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Glass-free low-temperature cofired ceramics: calcium germanates, silicates and tellurates

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Abstract

To reduce the complexity of LTCC systems, and so accelerate the development of LTCC tapes with new functionalities, it is necessary to reduce the number of phases within a particular tape. This can best be done by using glass-free single-phase ceramic systems. We performed a basic characterization of several low-temperature-sintered calcium silicates, germanates and tellurates in order to evaluate their potential as glass-free low-permittivity substrate LTCC materials. Special attention was focused on their microwave and 1 MHz dielectric properties, their sintering behavior and their compatibility with Ag. Two Ca-germanates, which were found to be the most interesting for LTCC applications exhibit a permittivity of ~10 and low dielectric losses; however, the temperature dependence of permittivity and the sintering temperature must be further reduced. For $CaGeO_3$ the temperature dependence of permittivity was fully suppressed by the addition of 10 mol% of $CaTiO_3$.

Keywords: Dielectric properties; Germanate and tellurate; LTCC; Silicate; Substrates

1. Introduction

In parallel with conventional printed-circuit-board technology, new technologies for the production of integrated multifunctional electronic chips are being developed. One of them is the low-temperature co-fired ceramic (LTCC) technology, which can be applied for the integration of passive elements into a monolithic, highly reliable and robust LTCC module. These modules consist of several layers of substrate material with integrated elements—inductors, capacitors, resonators, filters—that are interconnected with 3D stripline circuitry.

Although LTCC technology demonstrates some very advantageous features, its development is still in the early stages. The main problems relate to the rigorous demands placed on the materials. In general, it is believed that the main difficulties in 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. To produce a module the LTCC materials are co-fired with an inner-electrode structure and, as a consequence, the sintering temperature must be lower than the melting point of the electrode. In addition, a chemical compatibility between the LTCC material and the electrode must exist.[1] Silver is the usual choice for the electrode, which means the sintering temperature needs to be ~900 °C (the melting point of silver is 960 °C).

In terms of dielectric properties, newly developed materials are expected to exhibit a moderate temperature coefficient of permittivity (τ_κ in the range of the NP0-capacitor ceramics) and low dielectric losses ($\tan\delta \approx 1/Q$). There are two limiting factors that do not allow us to achieve high Q-values for the LTCC models. One is related to the conductive losses in the stripline circuitry and the other to the losses occurring in the glassy phase of the glass-ceramic composite substrate. Typically, the Q-values of such modules do not exceed 600 GHz.

1.1. Consideration of the LTCC phase interactions

Commercial LTCC tapes are mainly low-permittivity glass-ceramic composites that are used as a substrate material in the LTCC modules. For the successful co-firing of an LTCC module two material properties must

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be carefully considered: the sintering curves of all the materials present in the LTCC module must match and all of the phases present must be mutually chemically compatible. The only expected chemical reaction during the co-firing is the recrystallization of the glass, however; the products of the recrystallization must again be chemically compatible with the entire material system. After firing, the LTCC tape typically consists of the Al_2O_3 phase, the recrystallization products (e.g. anorthite), the residual glass and the phase for the modification of the dielectric properties ($SrTiO_3$, TiO_2,...).[2,3]

The presence of so many phases in the LTCC tape significantly increases the possibility of a chemical interaction with the metal electrode. To illustrate how the number of possible chemical interactions in the LTCC module increases with the number of the phases present we assume a material system where every LTCC tape consists of only two phases (Fig. 1). If just one LTCC tape is present its phases must be mutually compatible and both phases must be compatible with the electrode: three different phase interactions within the module. When two different LTCC tapes are present in the module we must consider the mutual phase interactions within the tapes, the interactions with the electrode as well as the interactions between the phases of both LTCC tapes. The number of interactions increases to 10 and when a third tape is added this number increases to 21. In general, the number of interactions can be calculated as $\sum_{n=1}^{N}(n-1)$, where N is the number of all the phases present in the module (including the electrode).

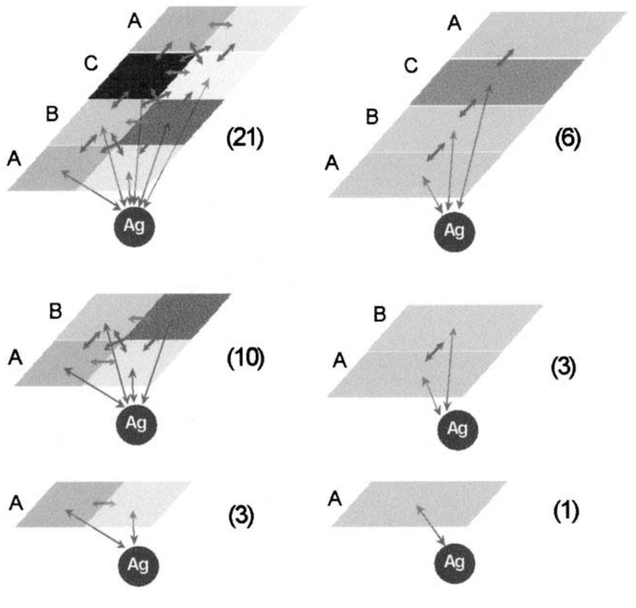

Fig. 1. Schematic representation of all possible interactions in the LTCC module with one, two and three types of tape for two-phase (left column) and single-phase tapes (right column). The number of all interactions for a particular case is in parenthesis.

In a typical commercial fired tape there are four or five phases present, none of which should react with the electrode. Moreover, with every further type of LTCC tape an additional four or five phases are introduced to the module, which significantly increases N and consequently $\sum_{n=1}^{N}(n-1)$. As an illustration: for three types of LTCC tapes with five phases $N=16$ and $\sum_{n=1}^{N}(n-1)=120$. Such a rapid increase in the number of interactions that must be controlled makes the system very complex and the development of new LTCC materials with new functionalities (high-permittivity layers, ferittes) extremely difficult. In the end, this problem may prevent the further development of new LTCC systems.

To reduce the complexity of LTCC systems it is necessary to reduce N by reducing the number of phases within the particular LTCC tape. Because in the glass-ceramic composite tapes the number of phases within the tape cannot be reduced below two, the glass-free systems have been considered. Such glass-free tapes can be single-phase tapes, and as a result $\sum_{n=1}^{N}(n-1)$ remains low even for a large number of different tapes.

The role of the glass phase in commercial tapes is mainly to enhance the sintering (to provide the mechanical properties) and through the process of recrystallization produce the phase with the appropriate dielectric properties. If the sintering of a glass-free ceramic material with the appropriate dielectric properties could be achieved at the required temperature then the mechanical properties would also be good and there would be no need for the glass phase to exist. By applying such an approach the simplicity of the LTCC system is maintained but special attention must be devoted to the sintering behavior of the materials with all the other requirements for the LTCC modules under consideration.

The basic material of every LTCC module is a low-permittivity substrate material that is used for the transmission lines or inductors. We characterized several low-temperature-sintered calcium silicates, germanates and tellurates in order to evaluate their potential as low-permittivity substrate LTCC materials. Special attention was focused on their microwave and 1MHz dielectric properties, their sintering behavior and their compatibility with Ag, which is the most commonly used material for the internal electrode in LTCC modules.

2. Experimental

The investigated compounds were synthesized using solid-state reaction techniques. Stoichiometric mixtures of dried reagent-grade oxides were homogenized and pre-reacted at 1000–1100 °C for 20 h, 1000–1200 °C for 20 h and 630–820 °C for 30 h for the germanates, silicates and tellurates, respectively. The reaction stage was performed with intermediate grinding stages to enhance the formation of the compounds. The powders were then milled with Y-stabilized ZrO_2 milling balls to an average particle size of 1 μm, uniaxially pressed into pellets at approximately 150MPa and sintered at temperatures ranging from 780 to 1300 °C (see Table 1). The relative densities of the samples were estimate from microstructural images and found to be >95% for all samples.

The progress of the reactions was monitored by powder X-ray diffraction (Bruker AXS, D4 Endeavor) using CuK_α radiation. Lattice parameters were calculated by least-squares refinement of X-ray diffraction data collected from $10° < 2\Theta < 90°$ with a step of 0.02°, counting time of 2 s per step and variable V12 slits. Powdered Ag was used as an internal standard. Microstructural analyses of the ceramics were conducted using an optical microscope (Olympus BX60) and a scanning electron microscope (Jeol, JXA 840A).

The microwave dielectric properties were characterized with the closed air-cavity method using a network analyzer (HP 8719C). Ceramic resonators with a diameter of 8.5 mm and a height of 3.5 mm were placed into a gold-plated resonant cavity with a diameter of 50 mm and a height of 30 mm. Permittivity and Q-values were calculated at the resonant conditions ($TE_{01\delta}$ mode) from S_{11} reflection coefficients as proposed by Kajfez et al.[4] The RF dielectric measurements were made at a frequency of 1MHz on silver-plated pellets using a high-precision LCR meter (Agilent 4824A). The temperature dependence of the permittivity was measured from-130 to 150 °C by placing the samples in an environmental chamber (Delta Design, Delta 9039).

3. Results and discussion

The first criterion used to select the interesting calcium compounds was the melting point. Only the compounds with the lowest melting points from each system were tested. In the $CaO–GeO_2$, $CaO–SiO_2$ and $CaO–TeO_2$ systems these compounds were $CaGe_2O_5$, $CaGeO_3$, $Ca_3Si_2O_7$, $CaSiO_3$, $CaTe_2O_5$ and $CaTeO_3$, respectively. In all cases the solid-state synthesis yielded a single-phase composition with a diffraction pattern that matched the corresponding PDF card.[5] The powders were sintered at a temperature that ensured a relative density >95% without using any sintering aid.

The sintering temperature, the reactivity with Ag, and the dielectric properties of these compounds are listed in Table 1. The results showed that Ca-tellurates exhibit the lowest sintering temperature of all the investigated compounds and have very low dielectric losses. However, $CaTe_2O_5$ exhibits a permittivity that is too high for the target application and, in addition, they both react with silver, which rules out any possibility of their use. Both Ca-silicates show sufficiently low permittivities and low dielectric losses. The temperature dependence is negative and must, for technological applications, be further suppressed. What is important is that they do not react with the silver. The major drawback of Ca-silicates is their high sintering temperature, which needs to be significantly lowered. Most probably, this can only be done by the addition of a significant amount of sintering aids, which would have an unpredictable impact on the dielectric properties.

The permittivities and dielectric losses of both investigated Ca-germanates are low enough for them to be used as substrate materials for LTCC modules. In addition, these materials do not react with silver and sinter at lower temperatures than silicates. $CaGeO_3$ and $CaGe_2O_5$ powders with an average particle size of ~1μm were sintered to >95% of relative density at 1180 °C. A further decrease in sintering temperature can be achieved by using finer powders and/or by the addition of a small amount of sintering aid. The property that significantly deviates from the requirements of LTCC technology is the materials' temperature dependence of permittivity. Several techniques, for example ionic substitution or microstructural engineering, can be used to modify the τ_k. To illustrate this, we attempted to suppress the τ_k of $CaGeO_3$.

Because of its highly negative τ_k (−1850 ppm/K), $CaTiO_3$ seems to be a good candidate for compensating the positive τ_k of $CaGeO_3$ (100 ppm/K). We synthesized four different $CaGeO_3$–$CaTiO_3$ compositions with 5, 10,

Table 1
Dielectric properties, sintering temperature and reactivity with Ag for the investigated compounds

	Permittivity		Dielectric losses		τ_k (ppm/K @ 1 MHz)	T_s (°C)	Reaction with Ag
	1 MHz	~10 GHZ	tanδ	$Q \times f$			
$CaGeO_3$	8.6	8.9	$1\cdot10^{-4}$	32200	100	1200	No
$CaGe_2O_5$	10.8	10.9	$<1\cdot10^{-4}$	39000	110	1180	No
$CaSiO_3$	9.2	8.4	$<1\cdot10^{-4}$	16000	70	1300	No
$Ca_3Si_2O_7$	6.5	7.8	$<1\cdot10^{-4}$	28400	140	1300	No
$CaTeO_3$	15.5	17.4	$2\cdot10^{-4}$	49300	140	840	Yes
$CaTe_2O_5$	23.6	19.3	$2.4\cdot10^{-3}$	13400	130	780	Yes

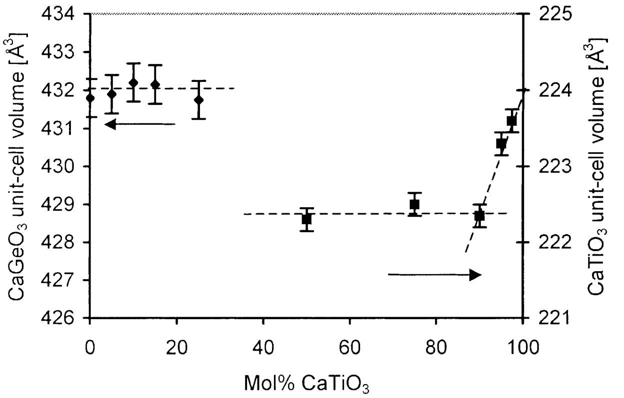

Fig. 2. Unit-cell volume of $CaGeO_3$- and $CaTiO_3$-based phase indicating no incorporation of Ti in $CaGeO_3$ and 10 at.% Ge in $CaTiO_3$.

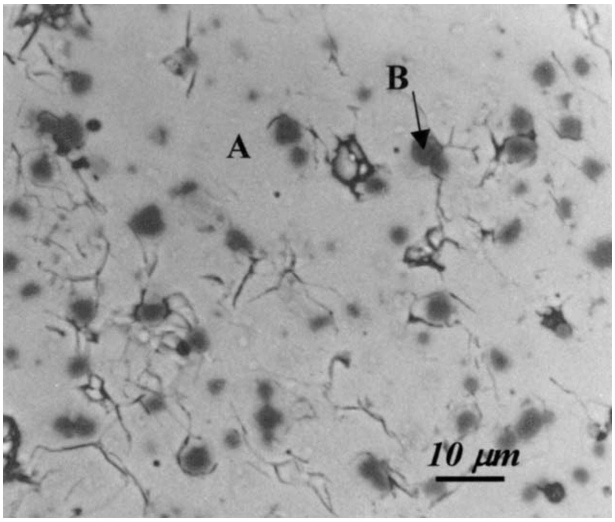

Fig. 3. Back-scattered electron image of ceramics with composition of $0.9CaGeO_3$:$0.1CaTiO_3$ (A…$CaGeO_3$, B…$CaTiO_{3\,(ss)}$).

15 and 25 mol% of $CaTiO_3$, sintered them and determined their dielectric properties. All of the ceramics were comprised of two phases: a wollastonite $CaGeO_3$ phase in which no solid solubility of Ti was detected and a perovskite $CaTiO_3$-based solid solution with approximately 10 at.% of Ge (Fig. 2). Interestingly, compared to the single-phase $CaGeO_3$ the sintering was significantly improved and the final relative densities were >97% (Fig. 3).

As expected, the τ_k of $CaGeO_3$ was suppressed by the addition of $CaTiO_3$. Adding 10 mol% of $CaTiO_3$ reduced the τ_k to ≈0 ppm/K (Fig. 4). The permittivity of this ceramic increased only slightly to 11.3, while the dielectric losses decreased to $\tan\delta > 1\cdot10^{-4}$ as a result of the improved sintering. From the point of view of the dielectric properties such a material fully satisfies the requirements of LTCC technology; however, further adjustments must be made to decrease the sintering temperature.

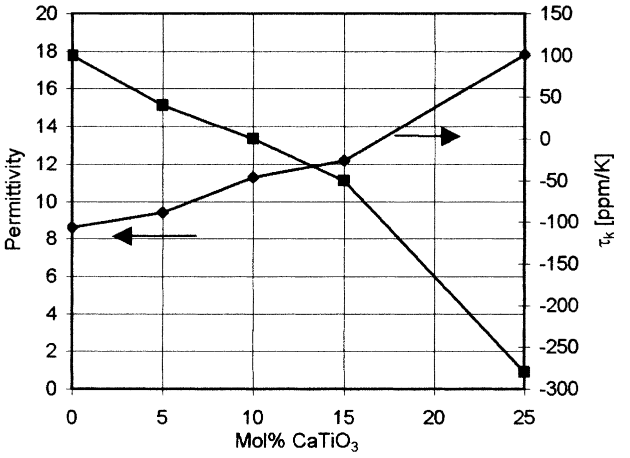

Fig. 4. Permittivity and temperature coefficient of permittivity as a function of $CaTiO_3$ concentration.

4. Conclusion

The multiphase nature of commercial LTCC tapes hinders the development of new types of tapes with new functionalities because of the problems related to mutual chemical compatibility. Our study showed that by eliminating the glass phase we can reduce this problem without any adverse effect on the other requirements.

We characterized several low-temperature-sintered calcium silicates, germanates and tellurates in order to evaluate their potential as glass-free, low-permittivity substrate LTCC materials. The results of the characterization revealed $CaGeO_3$ and $CaGe_2O_5$ as potential candidates for LTCC technology, but also showed on the main problems related to a further decrease of the sintering temperature and the fine tuning of the temperature dependence of permittivity. Both compounds exhibit low permittivities and low dielectric losses and, in addition, they do not react with silver. The temperature dependence of $CaGeO_3$ was successfully suppressed by the addition of 10 mol% of $CaTiO_3$. Further work is needed to reduce the sintering temperature from 1180 °C to ~900 °C, the temperature that is required by LTCC technology. In addition, the ultimate test of suitability for LTCC technology requires that a set of detailed and very specific tests and analyses be carried out. These tests should include investigations of the thermal expansion behavior, the tape casting, the warping behavior of multilayer structures, the mechanical properties, silver diffusion and optimization of the chemical composition of layers in order to tune the temperature dependence of permittivity and suppress the dielectric losses.

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