Dielectric properties of new LTCC material applied to high frequencies

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We have developed an LTCC (Low Temperature Co-fired Ceramics) material, which consists of Mg$_2$SiO$_4$, SrTiO$_3$ and highly crystallized Li–Mg–Zn–B–Si–O glass. The material was able to be co-fired with inner copper electrodes that have high electric conductivity. The dielectric constant is 8.8 and its Q value is 1620 at 25 GHz. Moreover, its temperature coefficient of dielectric constant $\tau_f$ is +16 ppm/°C, which is much smaller than that of the LTCC material reported previously. Using the new LTCC material, band-pass filter (BPF) was successfully fabricated. The BPF had no defects such as delamination or cracks, and its filter properties were confirmed.

Key-words : LTCC, Microwave, High Q value, Low temperature coefficient, Low dielectric constant, BPF

1. Introduction

Rapid progress continues to be made towards achieving high-speed and high-frequency processing of electronic devices, by realizing the electronic components and devices with ever-higher processing speed and higher integration density. To meet these requirements, low temperature co-fired ceramics (LTCC) materials are being used.\(^{1,4}\) LTCCs have excellent high-frequency properties and are widely used for electronic components because they can be co-fired with a high-conductivity wiring conductor, such as Cu, Ag, or Au, by lowering the sintering temperature of the ceramics used as the insulating layer.\(^{7,17}\) Furthermore LTCCs have lower dielectric loss, which affects the high-frequency properties, than organic resin, which is generally used as an insulating materials in electronic circuits.\(^{19}\)

Therefore, LTCCs are suitable materials for constructing filters mounted in high-speed radio communication equipments.\(^{19,21}\) LTCC components usually have a multilayered circuit structure, because multiple green tapes of LTCC with via-holes and wiring conductors are laminated in the manufacturing process.\(^{21,22}\) This multilayered circuit has capacitors and other element parts and has achieved downsized components such as filters. Especially for further development of to filters, higher conductivity of electric conductors and lower dielectric loss (high Q value) of LTCC are required.\(^{23-30}\)

Although Ag or Cu is generally selected for electrode material, we selected only the Cu electrode for the following reasons. Candidate materials for a conductor with a high conductivity and a low cost are limited to Cu and Ag. However, Ag easily causes a migration problem owing to the diffusion during sintering, and this problem is very difficult to overcome. In contrast, Cu has less possibility for migration. In addition, the melting point of Cu is approximately 100°C higher than that of Ag.\(^{30}\) Therefore, by using Cu as a wiring conductor, LTCC materials can be sintered at higher temperatures, which leads to a reduction in the quantity of the sintering aid added to LTCC materials. Because glass, which has a larger dielectric loss (lower Q value) than ceramics, is generally used as a sintering aid, reducing the quantity of this aid is advantageous in terms of the high-frequency properties of LTCCs. However, LTCC materials need to be sintered in a reducing atmosphere because Cu is easily oxidized at high temperatures.

For the smaller dielectric loss (higher Q value) of LTCC materials, LTCC material (LTCC-A),\(^{27,28}\) which has very high Q value for a LTCC material, was previously developed. Generally, the Q value of LTCC is lower than that of crystallized ceramics because LTCC contains a glass phase that has lower Q value. However, LTCC-A has a small residual glass phase because the glass phase is highly crystallized. Its dielectric constant and Q value are 7.4 and 2200 at 25 Hz, respectively. LTCC-A mainly consists of MgAl$_2$O$_4$, Mg$_2$B$_2$O$_6$, Mg$_2$B$_4$O$_7$, and Li$_2$MgSiO$_4$ crystal phases, which have high Q values. For achieving low temperature sintering and high Q value, highly crystallized Li–Mg–Zn–B–Si–O glass was used. Mg$_2$B$_2$O$_6$, Mg$_2$B$_4$O$_7$, and Li$_2$MgSiO$_4$ crystals are generated by crystallization of the glass, and the residual glass phase was scarcely, which contributed to the high Q value.

However, LTCC-A has a large temperature coefficient of dielectric constant ($\tau_f$) because all crystal phases of LTCC-A have large $\tau_f$. Therefore, its applications to microwave devices are limited to specific uses. To address this problem, new LTCC material that has both a high Q value and a low $\tau_f$ has been required.

In this paper, the investigation into new LTCC material (LTCC-B) and the relationships among the dielectric properties, crystal phases, and microstructures are discussed and an application, band pass filter (BPF) for a microwave by using LTCC-B is introduced.

2. Experimental procedure

2.1 Specimen preparation

Li–Mg–Zn–B–Si–O glass was prepared as follows: SiO$_2$
(99.9% purity) from Kojundo Chemical Laboratory, B₂O₃ (≥99%), Li₂CO₃ (≥99%), Mg(OH)₂ (≥99%), and ZnO (≥99%) from Nacalai Tesque were mixed using a ball mill with 5-mm-ϕ partially stabilized zirconia (PSZ) balls. They were melted in Pt–Rh crucibles at 1400°C for 2 h, rapidly quenched with twin-rollers, and crushed using a ball mill. Specimens of LTCC-B were prepared from Mg₂SiO₄, SrTiO₃, and Li₂O glasses. Mg₂SiO₄ and SrTiO₃ powder have high purity (≥99%) with mean particle diameters of 1.0 and 0.6 μm, respectively. Li–Mg–Zn–B–Si–O glass also has a mean particle diameter of 1.0 μm. Compound of Mg₂SiO₄, SrTiO₃, and Li–Mg–Zn–B–Si–O glass were mixed to make a slurry containing zirconia balls, an organic solvent and organic binder. The slurry was cast into green sheets using the doctor blade method. The sheets were cut, and pure Cu paste was printed on them by screen printing. They were then laminated to make blocks. The blocks were then red in a low-pressure atmosphere (mixture of N₂ and H₂) at 1400°C for 2 h, rapidly quenched with twin-rollers, and crushed using a ball mill. Specimens of LTCC-C were prepared from Mg₂SiO₄, SrTiO₃, and Li₂O glasses. Mg₂SiO₄ and SrTiO₃ powder have high purity (≥99%) with mean particle diameters of 1.0 and 0.6 μm, respectively. Li–Mg–Zn–B–Si–O glass also has a mean particle diameter of 1.0 μm. Compound of Mg₂SiO₄, SrTiO₃, and Li–Mg–Zn–B–Si–O glass were mixed to make a slurry containing zirconia balls, an organic solvent and organic binder. The slurry was cast into green sheets using the doctor blade method. The sheets were cut, and pure Cu paste was printed on them by screen printing. They were then laminated to make blocks. The blocks were then red in a low-pressure atmosphere (mixture of N₂ and H₂) at 1400°C in order not to oxidize Cu.

2.2 Measurements

The dielectric properties at microwave frequencies were measured using the circular cavity resonator method using a cavity with a hollow resonance frequency of 35 GHz. The measured specimens were about 400 μm thick. The dielectric constant was approximately 8.8, and the resonant frequency was approximately 25 GHz. Samples in the shape of a capacitor of LTCC-B, shown in Fig. 1, were prepared in order to measure εᵣ in the temperature range from −40 to 85°C using an LCR meter at 1 MHz. The specimens were investigated using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction analysis (XRD). The mechanical strength was measured using a three point bending test, and the thermal expansion coefficient (α) was measured using thermal mechanical analysis (TMA).

3. Results and discussion

3.1 Dielectric properties

Figure 2 shows εᵣ as a function of the amount of SrTiO₃ in LTCC-B. This figure shows εᵣ of a higher temperature range (25–85°C) and that of a lower temperature range (−40–25°C). |εᵣ| is smallest, 16 ppm/°C, when the amount of SrTiO₃ is 6.8 wt%.

Table 1 lists dielectric properties at a high frequency such as the dielectric constant, Q value, and τᵣ. τᵣ is the inverse of the dielectric loss. The table also lists properties of pre-developed material (LTCC-A)[27,28] and conventional LTCC material (LTCC-C). LTCC-C consists of CaZrO₃ and Li–Ca–B–Si–O glass. The dielectric constants of LTCC-A and LTCC-B are 7.3 and 8.8, respectively. The Q of LTCC-A and LTCC-B are 2200 and 1620 at 25 GHz respectively. On the other hand, the Q of LTCC-C is much lower. τᵣ of LTCC-A and LTCC-B are +180 ppm/°C and +16 ppm/°C, respectively. The above Q value of LTCC-B was very high, as was that of LTCC-A. τᵣ of LTCC-B was much smaller than that of LTCC-A. Dielectric constant (εᵣ), Q value, and τᵣ of SrTiO₃ were 270, 3000 (2 GHz), and −1200 ppm/°C, respectively. τᵣ of SrTiO₃ is a very negatively large and compensates positive τᵣ of Mg₂SiO₄ and the glass. The excellent Q value is attributed to highly crystallized glass. It is also thought that the high Q value significantly contributed to the low loss of the LTCC components.

The temperature coefficient of resonance frequency (τᵣ) is defined by

\[ τᵣ = -\frac{εᵣ}{f} \]  

where α is the Thermal expansion coefficient (TEC) of the dielectric specimen. By using the α (10.0 ppm/°C) of LTCC-B shown in Table 1 as α, the τᵣ of LTCC-B is calculated to be −18 ppm/°C. This is sufficiently small for the use of LTCC-B in electronic components such as filters. On the other hand, the τᵣ of LTCC-A is calculated to be −100 ppm/°C. Consequently, the dielectric characteristics of LTCC-B were very suitable for use in electronic components used with high-speed radio communication equipment.

3.2 Microstructure

Figure 3 shows the XRD pattern of LTCC-B. The main crystal phases detected were those of Mg₂SiO₄ (Forsterite) and SrTiO₃, but a small amount of Mg₁₂B₂O₁₉ (Kotoite) was also detected. The amount of Mg₁₂B₂O₁₉ is very small, and Mg₆B₂O₁₂ and Li₂MgSiO₄, which were detected in LTCC-A, were not detected because the amount of glass was small, 10 wt% though the amount of glass was 60 wt% in LTCC-A. Hollows indicating the presence of glass phase were not found, which means the glass was highly crystallized.

Figure 4 shows a SEM image (cross-section of ceramics) of LTCC-B, and Fig. 5 shows a SEM image and EDX images of LTCC-B. XRD, SEM, and EDX analyses revealed the presence of crystals of Mg₂SiO₄ and SrTiO₃ because Sr and Ti indicate
crystals of SrTiO₃ and those of Mg and Si indicate crystals of Mg₂SiO₄. Mg₂SiO₄ crystals were about 1 μm in diameter, and SrTiO₃ crystals were about 0.5 μm in diameter, did not show grain growth, and dissolved into glass. Mg₃B₂O₆ from crystallized glass was not found by SEM and EDX because its amount is very small.

3.3 Other properties
Table 1 shows other properties of LTCC-B. Mechanical strength of 260 MPa was obtained, which is sufficient for devices and substrates used at high frequencies. α from room temperature to 600°C was 10.4 ppm/°C.

3.4 Applications
Using LTCC-B, a band-pass filter for a microwave was made. Figure 6 shows BPF, which is 3.2 mm × 2.5 mm × 1.3 mm. Figure 7 shows a microscope image of BPF, whose inner and outer copper electrodes were co-fired. De-lamination, voids and cracks of LTCC and the electrode are not found in the BPF. Figure 8 shows frequency characteristics of the BPF at 2 GHz.
Those of BPFs using LTCC-A and LTCC-C are also shown. Insertion loss (I.L.) of BPF of LTCC-B is as good as that of LTCC-A and 0.1dB smaller than that of LTCC-C, which depends on Q values. The high Q value of LTCC-B is considered to be suitable for multilayered LTCC devices for high frequency.

4. Conclusion

Although LTCC-A has a very high Q value and low $\varepsilon_r$, $\tau_{\text{c}}$ of LTCC-A is very high and BPF made of LTCC-A has high $\tau_{\text{c}}$. Therefore, applications of LTCC-A are limited to specific uses for microwave devices. Thus, new LTCC material that has a high Q value, low $\varepsilon_r$, and low $\tau_{\text{c}}$ was developed. Highly crystallized glass and added SrTiO$_3$ contribute to high Q value and low $\tau_{\text{c}}$, respectively, which are very suitable for multilayered microwave devices. We made BPF for a microwave at 2 GHz. The BPF has good properties and an insertion loss is lower by 0.1dB than that made of conventional LTCC material.

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