New Generation of LTCC Materials

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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. Such a material system consisting of low- and high-permittivity LTCC materials was developed based on Bi eulytite (permittivity; κ'=16) and sillenite (κ'=40) compounds and the δ-Bi_2O_3 solid solution with Nb_2O_5 (κ'=90). The Ge and Si analogues of the sillenites and eulytites, and the $0.75Bi_2O_3 \cdot 0.25Nb_2O_5$ solid solution meet the main requirements for LTCC with respect to their sintering behavior (T_s=850-900ºC), their mutual chemical compatibility, their compatibility with a silver electrode as well as their dielectric properties.

Keywords: dielectric properties, substrates, capacitors, LTCC, Bi-based compounds

Nueva Generación de Materiales LTC

Para reducer la complejidad de los sistemas LTCC y así acelerar el desarrollo de láminas de LTCC con nuevas funcionalidades es necesario reducir el número de fases dentro de una determinada lámina. La mejor manera de hacer esto es usar sistemas cerámicos monofásicos libres de fase vítrea. Dicho sistema que consiste en materiales LTCC de baja- y alta-permitividad se ha desarrollado en base a compuestos de Bi-eulitita (permitividad; κ'=16) y silenita (κ'=40) y la solución sólida de δ-Bi_2O_3 con Nb_2O_5 (κ'=90). Los análogos de Ge y Si de las silenitas y eulititas, y la solución sólida $0.75Bi_2O_3 \cdot 0.25Nb_2O_5$ cumplen los principales requerimientos de los LTCC respecto a su comportamiento de sinterización (T_s=850-900ºC), su compatibilidad química mutua y su compatibilidad con electrodos de plata, así como en lo concerniente a sus propiedades dieléctricas

Palabras clave: propiedades dieléctricas, substratos, condensadores, LTCC, compuestos basados en Bi

1. INTRODUCTION

Intensive competition between the producers of electronic devices is increasing the pace of development in microwave wireless communication and information systems towards multi-functional pocket- or credit-card-size devices. This competition also stimulates the development of new systems and technologies, the expansion of the marketplace and, very importantly, the reduction of costs.

The "conventional" types of microwave materials that were developed prior to the mid 1990s - and are used world wide for the production of bulk microwave ceramic components, such as filters and resonators - have become insufficient and inappropriate for use in the newest applications and technologies. Consequently, several directions for the development of the next generation of high-frequency dielectric materials were identified in the last decade and the majority of the R&D work on these materials is still in progress. The current developments in high-frequency dielectric ceramics can generally be grouped into three major categories:

- Better frequency selectivity, improved filter performances, reduced insertion loss and interference from spurious modes, and more efficient manipulation with the determined frequency bands are driving the development of new materials in all permittivity classes with even *higher Q-values* than are available today.

- The miniaturization of today's systems is a permanent development trend and is crucially dependent on the development of new dielectric materials with substantially *higher permittivities*.

- Finally, the emergence of LTCC (low-temperature co-fired ceramics) technology is dictating the development of dielectric materials with a *sintering temperature low* enough to enable co-firing with an electrode metal.

1.1. New dielectrics with high Q-values

The fundamental structural conditions for achieving low dielectric losses have been recognized in the last few years. When developing high-Q materials, properties such as crystal-structure dynamics, tolerance factors, electronic and atomic structure, etc have to be considered. These fundamental properties translate into several structural criteria that must be met in order to produce the high-Q material: the structure must be packed as close as possible [1,2]; different ions residing at the particular crystallographic site should differ in size as little as possible [3]; the cation ordering should be induced to reduce the anharmonicity of the crystal-lattice dynamics and eliminate the effects of the disordered charge distribution and further constrain the structure [4,5]; the reduction (or oxidation) of the ceramics must be avoided to suppress the conductivity [6]; the concentration of structural defects must be minimized and not associated with the strain fields [4]; the ceramics must be free of deleterious secondary phases [7]; and the grain boundaries must be clean of precipitates and liquid phase [8].

Due to the number of structural conditions that a high-Q material must fulfill, the successful development of new high-Q materials is rare. Nevertheless, extensive research work in many laboratories around the world is focused in this direction. New microwave materials with a Q-value higher than that currently available are being asked for in all existing permittivity classes.

For the permittivity class around 80 the only commercially available material group is still based on the $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$ (R=La-Gd) solid solutions. The highest Q-values achieved in mass production today are already exceeding 10.000GHz but significant efforts are being invested to further improve the Q-value.[9]

The mid-permittivity class of materials with permittivities ~45

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is mainly covered by the perovskite solid-solution based on $CaTiO_3$-$NdAlO_3$.[10] This material combines a rather high permittivity with very low dielectric losses and was, therefore, investigated in detail over the last few years. The highest Q-value achieved for this system is around 50.000 GHz. Recently, a related system has been reported based on the $SrTiO_3$-$LaAlO_3$ [11] solid solution. It has a permittivity slightly lower than 40 and gives very high Q-values of 60.000 to 70.000 GHz. Further investigations of the reaction mechanism, the phase transition, and the structural and microstructural phenomena give hopes for further increases in the Q-values of both materials.

A requirement for materials with a permittivity of ~30 and a Q-value similar or even superior to the commercial perovskite tantalates (>100.000GHz) is particularly in demand in the field of wireless telecommunication infrastructure. The industry associates the development of new "super" high-Q materials with a requirement to eliminate, or at least reduce the use of tantalum because of the recent sharp increase in the tantalum price.

1.2. New dielectrics with high permittivity

The development of high-permittivity materials for the miniaturization of bulk components is still an important subject. The development of such materials is hindered by the unfortunate correlation between the permittivity and the two other important dielectric properties: the dielectric losses and the temperature dependence of the permittivity (τ_ε) - both of these properties are known to be adversely affected by an increase in the permittivity. A few papers have recently reported materials with permittivities >100. [12,13] However, from the commercial point of view the small increase in the permittivity does not compensate for the expense of introducing new production lines and re-designing the microwave circuits.

An important breakthrough was achieved with the development of temperature-stable low-loss $Ag(Nb,Ta)O_3$-based materials with permittivities ranging from 430 to 550.[14] These materials meet the requirements for several microwave electronic components, e.g. bandpass filters and high-capacity NP0 multilayer capacitors, that would lead to a significant miniaturization of these devices. For the case of bandpass filters, an eight-times volume reduction could be expected, allowing the production of ceramic filters with the size of surface acoustic wave (SAW) filters, but with significantly improved power handling and low dielectric losses across a wide temperature range. For capacitor technology, the implementation of ANT would lead to a new category of multilayer capacitors with characteristics between those of standard NP0 and X7R types. In addition, the replacement of high-frequency polymer capacitors (PPS-type) with ANT capacitors in, for instance, Bluetooth modules and the loop-filters of cellular phones offers the possibility for further size reduction and the enhancement of performance and reliability.

1.3. New dielectrics with low sintering temperature

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 a 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 (Fig. 1). These modules consist of several layers of substrate material with integrated elements -inductors, capacitors, resonators, filters - that are interconnected with 3D stripline circuitry.

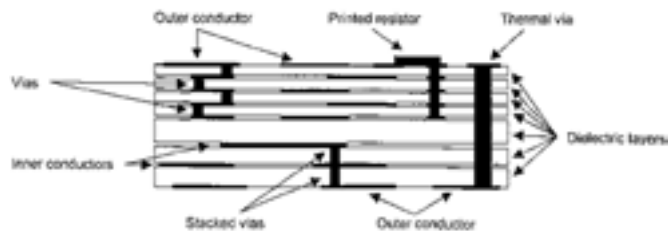Although LTCC technology demonstrates some very advantageous

Fig. 1: General cross-section of an LTCC module

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. [15] 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). To obtain such a low sintering temperature all commercially available materials are composites consisting of the crystallizing glass, Al_2O_3 and, eventually, the additive for the suppression of the temperature dependence of permittivity and/or increase of permittivity.

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.

2. CONCEPTUAL CONSIDERATION OF LTCC

2.1. 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 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, …).[16,17]

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. 2). 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

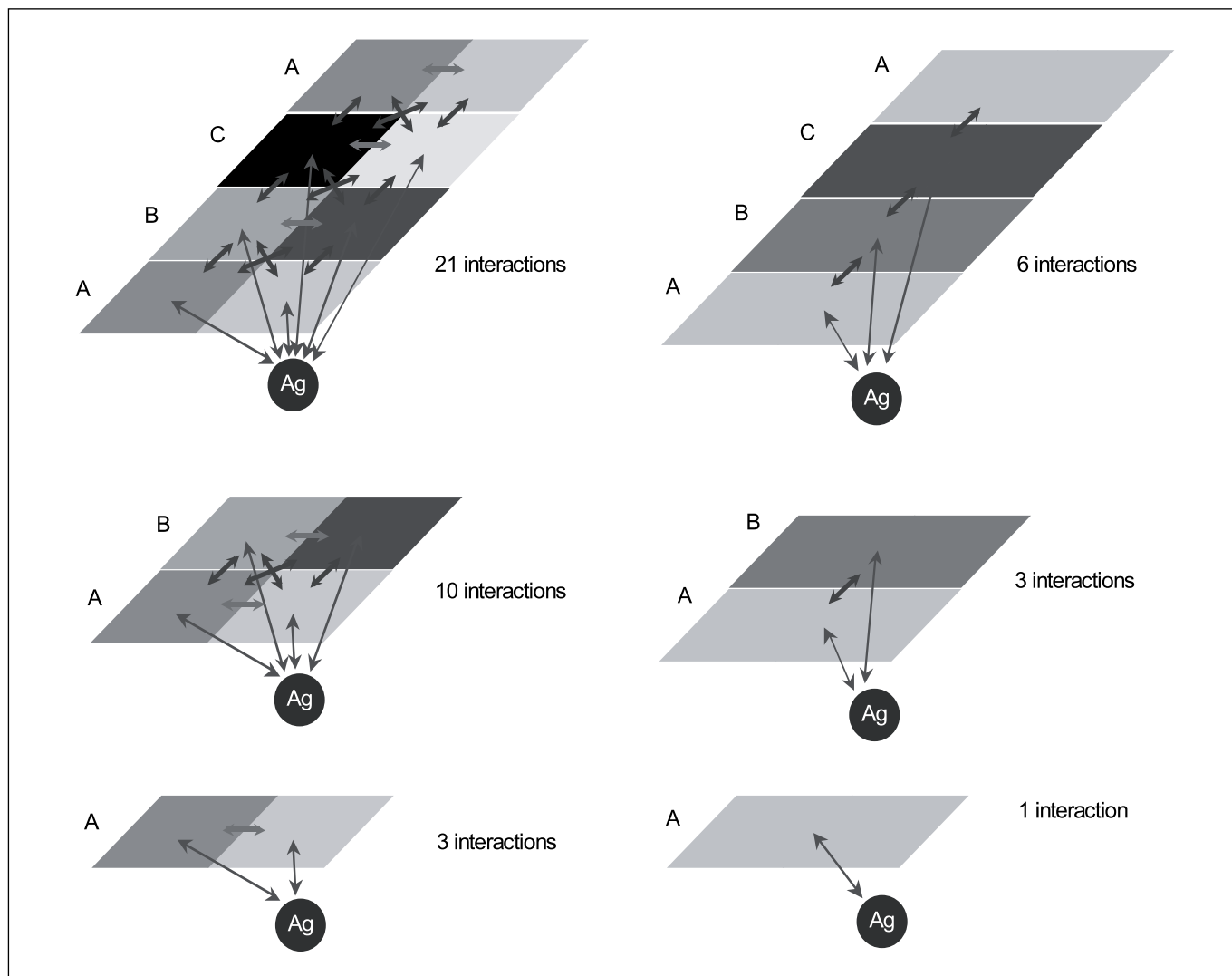Bol. Soc. Esp. Ceram. V., 43 [3] 634-639 (2004)

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Fig. 2: 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 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 $\Sigma(n-1)$, where n is the number of all the phases present in the module (including the electrode).

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 $\Sigma(n-1)$. As an illustration: for three types of LTCC tapes with five phases $n=16$ and $\Sigma(n-1)=120$. 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, feritttes) 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 LTCC tapes. Because in the glass-ceramic composite tapes the number of phases within the tape cannot be reduced below two the glass-free systems were considered. Such glass-free tapes can be single-phase tapes, and as a result $\Sigma(n-1)$ remains low even for a large number of different tapes.

2.2. A glass-free LTCC system

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.

Because the properties - chemical compatibility, sintering, permittivity - of all the tapes within a LTCC module must be mutually adjusted, particular tapes cannot be developed independently of each other but rather the simultaneous development of a complete glass-free LTCC system must be undertaken. Here we present a glass-free LTCC system that consists of a low-permittivity material for the substrate, and medium permittivity low-loss material and high-permittivity material for the capacitor structures (Table I). The system is based on Bi compounds. The framework of the system is represented by three structural families: *eulytite, sillenite* and δ-*Bi_2O_3 solid solution with Nb_2O_5*

(hereafter *BNss*). Several different Bi-based compositions that can be used for the LTCC tape exist in each of the structural families, which gives us important flexibility when it comes to modifying the electrical properties.

3. EXPERIMENTAL PROCEDURE

Syntheses of the all compounds were conducted using solid-state reaction techniques. Stoichiometric mixtures of dried reagent-grade oxides were homogenized and pre-reacted at 650°C–800°C for 20-50h with an intermediate grinding stage to enhance the formation of single-phase sillenite compounds. The powders were then milled with Y-stabilized ZrO_2 milling balls to the average particle size of 1μm, uniaxially pressed into pellets at approximately 150MPa and sintered at temperatures ranging from 850-900°C.

To check the chemical compatibility of the sillenite compounds and a silver electrode, *compatibility tests* were performed. Each *compatibility test* consisted of mixing and homogenizing 20 wt% of powdered Ag with the ceramic powder, pressing into pellets and firing in air at 850°C for 5h-15h to achieve equilibrium. The samples were analyzed with respect to the interaction of the ceramic phase with the silver.

Microstructural analyses of the ceramics were conducted using a scanning electron microscope (JEOL, JXA 840A). Characterization of the microwave dielectric properties was carried out at room temperature by the closed air-cavity method using a Network Analyzer (HP 8719C).[17] 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.[18] To determine the temperature dependence of resonant frequency, the test cavities were inserted into a temperature-controlled chamber. Dielectric characteristics of the samples were analyzed in the temperature range from 20°C to 60°C.

4. RESULTS

4.1. Bi eulytites

Eulytites are compounds that are isostructural with the natural mineral eulytine – $Bi_4Si_3O_{12}$.[19] Two analogues were closely examined for use with glass-free LTCC technology: $Bi_4Ge_3O_{12}$ and $Bi_4Si_3O_{12}$. Dielectric measurements performed at 1 MHz showed low permittivities of 15.9 and 14.9, and moderate temperature coefficients of permittivity (τ_k) of 130 and 115 ppm/K for $Bi_4Ge_3O_{12}$ and $Bi_4Si_3O_{12}$, respectively. Both compounds exhibit very low dielectric losses of $\tan\delta = 1\times10^{-4}$. $Bi_4Ge_3O_{12}$ was also investigated in the microwave frequency range. At 7.8 GHz the permittivity was determined to be 16.0, the Qxf-value was 12000GHz and the temperature coefficient of resonant frequency was -64 ppm/K. Evidently, the only property that requires further adjustment is τ_k. Because the eulytite structure offers great possibilities for isomorphous substitutions this mechanism can be applied for the adjustment of τ_k. [20,21]

4.2. Sillenites

The crystal structure of sillenites is isostructural with γ–Bi_2O_3. Stoichiometric sillenites with a fully occupied oxygen sublattice are compounds with the general formula $Bi_{12}MO_{20}$, where *M* represents a

tetravalent ion or combination of ions (and vacancies), which gives an average charge of 4+ (e.g. Ge^{4+}, Si^{4+}, $(Fe^{3+}_{0.35}P^{5+}_{0.59}\square_{0.06})$). [22] The sillenites exhibit a permittivity of ~40 regardless of the nature of the B-site ion. The temperature coefficient of resonant frequency (τ_f) increases with a decrease in the B-site ionic radius and reaches its highest value of ~ -20 ppm/K (τ_k ~ 5 ppm/K) for the $Bi_{12}SiO_{20}$ compounds. The τ_f of the $Bi_{12}GeO_{20}$ compound with its slightly larger B-site ion is –31 ppm/K. The Qxf-value reaches a maximum for the sillenite compounds with a near closed-packed arrangement of MO_4 tetrahedra. These compounds are $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$ with Qxf-values, measured at ~5.5 GHz, of 8100 GHz and 7800 GHz, respectively. [1] After considering the processing, the chemical and the dielectric properties of both the $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$ compounds appear to be good choices for the capacitor layers in LTCC technology.

4.3. δ-Bi_2O_3 solid solution with Nb_2O_5 – BNss

The BNss is well-known ionic conductor but it is also a p-type electronic conductor. The activation energy for the electronic conductivity increases with an increase in the Nb content. [23] From the crystallographic point of view, the fluorite-type f.c.c. BNss is isostructural with δ-Bi_2O_3. [24] The solid solutions with <19.5mol% Nb_2O_5 are high-temperature phases, which under cooling transform into a monoclinic modification isostructural with α-Bi_2O_3. With an increasing concentration of Nb the temperature of transformation decreases from an initial 730°C down to 610°C for the composition with 19.5 mol% Nb_2O_5. A higher concentration of Nb_2O_5 results in the formation of a pseudo-cubic analogue, which is a low-temperature stable modification. [25] The disputes about the nature and the stoichiometry of the end-member of the Bi_2O_5-Nb_2O_5 solid solution still exist in the literature.[24-26] At present, it is not clear whether the end-member is a proper compound with a stoichiometry of Bi_3NbO_7 or a composition with a pseudo-cubic crystal-structure modification of Bi_2O_3 with a stoichiometry of $0.77Bi_2O_3\cdot0.23Nb_2O_5$. As the proper nature of the end-member of the BNss is beyond the scope of this study, several different compositions, ranging from $0.73Bi_2O_3\cdot0.27Nb_2O_5$ to $0.81Bi_2O_3\cdot0.19Nb_2O_5$, were analyzed with respect to their dielectric properties. With an increasing concentration of niobium the permittivity decreases from 91 to 72. The compositions exhibit moderate dielectric losses that are the lowest for $0.75Bi_2O_3\cdot0.25Nb_2O_5$ (Qxf = 650 GHz, κ'=88.8 at 3.6 GHz). The temperature coefficient of resonant frequency can be easily adjusted by manipulating the Bi_2O_3 to Nb_2O_5 ratio. With the increasing concentration of Nb the τ_f decreases from 71 to –300 ppm/K. The composition that exhibits the most suppressed τ_f (36 ppm/K) is again $0.75Bi_2O_3\cdot0.25Nb_2O_5$, which means that in the range of the investigated BNss compositions it is the most suitable as an LTCC capacitor materials.

4.4. Sintering Characteristics

The ceramic components must be sintered at >50°C below the melting point of the electrode to avoid any deformation of the electrode structure and deterioration of functionality of the LTCC module. The sintering studies revealed that the sintering temperature of all three materials is sufficiently below the melting point of silver (960°C). The materials - eulytite, sillenite and BNss - can be sintered to >97% relative density at temperatures in the range 830 - 850°C. In addition, the sintering curves of these three types of material match closely, a necessary to be able to co-fire the tapes without warping (Fig. 3). If fine tuning of the sintering curves is needed it can be achieved by controlling the powder particle size.
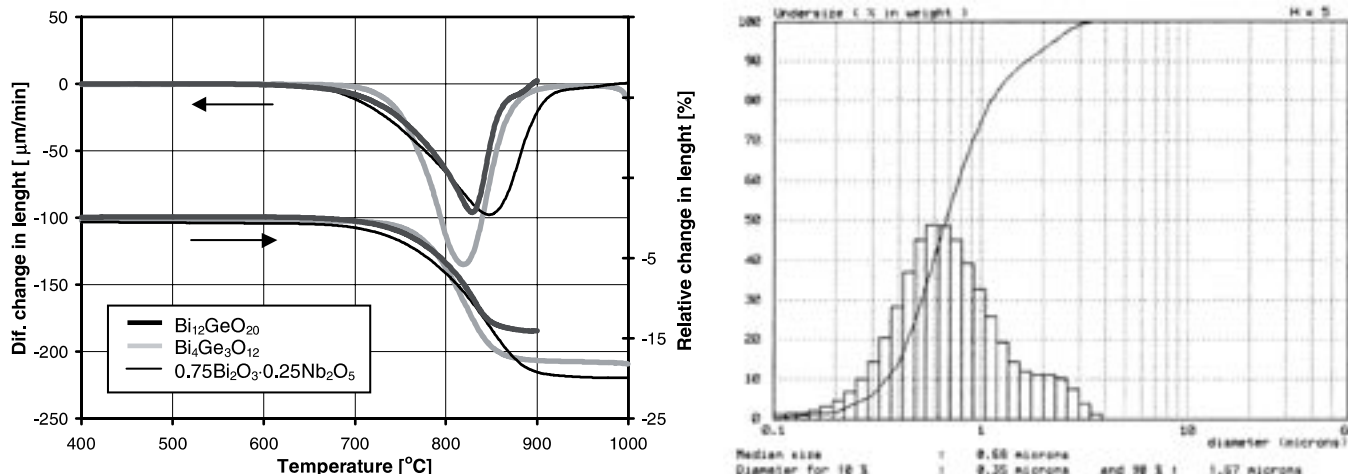
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Fig. 3: Sintering curves of $Bi_{12}GeO_{20}$, $Bi_4Ge_3O_{12}$, and $0.77Bi_2O_3\cdot0.23Nb_2O_5$, and a typical particle size distribution of the powders used for the sintering experiments

4.5. Chemical compatibility

Bi eulytites and sillenites are adjacent compounds in the Bi_2O_3-SiO_2 and Bi_2O_3-GeO_2 binary systems, [27,28] therefore, full mutual chemical compatibility is expected. To check whether they are also compatible with the BNss, $Bi_{12}SiO_{20}$ and $Bi_4Si_3O_{12}$ were mixed together with $0.75Bi_2O_3\cdot0.25Nb_2O_5$ and fired at a temperature typical for the firing of LTCC modules (900°C/2h). The microstructural analysis of such a sintered body revealed no interaction between the components. The phase composition corresponded to the phase composition of the starting mixture, the chemical composition of the phases remained unchanged and no reaction product was observed at the grain-boundary regions. The microstructure is shown in Fig. 4. The phase relations corresponding to this observation are schematically represented in Fig. 5 for the Bi_2O_3-SiO_2-Nb_2O_5 oxide system. The experiment shows that a thermodynamic equilibrium exists between these three compounds at 900°C, which is very important for their application in LTCC technology.

To check the chemical compatibility of the compounds and a silver electrode we performed *compatibility tests*. Each *compatibility test* consisted of mixing and homogenizing 20 wt% of powdered Ag with the ceramic powder, pressing into pellets and firing under the thermal conditions corresponding to the LTCC firing regime. Fired samples were examined by powder x-ray diffractometry and scanning electron microscopy. No interaction was detected for all three materials considered in this study, which confirms a chemical compatibility between silver and the ceramic phases (Fig. 6).

5. CONCLUSIONS

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. An example of such an LTCC-material system was shown. It consists of a low-permittivity material based on Bi eulytites, which can be used for the substrate layers, and a low-loss sillenite-based material and a high-permittivity δ-Bi_2O_3 solid solution with Nb_2O_5 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
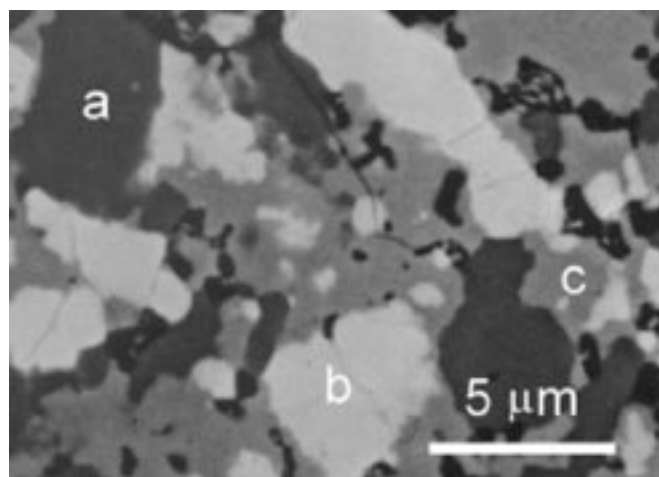

Fig. 4: SEM micrograph of the $Bi_{12}SiO_{20}$ - $Bi_4Si_3O_{12}$ - $0.75Bi_2O_3\cdot0.25Nb_2O_5$ three-phase ceramics, sintered at 900°C for 2h, showing no interaction between initial components

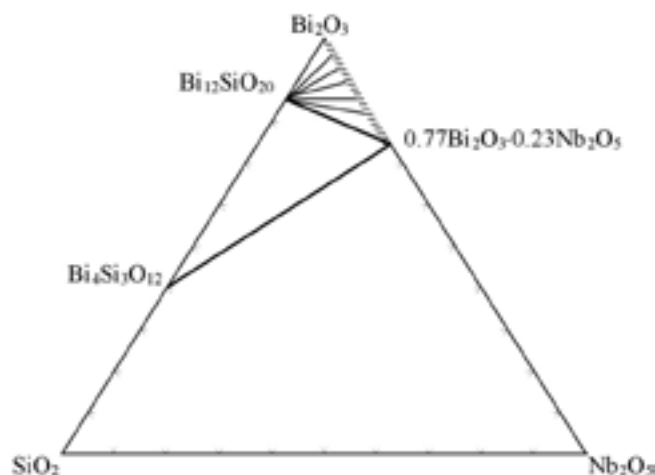Fig. 5: Schematic presentation of the phase relations between $Bi_{12}SiO_{20}$, $Bi_4Si_3O_{12}$ with $0.77Bi_2O_3\cdot0.23Nb_2O_5$ in the ternary Bi_2O_3-Nb_2O_5-SiO_2 diagram at 900°C. The phase relations are equivalent to the system Bi_2O_3-Nb_2O_5-GeO_2
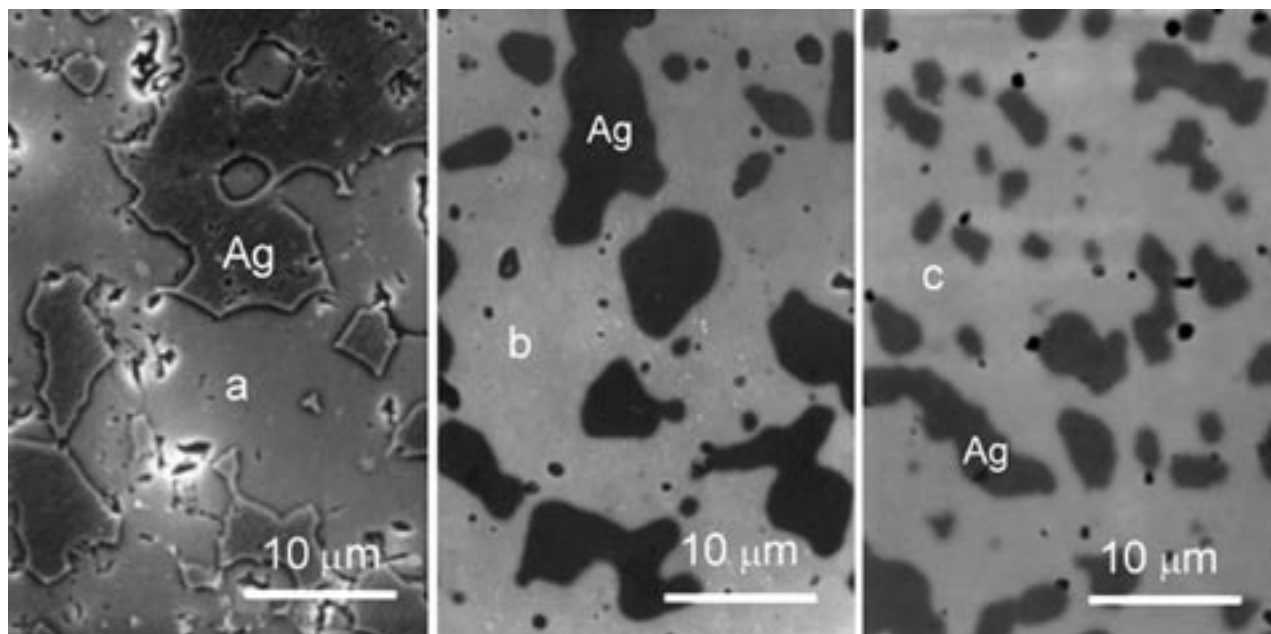
Fig. 6: SEM micrographs of the Ag - Bi$_4$Si$_3$O$_{12}$ (a), Ag - Bi$_{12}$SiO$_{20}$ (b) and
Ag - 0.77Bi$_2$O$_3$·0.23Nb$_2$O$_5$ (c) two-phase ceramics that confirm the compatibility of the Bi-based phases with the silver electrode. The ceramics were sintered at 850°C for 2h.

being compatible with respect to the sintering characteristics, which is essential for successful co-firing. In addition, they do not react with silver. However, the ultimate test of suitability for LTCC technology requires that a set of detailed and very specific tests and analyses must 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 etc.

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