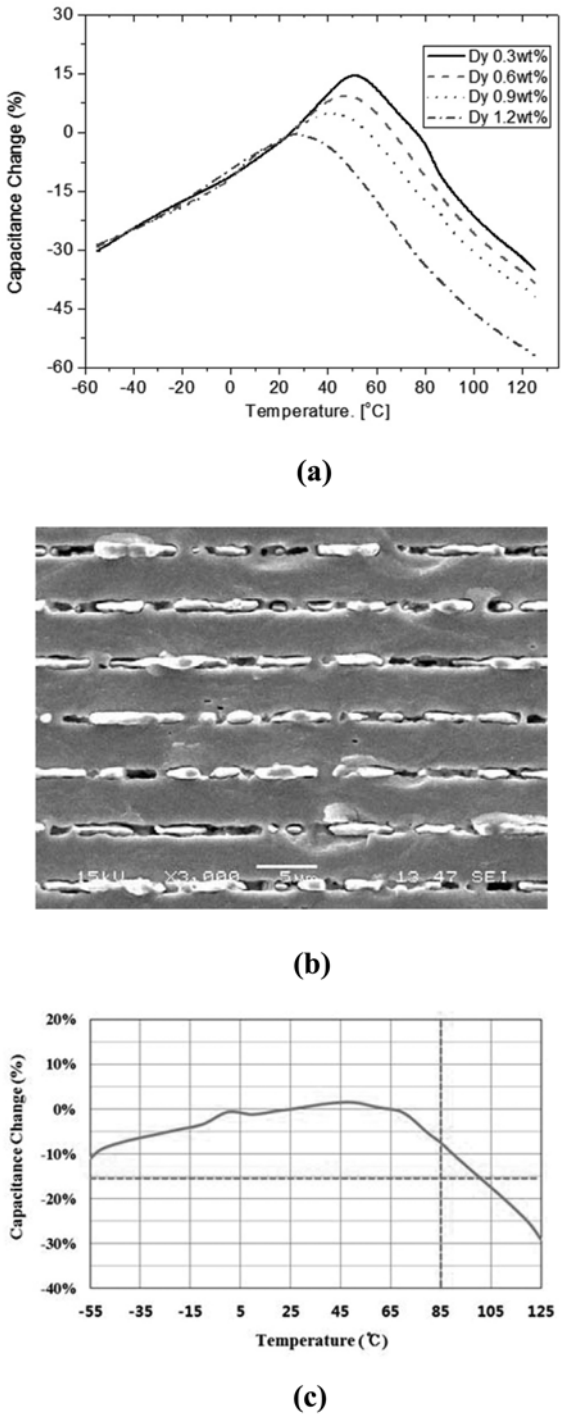

Fig. 5. TCC of BT-based ceramics as a function of Dy_2O_3 content sintered at 1230 ºC (a), SEM image of fabricated MLCC (b) and MLCC fabricated using 0.6 wt% Dy doped BT-based ceramic (c).

was conducted in the temperature range from −55 to 125 ºC. All samples similar behavior, however, the capacitance variations of BT-based ceramics doped 0.3, 0.6 wt % Dy doped satisfy X5R characteristics (−55 ºC ~ + 85 ºC, ± 15%). Other BT-based ceramics does not meet X5R characteristics. This result is influenced by a stable core-shell structure, as well as uniform particle growth. Two kinds of BT-based

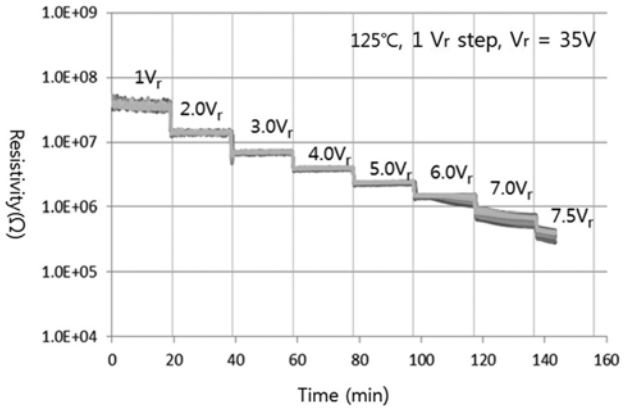

Fig. 6. Elelctrical resistivities at high temperature (125 °C) versus time of MLCC by applying voltage step of DC 1 Vr (1 Vr = 35 V) up to 7.5 Vr

ceramics doped 0.3 and 0.6 wt% Dy, we selected 0.6 wt% Dy doped BT-based ceramics owing to its superior dielectric properties than that of 0.3 wt%. Fig. 5(b) shows the SEM image of the fabricated MLCC and Fig. 5(c) shows the capacitance change of MLCC fabricated using 0.6 wt% Dy doped BT-based ceramic. The temperature stability of MLCC further enhanced and it also naturally satisfied X5R characteristics.

Fig. 6 shows the high temperature insulation resistance of MLCC (3.2 × 1.6 mm) at 125 °C under stepwise boosting voltage from 1 Vr ~ 7.5 Vr (1 Vr = 35 V). The degradation of insulation resistance was caused by oxygen vacancies which are moved into cathode under DC bias field stress as time goes by [7, 8]. However, Dy plays a crucial role in delay of oxygen vacancies move and thereby postpone insulation resistance degradation. Generally, the insulation resistance value decrease less than 10^{-6} Ω, we can regard that the reliability of products come to an end. It can be seen that fabricated MLCC stably satisfied 6 Vr. This confirms that high temperature insulation resistance of MLCC is applicable to the actual products.

Conclusions

The Dy_2O_3 was added to BT-based ceramics to improve their dielectric properties. Among them, when 0.6 wt% Dy_2O_3 was added to BT-based ceramics sintered 1230 °C, excellent electrical properties were obtained with high RC value and stable TCC ranged from −55 °C to 125 °C. Especially, the MLCC with 0.6 wt% Dy_2O_3 doped BT-based ceramics shows that this composition is a promising MLCC material for superior electrical properties with X5R type.

Acknowledgments

The research was support by a grant from the National Research Foundation (No. 10049864).

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