Synthesis of BaTiTe$_3$O$_9$ Ceramics for LTCC Application and Its Dielectric Properties

Do-Kyun KWON, Michael T. LANAGAN and Thomas R. SHROUT

Center for Dielectric Studies, Material Research Institute, The Pennsylvania State University, University Park, PA 16802

A new tellurate, BaTiTe$_3$O$_9$, was found in the BaO–TiO$_2$–TeO$_2$ ternary system. Using conventional solid state reaction, the new single phase compound, BaTiTe$_3$O$_9$, phase was synthesized and sintered over the very low temperature range of only 625–700°C. In addition, different calculations routes, including the effect of TiTe$_3$O$_9$ precursor in the phase formation, were examined. The dielectric properties of BaTiTe$_3$O$_9$ ceramics were determined in the microwave region as well as at low frequencies. The relative dielectric permittivity ($\varepsilon_r$) and the temperature coefficient of permittivity ($T_C$) of BaTiTe$_3$O$_9$ at 1 MHz were measured as 30 and 790 ppm/°C, respectively. The dielectric properties were maintained up to microwave region without degradation. The dielectric permittivity and $Q\times f$ product obtained were 29 and 1,700 GHz at 7.6 GHz, respectively. The temperature coefficient of resonance frequency ($TCF$) showed a large negative value of $-372$ ppm/°C.

[Received June 3, 2004; Accepted December 15, 2004]

Key-words: Dielectrics, Tellurium oxide, LTCC, Microwave, Precursor

1. Introduction

With the rapidly growing wireless industry, new high performance dielectric materials are needed to build low loss, high density, thermally stable integrated packages, such as Low Temperature Cofired Ceramics (LTCC). Multilayer microwave components have been investigated to miniaturize resonant devices. Promising candidate materials for multilayer type elements require the dielectric to be co-fireable with metal conductor layers at temperatures below their melting point. For the low temperature sintering of dielectric ceramics, low melting point glasses or oxide fluxes are frequently added so the dielectrics can be cofired with conductor layers such as silver, with a melting point of 961°C.

These approaches, however, often result in degradation of dielectric properties of the main formulations caused by the formation of secondary phases and lossy amorphous phases in the grain boundaries. For this reason, exploring low melting single phase dielectrics is preferred rather than the addition of sintering aids in the dielectric material development for LTCC application.

Tellurium dioxide is well known as a network-former in the glass industry with a melting point of 733°C. Because of their high IR transmission, high refractive index and low dispersion, tellurite glasses are of considerable interest for various optical devices. Many researchers have investigated non-linear optical glasses formed in the TeO$_2$ rich region in the BaO–TiO$_2$–TeO$_2$ ternary system and have investigated the coordination changes of tellurium ions with various BaO content resulting in structural changes. In contrast to glasses, tellurium based oxide ceramics in BaO–TiO$_2$–TeO$_2$ ternary system have not yet been seriously investigated for dielectric applications.

In the TiO$_2$–TeO$_2$ binary system, only one compound TiTe$_3$O$_9$ was reported as a thermodynamically stable single phase in air with the tellurium in the Te$^{4+}$ valence state. TiTe$_3$O$_9$ can be synthesized at 700°C in air in the form of CaF$_2$ cubic structure ($a = 1.095$ nm). The microwave dielectric properties of cubic TiTe$_3$O$_9$ polycrystalline ceramics was initially reported by Maeda et al., with a relative dielectric permittivity ($\varepsilon_r$) of 36, a $Q\times f$ of 10,200 GHz and a temperature coefficient of relative permittivity ($T_C\varepsilon_r$) of $-220$ ppm/°C, measured at 4 GHz with 12% porosity. Udovic et al. obtained improved dielectric properties of TiTe$_3$O$_9$ polycrystalline samples sintered at 720°C for 5 h by eliminating porosity. The obtained values were $\varepsilon_r$ of 50, $Q\times f$ of 30,600 GHz and a temperature coefficient of resonant frequency ($TCF$) of $+133$ ppm/°C, measured at 5 GHz. In this study, the new single phase ternary compound of BaTiTe$_3$O$_9$ was synthesized using TiTe$_3$O$_9$ precursor to prevent TeO$_2$ sublimation during firing process. Influences of processing factors on microstructure and dielectric properties were also considered by comparing the samples made through different calcination routes. In addition, the dielectric properties of BaTiTe$_3$O$_9$ compound were examined at various temperatures and frequencies up to the microwave range.

2. Experimental procedures

Ceramic compounds in the BaO–TiO$_2$–TeO$_2$ ternary system were prepared using conventional mixed oxide ceramic processing. Starting materials were reagent grade powders of BaCO$_3$ (Sakai Chemical Industry Co.), TiO$_2$ (Ishihara Corp.), and TeO$_2$ (Alfa Aesar). Raw materials were weighed stoichiometrically and mixed in alcohol media, accounting for combustion and hydration losses. Raw materials were ball milled with stabilized zirconia media for 24 h, and subsequently calcined. For single phase BaTiTe$_3$O$_9$ formation, two calcinations processing routes were applied.

Route 1: BaCO$_3$ + TiO$_2$ + 3TeO$_2$ $\rightarrow$ BaTiTe$_3$O$_9$ + CO$_2$ ↑ (700°C, 20 h)

Route 2: TiO$_2$ + 3TeO$_2$ $\rightarrow$ TiTe$_3$O$_9$ (650°C, 20 h)
$\rightarrow$ BaCO$_3$ + TiTe$_3$O$_9$
$\rightarrow$ BaTiTe$_3$O$_9$ + CO$_2$ ↑ (700°C, 10 h)

After calcinations, the ball-milled powders were pressed into disks 10 mm in diameter and 1–2 mm in thickness. Approximately 4 mass% organic binder was added to assist in the pressing. The disks were fired at 600–700°C for 2 h in closed crucibles. Phase determination was made using X-ray diffraction (XRD) (Scintag PADV and X2 diffractometers) and DMSNT (Scintag) data collection and analysis software. To
examine the grain morphology, polished surface microstructures were examined by scanning electron microscopy (SEM) (Hitachi S-3000H), and the chemical composition in localized areas of the samples was characterized by EDS attached to the SEM instrument.

For dielectric characterization, the disks were ground to provide parallel surfaces and gold electrodes were applied by sputtering. The temperature dependence of the complex dielectric permittivity and dielectric loss were determined in the frequency range of 100 Hz–1 MHz using a HP 4284 LCR meter with a programmable 9023 Delta Design oven. For high frequency measurement of the relative dielectric permittivity and $Q\times f$ values in GHz region, the post resonator method as suggested by Hakki and Coleman,\textsuperscript{11} was applied using on HP 8510 Network Analyzer. The temperature coefficient of resonant frequency (TCF) was determined by cavity resonator method\textsuperscript{12} using on INVAR cavity in the temperature range of 20 to 80°C.

3. Results and discussions
3.1 Formation of the BaTiTe$_3$O$_9$ compound

Figure 1 shows DSC & TGA data of BaTiTe$_3$O$_9$ formation, including the formation of the precursor TiTe$_3$O$_9$. Two processing routes were used for BaTiTe$_3$O$_9$ formation. The first route involved mixing of the three raw materials (BaCO$_3$, TiO$_2$, TeO$_2$), and the second one utilized the TiTe$_3$O$_9$ precursor. In the case of route 1, two exothermic and four endothermic reactions were observed during calcination. Weight loss accompanied the reactions up to 525°C, being attributed to BaCO$_3$ decomposition and unknown secondary reactions. The first two endothermic reactions in the temperature range of 450–525°C were considered to accompany these weight loss process of BaCO$_3$ decomposition as observed in the curve of route 2. However, it is unclear about the exothermic reactions that occurred below 400°C with accompanying weight loss. Based on the TiO$_2$ + 3TeO$_2$ reaction curve in Fig. 1, the second exothermic peak can be considered as the formation of TiTe$_3$O$_9$. However, it is still hard to explain the corresponding weight loss that occurred in this temperature range. The second exothermic reaction was identified with the formation of TiTe$_3$O$_9$. In the temperature range of 475–625°C, four endothermic reactions were observed. For route 2, the calcination process with the TiTe$_3$O$_9$ precursor, the DSC–TGA data showed different kinetics. Three endothermic reactions over 550°C which corresponded to the BaCO$_3$ decomposition and BaTiTe$_3$O$_9$ phase formation were observed. It is clear that the kinetics in calcination processes was simplified by utilizing the TiTe$_3$O$_9$ precursor. The phase formation temperature in route 2 was higher than that in route 1. The difference in phase formation temperature can be considered as the effect of the existence of highly reactive intermediate phases. When the stable TiTe$_3$O$_9$ was used as a precursor, the limitation of the reaction between BaCO$_3$–TeO$_2$ or BaCO$_3$–TiO$_2$–TeO$_2$ species resulted in high phase forming temperature. The extra weight loss related to the secondary reactions of tellurium species could also be prevented by using TiTe$_3$O$_9$ precursor.

The densification behavior of BaTiTe$_3$O$_9$ ceramics is shown in Fig. 2. For both samples, full densification was obtained at 625°C. It was about 100°C lower than the reported sintering temperature of TiTe$_3$O$_9$ single phase.'\textsuperscript{10} This extremely low sintering temperature implies the potential to be used in LTCC applications. However, different behavior in densification was observed by comparing samples from the two different processing routes. For samples prepared through route 1, the bulk density showed a maximum value at 625°C and then decreased at higher firing temperatures up to 700°C. In contrast, samples prepared using route 2 showed nearly constant bulk densities with increased sintering temperature. This different density change between processing routes 1 and 2 can be explained by the effect of the evaporation of tellurium species in the tellurates secondary phases. As shown in the XRD patterns of sintered samples, the calcination route 1 (Fig. 3(a)) produced secondary phases indexed as BaTe$_2$O$_6$ and TiTe$_3$O$_9$ while route 2 (Fig. 3(b)) produced BaTiTe$_3$O$_9$ single phase after the sintering at 650°C for 2 h. For both samples, partial melting was observed when sintered at higher than 700°C.

Grain morphology was analyzed using scanning electron microscopy. Figure 4 shows the thermally etched surface of BaTiTe$_3$O$_9$ specimen sintered at (a) 650°C and (b) 700°C for 2 h, respectively. After sintering at 650°C, plate shaped uniform grains were observed with submicron grain sizes. Abnormal grain growth with well-developed plate morphology was observed at higher temperatures. It was confirmed by EDS analysis that all grains in the microstructure had the same chemical compositions with the Ba–Ti–Te ratio of 1 : 1 : 3.

3.2 Dielectric properties of BaTiTe$_3$O$_9$

Dielectric properties of BaTiTe$_3$O$_9$ ceramics sintered at the temperature range of 625–675°C are exhibited in Fig. 5. Relative dielectric permittivity and dielectric loss were measured at 1 MHz, and the temperature coefficient of permittivity (TC$\varepsilon$)
was measured in the temperature range of 20 to 80°C. The dielectric properties of single phase BaTiTeO₃ (route 2) were obtained, with a dielectric permittivity of 30, TCE of 790 ppm/°C and dielectric loss (\(\tan \delta\)) of \(5 \times 10^{-3}\). According to Harrop, most dielectrics having a dielectric permittivity of 30 exhibit large negative values of TCE (\(\sim -300\) ppm/°C), proportional to \(-\alpha\)\(\varepsilon\).\(^{13}\) However, BaTiTeO₃ shows an anomaly in TCE with a large positive value. This anomaly in TCE makes it possible to develop low firing, high dielectric constant dielectrics by the formation of composite with high dielectric constant (\(\sim 100\)), negative TCE dielectrics such as rutile TiO₂.

The dielectric permittivity and TCE varied with sintering temperature for the samples prepared using route 1, while those of samples prepared by the precursor method (route 2) remained constant. Decrease of dielectric permittivity and increase of TCE with increasing sintering temperature are considered as the effect of secondary phases, such as TiTeO₃. The dielectric permittivity and TCE changes agree with the elimination of high dielectric permittivity TiTeO₃ phase (\(\varepsilon = 50, \text{TCE} = -300\) ppm/°C) at high temperatures, as shown in Fig. 3.

It is unclear which factor causes higher dielectric loss in the sample of route 1. But, with consideration of the weight loss shown in Fig. 1, it might be related to the porosity or defects resulting from volatilization of tellurium species.

The microwave dielectric properties were also measured using the post resonator method. The TE₀₁₁ resonance peaks were observed at 7.6 GHz and 10.3 GHz for post samples with the diameter of 10 mm and 8 mm, respectively. For both samples, the dielectric permittivity was 29 and \(Q / f\) was calculated to be 1,700 GHz. As shown in the Fig. 6, frequency dependence of dielectric properties was observed only in low frequency region (below 10 kHz), which can be explained by space charge effect. However, in the high frequency region from 1 MHz to 10 GHz, dielectric relaxation causing significant decrease in dielectric permittivity and increase in dielectric loss was not observed. The temperature coefficient resonance frequency (TCR) was \(-372\) ppm/°C over the temperature range of 20 to 80°C.

4. Conclusion
A new dielectric composition in the BaO–TiO₂–TeO₂ ternary...
The relative dielectric permittivity and the temperature coefficient of permittivity of BaTiTe$_3$O$_9$ at 1 MHz were determined to be 30 and 790 ppm/$^\circ$C, respectively. The dielectric properties were maintained up to the microwave region without degradation. The dielectric permittivity and $Q \times f$ obtained as 29 and 1700 GHz at microwave frequency, respectively. The temperature coefficient of resonance frequency (TCF) showed large negative value of $-372$ ppm/$^\circ$C. The $Q \times f$ value of BaTiTe$_3$O$_9$ single phase itself is not high as compared with other microwave dielectrics. However, exceptionally large negative TCF value (i.e. large positive $\kappa$) relative to dielectric permittivity and its low sintering temperature promise the application of BaTiTe$_3$O$_9$ ceramics as high $k$, microwave NP0 dielectrics end member with LTCC technology. The use of the TiTe$_3$O$_8$ precursor in the replacement of TiO$_2$ in various dielectrics, such as MgTiO$_3$, (Zr, Sn)/TiO$_2$, Ba$_2$Ti$_4$O$_9$, etc., should enable the synthesis of excellent dielectrics that can be processed at very low temperatures.

Acknowledgment This work was supported by the National Science Foundation, as part of the Center for Dielectric Studies under Grant No. 0120812.

References