Bi-Based Compounds for Glass-Free LTCC Technology

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A review of the low-temperature co-fired ceramic (LTCC) materials that are currently in production, or under investigation, suggests that they can be grouped into three classes: glass-ceramic composites, recrystallized glasses and glass-free ceramics. Whereas the first two of these classes of materials are already in commercial production, glass-free ceramics are still in the development stage. In this study we have investigated a glass-free LTCC material system that consists of low- and high-permittivity LTCC materials based on Bi eutylite (permittivity, \(\kappa' = 16\)), silicate (\(\kappa' = 40\)) compounds and a \(\delta\)-BiO\(_2\) solid solution with Nb\(_2\)O\(_5\) (\(\kappa' = 90\)). All these phases meet the main requirements for LTCCs with respect to their sintering behavior \((T_s = 850-900^\circ C)\), their chemical compatibility with each other, their compatibility with a silver electrode, and their dielectric properties.

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Introduction

Commercial interest in highly sophisticated, reliable and convenient electronic devices puts a continuous pressure on the electronics industry to develop complex, robust and miniaturized circuits. While the integration of active electronic components has resulted in the miniaturization and integration of electronic circuits, the majority of the passive elements remain discrete, despite the fact that significant improvements have been made in reducing their size and cost. In parallel with conventional printed-circuit-board technology, new technologies are being developed based on the use of ceramic multilayer substrates. By applying a low-temperature co-fired ceramic (LTCC) technology, passive elements can be integrated in monolithic, highly reliable and robust LTCC modules consisting of several layers of ceramic substrates with integrated elements (inductors, capacitors, resonators), which are interconnected with 3D stripline circuitry.

LTCC technology has a number of very important advantages that make it one of the most potentially profitable technologies in the information and telecommunications industries. Because of the parallel processing of particular module layers, the production is fast, and this allows intermediate quality control. Potential production faults can be eliminated during the manufacturing and before final co-firing, which reduces the production costs. The LTCC modules are highly reliable because the circuitry is hermetically sealed, and almost no additional thermal shocks are applied as there is a reduced need for soldering. This also eliminates the problems that can occur at the contacts between the mounted component and the electrode. The LTCC modules are robust, as well as being thermally and mechanically very stable.

LTCC Materials

Although LTCC technology demonstrates a number of advantageous features, its development is still in the early stages. The main problems relate to the rigorous demands that are placed on the materials. In terms of dielectric properties, any newly developed materials are expected to exhibit temperature-stable permittivities with values similar to those of conventional microwave materials; they are also expected to have low dielectric losses \((\tan \delta = 1/Q)\). The magnitude of the dielectric losses is not necessarily the same as those exhibited by conventional microwave materials, because the overall losses associated with LTCC modules are predominantly determined by the losses in the conductive components.

A Q value of a few thousand at 1 GHz is acceptable.

In order to minimize conductor losses, the choice of an appropriate electrode is limited to highly conductive metals like copper and silver. The main disadvantage of copper is related to its affinity for oxygen, which demands a slightly reducing atmosphere during firing that can be detrimental to the ceramics. In this respect, silver is the better choice; it does, however, exhibit a lower melting point \((960^\circ C)\). The melting point of the electrode metal determines the sintering temperature of the module because the ceramic components must be sintered at approximately 50–100°C below this temperature. Another very restrictive requirement is the necessity for the electrode material and the ceramic to be chemically compatible. Fine stripline circuitry—as fine as 10-μm thick, and with lines that are 80-μm wide—that is screen printed on ceramic green sheets must maintain its structure, even after co-firing. Every reaction that occurs between the electrode and the ceramic can destroy the functionality of the module or at least change its characteristics. In general, it is believed that the main difficulties with the development of new LTCC materials are not related to their dielectric properties but to their sintering behavior, their thermo-mechanical properties, and especially to their chemical compatibility.

LTCC materials that are commercially used today, or are in the process of being developed and introduced into production, can be divided into three major groups:

1. Glass-ceramic composites
2. Recrystallized glasses
3. Glass-free ceramics

**Glass-ceramic composites:** The first group of LTCC materials, glass-ceramic composites, includes conventional microwave dielectric materials, which on their own have a sintering temperature that is far too high. However, the glass phase that is added to such microwave dielectrics can reduce the sintering temperature to a suitable level. The main component of the composite is the crystalline phase, and this phase makes the largest contribution to the dielectric properties of the composite. Nevertheless, the influence of the glass phase cannot be ignored, because it significantly reduces the permittivity and increases the dielectric losses. The dissolution of the crystalline filler in the glassy phase has an important influence on the viscosity of the melt during the firing, and on the mechanical properties of such composites.

Based on the reactivity between the glass and the crystalline filler, two sub-groups can be distinguished. The first includes
composites for which no significant chemical reaction takes place during the firing. An example of such a reduction in sintering temperature is provided by the composite composed of a BaNd₃Ti₅O₁₂ ceramic and glass with the composition La₂O₃/B₂O₃/TiO₂. On its own, the BaNd₃Ti₅O₁₂ ceramic sinters at ~1400°C, whereas the composite with ~65 vol% of glass sinters as low as ~840°C. After firing, such a glass-ceramic composite exhibits $\kappa' = 30$, $Q\cdot f > 6.000$ GHz (measured at 6 GHz) and $\tau_r \sim 0$ ppm/K. The second sub-group involves systems for which the reaction between the glass and the ceramic phase occurs during firing. Using such an approach, the sintering temperature of BaNd₃Ti₅O₁₂ can be reduced to ≤900°C with the addition of a significantly smaller amount of glass. The addition of only 10 vol% of B₂O₃/B₂O₃/SiO₂/ZnO glass gives a composite LTCC material with $\kappa' = 68$, $Q\cdot f > 6.000$ (at 6 GHz) and $\tau_r \sim 0$ ppm. Many other systems have already been developed for which the same mechanism for reducing the sintering temperature can be applied. Interestingly, in some systems, e.g. MgTiO₃-CaTiO₃, the characteristics of the starting glass powder proved to be very important. For example, the presence of unreacted oxide in the amorphous glass powder can influence the phase development, the microstructure characteristics and, consequently, the properties of such an LTCC composite.

**Reconstituted glasses:** The next group of LTCC materials includes materials based on reconstituted glasses. Today, this is the most frequently used group of LTCC materials in industry. The amorphous glass, which might contain a small amount of crystalline phase that acts as nucleating agent or a dielectric-property modulator, crystallizes during the firing. During this process the crystalline phases that determine the dielectric properties of such a material are formed. An example is the commercial Ferro A6-M powder, which contains CaO/SiO₂/B₂O₃ glass. During firing at 850°C, the crystallization of wollastonite (CaSiO₃) takes place. At the end of the procedure, the material contains the wollastonite phase and residual borosilicate glass. The residual glass would crystallize at 930°C, thereby reducing the dielectric losses; however, this step is usually not applied because the temperature is close to the melting point of the electrode. A similar mechanism was also used in some other systems, for example, the CaO-Al₂O₃-SiO₂-TiO₂ system. During the firing of the mixture, which is composed of the glass from this system and a crystalline Al₂O₃, anorthite (CaAl₂Si₂O₆) is formed (Fig. 1). By varying the concentration of the B₂O₃/TiO₂ additives and the processing conditions, we can influence the phase crystallization, the microstructural characteristics, the sintering behavior and the dielectric properties. Typical microwave dielectric properties for such reconstituted LTCC materials are: $\kappa' = 10$, $Q\cdot f = 14.200$ GHz (at 10 GHz). The temperature dependence of the resonant frequency is not linear and shows a $\tau_r$ of ~ -20 ppm/K and ~ -60 ppm/K in the temperature ranges of ~ -55 to 25°C and 25 to 155°C, respectively.

**Glass-free ceramics:** Today, LTCC modules have been developed to the level where further improvements will require the integration of new layers with specific functions. This means there is a demand for new LTCC materials that must possess very specific electrical properties in addition to all the LTCC-relevant properties. Such a group of materials, which can be used as capacitors, couplers, LC filters, are those
materials with a high permittivity. The use of high-permittivity materials in LTCC technology would contribute to the miniaturization of modules, which in turn results in an increase in the volume density of the electrodes and the thermal vias. This further complicates the production process because of the much lower geometrical tolerances that are required.\(^{14}\) To avoid this, materials with significantly lower dielectric losses must be applied to reduce the generation of heat.

All the LTCC materials that are commercially used today include a significant amount of glass phase. Apart from its advantageous influence with regard to the sintering behavior, the glass phase also has some detrimental influences. The presence of the glass phase increases the dielectric losses of such composites, which results in poorer performance of the module and increased heat generation. The diffusion of the silver electrode through the amorphous phase is also enhanced. The reproducibility of the production process can present problems, and small variations in the processing conditions can have a significant influence on phase formation and crystallization. Finally, the presence of the glass phase, together with the products of the crystallization and the different modulators, makes the LTCC materials very complex. To keep the physical properties of particular layers intact, mass transport through the interfaces must be minimized. In the case of multiphase layers, this is very difficult to ensure, especially when several different layers are combined within a single module.\(^{15}\) The complexity of existing LTCC materials makes the development of new functional layers difficult. For future systems, simple single-phase layers would be more appropriate. Many of these problems can be effectively overcome by eliminating the glass phase.

So-called glass-free LTCC materials are currently the subject of intense investigations in many R&D laboratories. Many studies of BiNbO\(_5\) (\(\kappa = 44\)), temperature coefficient of resonant frequency \(\tau_r = -10 \text{ ppm/K}\), quality factor \(Q = f = 4000 \text{ GHz at 4 GHz}\) were performed in order to tune the dielectric properties and adjust the sintering temperature to the requirements of LTCC technology.\(^{16-18}\) Unfortunately, later investigations clearly demonstrated that BiNbO\(_5\) is not an appropriate material for LTCC applications because it reacts with Ag,\(^{20}\) which is, due to its high conductivity, the most commonly used metal for transmission lines within LTCC modules. The sintering temperature of Zn niobates (\(\text{Zn}_2\text{Nb}_2\text{O}_6\) and \(\text{ZnNb}_2\text{O}_4\)) was successfully decreased by adding Cu compounds without deteriorating the initial high \(Q\)-value.\(^{20,21}\) The major drawback of these materials is the low permittivity of the Zn niobates (\(\sim 20\)), which significantly reduces their technological value. The Zn-doped Bi\(_x\)Ca\(_y\)Nb\(_2\)O\(_x\) compound was claimed to exhibit useful dielectric properties (\(\kappa = 79\), \(Q = f = 1150 \text{ GHz, } \tau_r = 1 \text{ ppm/K}\)) in combination with a low sintering temperature, but the authors did not report on the possible interaction with Ag.\(^{22}\)

By far the most extensively investigated NP0-type LTCC materials are the two ternary phases from the Bi\(_2\)O\(_3\)-Nb\(_2\)O\(_3\)-ZnO system: the cubic pyrochlore Bi\(_2\)ZnNb\(_2\)O\(_7\) (\(\kappa = 150\), \(\tau_r = -400 \text{ ppm/°C}\)) and the monoclinic zirconolike Bi\(_3\)Zn\(_2\)Nb\(_3\)O\(_{12}\) (\(\kappa = 80\), \(\tau_r = +200 \text{ ppm/°C}\)) (for example, see ref. 23, 24, 25, 26, 27, 28). They both exhibit a high permittivity and because they exhibit opposite signs for the temperature dependence of permittivity they have been considered as a good pair, which when combined can provide temperature-compensated ceramics. The dielectric properties of these two compounds were mainly investigated at frequencies \(<1 \text{ MHz}\), and under these conditions both showed very low dielectric losses. However, recent investigations of Bi\(_{1.2}\)ZnNb\(_{3}\)O\(_2\) revealed an enormous increase in the room-temperature dielectric losses in the microwave range. The increase results from a low-temperature, frequency-dispersive relaxation phenomenon in Bi\(_{1.2}\)ZnNb\(_{3}\)O\(_2\).\(^{29}\) The Q-value of Bi\(_{1.2}\)ZnNb\(_{3}\)O\(_2\), measured by the authors of this paper at \(~4 \text{ GHz}\), was determined to be \(< 30\), which significantly decreases the overall Q-value of the temperature-compensated Bi\(_{1.2}\)ZnNb\(_{3}\)O\(_2\)-Bi\(_2\)Zn\(_2\)Nb\(_3\)O\(_4\) composite ceramics. Higher values were determined for an analogous Ta-based system;\(^{30}\) however, due to the high price of Ta\(_2\)O\(_5\), such a system is not interesting from the commercial point of view.

The concept of a glass-free multi-material structure for an LTCC

Because the properties—the chemical compatibility, the sintering temperature, and the permittivity—of every tape within an LTCC module must be adjusted to take into account the properties of every other tape, particular tapes cannot be developed independently of each other, rather the simultaneous development of a complete glass-free LTCC system must be undertaken. Bi-based compounds seem to be very promising candidates for such a system because they are able to meet all the requirements: the high ionic polarization of Bi\(^{3+}\) and the lone electron pair can contribute to an increased polarization and therefore to a higher dielectric constant; Bi\(_2\)O\(_3\) is characterized by a low melting temperature (830°C), which leads us to believe that Bi-based compounds will also sinter at temperatures lower than 900°C; and most of these Bi-based compounds are also compatible with silver.

An example of such an LTCC-material system was investigated and reported by the authors of this paper.\(^{19}\) In our earlier article, we presented a glass-free LTCC system that consists of a low-permittivity material for the substrate, together with a medium-permittivity low-loss material and a high-permittivity material for the capacitor structures. The system is based entirely on Bi compounds. The framework of the system is represented by three structural families: eutylite, silenite, and a \(\delta\)-Bi\(_2\)O\(_3\) solid solution with Nb\(_2\)O\(_5\) (hereafter BNSs). The low-permittivity material is based on Bi eutylites and can be used for the substrate layers, whereas a low-loss silenite-based material and a high-permittivity BNS can be used for the two different types of capacitor layers. A characterization of these materials showed that they meet all the major criteria for application in LTCC modules. They are mutually chemically compatible as well as being compatible with respect to the sintering characteristics, which is essential for successful co-firing. In addition, they do not react with silver.

For the two investigated compounds from the Bi-eutylite family, namely Bi\(_2\)Ge\(_2\)O\(_6\) and Bi\(_2\)Si\(_2\)O\(_7\), the dielectric measurements performed at 1 MHz showed low permittivities of 15.9 and 14.9, and moderate temperature coefficients of permittivity (\(\tau_p\)) of 130 and 115 ppm/K for Bi\(_2\)Ge\(_2\)O\(_6\) and Bi\(_2\)Si\(_2\)O\(_7\), respectively. Both compounds exhibit very low dielectric losses of tan \(\delta <1 \cdot 10^{-4}\). For the Bi\(_2\)Ge\(_2\)O\(_6\) compound the measurements of the dielectric properties at 7.8 GHz showed permittivity 16, \(Q = f = 12000 \text{ GHz}\) and \(\tau_p = -64 \text{ ppm/K}\). Due to the nature of the eutylite structure, \(\tau_p\) can be suppressed to a value close to zero by using different isomorphous substitutions.

Investigating the structural and crystallographic properties of various silenites, we described a stoichiometric model\(^{52}\) in which a general formula was developed. All stoichiometric silenites can be described by a general formula Bi\(_{1.2}\)(Bi\(_{0.5-x}\)\(Y\text{M}^{4+}\))\(_{0.2}\text{O}_{1.2} + x\). They show higher dielectric constants (up to
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Fig. 2. Qxf-values and the temperature coefficient of resonant frequency for silellites as a function of the ionic radius of the M ion. The ideal radius corresponds to the radius of the tetrahedral interstice.

40) regardless of the nature of the B-site ion. The temperature coefficient of resonant frequency \( (\tau_f) \) increases with a decrease in the B-site ionic radius and reaches its highest value of \( \sim -20 \text{ ppm/K} \) \( (\tau_f \sim 5 \text{ ppm/K}) \) for the Bi\(_2\)SiO\(_3\) compounds. The \( \tau_f \) of the Bi\(_2\)GeO\(_3\) compound with its slightly larger B-site ion was found to be \( -31 \text{ ppm/K} \). The \( Qxf \)-value reaches a maximum for the silellite compounds with a near-closed-packed arrangement of MO\(_4\) tetrahedra. These compounds are Bi\(_2\)SiO\(_3\) and Bi\(_2\)GeO\(_3\) with Quf-values, measured at \( \sim 5.5 \text{ GHz} \), of 8100 GHz and 7800 GHz, respectively (Fig. 2).33

Even higher dielectric constants can be achieved for the \( \delta \)-Bi\(_2\)O\(_3\) solid solution with Nb\(_2\)O\(_5\). We found that the permittivity is related to the Nb content: in different compositions, ranging from 0.74Bi\(_2\)O\(_3\)-0.26Nb\(_2\)O\(_5\) to 0.90Bi\(_2\)O\(_3\)-0.10Nb\(_2\)O\(_5\), with an increasing concentration of niobium the permittivity decreases from 91 to 72. The compositions exhibited moderate dielectric losses, which were the lowest for 0.76Bi\(_2\)O\(_3\)-0.24Nb\(_2\)O\(_5\) \( (Qxf=1000 \text{ GHz}, \ k'=88.8 \text{ at } 3.6 \text{ GHz}) \). The temperature coefficient of resonant frequency can be easily adjusted by manipulating the Bi\(_2\)O\(_3\)-to-Nb\(_2\)O\(_5\) ratio. With the increasing concentration of Nb the \( \tau_f \) decreases from 71 to \( -300 \text{ ppm/K} \). The composition that showed the most suppressed \( \tau_f \) \( (36 \text{ ppm/K}) \) was 0.74Bi\(_2\)O\(_3\)-0.26Nb\(_2\)O\(_5\).34

Apart from very promising dielectric properties, such materials must exhibit very similar sintering characteristics since they are sintered in a one-step heating process. In addition, they must sinter below the melting point of silver to avoid any deformation of the electrode structure and deterioration of the LTCC module. Sintering curves for selected compositions from all three Bi-based families are shown in Fig. 3. One can see that the sintering curves of these three types of materials match closely, and that they achieve their final relative density of \( >97\% \) at sintering temperatures \( \sim 850\degree \text{C} \). The eutectics, the silellites and the \( \delta \)-Bi\(_2\)O\(_3\) solid solution with Nb\(_2\)O\(_5\) are also shown to be chemically compatible with each other (Fig. 4), as well as being compatible with silver (Fig. 5).

Conclusions

With respect to their phase composition, LTCC materials can be grouped into three classes. Glass-ceramic composites exhibit a large amount of glass phase, which mainly acts as a sintering aid. During the firing, almost no chemical interaction occurs between the ceramic and the glass phase. In contrast, a much smaller amount of the glass phase is present in recrystallized LTCC materials. The characteristic of this class of materials is that during the firing, the initial glass powder sinters and recrystallizes to form a dielectric crystalline phase, which originally would exhibit a much higher sintering tem-
Fig. 3. Sintering curves of eulytite, sillenite and $\delta$-Bi$_2$O$_3$ solid solution with Nb$_2$O$_5$.

Fig. 4. SEM micrograph of the Bi$_2$SiO$_5$-Bi$_2$SiO$_3$-0.75Bi$_2$O$_3$-0.25Nb$_2$O$_5$ three-phase ceramics, sintered at 900°C for 2 h, showing no interaction between the initial components.

The presence of the glass phase in both these classes of LTCC material induces some detrimental influences, for example, increased dielectric losses or an increased complexity of the system. To avoid these problems, a new class of LTCC materials, glass-free materials, has recently been subject to intensive investigation. Our investigations have shown that because of the required inter-compatibility, particular tapes cannot be developed independently of each other, rather the simultaneous development of a complete glass-free LTCC system must be undertaken. We have developed an LTCC system of materials that is entirely based on Bi compounds. The low-permittivity material is based on Bi eulytites and can be used for the substrate layers, whereas a low-loss sillenite-based material and a high-permittivity $\delta$-Bi$_2$O$_3$ solid solution with Nb$_2$O$_5$ can be used for the two different types of capacitor layers.

References
Fig. 5. SEM micrographs of the Ag–Bi$_2$SiO$_3$ (a), Ag–Bi$_2$SiO$_3$ (b) and Ag–0.77Bi$_2$O$_3$–0.23Nb$_2$O$_5$ (c) two-phase ceramics that confirm the compatibility of the Bi-based phases with the silver electrode. The ceramics were sintered at 850°C for 2 h.