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LTCC glass-ceramic composites for microwave application

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Abstract

Advanced materials of rare earth derived glass–and reactive bonded glass–ceramic composites are exceptionally interesting for IC packaging, radar, antennas and wireless technologies for the next generation of miniature electronic devices. Glass–ceramic composites in the system 1:1:4 $BaO–Nd_2O_3–TiO_2$ and modified rare earth glasses based on boron oxide for passive integration in LTCC demonstrate excellent dielectric properties in the middle permittivity ε range of 20–70 with high quality factor Q and low temperature coefficient TCf at microwave frequencies. Depending on the glass–ceramic system, concentration, significant processing parameters e.g. powder preparation techniques and sintering of dense composite at temperatures $<900°C$ were achieved. Dielectric properties were studied by a cavity resonator method at frequencies 1–6 GHz in correlation of the crystalline microstructure. This work was supported by tridimensional modeling systems to estimate dielectric behavior of multiphase glass–ceramic composites.

Keywords: Dielectrical properties; Glass ceramics; LTCC; Microwave processing

1. Introduction

Low-temperature-cofired ceramics (LTCC) for microwave application represent a key position in the development of future electronic products in a high frequency application for IC packaging radar, antennas and wireless technologies. The integration of passive components in LTCC is, therefore, particularly interesting in multi-layers technology. Integration of passive devices in wireless application corresponds to the trend of mobilization and miniaturization with high electrical performance using conductive electrode materials such as gold, silver and copper. The melting temperature of silver electrodes in a multi-layer device limits the sintering temperature to 900°C. Material systems of $BaO–Re_2O_3–TiO_2$ (Re = La, Sm, Nd, Eu) in 1:1:4 composite are especially suited for the development of dielectric materials[1,2] which are characterized by excellent dielectric constant ε, high quality factor Q as inverse of dielectric loss $Q = (\tan\delta)^{-1}$ and low temperature coefficient of frequency TCf characteristics.

Exceptional dielectric characteristics of 1:1:4 composite are achieved at sintering temperature $>1300°C$ and, therefore, contrary compared to the demanded temperatures of 900°C in the case of LTCC technology with Ag-electrodes. Development trends of LTCC materials are glass–ceramics systems, including low softening glasses and high sintering microwave ceramic. Typical glass systems are borosilicate, lead borosilicate or earth alkali $CaO–B_2O_3$ SiO_2 glass which crystallize at optimized processing parameters.[3] The requirement catalogue for glass–ceramic composites is: densification temperature $<900°C$, combined with dielectric characteristics ε 20…70, Q 1000 and TCf approximately 0 ppm/°C of composite. Promising candidates of middle ε 20…30 composite are glass–ceramic by restricting on lead-free glasses especially rare earth derived microwave glasses La–B–Ti–O (LBT).[4] An alternative route for high ε materials 60–80 are low viscosity reactive glasses in a B–Bi–Zn–O (BBSZ) system. $BaNd_2Ti_4O_{12}$ microwave ceramic filler was added with earth alkali ZnO less 1 wt.% to optimized sintering and dielectric properties in adjustment of glasses.

2. Experimental

Microwave ceramic compositions in the $BaO–Nd_2O_3–TiO_2$ system were prepared using a conventional mixed-oxide method. The $BaNd_2Ti_4O_{12}$ ceramic was derived by

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$BaCO_3$, TiO_2, Nd_2O_3 high purity powders with and without functional additives less 1 wt.%. Ball milled powders were calcinated at 1100–1270°C depending on additives and milled again for 24 h. Ground powder (average particle size $D_{50}=3$ μm) were granulated by mixing with 10% polyvinylalcohol solution and pressed into a disk of 12 mm diameter and 5 mm thickness. Pellets were sintered in a temperature range of 1300–1400°C for 2 h in air with a typical heating rate of 5°C/min.

Reactive sintering glass composition containing B_2O_3 27%, Bi_2O_3 35%, SiO_2 6% and ZnO 32% (in mol%) BBSZ was prepared by firing in platinum crucible at temperatures <1000°C. BBSZ glass frit was milled with a mixture of agate balls in different diameters 10–25 mm in generally ground to an average particle size of less than 6 μm.

Passive sintering glass composition containing La_2O_3 23%, B_2O_3 35%, TiO_2 42% (in mol%) modified by addition of ZrO, BaO, SrO <3 mol% to realized "long glasses" and inhibit the crystallization of glasses at elevated temperature. Mixtures of calcinated ceramic powder of the $BaRe_2Ti_4O_{12}$ ceramic with reactive BBSZ glass and passive LBT were attritated 4 h (average size $D_{50}=0.5$ μm) respectively 2 h (average size $D_{50}=4$ μm), dried in rotation evaporator by addition of polyvinylalcohol solution. After drying and granulation the powders were pressed in disks 12 mm in diameter and 5 mm thick. Microwave ceramic compositions with LBT glass were sintered in the temperature range of 750–850°C, reactive sintering of BBSZ glass was studied at 850–950°C.

Fig. 1 shows processing of the glass–ceramic composition alternative route of passive and reactive glass bonded ceramic composition for LTCC. Dielectric properties were measured at disks as fired.

Density of sintered products were measured by helium pycnometry (Accupyc 1330, Micromitrics, Duesseldorf, FRG). Temperature and time-controlled sintering behavior was investigated in situ using dilatometry (Model STA 409C, Netzsch, Selb FRG). Viscosity of the glass was determined by the deflection method and approximated by the conventional Vogel–Fulcher–Tammann equation.

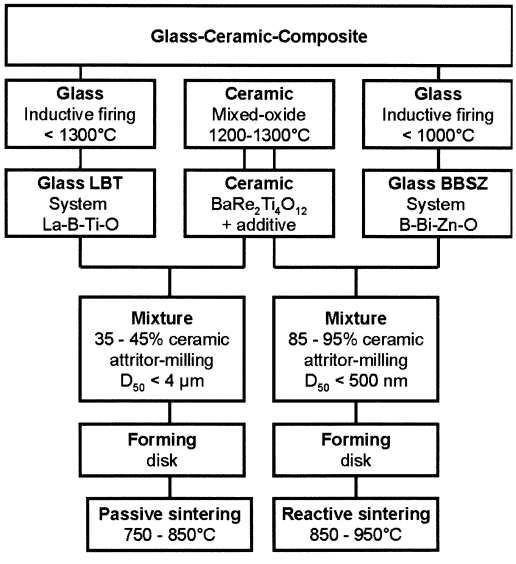

Fig. 1. Manufacturing of glass–ceramic composites.

Phase composition of glass–ceramic constituents were examined by X-ray analysis (Siemens Diffrac 500).

Dielectric properties were studied by cavity resonator method at frequencies 1–6 GHz with a Networkanalyzer HP8510B (Hewlett Packard, Palo Alto, USA) and integrated climber chamber. Temperature coefficient of frequency TCf was investigated in the temperature range of -30 to 80°C.

Dielectric properties were calculated by a modified Bruggemann effective-medium-theory considering the microstructure of a reactive sintered microwave composite in separated and coating phases.[5] Multiphase Bruggemann effective-medium-theory simulate dielectric properties of glass–ceramic composites, where v is the volume fraction and ε the complex dielectric constant of the corresponding phase.

$$\sum_{j=1}^{N=3} v_j \cdot \frac{\varepsilon_j - \varepsilon_{\text{eff}}}{\varepsilon_j + 2\cdot\varepsilon_{\text{eff}}} = 0 \tag{2.1}$$

$$(v_1+v_2)\cdot\frac{(\varepsilon_1-\varepsilon_{\text{eff}})\cdot(\varepsilon_2+2\varepsilon_1)+\dfrac{v_2}{v_1+v_2}.(\varepsilon_2-\varepsilon_1)\cdot(\varepsilon_{\text{eff}}+2\varepsilon_1)}{(\varepsilon_1+2\varepsilon_{\text{eff}})\cdot(\varepsilon_2+2\varepsilon_1)+2\cdot\dfrac{v_2}{v_1+v_2}.(\varepsilon_2-\varepsilon_1)\cdot(\varepsilon_1-\varepsilon_{\text{eff}})} + v_3\cdot\frac{\varepsilon_3-\varepsilon_{\text{eff}}}{\varepsilon_3+2\varepsilon_{\text{eff}}} = 0 \tag{2.2}$$

Temperature coefficient of dielectric permittivity TCε is generally given by ε(T)

$$\text{TC}\varepsilon = \frac{1}{\varepsilon}\cdot\frac{\partial\varepsilon}{\partial \text{T}} \tag{2.3}$$

and substitution of ε by TCε [Eq. (2.3)] in Bruggemann [Eq. (2.1)] results in the simplified formula

$$\sum_{j=1}^{N=3} v_j \cdot \frac{\text{TC}\varepsilon_j - \text{TC}\varepsilon_{\text{eff}}}{\varepsilon_j\cdot(1+2\varepsilon_{\text{eff}}/\varepsilon_j)^2} = 0 \tag{2.4}$$

which $\text{TC}_{\varepsilon(\text{eff})}$ solved explicitly. Relation of TCε, TCf and linear temperature coefficient α is

$$\text{TC}\varepsilon = -2\cdot(\text{TC}f + \alpha_l) \tag{2.5}$$

This modified model is simulated by tridimensional phases considered as complexity multiphase glass-ceramic composite which transform depending on temperature in

multi-crystalline and glass phases, including the interface reaction of ceramic and glasses as coating.

3. Results and discussion

3.1. Microstructure and dielectrics

For a glass-ceramic system with rare earth derived glass LBT the microwave ceramic filler content is limited <45 vol.% by the crystallization of glasses at temperatures $<900°C$. Ceramic filling material contents >80 vol.% are realized by sinter active glass BBSZ with low viscosity at a temperature of 400°C and a high solubility of rare-earth derived ceramic. Glass softening point T_s (log $\eta = 7.6$ d·Pas) as significant processing parameter is 725°C for LBT and 430°C for BBSZ, respectively.

Dielectric high frequency properties of the glass system LBT amount TC$f = -100$ ppm/°C, $\varepsilon = 16$ and unfilled BBSZ TC$f = -152$ ppm/°C, $\varepsilon = 21$ with low $Q < 100$. Densification behavior of reaction bonded and passive glass-ceramic via LBT and BBSZ composite with 90 and 35 vol.% $BaNd_2Ti_4O_{12}$ ceramics are demonstrated by dynamical dilatometry in Fig. 2. Phenomenological investigation during heat treatment shows densification $>98\%$ of passive glass–ceramic systems at sintering temperature less 750°C with a high densification rate -30%/min. Addition of 10 vol.% BBSZ reactive glass is characterized by the maximum densification rate of -7%/min at 880°C which indicate densification $<900°C$ by introducing a dwell time.

3.2. Passive and active sintering glass–ceramics

Fig. 3 shows the results of the X-ray investigations of sintering phases depending on temperature 25–900°C in the system 35 vol.% $BaNd_2Ti_4O_{12}$ / 65 vol.% LBT. In

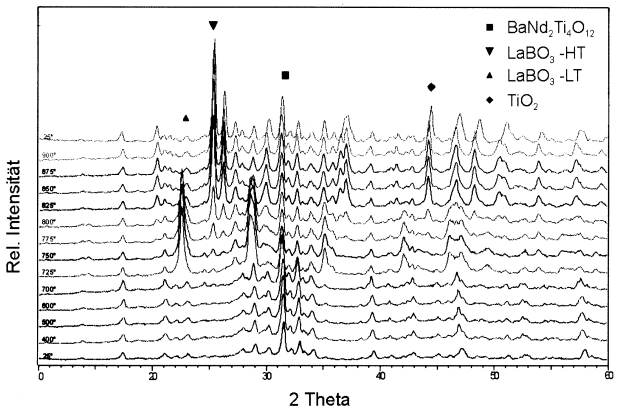

Fig. 3. Temperature dependent X-ray investigation of specimen containing 35 $BaNd_2Ti_4O_{12}$/65 LBT in vol.%.

agreement with the softening temperature $T_s = 725°C$ crystallization of glasses starts by generation of the LT-$LaBO_3$ phase which transforms to a high temperature modification HT-$LaBO_3$ at 800°C. Simultaneously, interactions of glass and ceramic composition results in the degradation of LBT glass into $LaBO_3$ and TiO_2 phases. Rare earth derived glass crystallization simplified the complete decomposition of $LaBO_3$–B_2O_3–TiO_2 glass in separated $LaBO_3$, TiO_2 and B_2O_3 phases.

$$(La_2O_3 + 2TiO_2 + B_2O_3)_{(glass)} \xrightarrow{>800°C} 2LaBO_{3(s)} + 2TiO_{2(s)} + 0.5B_2O_{3(l)} \quad (3.1)$$

In agreement with X-ray analyses interactions of B_2O_3 containing glass with microwave ceramics ($D_{50} \approx 4$ μm) at temperature less 900°C are negligible.

Complexity reduction of glass–ceramic multi-crystallization is simulated by the modified Bruggemann effective medium model. Fig. 4 shows modeling of five phases which considered x vol.% LBT glass, y vol.%

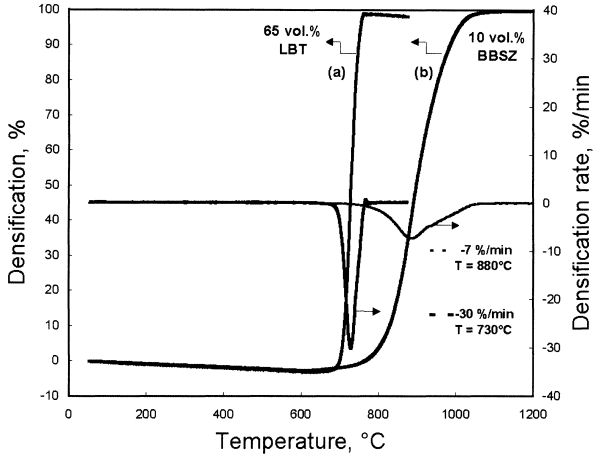

Fig. 2. Densification of glass–ceramic composites containing $BaNd_2Ti_4O_{12}$ ceramic with (a) 65 LBT and (b) 10 BBSZ in vol.%.

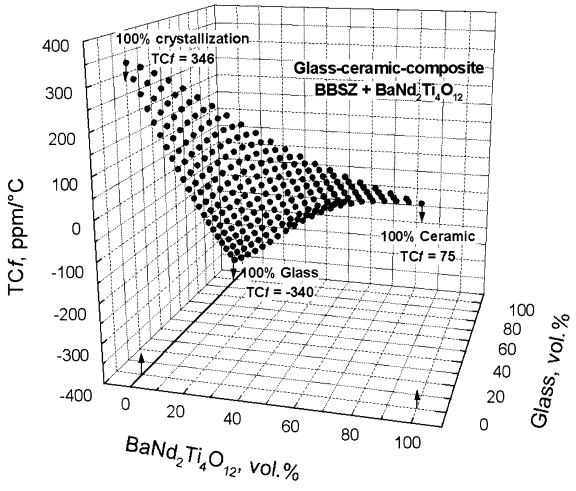

Fig. 4. Tridimensional modelling systems of TCf of glass–ceramic composites, with $BaNd_2Ti_4O_{12}$ and crystallization of LBT glass.

microwave ceramic and the decomposition of LBT glass into (100-x-y) vol.% ($LaBO_3$, B_2O_3 and TiO_2) phases. On the condition of microwave ceramic $BaNd_2Ti_4O_{12}$ (TCf = 75 ppm/°C) at temperature < 900 °C is stable and chemical inert.

Simulation parameters are $LaBO_3$ (TCf = 670 ppm/°C), B_2O_3 (TCf = −6400 ppm/°C)[6] and TiO_2 (TCf = 450 ppm/°C) phases accrue by glass crystallization and generate in a constant mole volume relationship according to formula (3.1). Glass and ceramic parameters for result are taken as LBT TCf = 340 ppm/°C and $BaNd_2Ti_4O_{12}$ (+ZnO 1 wt.%) TCf = 75 ppm/°C. Result of modeling of ceramic–glass ceramic describes an area which indicates increasing crystallization of glass and the TCf of 0 ppm/°C is achievable. The dielectric composite shows at controlled phase transformation of LBT glass a TCf of 0 ppm/°C with 35 vol.% $BaNd_2Ti_4O_{12}$ and glass crystallization of 40 vol.%.

Corresponding to simulation measurements and X-ray analyses the temperature controlled crystallization determines the dielectric properties. Fig. 5 shows microwave properties at a frequency of 5 GHz for sintered specimens. Interrelationship of temperature coefficient TCf and permittivity ε demonstrate a linear function correlated to temperature which was expected by the result of computation. Increase of TCf is coherent to the decrease of permittivity ε explained by the formation of $LaBO_3$ and TiO_2 as dominat phases.

Decomposition and separation processes in the case of glass–ceramics transformation results in dielectric characteristic of ε, Q and TKf. Best results with the composite 35 vol.% $BaNd_2Ti_4O_{12}$/65 vol.% LBT concerning high densification, dielectric properties TCf approximately 0 ppm/°C, $\varepsilon = 30$ and $Q > 1000$ at densification temperature 840°C and 15°C/min heating rate were achieved.

X-ray investigation analyses in the system 90 vol.% $BaNd_2Ti_4O_{12}$ (+1 wt.% ZnO)/10 vol.% BBSZ indicate $BaNd_2Ti_4O_{12}$ as the dominating phase. Fig. 6 shows

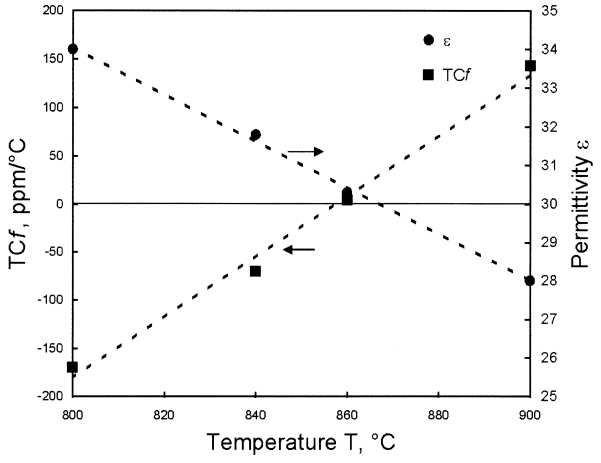

Fig. 5. Dielectric characterization of glass–ceramic 35 $BaNd_2Ti_4O_{12}$/65 LBT in vol.%.

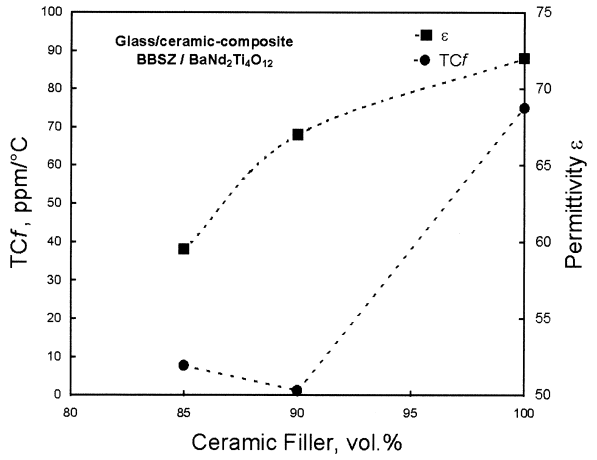

Fig. 6. Dielectric characterization of reaction bonded glass–ceramic (100-x) $BaNd_2Ti_4O_{12}$/x BBSZ in vol.% at 900°C/3 h (100% $BaNd_2Ti_4O_{12}$ sintering 1420°C).

TCf and ε of reactive sintering glass in variation of glass concentration at 900°C. Optimization of the glass concentration resulted in TCf + 4 ppm/°C, $\varepsilon = 67$ and $Q >$ 1000 at a frequency of 6 GHz.

4. Conclusion

Glass–ceramic composites of defined dielectric material with TCf = 0 ppm/°C, quality factor $Q > 1000$, permittivity ε of 25–70 in the frequency range of 0.5–3 GHz for high frequency application are demonstrated. Depending on the glass–ceramic concentration evaluated by modified tridimensional modeling and significant processing parameters e.g. powder preparation techniques dielectric properties and sintering modification at temperature <900°C were controlled. Processing parameters of passive sintering glass–ceramic with nucleation and crystal growth rate controlled by concentration, particle size, sintering temperature and heating rate. Middle ε 30 developed by lead-free rare earth derived boron glass in addition of 35 vol.% 1:1:4 BaO–Nd_2O_3–TiO_2 ceramic enable sintering temperature <780°C. Controlled phase transformation of ceramic filled LBT glass at 850°C with HT-$LaBO_3$ and TiO_2 phases optimized the dielectric properties. An alternative route of high filled reaction bonded lead-free B–Bi–Zn–O glass–ceramic composite contains $BaRE_2Ti_4O_{12}$ >90 vol.%. Characterized by high solubility of microwave ceramic and tailored generated microwave phases by addition of earth alkali in glass and ceramics in order to achieve TCf approximately 0 ppm/°C, $\varepsilon = 68$, $Q > 1000$ at 6 GHz and temperature 900°C. Development of passive glass ceramics systems in addition of reactive bonded glass ceramics materials characteristics with excellent dielectrics are promising candidates for the integration of passive components into LTCC modules.

Acknowledgements

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