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Characterization and improvement of LTCC composite materials for application at elevated temperatures

Christian Bienert*, Andreas Roosen

University Erlangen-Nuremberg, Department of Materials Science, Glass and Ceramics, Martensstrasse 5, 91058 Erlangen, Germany

Abstract

Glass–ceramic composites combine the material properties of its ceramic filler material and the ability of densification via glass assisted sintering. Especially for LTCC materials, were densification has to be achieved at temperatures below 900 °C to enable the usage of metals of improved conductivity in conducting pastes, this densification mechanism in combination with crystallization of the glassy matrix is used successfully. However, the glass' softening point also limits the use of LTCCs at elevated temperatures, since their mechanical stability is dependent on the remaining glass composition's transition range and its crystallization products. Because LTCC multilayers gain increasing interest in manufacturing sensor devices, a better understanding of their mechanical and electrical behavior in the elevated temperature regime is needed to broaden their field of applications. Therefore, five commercially available LTCC materials were investigated in regard to their temperature dependence of mechanical and electrical properties. Based on the understanding gained from these results, a novel LTCC will be presented and its properties will be discussed.

Keywords: LTCC; Composites; Thermal properties; Electrical properties; Glass–ceramics

1. Introduction

Nowadays, the fields of application for LTCC composite materials have increased far beyond microelectronics where they were first introduced in the early 90s.[1] Electronic packaging and microsystems rely on the advantages of small power loss, high signal density and high signal velocity which are required to precede towards the latest trends in miniaturization.[2,3] Filled glass–ceramic composites combine the possibilities of the thick film technology and the high temperature co-fired ceramics technology with the advantage of low sintering temperatures of <900 °C.[1,4] This allows the usage of metal pastes with high electrical conductivity. Thus, the performance of multilayer devices can be improved when using metal pastes containing Ag, AgPd, and Au.[4] After lamination, de-bindering and densification via viscous sintering, which is accompanied by partial crystallization of the glassy matrix, a multilayer device is achieved, whose performance depends on the degree of crystallization, the crystallization products and the choice of ceramic filler.[5] The possibilities of tailoring properties and performance of LTCC devices lead to their broad establishment in communication, automotive and medical industries.[6,7] Hence, the technical possibilities of highly integrated LTCC multilayers with compact electrical assemblies have extended into new fields like sensor technique and microfluidsystems.

Due to the fact that novel applications for LTCC composites often take place at elevated temperatures, this paper contributes to the characterization and improvement of LTCC composite materials by the investigation of commercial LTCC systems in a temperature regime up to 750 °C.[8,9] Taking into account that these materials had originally not been developed for usage at elevated temperatures, knowledge gained from these experiments is used to design novel LTCC systems for high temperature application.

2. Experimental procedure

For these investigations, the commercial LTCC systems DP 951 (sintered thickness 180 μm) and DP 943 (sintered thickness 250 μm) from Du Pont, Bristol, UK, GC (sintered thickness 230 μm) from CeramTec AG, Marktredwitz, Germany, and CT 800 (sintered thickness 190 μm) as well as Heratape AHT01-005 (sintered thickness 94 μm) from W.C. Heraeus GmbH, Hanau, Germany, were chosen. The tapes were cut with a hot cutting

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* Corresponding author. Tel.: +49 09131 85 27 547;
fax: +49 09131 85 28 311.
E-mail address: andreas.roosen@ww.uni-erlangen.de (C. Bienert).

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blade at 60 °C (Grotz-Beckert KG, Albstadt, Germany) to gain a sintered sample size of 3 mm × 14 mm. The samples were sintered in a chamber furnace (Nabertherm GmbH, Lilienthal, Germany) of improved temperature uniformity following the sintering profiles recommended by the tape producers.

The inorganic chemical composition was determined by ICP chemical analysis (ICP Moldula, Spectroflame, Kleve, Germany) on all green tapes but Heratape AHT01. The phase composition was analyzed by X-ray analysis measurements (Siemens Diffract 500, Siemens AG, Karlsruhe, Germany) on all sintered substrates.

3-Point bending tests were performed in a thermo-mechanical analyzer (TMA-60 H, Shimadzu, Tokyo, Japan). A pressure of 100 MPa was applied on the sintered specimens (3 mm × 14 mm) which were supported by alumina stages in a 3-point bending setup. Two different cases were investigated: for case a, loading of the sample started at 400 °C with a loading rate of 0.1 N/min and a consecutive heating rate of 10 K/min to 750 °C and 950 °C, respectively. Case b involved loading of the sample at 600 °C with 0.01 N/min and a consecutive heating rate of 1 K/min to maximum temperature. The complete test conditions for the 3-point bending tests are summarized in Table 1. The deviation of the loading beam was monitored throughout the experiment and from this plot, softening and failure of the specimens were determined. To analyze the samples' creep behavior, loaded samples were held for 5 h at 650 °C before heated to 750 °C at 10 K/min in the 3-point bending setup.

For measurement of the electrical resistivity, four layers of tape were laminated by thermo-compression (Polystat 200T, Servitec, Wustermark, Germany) at a pressure of 37.5 MPa at 70 °C for 15 min. Cylindrical specimens with a diameter of 32 mm were punched out, fired and finally contacted with Pt paste on both sides. The electrical resistivity was measured at 600 °C in air in a tube furnace in AC mode (1 V, 20,000 Hz), neglecting a third electrode since surface conductivity is minimal at elevated temperatures. The measurement setup consists of two loops of Pt wire contacting the specimen and a 4284A Precision LCR Meter (Hewlett-Packard, Tokyo, Japan).

In addition to the commercial systems, four alumina filled LTCC composites of novel glass composition were investigated and compared to the five commercial systems. SiO_2–Al_2O_3–CaO–B_2O_3 glasses with slight variations were melted. The basic glass B-1 in addition contained K_2O and Na_2O, La_2O_3 and TiO_2. The variations from B-1 concern either the depletion of K_2O and Na_2O (B-2) to detect their influence on the glass transformation temperature or the depletion of titanium oxide (B-3), which was used as nucleation agent in the other three compositions. Lanthanum oxide, used to enhance the decrease of boron oxide in the glass by crystallization of borate phases was depleted in B-4. Table 2 summarizes the compositional differences of the glasses. Each glass composition was melted from the raw materials in a Pt crucible at 1450 °C for 1 h and quenched in water. The glass was dried and milled down to a median particle size d_{50} of approximately 6 μm using a disk mill (Siebtechnik, Mühlheim an der Ruhr, Germany). Glass–ceramic composites were prepared by mixing 43 wt% of the alumina filler (d_{50}: 0.8 μm, Almatis GmbH, Ludwigshafen, Germany) with 57 wt% of the respective glass. Milling to a median particle size of a d_{50} value of 2 μm was carried out in isopropanol using an attrition mill at 1200 rpm. To avoid contamination of the LTCC system, alumina milling balls with a diameter of 1–1.5 mm were used. The dried powders were uniaxially pressed at 158 MPa and 25 MPa to cylindrical specimens of 10 mm and 25 mm in diameter, respectively, and approximately 2.3 mm in height.

Table 1
3-Point bending test conditions.

	Case a	Case b
100 MPa applied at	400 °C	600 °C
Stress rate	0.1 N/min	0.01 N/min
Consecutive heating rate	10 K/min	1 K/min

Table 2
Variation of the glass composition.

	B-1	B-2	B-3	B-4
Alkali ions	X		X	X
TiO_2	X	X		X
La_2O_3	X	X	X	

X: component contained in the glass composition

For a first screening, penetration experiments using a steel tip were performed in the thermo-mechanical analyzer on sintered powder compacts which were heated to 400 °C at 10 K/min. At this temperature, the initial load of 0.25 MPa was increased to 25 MPa at 0.5 N/min before heating was continued to 750 °C at 10 K/min.

For tape casting, B-1 and B-4 LTCC powders were further milled to a median particle size of a d_{50} value of 1 μm. The powder then was dispersed in an aceotropic solvent mixture of toluene/ethanol using fishoil as the dispersant agent. For deagglomeration of the particles, the suspension was milled in a ball mill for 24 h. After addition of the binder polyvinylbutyral and the plasticizer benzylphthalate, the slurry was homogenized for another 24 h in a ball mill. After degassing, the slurry was cast on a tape casting machine using a double chamber doctor-blade system. The LTCC tape was then cut with a hot cutting blade at 60 °C to gain a sintered sample size of 3 mm × 14 mm. The samples were fired in air in a chamber furnace (Nabertherm GmbH, Bremen, Germany) at a heating rate of 10 K/min to 895 °C. A dwell time of 30 min was applied before cooling to room temperature at 5 K/min.

Under the same conditions as described for the commercial systems, the 3-point bending tests and, for B-4, creep behavior tests were carried out on the LTCC tapes. The measurement of the electrical resistivity was carried out on powder compacts of these novel LTCC compositions. Additionally, their phase composition was characterized by X-ray analysis.

3. Results and discussion

Fig. 1 shows the results gained from the 3-point bending tests in the thermo-mechanical analyzer for the five commercial

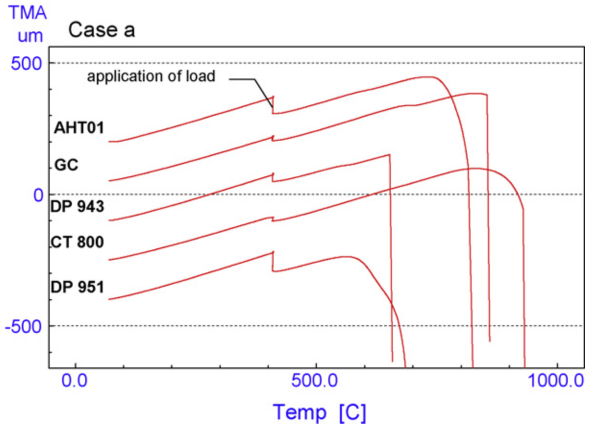

Fig. 1. 3-Point bending experiment on commercial LTCC tapes (case a).

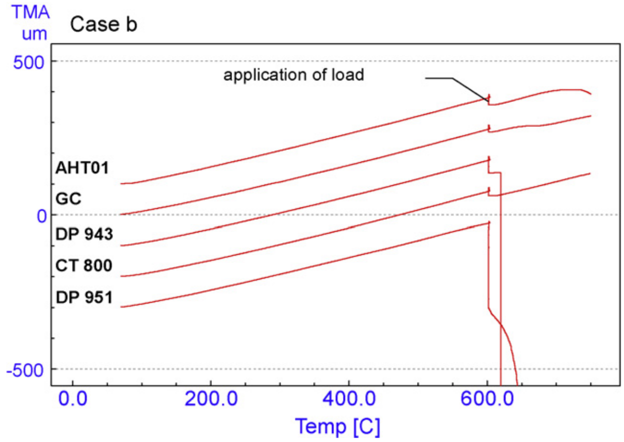

Fig. 2. 3-Point bending experiment on commercial LTCC tapes (case b).

tapes and loading at 400 °C, whereas Fig. 2 shows the results for loading at 600 °C. In all cases, the sample first expands due to the increase in temperature. The deviation of the loading beam is depicted over temperature with its characteristic step caused by the loading of the specimen with 100 MPa at 400 °C and 600 °C, respectively.

As can be seen, the material's response to bending stress with an increase in temperature differs in a wide spectrum. DP 951 exhibits softening of the tape at temperatures above 575 °C. As can be seen in the excerpt of the ICP analysis in Table 3, Du Pont 951 is the only system investigated which uses PbO to reduce the glass transformation temperature T_g. Additionally, SiO_2, Al_2O_3, CaO, B_3O_2 and Na_2O are the major components of this glass composition which crystallizes into anorthite $CaAl_2Si_2O_8$. Being stressed at 600 °C (case b), this material already is beyond its softening point and thus does not exhibit any temperature stability. Therefore, the single tape softens immediately during stress application and starts bending under the applied stress.

Table 3
Excerpt of ICP analysis of commercial tapes (wt%).

	DP 951	DP 943	GC	CT800
SiO_2	31.2		32.8	32.6
Al_2O_3	50.3	54.9	46.9	29.2
CaO		7.6	15.1	
SrO				5.2
BaO				16.7
PbO	9.0			
B_2O_3		18.9		
La_2O_3		17.8		
Others	9.8	0.8	5.2	16.3

On the other hand, DP 943 simply breaks at 650 °C without any characteristics of softening (case a). The glass composition of this system was developed to exhibit an excellent RF behavior[10] and is more complex than the one of Du Pont 951. Instead of using a Si–O-network, DP 943 incorporates B_2O_3, Al_2O_3, and La_2O_3 to build the glass network (Table 3). The crystallization products detected by X-ray analysis are lanthanum borate $LaBO_3$, calcium aluminum borate $CaAl_2B_2O_7$ and lanthanum aluminum borate oxide $LaAl_{2.03}(B_4O_{10})O_{0.54}$.[11,12] When stressing this LTCC material at 600 °C (case b), using a lower stressing and consecutive heating rate, the temperature of failure drops to 620 °C as can be seen in Fig. 2. It was expected to also see softening and bending when using lower rates for stressing and heating, however, the results indicate that both, the stressing and heating rates do not have an impact on the materials' behavior and failure.

For CeramTec's GC tape, failure of the tape was detected at a temperature of 850 °C after a very short interval of softening (case a). It does not show any softening and bending when analyzed up to 750 °C (case b). Chemical analysis indicates that the glass used in this tape is a four-component composition of Al_2O_3, SiO_2, CaO and B_2O_3.[13,14] X-ray analysis detects wollastonite $CaSiO_3$ and anorthite $CaAl_2Si_2O_8$ as crystalline phases in addition to the alumina filler.

For Heraeus' CT800, softening was detected from 815 °C on, whereas the tape broke at 930 °C. Chemical analysis indicates a more than 10-component composition which incorporates BaO, SrO, ZnO and TiO_2 additionally to the common oxides SiO_2, Al_2O_3, CaO. However, barium strontium aluminum silicate $Ba_{0.75}Sr_{0.25}Al_2Si_2O_8$ and strontium aluminum silicate oxide $Sr_2Al_2SiO_7$ are the only crystalline phases detected next to the ceramic filler material Al_2O_3.

Also for Heraeus' Heratape AHT01-005, a great softening interval of 75 °C could be detected. Starting to soften at 740 °C, the tape fails at a temperature of 815 °C (case a). The steep decrease of the plot indicates a rapid change of viscosity of the system. This Willemite containing composite crystallizes into calcium sodium silicate $Ca_{0.8}Na_{0.2}Al_{1.8}Si_{2.2}O_8$ and Gahnite $ZnAl_2O_4$, whereas alumina is the filler material.

The results gained from the 3-point bending experiments under both test conditions indicate that the systems investigated show very different material's response to temperature. Since all systems incorporate alumina as filler material, the main differences result from the glass compositions, its crystallization products, the amount of residual glass phase and its corresponding T_g. DP 951 exhibits a broad softening interval and a low transition temperature T_g, the latter being controlled by the large PbO-content. It seems that the remaining glass phase in DP 943 and the large amount of crystallized crystalline phases have created a microstructure which avoids softening before failure. For

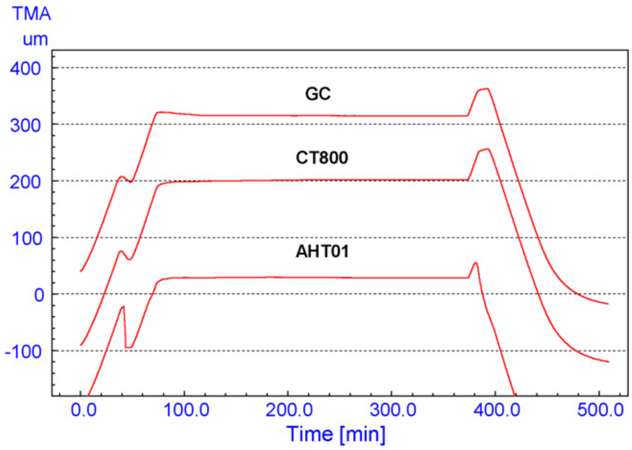

Fig. 3. Creep behavior test of commercial LTCC tapes.

GC, it seems very likely that the crystallization products deplete the remaining glass phase and therefore increases its T_g. This improves the softening characteristics of the tapes. AHT01 and CT 800 exhibit broad softening intervals at higher temperatures, with a pronounced softening of the tapes starting at 740 °C and 815 °C, respectively.

With the same setup as described for case a, a creeping test of 5 h was performed on the three commercial LTCC systems withstanding 650 °C. As can be seen in Fig. 3, the three tapes do not exhibit any creeping during the holding time. As can be seen in Fig. 4, however, after heating them to 750 °C and subsequent cooling, the plot of deflection over temperature shows a hysteresis for two of the three tapes. In contrast to CT 800, GC and AHT01 do not return to their origin but exhibit a deviation in the order of 50 μm and more than 200 μm, respectively. This deviation is due to the beginning of softening or structural rearrangement at temperatures around 750 °C and has to be considered for applications in that temperature regime.

The LTCC systems incorporating the novel glass compositions were tested by penetration experiments. Instead of sintered tapes, sintered powder compacts were used for a first screening. Fig. 5 shows the results gained from these experiments. As can

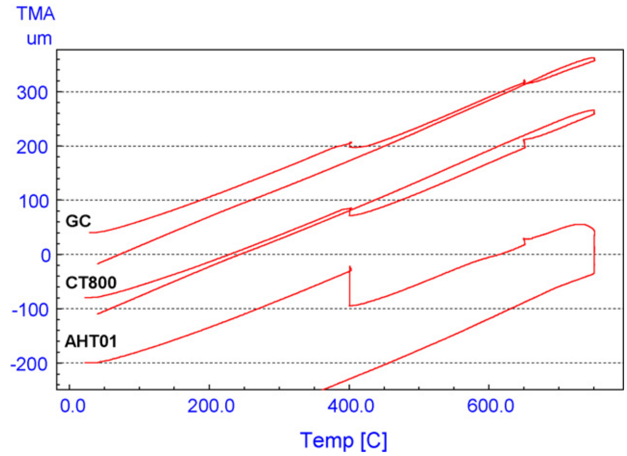

Fig. 4. Hysteresis after creep behavior test and consecutive heating to 750 °C at 10 K/min.

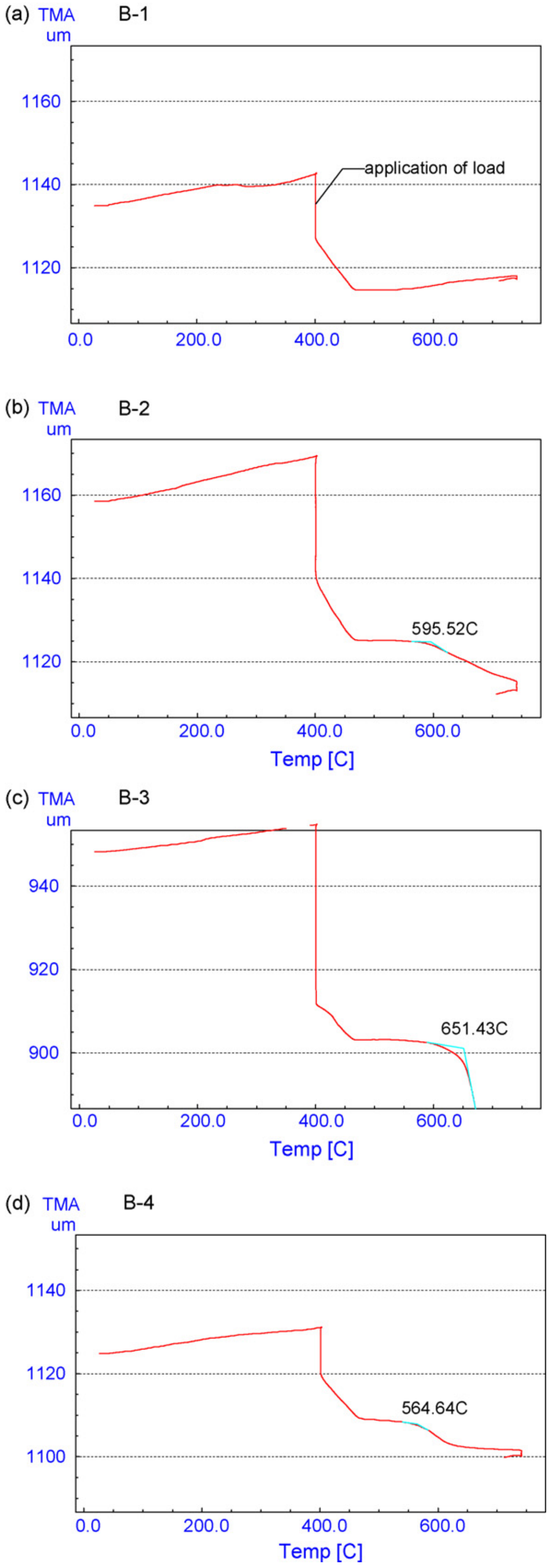

Fig. 5. Penetration experiments on powder compacts of novel LTCC composites (a–d) stressed with 25 MPa at 400 °C and consecutive heating at 10 K/min to 750 °C.

be seen, glass composition B-1 (Fig. 5a) containing alkali, as well as nucleation agents and lanthanum oxide, exhibits no softening. X-ray analysis detects the formation of multiple crystal phases such as anorthite $CaAl_2Si_2O_8$, perovskite $CaTiO_3$, quartz SiO_2 and calcium aluminium oxide $CaAl_2O_4$. All X-ray patterns also show the filler material aluminum oxide Al_2O_3.

When leaving out the alkalines, the remaining glass composition (B-2) becomes slightly richer in borate and lanthanum. This causes the LTCC system to exhibit softening at a temperature of 595 °C and a low penetration rate (Fig. 5b). Instead of perovskite $CaTiO_3$, calcium titanium oxide $Ca_4Ti_3O_{10}$ can be detected, as well as calcium aluminum silicate $CaAlAlSiO_6$ instead of calcium aluminum oxide $CaAl_2O_4$. The crystal phases of anorthite and alumina oxide, however, are still detected. Slight traces of titanium oxide Ti_7O_{13} complete the X-ray pattern.

As can be seen in the results, the addition of higher amounts of borate oxide (B-3) also leads to softening of the glassy phase. The softening temperature shifts to 650 °C, however, the penetration rate increases considerably (Fig. 5c). The lack of nucleation agent has a direct impact on the number of crystalline phases in this composition. Only anorthite $CaAl_2Si_2O_8$ and aluminum oxide Al_2O_3 could be detected. However, the increase in lanthanum and borate does not result in enhanced crystallization of lanthanum borate, which was intended to shift the softening point of the remaining glassy phase to higher temperatures.

The simultaneous increase of CaO and B_2O_3 in glass composition B-4 compared to B-1 causes a change in structure at about 564 °C. However, no further penetration was detected and thus, it cannot be considered softening (Fig. 5d). This LTCC composition also exhibits crystallization of anorthite $CaAl_2Si_2O_8$, as well as rutile TiO_2 and Kyanite Al_2SiO_5.

Overall, B-1 and B-4 have the attributes for further development as LTCC composite materials for usage at elevated temperature. In contrast to B-2 and B-3, which exhibit softening at temperatures of 595 °C and 650 °C, these compositions are not penetrated under a load of 25 MPa up to 750 °C.

Further characterization of these materials includes the 3-point bending tests on tape specimens. The test conditions were the same as for the commercial tapes. As can be seen in Fig. 6, tape B-1 does not withstand loading with a bending stress of 100 MPa in both case a and b. In contrast to DP 951, however, it does not exhibit any softening but shows an even expansion up to the temperature of loading. Thus, B-1's material behavior is more similar to DP 943 which also does not exhibit any softening. B-4, however, exhibits softening in case a at 710 °C and fails at 745 °C. For case b, the system is exposed for a longer period to the respective temperature, since both, heating and loading rate are reduced by a factor of 10 compared to case a. Thus, B-4 starts to soften at 680 °C and fails at a temperature of 725 °C.

For usage as substrate material at higher temperatures, the electrical resistivity must be high enough to guarantee electrical insulation. Thus, the measurement of the electrical resistivity at elevated temperature was carried out on all LTCC systems presented in this paper (Table 4). It can be seen, that the electrical resistivity of the commercial tapes depends on the material's performance. For all three of the tapes withstanding high temperature bending, an electrical resistivity higher than 10^6 Ω m could be measured at 600 °C. For the two Du Pont tapes, the electrical resistivity at 600 °C exhibits values two orders of magnitude lower. Again it has to be stressed, that these materials where not developed for this temperature regime. However, for application at elevated temperatures this behavior becomes essential.

For the novel glass compositions, however, it seems that electrical resistivity is independent of the composites' performance, since values higher than 10^6 Ω m could be measured for all four powder compacts. The value for B-2, one of the specimens showing softening at temperatures higher than 595 °C, as well as for CeramTec GC, the resistivity is even higher than the upper limit measurable with the measurement setup.

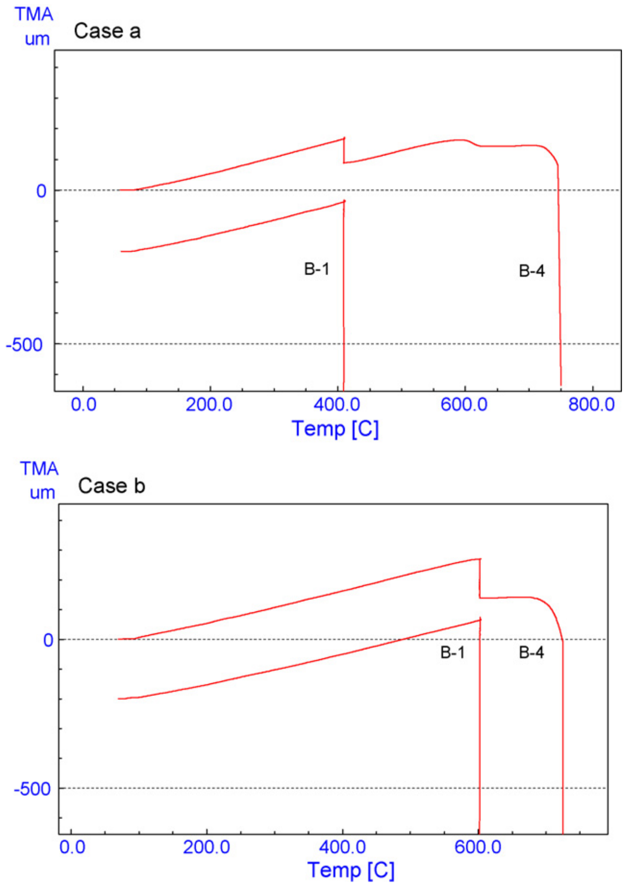

Fig. 6. 3-Point bending experiments on novel LTCC composite tapes (case a and case b).

Table 4
Electrical resistivity ρ of commercial and novel LTCC systems at 20,000 Hz, 1 V, and 600 °C.

	DP 951	DP 943	GC	CT800	AHT01
ρ [Ω m]	2.6×10^4	4.7×10^4	$>10^7$	4.8×10^6	1.3×10^7
	B-1	B-2		B-3	B-4
ρ [Ω m]	3.0×10^6	$>10^7$		3.6×10^6	4.6×10^6

4. Conclusion

The performance of the five commercial LTCC systems at elevated temperature was investigated and showed their limitations. 3-Point bending tests of the sintered tapes indicated softening of the glassy matrix at 575 °C for Du Pont 951. DP 943 broke at temperatures between 620 °C and 650 °C without showing any softening. Heratape AHT01-005 began softening at 740 °C, whereas CeramTec's GC and Heraeus' CT 800 tape did not exhibit softening up to 750 °C but withstood temperatures up to 850 °C and 930 °C, respectively. These three commercial systems also showed a electrical resistivity higher than $10^6\ \Omega$ m at 600 °C, whereas the two Du Pont tapes only showed values of $10^4\ \Omega$ m.

The novel glass compositions introduced in this paper showed good performance concerning their behavior at elevated temperatures, and are comparable to the commercial ones. Processed as a LTCC tape, composition B-4 withstood loading with a bending stress of 100 MPa up to 680 °C and 710 °C, dependent on the applied heating rate. For all novel systems, a specific electrical resistance of higher than $10^6\ \Omega$ m could be measured at 600 °C.

Further work will include refining of the glass compositions to enhance temperature stability and crystallization of the glassy matrix as well quantitative determination of the amorphous phase by Rietveld-refinement method.

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