

## Development of high-permittivity glasses for microwave LTCC tapes

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One of today's leading packaging concepts in microelectronics and microsystems is the technology of Low Temperature Cofiring Ceramics (LTCC). It is based on ceramic tapes that sinter at low temperatures ( $< 950^{\circ}\text{C}$ ) and are capable of fine-line wiring by use of high-conductivity metals, preferably silver ( $\vartheta_{\text{m}} = 961^{\circ}\text{C}$ ).

To lower sintering temperatures of crystalline powders, glass powder is added. Depending on the amount of glass added, two mechanisms of sintering are possible: reactive or nonreactive liquid phase sintering. Reactive sintering requires small amounts ( $< 10 \text{ vol.}\%$ ) of a very low softening glass ( $\vartheta_{\text{soft}} < 400^{\circ}\text{C}$ ). If the glass amount is increased to more than 50 vol.%, nonreactive sintering occurs in the glass softening range. According to the microstructure observed for each case, the respective types of materials are called Glass Bonded Ceramics (GBC) and Glass Ceramic Composites (GCC).

Integration of microwave filters in LTCC multilayers requires inner dielectric layers with medium, temperature-stable permittivities ( $\epsilon_r = 30$  to 60) and low dielectric loss ( $\tan \delta < 2 \cdot 10^{-3}$ ). Up to now, appropriate materials have been realized only by GBC sintering at  $900^{\circ}\text{C}$  and above. Hence, pure silver metallization is not possible. To overcome this limitation, GCC are a promising way. Therefore, crystalline substances possessing  $\epsilon_r$  of about 100 and low dielectric loss – for example  $\text{Ba}(\text{La}, \text{Nd})_2\text{Ti}_4\text{O}_{12}$  – were combined with special high-permittivity glasses. A development of such glasses is presented in this work. Addition of oxides of easily polarizable elements (e. g.  $\text{Nb}_2\text{O}_5$ ,  $\text{La}_2\text{O}_3$ ,  $\text{TiO}_2$ ) effects an increase in permittivity of selected basis compositions from the systems  $\text{BaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$  ( $\epsilon_r$  up to 15) and  $\text{La}_2\text{O}_3-\text{Ba}_2\text{O}_3-\text{TiO}_2$  ( $\epsilon_r$  up to 20). GCC mixtures made of 65 vol.% of these glasses and 35 vol.%  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  showing microwave properties and sintering temperatures below  $900^{\circ}\text{C}$  are introduced.

### 1. Introduction

In the fabrication of ceramic substrates and housings for microelectronic devices, glass powder is widely employed to lower the sintering temperature of common crystalline materials ( $\alpha\text{-Al}_2\text{O}_3$  sinters around  $1650^{\circ}\text{C}$ ). A slurry is made by adding organic adjuvants to a mixture of glass and ceramic powder and a tape is cast (ceramic tape technology [1]). Via holes are punched and conductors as well as thick film resistors are screen-printed on the green tape. Once all the layers are processed, they are stacked, laminated and then co-fired to form a high density, fully integrated multilayer substrate (figure 1) at low cost level. Lowering sintering temperatures below  $900^{\circ}\text{C}$  enables one to cofire high-conductivity metals such as gold, copper and especially silver ( $\vartheta_{\text{m}} = 961^{\circ}\text{C}$ ). In contrast to the HTCC technology (High Temperature Cofiring Ceramics as for example  $\text{Al}_2\text{O}_3$  ceramics) where high melting metals with lower conductivity have to be processed, this method is called LTCC (Low Temperature Cofiring Ceramics) [2 to 4]. LTCC provide advantages like

- fine-line metallization,

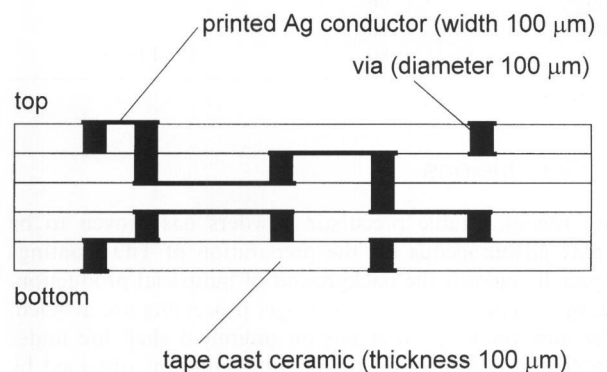


Figure 1. Cross section of a Low Temperature Cofiring Ceramics (LTCC) multilayer substrate (schematic).

- easier integration of passive components into multilayers,
- high-velocity signal processing, and
- high-frequency applications.

Microintegration and at the same time miniaturization in packaging of hybrid electronic circuits are achieved at low production costs. Hence, LTCC technology is currently considered as one of the most innovative packaging concepts.

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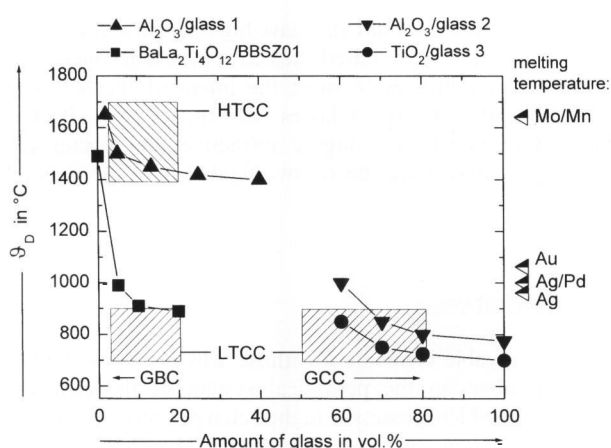


Figure 2. Dependence of the lowest temperature of full densification  $\vartheta_D$  on the amount of glass powder of selected glass/ceramic powder mixtures; glass 1:  $\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  type, glass 2:  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$  type, glass 3:  $\text{BaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$  type. Technological windows are hatched: High Temperature Cofiring Ceramics (HTCC) are usually made of Glass Bonded Ceramics (GBC). Low Temperature Cofiring Ceramics (LTCC) are favourably made of Glass Ceramic Composites (GCC).

In wireless applications and mobile communication the miniaturization of microwave filters (1 to 3 GHz) becomes more and more desirable [5]. Therefore, LTCC materials showing medium permittivities ( $\epsilon_r = 30$  to 100) in the microwave range are necessary. Moreover, their temperature coefficient of permittivity,  $\text{TC}\epsilon$ , has to amount to  $< \pm 15 \cdot 10^{-6} \text{ K}^{-1}$  and the dielectric loss must be very small ( $\tan \delta < 2 \cdot 10^{-3}$ ) [6]. These characteristics, called microwave properties, have not been achieved yet on ceramics sintering below  $900^\circ\text{C}$ . This work reports on the development of microwave LTCC within a BMBF MaTech project [7].

## 2. Sintering of composite materials consisting of glass and ceramic powders

Depending on the mix proportions of a glass powder and a powder of a crystalline material (here denoted as ceramic powder), there are two different temperature-dependent ways to obtain dense composite materials: reactive or non-reactive liquid phase sintering. Respective microstructures consist of amorphous and crystalline parts and can be properly termed as Glass Bonded Ceramics (GBC) and Glass Ceramic Composites (GCC) (figure 2). Between GBC and GCC there exists a range of compositions that do not yield dense materials under normal conditions.

### 2.1 Reactive liquid phase sintering – Glass Bonded Ceramics (GBC)

To decrease the lowest temperatures of full densification  $\vartheta_D$  of a crystalline material, small amounts of glass powder or glass batch (3 to 20 vol.%) can be added. The glass must show very low viscosity at the processing temperatures and high solubility of the crystalline material. Sintering and densification then occurs by rearrangement of the crystal-

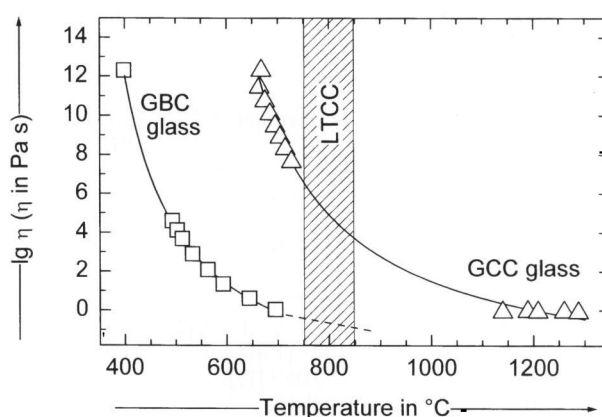


Figure 3. Viscosity-temperature charts of glasses for Glass Bonded Ceramics (GBC) (BBSZ01, left) and for Glass Ceramic Composites (GCC) (LBT2, right). The temperature range of Low Temperature Cofiring Ceramics (LTCC) manufacturing is hatched. Data above  $\vartheta_{\text{soft}}$ : rotation viscosimeter, below  $\vartheta_{\text{soft}}$ : cylinder compression method. Data for  $\eta = 10^{12-3} \text{ Pa s}$ : dilatometer. Curves were fitted using VFT equation.

line particles in the liquid phase and by solution-precipitation processes. Figure 2 (top left) is given as typical example: the  $\vartheta_D$  temperature of  $\text{Al}_2\text{O}_3$  drops significantly by  $200 \text{ K}$  within addition of glass powder up to approximately 10 vol.% [8]. Consequently, the first approach to microwave LTCC is to reduce the sintering temperatures of typical microwave ceramics [9] by small additions of glass. This effect is demonstrated in figure 2 (bottom left) for the crystalline compound  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  (BLT), ( $\epsilon_r = 108$ ;  $\tan \delta = 3 \cdot 10^{-3}$ ) and the glass (composition in mol%)  $6\text{SiO}_2 - 32.5\text{ZnO} - 34\text{Bi}_2\text{O}_3 - 27.5\text{B}_2\text{O}_3$  (BBSZ01) [7]. The viscosity of this glass melt is very low in the LTCC processing range (figure 3, GBC glass). A considerable drop by approximately  $600 \text{ K}$  towards  $900^\circ\text{C}$  occurs. Although there have been many attempts to develop lower sintering GBC, up to now there is no significant success [10 to 12].

### 2.2 Nonreactive liquid phase sintering – Glass Ceramic Composites (GCC)

A decrease in the sintering temperature below  $900^\circ\text{C}$ , and hence the possibility of silver metallization, is achieved easily when the amount of glass powder in the mixture exceeds 50 vol.%. Such a composite powder sinters by viscous flow of the glass melt in the temperature range around the glass softening point  $\vartheta_{\text{soft}}$  (see figure 3, GCC glass). The result of this process is a dense glass matrix-inclusions microstructure showing a residual porosity near to zero. In contrast to GBC a reaction between glass melt and crystalline inclusions is not required in order to reach full densification. For this reason, this technology is called non-reactive liquid phase sintering. Appropriate dense composite materials are termed Glass Ceramic Composites (GCC). Yet, it should be noted here that, to some extent, reactions at the interface between glass melt and crystalline phase as well as crystallizations of the glass melt can accompany the sintering process in its later stage.

To achieve GCC with microwave properties,  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  (BLT) and  $\text{TiO}_2$  (rutile) were selected as crystalline

Table 1. Physical properties of TiO<sub>2</sub> (rutile) and BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT)

	TiO <sub>2</sub> (rutile)	BaLa <sub>2</sub> Ti <sub>4</sub> O <sub>12</sub> (BLT)
calcination temperature in °C	1300 [17]	1350**
melting temperature in °C	1845 [18]	
density in g/cm <sup>3</sup>	4.25 [19]	5.57
$\alpha_{th}$ in 10 <sup>-6</sup> K <sup>-1</sup>	9.2   , 7.1 $\perp$ * [20]	10.3
$\epsilon_r$	100 <sup>1)</sup> [17]	108 <sup>2)</sup> **
$\tan \delta$ in 10 <sup>-3</sup>	0.05 <sup>1)</sup> [17]	3 <sup>2)</sup> **
TC $\epsilon$ in 10 <sup>-6</sup> K <sup>-1</sup>	-900 <sup>3)</sup> [21]	-99 <sup>2)</sup> **

1) 1.0 GHz

2) 3.3 GHz

3) 10 GHz

\* || parallel,  $\perp$  perpendicular to *c*-axis.

\*\* Measurement of Siemens AG in the context of [7].

compounds. Properties of these materials are specified in table 1.

However, the glass phase will dominate the effective dielectric properties of the composites because of its higher amount in the mixture. Consequently, the glass used must have a permittivity as high as possible and, at the same time, a low dielectric loss.

In general, glasses are known to show  $\epsilon_r$  values below 10 or, if higher, they also show higher dielectric loss. The first step approaching microwave LTCC was a development of glasses with high permittivities and low dielectric loss.

### 3. Development of glasses for microwave LTCC

#### 3.1 Development strategies

Glasses that are suited to make microwave LTCC have to meet certain thermal and technological criteria, such as

- = softening point 700 °C <  $\vartheta_{soft}$  < 800 °C,
  - = coefficient of thermal expansion at  $\alpha_{th} \leq 8 \cdot 10^{-6} \text{ K}^{-1}$ ,
  - = small water solubility of glass powders,
  - = dense sintering of glass powder pressings,
- as well as specific dielectric properties in the microwave region, like
- = permittivity  $\epsilon_r > 10$ ,
  - = dielectric loss  $\tan \delta < 5 \cdot 10^{-3}$ .

Appropriate glasses are not known in literature.

##### 3.1.1 Basic glasses

The thermal requirements are met by several alkaline earth alumoborosilicate glasses that are in use to make common LTCC. For our first development strategy, such a glass will be modified in its dielectric behavior by addition of suitable oxides in such a way that it obtains the required properties. For this investigation the BaO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (BABS) system was chosen.

Our second development strategy was based on the Maxwell relation:  $\epsilon_r = n^2$ . Glasses that possess high values

of refractive index should also have high permittivities. Such a glass showing the required dielectric properties has to be trimmed via additives to meet the intended thermal and technological criteria. Glasses of the La<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> (LBT) system are highly refractive and chemically stable [13] and have been investigated for the second strategy.

##### 3.1.2 Additives

Easy polarizable elements are those which possess higher order numbers in the periodical system of the elements (PSE), i. e. which possess a higher charged atomic nucleus and rather many electrons. The higher the charge of the nucleus the more the electrons are attracted. The highest electronic polarizabilities are expected for big alkaline earth metal and rare earth metal ions like Ba<sup>2+</sup>, Sr<sup>2+</sup> and La<sup>3+</sup>, Nd<sup>3+</sup>.

Analogously, but, because of smaller size of the ions, less imperative, this is valid for certain transition elements like Ti<sup>4+</sup>, Zr<sup>4+</sup> und Nb<sup>5+</sup>. In dependence on the glass composition, these elements can act both as network modifier and as network former.

Along with European environment politics, the well suited element lead was categorically excepted. Tellurium, which is also well suited [14 and 15], was disqualified because of its toxicity.

##### 3.1.3 Experimental

Glass batches of 100 g were molten in PtRh crucibles. The temperature of the melt was set in such a way that the viscosity amounted to approximately  $\eta = 10^3 \text{ Pa s}$  and drops with a diameter of  $D \approx 15 \text{ mm}$  could be poured. These were taken into the cooling furnace which had a temperature of about 20 K above  $T_g$ , and were cooled down to room temperature at a rate of 1 to 3 K/min. From these glass drops standard specimens having a height *h* of 1 mm and a diameter *D* of 15 mm were ground. Dielectric measurements were performed in the frequency range 0.01 to 1 GHz by use of an impedance analyzer HP4291A (Agilent, Böblingen (Germany)). A comparison between different measuring methods yielded a fair agreement between results in this range and those between 1 to 6 GHz (resonant methods). Deviations amounted to 10 % at their maximum [16]. The theoretical coefficient of thermal expansion  $\alpha_{th}$  as well as  $T_g$  were measured using standard specimens.

Glasses showing promising thermal and dielectric properties were fritted into desalted water and milled to powders. Cylindrical pressings were formed and characterized in their sintering and crystallization behavior by dilatometric shrinkage. All sintered glass pressings showed a high relative densification  $\rho_{rel} \approx 99 \%$ . Dielectric characteristics of these specimens matched those of poured glass samples.

Standard composite batches were made from 65 vol.% glass powder and 35 vol.% ceramic powder by milling. The particle average diameter  $d_{50}$  was set to about 1 to 3  $\mu\text{m}$ . Courser fractions hinder the densification process, more fine-grained fractions support unwanted reactive interac-

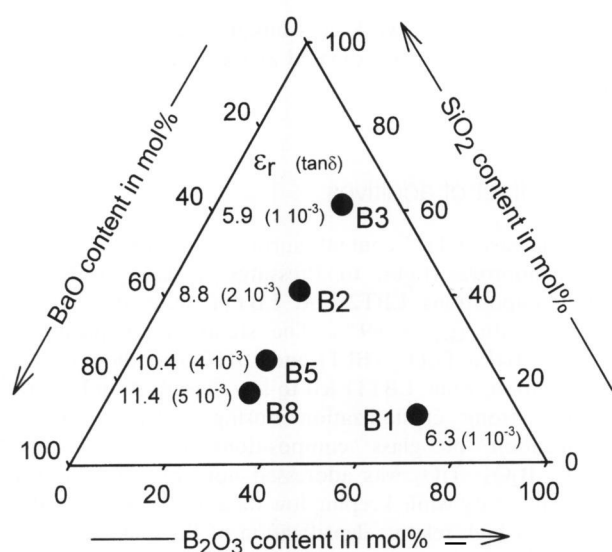


Figure 4. Quasi ternary cut through the four-compound system BaO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (cut at 7.5 mol% Al<sub>2</sub>O<sub>3</sub>). Compositions of molten glasses (●), their dielectric properties  $\epsilon_r$  and  $\tan \delta$  in  $10^{-3}$  (shown in brackets) are given in the diagram.

tions. To have an appropriate preparation method for serial investigations, the dielectric standard measurements were first carried out using cylindrical pressings ( $h \approx 1.5$  mm,  $D \approx 17$  mm). The manufacturing process was the same as that for ceramic tape casting slurries. The slurry of the batch milling contains, in addition to the dispergator, an organic support medium, that reduces the friction between the particles and between the particles and the wall of the pressing form. This provides a sufficient green densification of the pressing.

The specimens were sintered slightly above the temperature of the highest dilatometric shrinkage rate. They were heated up at a rate of 10 K/min, kept at the highest temperature for 10 min and cooled at a rate of 10 K/min. The bulk densities were measured by the Archimedes method. Relative densities were obtained by dividing bulk densities by pure densities of the composite batch ( $q_{rel}$  in % of theoretical density, see tables 4 and 5). At increased sintering temperatures changes may appear in the pure density because of reactions or crystallizations. Thus, the true pure densities of selected milled samples were measured.

Dense specimens ( $q_{rel} > 95\%$ , porosity  $< 5\%$ ) were characterized in their dielectric behavior. Therefore, they were ground coplanar to  $h = 1$  mm using disks of grain size 15  $\mu$ m.

### 3.2 System BaO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (BABS)

A thermally and chemically stable borosilicate glass is AF 45 (Schott DESAG, Gr $\ddot{u}$ nenplan (Germany)), a barium alu-borborosilicate glass for LCD displays and solar cells. Its composition approximately agrees with that of glass B3 in figure 4.

Glass B3 contains 7.5 mol% Al<sub>2</sub>O<sub>3</sub> to avoid the well known mixing gap in the three-compound system BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> [22]. Based on B3 several compositions were made to move stepwise into the barium-rich area of

the system by substitution of BaO for SiO<sub>2</sub> (B3–B2–B5–B8). A boron-rich glass composition (B1) was also prepared. The percentage of Al<sub>2</sub>O<sub>3</sub> content in all investigated glasses was constant.

The permittivities increase with barium content, from  $\epsilon_r \approx 6$  in the barium-poor region (B1, B3) to  $\epsilon_r > 11$  (B8). In the same direction the dielectric losses grow from 1 to 5  $\cdot 10^{-3}$ .

#### 3.2.1 Effect of additives

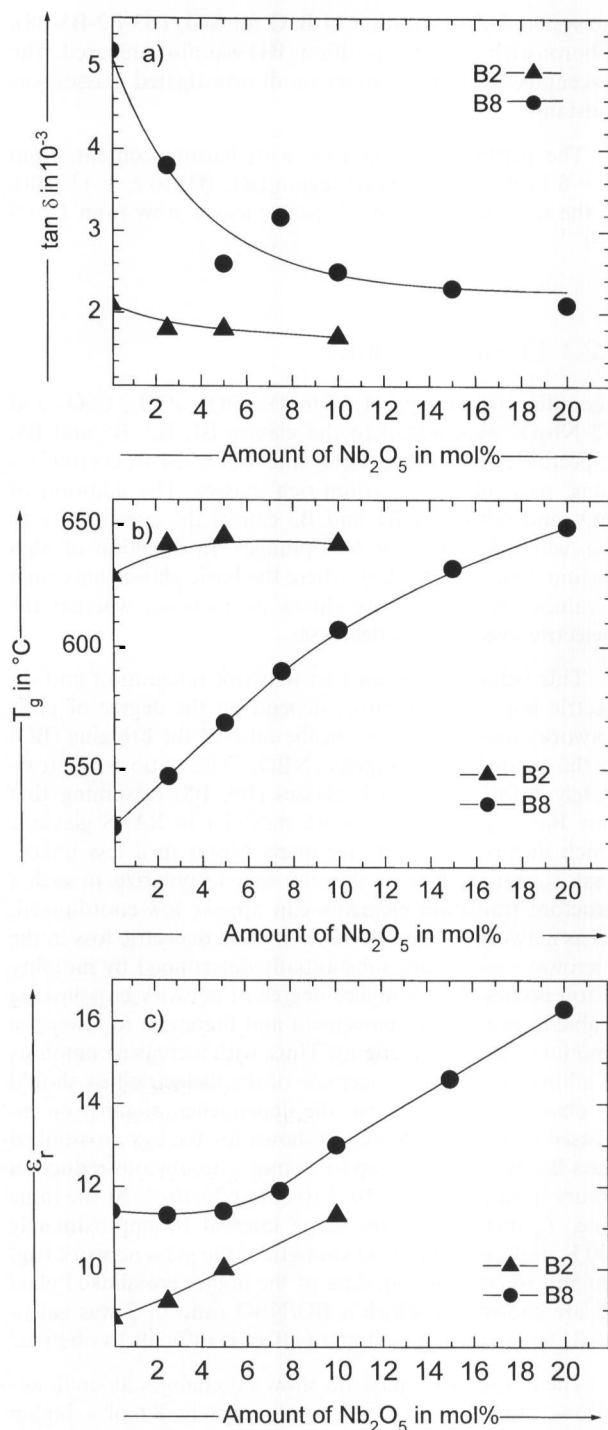
According to strategy (1), 5 mol% TiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> and 1/2 Nb<sub>2</sub>O<sub>5</sub> were added to the glasses B1, B2, B5 and B8, respectively. The oxides ZrO<sub>2</sub> and CeO<sub>2</sub> led to crystallizations, particularly in barium-rich glasses. The addition of TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> in B1 and B3 causes the permittivity to rise, while the dielectric loss plunges. In direction of high barium contents (B5, B8), where the basic glasses have high  $\epsilon_r$ -values, the permittivity shows no increase, whereas the dielectric loss strongly decreases.

This behavior implies that network integration and dielectric impact of additives depend on the degree of glass network crosslinking, i. e. on the ratio of the bridging (BO) to the nonbridging oxygens (NBO). This ratio is approximately 1 for barium-rich glasses (B5, B8) (assuming that only Ba<sup>2+</sup> appears as network modifier in BABS glasses), which means that there are many NBOs in a less linked, weak structure. Because they are easy to polarize, in such a structure transition elements can appear low-coordinated, i.e. as network former. Permittivity and dielectric loss in the microwave region are substantially determined by mobility of ion bodies [23]. A higher degree of network crosslinking is able to restrict this movement and therewith to lower the amount of dissipated energy. Thus, with increasing amounts of additives a stronger decrease of the dielectric loss should be observed. In figure 5a, the dependence of  $\tan \delta$  on increased amounts of Nb<sub>2</sub>O<sub>5</sub> is shown for the low crosslinked glass B8. For additions up to 10 mol% an obvious reduction occurs from  $\tan \delta = 5 \cdot 10^{-3}$  to about  $2 \cdot 10^{-3}$ . At the same time,  $T_g$  increases in the same interval by approximately 100 K, indicating growing strength of the glass network (figure 5b). In comparison, data of the higher crosslinked glass B2 are shown, for which a BO/NBO ratio of 3 was calculated. For this composition an effect is difficult to observe.

The  $\epsilon_r$ -values of glass B8 show no changes at small additions, but starting from approximately 8 mol% higher amounts of easily polarizable ions lead to an almost linear permittivity increase while the dielectric losses remain low (figure 5c). This increase occurs in the higher crosslinked glass B2 immediately with first additions. The weak glass B8 shows an equivalent behaviour to that of the more strengthened glass B2, if it contains more than 10 mol% Nb<sub>2</sub>O<sub>5</sub>.

#### 3.2.2 Selection of glasses for LTCC

To manufacture LTCC, modified BABS glasses given in table 2 were chosen. Pure glass pressings predominantly densified in the temperature range 700 °C  $< \vartheta_D < 800$  °C ( $q_{rel} > 95\%$ ). The permittivities of the glasses could be in-



Figures 5a to c. Dielectric loss (a),  $T_g$  (b) and permittivities (c) of the glasses B8 and B2 in dependence on their Nb<sub>2</sub>O<sub>5</sub> content.

creased up to 10 by additives and the dielectric loss shows small values below  $3 \cdot 10^{-3}$ .

### 3.3 System La<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> (LBT)

The glass forming range of the system La<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> according to [24] is shown in figure 6. Permittivities of molten glass compositions increase with growing TiO<sub>2</sub> content from about  $\epsilon_T = 13$  (LBT7) to 18 (LBT11). The dielectric loss remains at low level below  $3 \cdot 10^{-3}$ . This indicates

a high degree of network crosslinking. In LBT2, 48 % of boron ions are four-coordinated as indicated by <sup>11</sup>B-MAS-NMR.

#### 3.3.1 Effect of additives

With increasing Ti<sup>4+</sup> content, surface crystallization in the system improves (figure 6). Pressings of glass powders of both compositions LBT2 and LBT11 sintered to dense samples with  $\rho_{\text{rel}} \approx 99\%$ . The standard composite of 35 vol.% BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT) and LBT2 also showed high densification, while LBT11 led to low densification because of too strong crystallization during sintering. Hence, optimization of glass compositions of the systems La<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> was addressed not only to maximize the permittivity while keeping low dielectric losses, but also to reach a high relative densification of the Glass Ceramic Composites.

To reduce the strong tendency towards surface crystallization of LBT11, suited glass formers had to be added. Nb<sub>2</sub>O<sub>5</sub> supports glass formation and can increase the permittivity [25]. The glass forming range of a system can be enlarged by adding several oxides which have different charges and sizes [26].

#### 3.3.2 Selection of glasses for LTCC

Table 3 shows compositions, dielectric and thermal properties of the ternary glasses LBT2 and LBT11 as well as those of the optimized modifications of the glass LBT11 to the glasses LBT11NB (substitution of 5 mol% Nb<sub>2</sub>O<sub>5</sub> for TiO<sub>2</sub>), LBT11M01 (addition of 1 mol% BaO, SrO and ZrO<sub>2</sub>, respectively) and LBT11M01N (LBT11M01 with addition of 6 mol% Nb<sub>2</sub>O<sub>5</sub>). In contrast to LBT11, all these slightly modified glasses sinter in combination with BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT) to high values of relative density  $\rho_{\text{rel}} > 95\%$ . The permittivities of the glasses attain the range between 18 and 20 and exceed that of LBT11.

LBT glasses show obviously higher permittivities than BABS glasses and are more consistent with the design target. An adjustment of thermal and technological data is not necessary.

## 4. Results

Tables 4 and 5 specify results of sintering experiments (maximum relative density  $\rho_{\text{rel}}$ , lowest temperature of full densification  $\vartheta_D$ ) and dielectric parameters ( $\epsilon_r$ ,  $\tan \delta$ ) of GCC made of selected BABS and LBT glasses. In the first column there are listed criteria that must be met by composite materials. Not matched criteria are given in bold type in composite columns. Appropriate composites are not applicable.

### 4.1 Sintering behaviour

GCC of the glasses B2N (table 4) and LBT2 (table 5) show the dependence of the sintering process on the combination

Table 2. Chosen glass compositions in mol% and their physical properties of the system BaO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (BABS)

	B5T	B2N	B84N	B2NN	B2LL	B2LT
SiO <sub>2</sub>	23.48	39.16	13.55	37.10	37.10	37.10
B <sub>2</sub> O <sub>3</sub>	20.37	19.16	17.39	18.16	18.16	18.16
Al <sub>2</sub> O <sub>3</sub>	7.12	7.12	5.99	6.74	6.74	6.74
BaO	44.03	29.56	43.06	28.00	28.00	28.00
Nb <sub>2</sub> O <sub>5</sub>		5.00	20.00	10.00		
La <sub>2</sub> O <sub>3</sub>					10.00	5.00
TiO <sub>2</sub>	5.00					5.00
physical properties:						
$\epsilon_r$ <sup>4)</sup>	10.4	10.0	16.3	11.3	10.8	10.3
$\tan \delta$ in $10^{-3}$ <sup>4)</sup>	3.1	1.8	2.1	1.7	2.9	2.3
$\rho$ in g/cm <sup>3</sup> <sup>5)</sup>	4.035	3.677	4.499	3.753	4.107	3.854
$\alpha_{th}$ in $10^{-6}$ K <sup>-1</sup>	10.4	7.9	9.1	7.5	9.2	8.7
$T_g$ in °C	562	645	649	642	644	645
$\vartheta_D$ in °C <sup>6)</sup>	650	757	730	760	752	746

<sup>4)</sup> Standard measurement: HP 4291 A, Agilent, Böblingen (Germany); average value of  $\epsilon_r$  0.01 to 1 GHz.

<sup>5)</sup> Density of glassfrit of the fraction  $d_{50} < 40 \mu\text{m}$  after 2 h milling was measured with a pycnometer.

<sup>6)</sup> Lowest temperature of full densification,  $q_{rel} > 95\%$ .

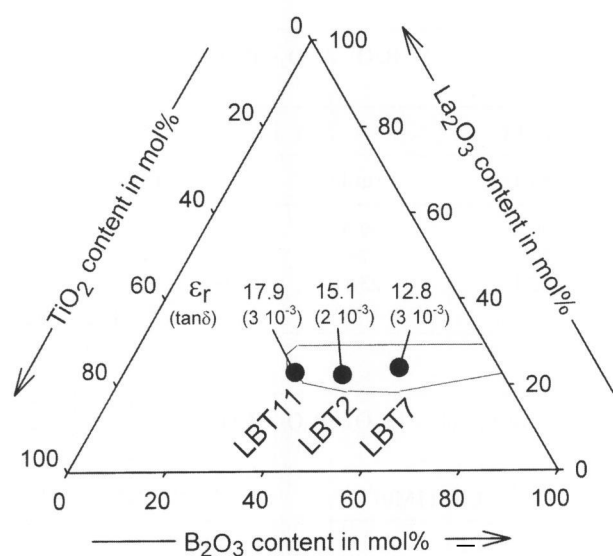


Figure 6. Ternary system La<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub>. Compositions of molten glasses (●), their dielectric properties  $\epsilon_r$  and  $\tan \delta$  in  $10^{-3}$  (shown in brackets) are given in the diagram.

of glass and ceramic components. While the combination of glass B2N with BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT) results in a rather poor densification because of the crystallization of barium niobate, the sample with rutile densifies without disturbing crystallizations. In contrast, composites of glass LBT2 and BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT) completely densify and the combination with rutile leads to a sintering blockade ( $q_{rel} < 90\%$ ) because of the crystallization of LaBO<sub>3</sub> and La(BO<sub>2</sub>)<sub>3</sub>.

BABS glass powders are capable of yielding high sintering densities with both compounds (B2LL in table 4), whereas all investigated composites of LBT glasses with rutile showed a sintering blockade.

#### 4.2 Dielectric properties of the dense-fired samples

Tables 4 and 5 list the dielectric data of pressings that were fired at their lowest temperatures of full densification  $\vartheta_D$ .

The permittivities of GCC with BABS glasses amount to 20 and more. GCC containing LBT glasses show values of 30 and above. The glass LBT11M01 with BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (table 5) features the highest permittivity (ca. 36) and very low dielectric loss. Appropriate GCC are suited to microwave LTCC and permit a metallization of pure silver because of low sintering temperatures of 750 °C.

In figure 7 measured permittivities given in tables 4 and 5 are compared to calculated data. Calculation is based on a three-phase effective-medium model for glass matrix (data from tables 2 and 3), crystalline disperse phase (data from table 1) and pore phase [27]. Volume fraction of pores were approximated from the difference of relative densities in tables 4 and 5 to 100%. Dielectric data for pores are  $\epsilon_r = 1$  and  $\tan \delta = 0$ . The chart shows that there exists a very good agreement between experimental and calculated data for GCC B2N/BLT and LBT11M01/BLT. For other composites the match is not so good: some measured values show deviations (e. g. LBT2/BLT, B2NN/BLT). The differences can be explained if the constitution of the microstructure changed during sintering. New phases can appear by reactions and/or crystallizations.

The decreased permittivity of GCC B2LL/rutile is caused by partial crystallization of celsian which has low  $\epsilon_r$ . In composites containing LBT glasses small amounts of LaBO<sub>3</sub> ( $\epsilon_r$  around 10) crystallize. Moreover, XRD as well as REM pictures of the microstructure show a partial solution of the crystalline compound BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT) by the glass melt.

In GCC B2NN/BLT the new crystalline phase Ba<sub>5</sub>LaTi<sub>3</sub>Nb<sub>7</sub>O<sub>30</sub> could be identified. Because in this case measured values for  $\epsilon_r$  lie above calculated ones, it has to be assumed that the crystallization of a high- $\epsilon_r$  phase succeeded.

#### 4.3 Dielectric properties for higher firing temperatures

The temperature range for LTCC processing scales up to about 875 °C. This is remarkably higher than the lowest

Table 3. Chosen glass compositions in mol% and their physical properties of the system  $\text{La}_2\text{O}_3\text{-B}_2\text{O}_3\text{-TiO}_2$  (LBT)

	LBT2	LBT11	LBT11M01	LBT11NB	LBT11M01N
$\text{La}_2\text{O}_3$	22.41	23.00	22.31	23.00	20.93
$\text{B}_2\text{O}_3$	44.95	35.00	33.95	35.00	31.85
$\text{TiO}_2$	32.64	42.00	40.74	37.00	38.22
BaO			1.00		1.00
SrO			1.00		1.00
ZrO <sub>2</sub>			1.00		1.00
Nb <sub>2</sub> O <sub>5</sub>				5.00	6.00
<u>physical properties:</u>					
$\epsilon_r$ <sup>7)</sup>	15.1	17.9	18.3	19.3	19.8
$\tan \delta$ in $10^{-3}$ <sup>7)</sup>	2.4	2.6	2.4	2.5	2.5
$\alpha_{\text{th}}$ in $10^{-6} \text{ K}^{-1}$	7.9	8.2	8.9	8.5	8.1
$\rho$ in $\text{g/cm}^3$ <sup>8)</sup>	4.399	4.622	4.530	4.588	4.588
$T_g$ in °C	662	668	668	664	662
$\vartheta_D$ in °C <sup>9)</sup>	727	743	737	727	733

<sup>7)</sup> Standard measurement: HP 4291 A, Agilent, Böblingen (Germany); average value of  $\epsilon_r$  0.01 to 1 GHz.

<sup>8)</sup> Density of glassfrit of the fraction  $d_{50} < 40 \mu\text{m}$  after 2 h milling was measured with a pycnometer.

<sup>9)</sup> Lowest temperature of full densification,  $\rho_{\text{rel}} > 95\%$ .

Table 4. Physical properties of Glass Ceramic Composites (GCC) produced of 65 vol.% BaO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (BABS) glass powder and 35 vol.% ceramic powder

	glass-ceramic	B2N		B2LL		B2NN
		BLT	rutile	BLT	rutile	BLT
$\rho_{\text{rel}}$ (max) in %	>95	<b>93.4</b>	96.4	99.4	99.9	94.8
$\vartheta_D$ in °C	<900	850	825	775	775	850
$\epsilon_r$	>20	23	22.8	22.1	23.1	33.7
$\tan \delta$ in $10^{-3}$	<2	5	1	<1	1.6	<b>7.4</b>

Table 5. Physical properties of Glass Ceramic Composites (GCC) produced of 65 vol.%  $\text{La}_2\text{O}_3\text{-B}_2\text{O}_3\text{-TiO}_2$  (LBT) glass powder and 35 vol.% ceramic powder

	glass-ceramic	LBT2		LBT11M01		LBT11NB
		BLT	rutile	BLT		BLT
$\rho_{\text{rel}}$ (max) in %	>95	99.5	<b>&lt;90</b>	98.5		98.4
$\vartheta_D$ in °C	<900	725	n.a.	750		750
$\epsilon_r$	>20	29.4	n.a.	36.4		29.1
$\tan \delta$ in $10^{-3}$	<2	1.7	n.a.	<1		<1

temperatures of full densification of the investigated GCC ( $\vartheta_D$  725 to 825 °C). Firing at temperatures higher than  $\vartheta_D$ , for example co-firing together with common LTCC materials, improves reactions and crystallizations that change the dielectric data of the samples.

Already small variations in the glass composition are sufficient to influence the reaction and crystallization behaviour crucially, as it is shown in the case of GCC LBT11M01/BLT and LBT11NB/BLT (table 5). Both glass compositions are derived from glass LBT11 (table 3), which features a sintering blockade in combination with BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT).

Dielectric data of LBT11M01/BLT specimens that were sintered at increasing firing temperatures are plotted in figure 8. Also given is the DTA chart of the same powder

mixture. In the range of crystallization, a sharp exothermic peak appears at 770 °C.

The permittivity of the material LBT11M01/BLT decreases with increasing sintering temperatures  $\vartheta_S$  from 36 at 750 °C to about 32 at 775 °C, but remains at this level up to very high temperatures. The dielectric loss is very low ( $\tan \delta = 1 \cdot 10^{-3}$ ) in the whole temperature range. In the sintering interval from 750 to 950 °C, the relative density of the specimens amounts to > 95 %. With the help of XRD and REM investigations this behaviour can be described by an initial partial dissolution of BaLa<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (BLT) in the glass melt and the appearing segregation of the TiO<sub>2</sub> and LaBO<sub>3</sub> phases at the same time, which is almost completely finished at 775 °C.

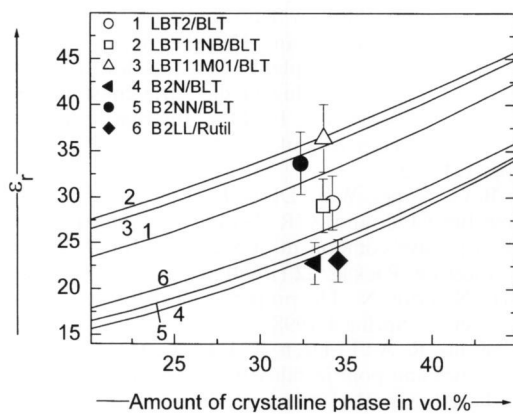


Figure 7. Permittivities of GCC made of BABS and LBT glasses as a function of the amount of crystalline phase in the microstructure. Comparison between measured permittivities (symbols) and calculated permittivities after effective medium theory [27] (lines). Calculated values are based on data for three phases, respectively: glass matrix, crystalline disperse phase, pore phase. Error bars show specified error of the impedance analyzer.

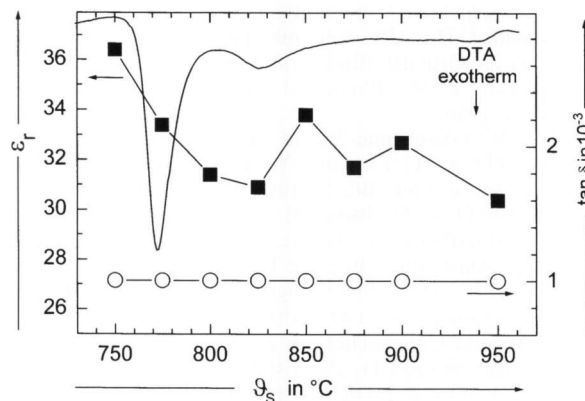


Figure 8. Dependence of the dielectric properties on the sintering temperatures  $\vartheta_s$  of the GCC LBT11M01/BLT. For comparison the DTA chart (5 K/min) is given.

Thus, a reasonable independence of the dielectric data of the sintering temperature in the LTCC processing range was achieved. In addition, the substitution of the crystalline compound  $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$  for  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  enables one to set the thermal coefficient of the permittivity  $\text{TC}\varepsilon$  to  $\leq 15 \cdot 10^{-6} \text{ K}^{-1}$  [28].

Figure 9 shows the dielectric data of LBT11NB/BLT samples as a function of the sintering temperature  $\vartheta_s$ . The DTA plot of the powder shows a sharp crystallization peak similar to that of the LBT11M01/BLT composite, but it is followed by a second wide crystallization peak at higher temperatures. Crystallization behaviour at lower temperatures is analogous to that of the above reported LBT11M01/BLT composite. Due to a stronger  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  dissolution, permittivities decrease to below 30 while the growing content of segregated rutile only effects partial equalization. However, above  $850^\circ\text{C}$  a new phase,  $\text{Ba}_2\text{LaTi}_2\text{Nb}_3\text{O}_{15}$ , crystallizes whereby a GCC forms with  $\varepsilon_r > 35$  and low dielectric loss of  $1 \cdot 10^{-3}$ , i. e. very good microwave properties. More-

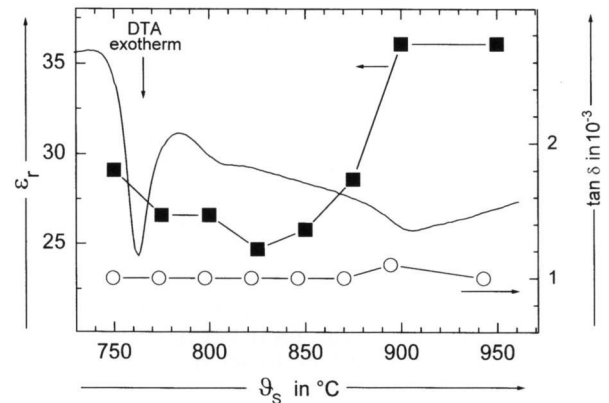


Figure 9. Dependence of the dielectric properties on the sintering temperatures  $\vartheta_s$  of the GCC LBT11NB/BLT. For comparison the DTA chart (5 K/min) is given.

over, a zero-crossing of  $\text{TC}\varepsilon$  is linked to the segregation of this phase, which enables to set the  $\text{TC}\varepsilon$  to  $\leq 15 \cdot 10^{-6} \text{ K}^{-1}$ .

## 5. Conclusions

Glasses open up new possibilities in the development of innovative electroceramics for microelectronics and microsystem technologies. Up to now, glass powders have been employed in many cases only to lower the sintering temperatures of common ceramic compounds.

This work shows that glasses can gain a variety of functions in modern substrates. On the one hand, Glass Ceramic Composites (GCC) consisting of  $\geq 50 \text{ vol.}\%$  glass powder and  $\leq 50 \text{ vol.}\%$  crystalline (ceramic) powder sinter below  $900^\circ\text{C}$  by viscous flow of the glass melt. On the other hand, glasses enable one to adjust crucial dielectric properties of GCC.

To produce GCC eligible for miniaturization of microwave filters for wireless communication (1 to 3 GHz), special glasses with high permittivities and low dielectric loss in the microwave range were developed.

Addition of suitable oxides (e. g.  $\text{Nb}_2\text{O}_5$ ,  $\text{La}_2\text{O}_3$ ,  $\text{TiO}_2$ ) increases the permittivities of commercial  $\text{BaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$  (BABS) glasses to approximately 15. Combinations of these glasses with crystalline compounds like for example  $\text{Ba}(\text{La},\text{Nd})\text{Ti}_4\text{O}_{12}$  show permittivities up to about 25. The dielectric loss was measured to be below  $2 \cdot 10^{-3}$ . Sintering temperatures of  $850^\circ\text{C}$  and below permit pure silver metallization structures. In the high refractive  $\text{La}_2\text{O}_3-\text{B}_2\text{O}_3-\text{TiO}_2$  (LBT) system, glasses with permittivities up to 20 were obtained by targeted modification. The use of these glasses in GCC yields microwave LTCC with sintering temperatures below  $800^\circ\text{C}$ , permittivities up to 40 and low dielectric loss below  $2 \cdot 10^{-3}$ .

In conclusion, by small variations of glass composition the following results were obtained:

- a sintering blockade was avoided and a substrate material showing 98.5% relative density was produced (LBT11M01/BLT instead of LBT11/BLT),
- strong partial dissolution of  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  at high firing temperatures was decreased and a material with approximately constant dielectric properties in a wide sintering



- interval was achieved (LBT11M01/BLT instead of LBT11NB/BLT),
- crystallization of a new phase was initiated, which has a high permittivity and low dielectric loss and thus complies with targeted dielectric properties (LBT11NB/BLT instead of LBT11M01/BLT).

\*

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