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The Effects of $(Ba_{0.4}Ca_{0.6})SiO_3$ Nano Spheroidization Glass Additives on the Microstructure and Microwave Dielectric Properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$ Ceramics

Cheal Soon Choi*, Ki Soo Kim, Dong Hee Rhie*** and Jung Rag Yoon†**

Abstract – In this study, the microwave dielectric properties of nano spheroidization glass powders added $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics prepared by solid state reaction have been investigated. Adding $(Ba_{0.4}Ca_{0.6})SiO_3$ nano spheroidization glass powders could effectively promote the densification even in the case of decreasing the sintering temperature. When the glass frit is 0.3 wt% and sintering is carried out at a temperature of 1500 ℃ for 6 hr, a temperature stable microwave dielectric ceramic could be obtained, which has a dielectric constant (ε_r) of 30.2, a quality factor ($Q\times f_0$) of 124,000 GHz and a temperature coefficient of resonance frequency (τ_f) of 2 ppm/℃.

Keywords: Nano spheroidization glass powder, Dielectric constant, Quality factor, Temperature coefficient of resonance frequency

1. Introduction

With the recent development of the wireless communication field, there has been a development from communication service mainly for voice transmission and reception to various multimedia application services. According to the requirements for various multimedia application services, an increase in the frequency of use and the use of a high-frequency of 60GHz, 77GHz or 94GHz that enables broadband services have been reviewed. Thus, the requirement for a microwave dielectric resonator having high performance, which can be used in this high-frequency band, has increased. The three important characteristics required for a microwave dielectric resonator are suitable dielectric constant for use, a high quality factor ($Q\times f_0$), and a stability of the temperature coefficient of resonant frequency [1]. Typical compositions having a high quality factor among microwave dielectric properties include complex perovskite $A^{2+}(B^{2+}{}_{1/3}B^{5+}{}_{2/3})O_3$, wherein the A-site includes Ba or Sr, and the B-site includes divalent ions such as Zn or Mg, or pentavalent ions such as Ta or Nb. Among them, typical compositions include $Ba(Zn_{1/3}Ta_{2/3})O_3$ known to have a quality factor ($Q\times f_0$), higher than 120,000 and a stable temperature coefficient of resonant frequency [2,3]. It is known that, to increase the quality factor of this composition, the ordering of the B-site (Zn and Ta) is required, and for this ordering, heat treatment at a temperature of 1600 ℃ or higher for a long time is required [4,5,6]. Methods that are generally used to lower the sintering temperature of microwave dielectric ceramics include a method of reducing the size of power, a method of adding V_2O_5, CuO, SiO_2, B_2O_3 and the like as sintering aids for promoting liquid-phase sintering, or a method of adding glass powder that forms a liquid phase by itself [7]. Addition of glass powder for low-temperature sintering is effective in lowering the sintering temperature, but results in deterioration in microwave dielectric properties due to a glass phase remaining after sintering. Glass powder compositions that are generally added to microwave dielectric materials include lanthanum borate glass ($20RO\text{-}20La_2O_3\text{-}60B_2O_3$; R = Ca, Mg, Zn), anorthite glass ($CaO\text{-}Al_2O_3\text{-}2SiO_2$) and the like. A mutilayer ceramic capacitor (MLCC) that is a typical part composed of a dielectric material is manufactured using barium calcium silicate glass ($BaO\text{-}CaO\text{-}SiO_2$) or borosilicate glass ($R_2O\text{-}B_2O_3\text{-}SiO_2$; R: alkali metal) in order to low-temperature and dielectric characteristics [8, 9]. In this study, various amounts of barium calcium silicate-based nano spheroidization glass powders synthesized by a radio-frequency (RF) thermal plasma process were added to $Ba(Zn_{1/3}Ta_{2/3})O_3$, and the crystalline phases and microstructures of the microwave dielectric ceramics were analyzed. In addition, the dielectric properties of the microwave dielectric materials were studied.

2. Experimental Method

As starting materials for preparing a $Ba(Zn_{1/3}Ta_{2/3})O_3$ composition, $BaCO_3$ (99.9%, Sakai, Japan), ZnO (99.9%, Kojundo Chemical, Japan) and Ta_2O_5 (99.9%, Kojundo Chemical, Japan) were used. $Ba(Zn_{1/3}Ta_{2/3})O_3$ was mixed using a general ceramic process, and the powder was

† Corresponding Author: R&D center, SAMWHA CAPACITOR Co. LTD. Korea. (yoonjungrag@samwha.com)
* InT Co. Ltd. Korea. (changjo1225@hotmail.co.kr)
** Dept. of Materials Science Engineering, Hongik University, Korea. (kisoo@hongik.ac.kr)
*** Dept. of Electrical Engineering, Suwon University, Korea. (dhrhie@suwon.ac.kr)
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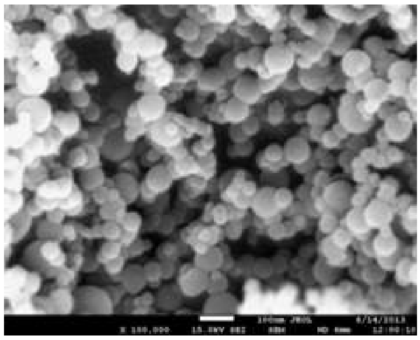
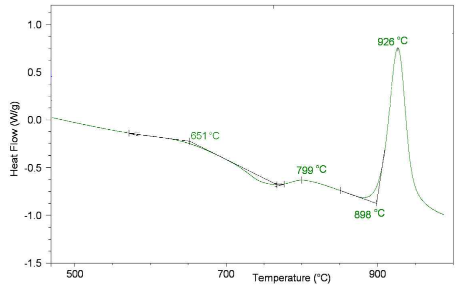
calcined at a temperature of 1200℃ for 2 hours. Nano spheroidization glass powder was added to the calcined powder, and the mixture was mixed and ground using ethanol and zirconia balls. The powder was added to PVA, after which it was granulated, and then molded using a disk mold, and the molded sample was sintered at 1400 ~ 1550℃ for 4 hr. As raw materials for the RF thermal plasma treatment, nano spheroidization glass powder with the composition of SiO_2-0.4BaO-0.6CaO was prepared by the following procedure. Reagent-grade SiO_2, $BaCO_3$, and $CaCO_3$ (Kojundo chemical, Japan) were weighed in the composition ratio and ball-milled in ethanol with zirconia balls for 24 hr. The dried powders were melted at 1550℃ for 1 h using a platinum crucible, and the melted mixture was poured into a twin roller to produce a glass cullet. These cullet flakes were ball milled into glass powders with an average size of ~1㎛. The sub-micrometer-sized coarse glass powders were nano spheroidized using the RF thermal plasma system (model TDU-60, Tekna Plasma System Inc., Canada). The induction plasma powder synthesis was performed at pressure of 80~100 torr and 30~50 kW of power under a flow rate of 20 slpm (standard liter per minute) of Ar as a central gas and 80 slpm of O_2 as a sheath gas. The crystallization temperature of glass was analyzed using thermogravimetry (TG-DTA SDT Q-600, TA Instruments) at a heating rate of 20℃/min. The phases of the sintered sample were analyzed by X-ray diffraction (XRD) using Cu-Kα rays in the range of 20-60°. The surface of the sintered sample was polished and thermally etched, and then the microstructures were observed using a scanning electron microscope (SEM). The dielectric constant (ε) was measured using the Hakki-Coleman method, and the quality factor ($Q \times f_0$) was measured using the cavity perturbation method that shows high accuracy [10, 11]. The temperature coefficient of resonant frequency (τ_f) was determined by placing the sample in a cavity resonator made of copper and measuring the resonant frequencies f_{25} and f_{80} at room temperature and 80℃.



(a)



(b)

Fig. 1. The DTA results and powder shape with plasma treated nano spheroidization glass powder: (a) Powder shape with plasma treated glass powder; (b) The DTA results with plasma treated nano spheroidization glass powder.

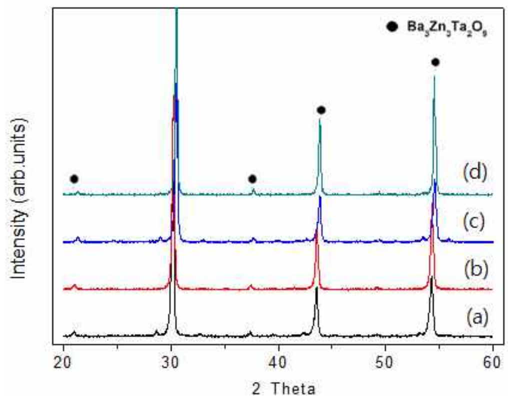


Fig. 2. XRD results of sintered BZT ceramics with nano spheroidization glass powder addition: (a) glass powder (0.0 wt%); (b) glass powder (0.3 wt%); (c) glass powder (0.6 wt%) (d) glass powder (1.0 wt%)

3. Results and Discussions

Fig. 1 shows the shape and the results of DTA analysis of nano spheroidization glass powder. As shown in Fig. 1, plasma-treated glass powders have a spherical shape, an average particle size (D_{50}) of 120 nm and a BET surface area of 13.86 m^2/g. The results of thermo gravimetric analysis (TGA) indicate that the of nano spheroidization glass powder have a Tg of 651℃, a crystallization initiation temperature of 799℃ and a main crystallization temperature of 926℃.

Fig. 2 shows the results of XRD analysis of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics as a function of nano spheroidization glass powder content and sintered at 1450℃. As can be seen in Fig. 2, the main peak is shifted to a higher angle due to the addition of nano spheroidization glass powder, and a secondary phase is produced as the of nano spheroidization glass powder content increases.

Fig. 3 shows the changes in bulk density of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics as a function of nano spheroidization glass powder content and sintering temperature. As can be seen therein, at a sintering temperature of 1500℃, the density increases as the nano spheroidization glass powder content and the sintering temperature increase, but at a nano spheroidization glass powder content of 1.0 wt%, the

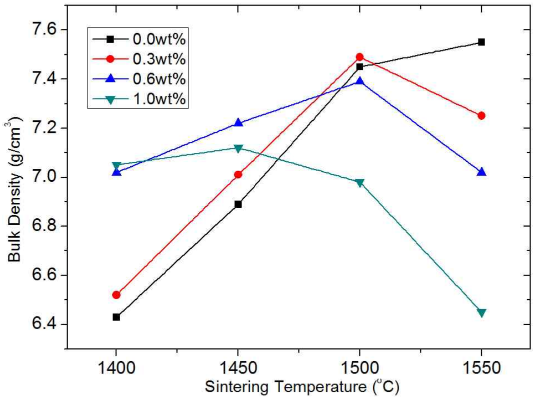


Fig. 3. Bulk density of BZT ceramics according to sintering temperature for various nano spheroidization glass powder addition

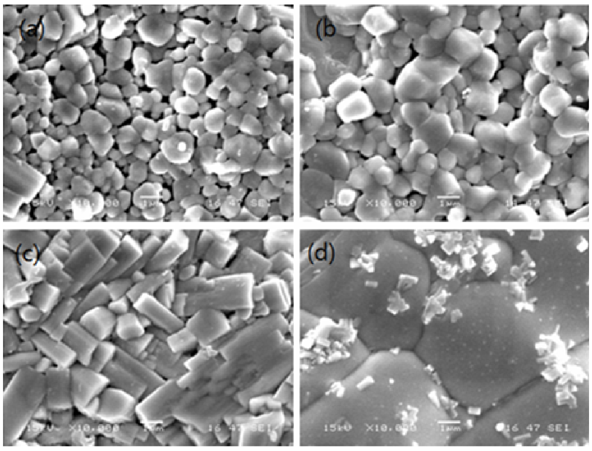


Fig. 4. SEM image of sintered BZT ceramics with nano spheroidization glass powder addition: (a) glass powder (0.0 wt%); (b) glass powder (0.3 wt%); (c) glass powder (0.6 wt%); (d) glass powder (1.0 wt%)

bulk density significantly decreases regardless of the sintering temperature. Generally, in the case of pure $Ba(Zn_{1/3}Ta_{2/3})O_3$, a sintering temperature of 1600℃ or a long sintering time is required to obtain a bulk density of 7.953 g/cm^3 or higher, but a bulk density of 7.53 g/cm^3 is shown even at a nano spheroidization glass powder content of 0.3 wt%, suggesting that the sintering temperature can be lowered by the addition of nano spheroidization glass powder.

Fig. 4 shows the microstructures of the sintered sample having nano spheroidization glass powder contents and sintered at a temperature of 1500℃. As can be seen therein, the microstructures become more dense and angular as the glass powder content increases. In the case of nano spheroidization glass powder content 1.0 wt%, the microstructures look dense, but the bulk density decreases, and this decrease in the bulk density is believed to be because of abnormal grain growth caused by excessive liquid-phase sintering and the influence of a secondary phase caused by glass. Fig. 5 shows the changes in dielectric

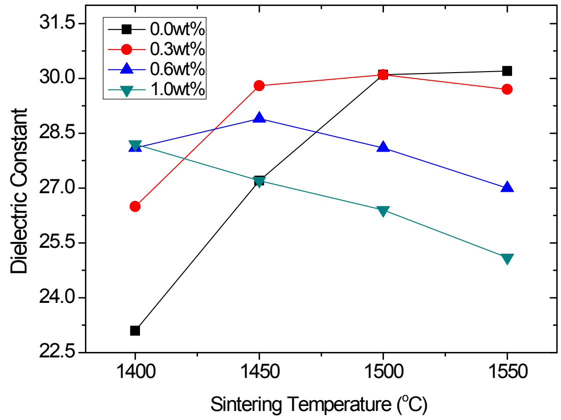


Fig. 5. Dielectric constant of BZT ceramics according to sintering temperature for various nano spheroidization glass powder addition

constant of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics as a function of nano spheroidization glass powder content and sintering temperature. As can be seen therein, in the case of pure $Ba(Zn_{1/3}Ta_{2/3})O_3$, the dielectric constant increases as the sintering temperature increases, and a dielectric constant of 30 or higher is shown at a sintering temperature of 1550℃ or higher. In the cases of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics containing nano spheroidization glass powder, a dielectric constant of 30 or higher is shown even at a sintering temperature of 1450℃. It is generally known that, when glass powder having a low dielectric constant is added to a dielectric material, the dielectric constant of the dielectric material is reduced [7]. However, the $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics having a nano spheroidization glass powder content of 0.3 wt% or lower showed a dielectric constant similar to that of pure $Ba(Zn_{1/3}Ta_{2/3})O_3$, suggesting that nano spheroidization glass powder was solid-dissolved in $Ba(Zn_{1/3}Ta_{2/3})O_3$ without forming a secondary phase. It is known that the increase in dielectric constant of a dielectric material with an increase in sintering temperature is determined by the composition of the dielectric material, but in the case of the same composition, the dielectric constant increases as the grain size increases. However, it is believed that the increase in dielectric constant with an increase in sintering temperature in this experiment is due to bulk density.

Fig. 6 shows the changes in quality factor ($Q\times f_o$) of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics as a function of nano spheroidization glass powder content and sintering temperature. As can be seen therein, in the case of pure $Ba(Zn_{1/3}Ta_{2/3})O_3$, the quality factor ($Q\times f_o$) value increases as the sintering temperature increases, and in the case of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics containing glass powder, at a sintering temperature of 1500℃ or lower, the quality factor ($Q\times f_o$) value increases as the nano spheroidization glass powder content increases, but at a sintering temperature of 1550℃, the quality factor value decreases as the nano spheroidization glass powder content increases. It is generally known that the quality factor of a dielectric material is greatly

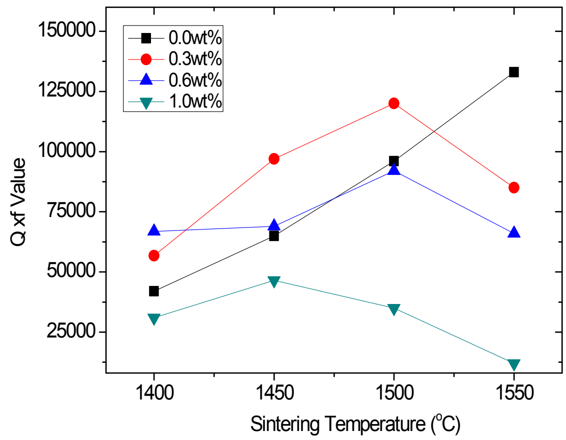


Fig. 6. Quality factor of BZT ceramics according to sintering temperature for various nano spheroidization glass powder addition

influenced by the composition and microstructure of the dielectric material, and a combination of point defects, grain boundaries, voids, secondary phases and the like is attributable to a decrease in quality factor. In particular, it is known that the quality factor ($Q\times f_0$) of complex perovskite $A(B', B'')O_3$ is influenced by the ordering of Zn and Ta ions at the B lattice position. It is believed that the increase in the quality factor ($Q\times f_0$) value with an increase in sintering temperature is attributable to the ordering of ions as previously reported and that the decrease in quality factor by the addition of nano spheroidization glass powder is attributable to a secondary phase caused by the glass phase. The temperature coefficient of resonant frequency that is the important property of a dielectric resonator was in the range of 3-7.5 ppm/℃ for pure $Ba(Zn_{1/3}Ta_{2/3})O_3$ depending on the sintering temperature and time, and this temperature coefficient value was shown to be similar to a previously reported value [2, 3, 4]. In the case of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics containing glass powder, the temperature coefficient of resonant frequency decreased as an increase in the nano spheroidization glass powder content and was shown to range from -7 to 2 ppm/℃. The temperature coefficient of resonant frequency is influenced by the temperature coefficient of dielectric constant (τ_ε) and the coefficient of thermal expansion (α_l). It can be seen that the decrease in the temperature coefficient of resonant frequency with an increase in the nano spheroidization glass powder content is attributable to the change in thermal expansion coefficient by the glass phase.

4. Conclusion

In this study, nano spheroidization glass powder was added to a composition of $Ba(Zn_{1/3}Ta_{2/3})O_3$, and the microwave dielectric properties and microstructures of the resulting $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics having glass powder contents and sintered at various temperatures were examined. The experimental results revealed that, as the nano spheroidization glass powder content increased, the microstructures of the dielectric ceramics became denser even at low temperatures. On the other hand, in the case of the microwave dielectric properties of the dielectric ceramics, it could be seen that the dielectric constant and the quality factor decreased as the nano spheroidization glass powder content increased. Excellent microwave dielectric properties could be obtained under the conditions of suitable nano spheroidization glass powder content and sintering temperature. Particularly, when the nano spheroidization glass powder is 0.3 wt% and sintering is carried out at a temperature of 1500℃ for 6 hr, a temperature stable microwave dielectric material is obtained, which has a dielectric constant (ε_r) of 30.2, a quality factor ($Q\times f_0$) of 124,000 GHz and a temperature coefficient of resonance frequency (τ_f) of 2 ppm/℃.

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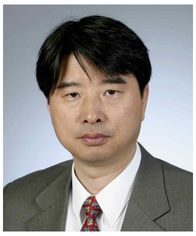
Cheal Soon Choi He received B.S degree in the department of materials science & engineering from Ganneung university. Korea, 1993. He is currently pursuing his M.S degree in Hongik University, Korea. His research interests are dielectric material and microwave passive device. Currently, he serves as a director for InT. Co. Ltd.



Ki Soo Kim He received B.S, MS degree in the department of materials science & engineering from Seoul National University. Korea 1979 and 1981, respectively. He completed Ph.D degree in Materials from Stanford University in 1993. His research interests include dielectric, ferroelectric, piezoelectric materials and their applications. Currently, he serves as a professor in Hongik University, Korea.

Dong Hee Rhie He received Ph.D degree in electrical engineering from Korea University. Korea 1990. His research interests include dielectric, semiconductor, piezoelectric materials and their applications. Currently, he serves as a professor in Suwon University, Korea.

Jung Rag Yoon He received B.S, MS, and Ph.D degree in electrical engineering from Myoung Ji university.. Korea, 1991, 1993, and 1999, respectively. His research interests are dielectric material and energy storage device. Currently, he serves as an R&D Center Manager for Samwha Capacitor Co. Ltd.