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ScienceDirect
Journal of the European Ceramic Society 30 (2010) 81–86
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Low temperature sintering of barium titanate ceramics assisted by addition of lithium fluoride-containing sintering additives

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Received 11 February 2009; received in revised form 2 July 2009; accepted 8 July 2009
Available online 19 August 2009

Abstract

By addition of LiF-containing sintering additives to commercial $BaTiO_3$ powder, more than 98% of the theoretical density was reached at a sintering temperature of 900 °C both on powder compacts and laminates. Dielectric measurements were performed on ceramic samples in the temperature and frequency ranges from −20 °C to 125 °C and from 10^3 to 10^6 Hz, respectively. High relative permittivity ($\varepsilon_r \sim 3160$) and low dielectric loss ($\tan\delta \sim 0.014$) were measured for tapes of the favoured material. The breakdown strength for tapes with a thickness of about 80 μm is 30 kV/mm. The microprobe analysis showed, that no interfacial reaction between the dielectric layer and the Ag-electrode had occurred.

The newly developed barium titanate ceramics completely densifying at 900 °C turned out to be promising for integration of buried capacitors in LTCC multilayers.

Keywords: LTCC; $BaTiO_3$; LiF; Capacitors

1. Introduction

Low temperature Co-fired ceramics (LTCC) modules consisting of dielectric tapes and Ag conductors must be sintered at temperatures ≤900 °C due to the low melting temperature of silver (961 °C). Miniaturization of LTCC modules would be possible if buried capacitors could be realized inside the multilayer instead of additional soldering of discrete elements (e.g. multilayer capacitors) at the surface. Therefore, inner layers with a high dielectric constant are necessary. Barium titanate is a well known ferroelectric material for capacitor manufacturing due to its high dielectric constant but commercially available barium titanates (sintering temperature >1250 °C) do not reach satisfactory density (>90% theoretical density) during sintering at 900 °C.

Many researchers have already investigated the low-temperature sintering of $BaTiO_3$-based ceramics.[1–3] In order to decrease the sintering temperature, addition of various types of sintering aids, mostly fluxes, have been tested in recent years. Any flux material must satisfy a set of requirements. Fluxing should decrease the sintering temperature drastically without deterioration of dielectric properties of the host material. The desirable dielectric properties include high and almost temperature-independent dielectric constant, low dissipation factor and high breakdown strength. The addition of lithium fluoride as flux to barium titanate was first reported by Walker et al.,[4] who found that an addition of 0.5–3 wt.% of LiF allowed densification of $BaTiO_3$ at a temperature much lower than that normally required for pure $BaTiO_3$. In another study, Haussonne et al.[3] reported that by addition of excessive $BaCO_3$ to the mixture of $BaTiO_3$ and 1–2 wt.% LiF, a pseudo-cubic perovskite phase ($BaTi_{(1-x)}Li_xO_{(3-3x)}F_{3x}$) formed during liquid phase sintering, which was responsible for the densification behaviour and resulting dielectric properties. Many other references document that $BaTiO_3$ with LiF-addition can be densified at very low temperatures with acceptable dielectric properties.[5–8]

In this work, we investigated the influence of different LiF-containing mixtures on sintering behavior and dielectric characteristics of the commercially available $BaTiO_3$-powder both on powder compacts and laminates.

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doi:10.1016/j.jeurceramsoc.2009.07.005

2. Experimental

The starting powders were high-purity raw materials of $BaTiO_3$ (ABT-O-21, Ferro Corp.), $SrCO_3$ (Riedel-deHaën), $CaCO_3$ (Riedel-deHaën), $BaCO_3$ (Merk), and LiF (Fluka). The appropriate amounts of LiF and carbonates with a LiF/carbonates molar ratio of 2.5 were doped to $BaTiO_3$ and mixed/milled for 2 h in ethanol by attrition milling (Netzsch, typ. 4V1M) using 2 mm diameter ZrO_2 balls. The dried powders were then pressed into discs of 20 mm diameter and sintered at 900 °C for 2 h. For preparation of ceramic tapes, the powders were mixed with suitable solvent, dispersant, plasticizer and binder to form a slurry for tape casting. Tapes with a thickness of about 90 μm were casted. After screen printing of silver conductors the tapes were laminated and sintered at a temperature of ≤900 °C for 2 h in air. Linear shrinkage was monitored using a dilatometer Bähr 802-S and the coefficient of thermal expansion (CTE) measurements were carried out by dilatometer Netzsch 402E.

The heating rates for dilatometric measurements were 5 K/min. XRD measurements were processed with Philips PW 1710 powder diffractometer. SEM micrographs and microprobe analysis were carried out by a JEOL JXA-8900 RL electron microprobe. The detailed microstructure of the samples was examined using transmission electron microscopy (STEM, Joel JEM-2200FS). The STEM is equipped with energy dispersive X-ray (EDX) for the element analysis. The dielectric properties were measured as a function of temperature and frequency using an impedance analyser HP 4194.

3. Results and discussion

Fig. 1 shows the linear shrinkage of $BaTiO_3$ (BT) samples containing 2 wt.% LiF·$SrCO_3$ and 2 wt.% LiF·$BaCO_3$. The samples doped with LiF·$SrCO_3$ and LiF·$BaCO_3$ can be densified at about 400 °C below the sintering temperature of pure BT. The samples start to shrink at about 630 °C and densification is completed at about 860 °C and 900 °C, respectively. The density of 2 wt.% LiF·$SrCO_3$ containing BT ceramics after sintering at 900 °C for 2 h was more than 98% of the theoretical density.

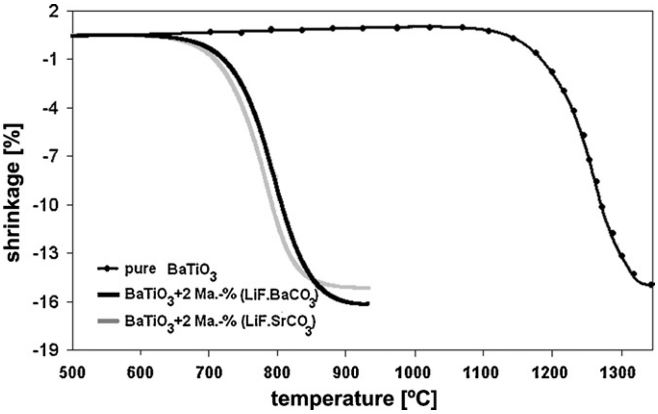

Fig. 1. Shrinkage behaviour of pure and doped $BaTiO_3$, measured at a heating rate of 5 K/min.

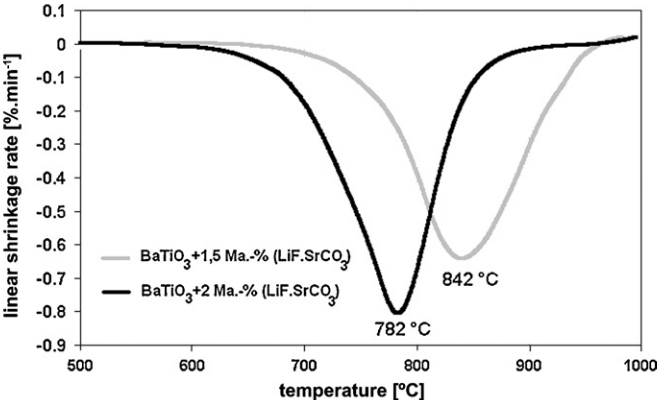

Fig. 2. Shrinkage rate of $BaTiO_3$ contained LiF·$SrCO_3$ additives.

Fig. 2 shows the shrinkage behaviour of BT with additions of 1.5 wt.% and 2 wt.% LiF·$SrCO_3$. The small change (0.5 wt.%) in the amount of LiF·$SrCO_3$ additives causes a remarkable change of the temperature at which the maximum shrinkage rate occurs (about 60 K). The influence of different carbonates on the shrinkage behaviour of LiF doped BT is shown in Fig. 3. LiF·$SrCO_3$ in comparison with LiF·$BaCO_3$ and LiF·$CaCO_3$ seems to be the more effective sintering additive for BT. The shrinkage of BT sample containing LiF·$SrCO_3$ begins and ends at lower temperatures. The properties of different compositions sintered at ≤900 °C are listed in Table 1. By addition of only 2 wt.% LiF·$SrCO_3$ to BT excellent densification was obtained both on powder compacts and laminates.

Fig. 4 shows CTE curves for pure and LiF·$SrCO_3$ containing BT. The cubic-tetragonal transformation and the corresponding change in the relative expansion at a temperature close to 130 °C, which is observed for pure BT, is absent for the LiF·$SrCO_3$ containing BT. Thus the cubic-tetragonal phase transformation does not occur in the LiF·$SrCO_3$ containing BT and this causes the difference in the CTE-values (30–600 °C) as listed in Table 1.

The evolution of domain structures in LiF·$SrCO_3$ containing BT ceramics was studied by TEM. The core part of the grains shows ferroelectric domains, and these regions are surrounded by featureless areas called the shell. The shells are paraelectric and free from domain wall contrast. This microstructure, fea-

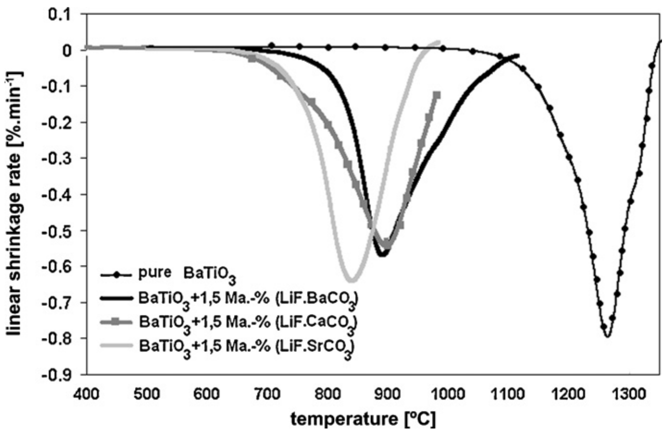

Fig. 3. Shrinkage rate of pure and doped $BaTiO_3$.

Table 1
Properties of $BaTiO_3$ with different sintering additives.

Sintering additives amount and type	LiF-content [wt.%]	Sample shape	Sintering temperature [°C]	CTE 30–400 °C [ppm/K]	Bulk density [g/cm^3]	Open porosity [%]	Densification [% of theor. density]
–	–	Powder compacts	1300	10.47	5.81	0.833	98
2 wt.% (LiF·$SrCO_3$)	0.61	Powder compacts	900	11.73	5.84	0.81	98.51
2 wt.% (LiF·$SrCO_3$)	0.61	Laminates	860	–	5.9	0.16	99.5
1.5 wt.% (LiF·$SrCO_3$)	0.46	Powder compacts	900	–	5.79	1.10	97.63
2 wt.% (LiF·$BaCO_3$)	0.5	Powder compacts	900	–	5.71	2.06	96.23
1.5 wt.% (LiF·$BaCO_3$)	0.37	Powder compacts	900	–	5.49	6.45	92.46
1.5 wt.% (LiF·$CaCO_3$)	0.59	Powder compacts	900	–	5.41	5.78	91.13

turing the coexistence of core and shell in one grain is called the ‘core-shell’ structure as shown in Fig. 5. This ‘core-shell’ structure has a significant effect on the dielectric properties of the materials especially on temperature dependency of the dielectric constant.

The results of EDX analysis (line scan) are shown in Fig. 5. As expected, the concentration of additive ions such as strontium is much higher in the shell. The small counts of strontium in the core are probably caused by the underlying grain shell. These observations are consistent in all core-shell regions.

The XRD patterns of sintered specimens are shown in Fig. 6. The crystalline phase of pure BT at room temperature is tetragonal. As shown in the XRD pattern of pure BT the characteristic peak splitting of the (2 0 0)/(0 0 2) reflections, which indicates a tetragonal phase, is observed. BT containing LiF·$SrCO_3$ ceramics do not exhibit this characteristic peak splitting. The main crystalline phase in LiF·$SrCO_3$ doped BT is cubic. This observation agrees well with the CTE results.

Based on this and TEM evidence, it is suggested that the lattice of the tetragonal core of the grain is distorted into a pseudo-cubic structure by stresses imposed by the cubic shell.[9] In the XRD pattern only a cubic BT phase is observed.

Despite the present of the sintering additives no formation of new phases was observed in the XRD-analysis of doped BT ceramics. It is suggested that the additives perform their function in the densification process due to liquid phase sintering, after which they become a dopant in the shell.[8]

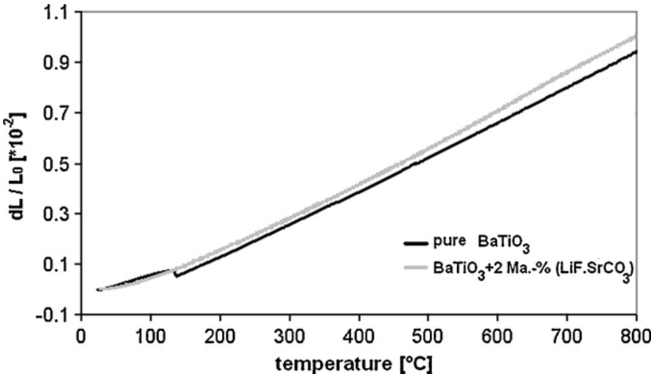

Fig. 4. CTE-curves of pure and doped $BaTiO_3$.

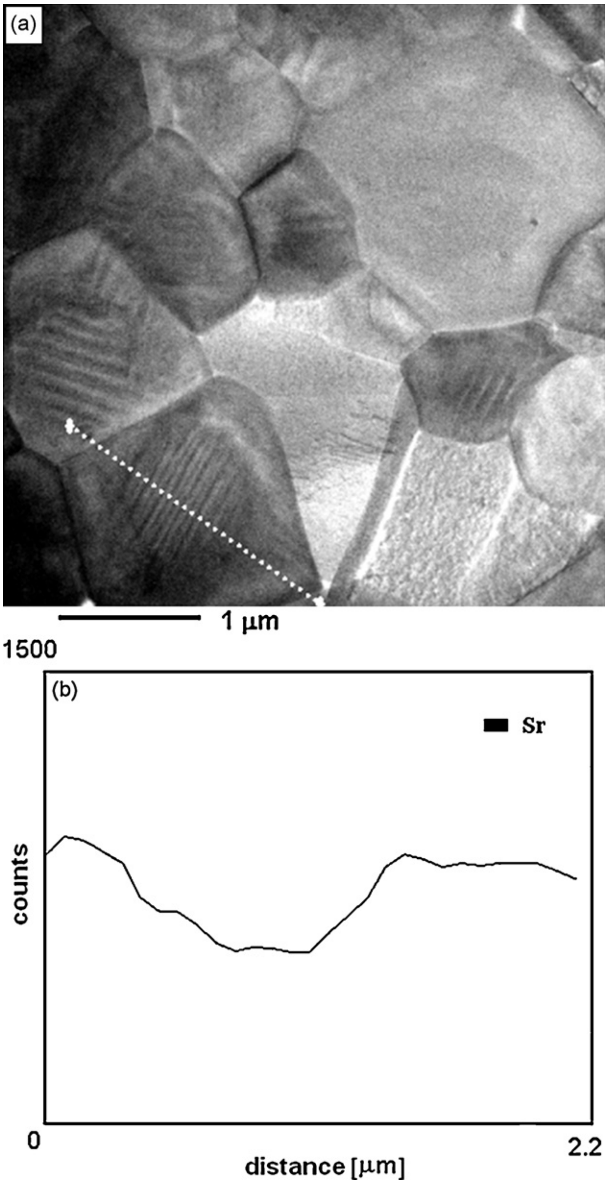

Fig. 5. TEM image (a) and EDX analysis of strontium along the dotted line (b) for LiF·$SrCO_3$ doped $BaTiO_3$ ceramics sintered at 900 °C.

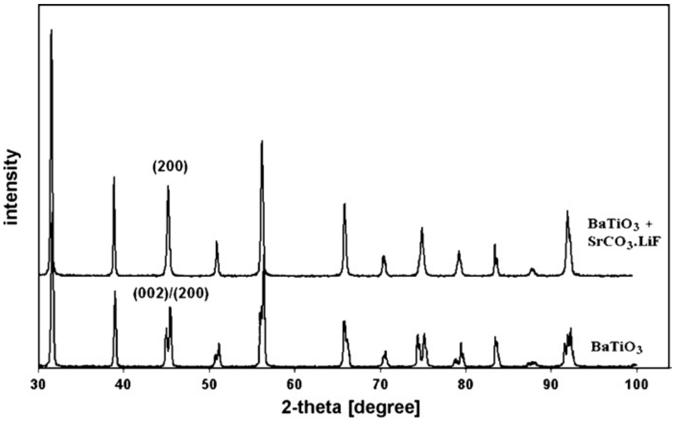

Fig. 6. XRD patterns and splitting of the (2 0 0) reflection for pure and doped $BaTiO_3$ sintered compacts (900 °C/2 h).

SEM analysis of LiF·$SrCO_3$ doped BT sintered ceramics in Fig. 7 revealed a dense microstructure with a uniform distribution of grain sizes and an average grain size of about 1 μm. Compared to the BT starting powder with average grain size of about 0.5 μm a limited grain growth is occurred during sintering.

Compatibility to co-fired pure silver conductors is an important topic in today's LTCC development. Fig. 8 shows a cross-section of LiF·$SrCO_3$ doped BT laminates co-fired with Ag-conductors at 900 °C. No evidence of interfacial reaction between the dielectric layer and the Ag-electrode or Ag-diffusion in the dielectric layer was found by microprobe measurements (line scanning).

The dielectric characteristics of sintered specimens measured at 1 kHz are summarized in Table 2. The rel. dielectric constant at room temperature for most doped BT ceramics is higher than that for pure BT. The sample with 2 wt.% LiF·$SrCO_3$ possesses the highest dielectric constant at room temperature. Fig. 9 illustrates the temperature dependence of the dielectric constant in the temperature range between −20 °C and 125 °C for pure and doped BT ceramics. The value of the ferroelectric Curie temperature (T_c) of doped samples is much lower than that of pure BT, which is about 130 °C. The dielectric constant of doped samples exhibits a broadened and diffuse ferroelectric–paraelectric phase transition. The higher dielectric constant at room temperature for doped BT ceramics compared to pure BT is due to lower Curie temperatures and the broad ferroelectric–paraelectric phase transitions of doped BT ceramics. It is supposed that the substitution of oxygen by fluorine[6,7] and barium by strontium or calcium in the $BaTiO_3$ structure is responsible for this behaviour. These substitutions also support the sintering process and reduce the volume fraction of low dielectric constant phase.[1] The solubility of strontium in barium

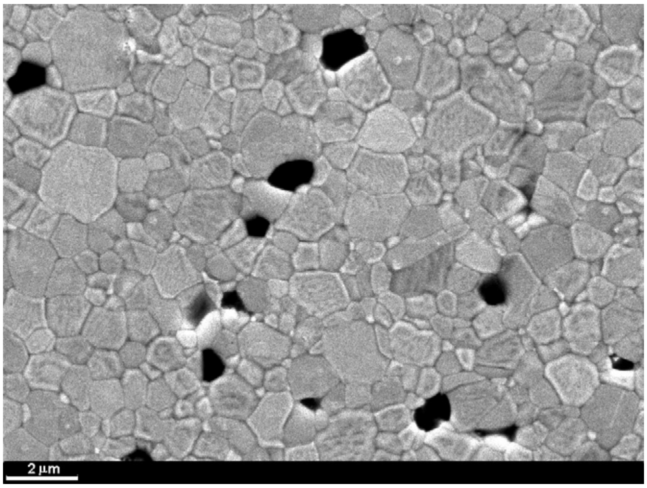

Fig. 7. SEM micrograph of LiF·$SrCO_3$ containing $BaTiO_3$ ceramics sintered at 900 °C/2 h.

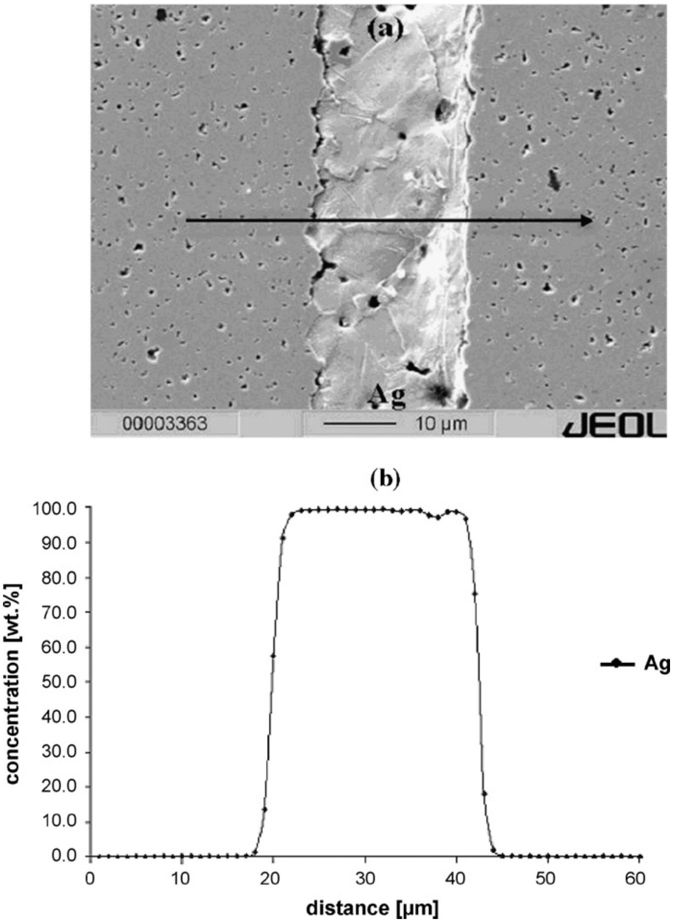

Fig. 8. The cross-section of LiF·$SrCO_3$ added $BaTiO_3$ laminate co-fired with Ag-conductors (a) and the corresponding line scan of silver (b).

Table 2
The dielectric parameters at a frequency of 1 kHz and room temperature for doped BT ceramics sintered at 900 °C/2 h (laminates sintered at 860 °C/2 h), and for pure BT sintered at 1300 °C/2 h.

Sintering additives	Rel. dielectric constant	Dielectric loss
Pure BT	2500	0.03
2 wt.% (LiF·$SrCO_3$)	3591	0.038
2 wt.% (LiF·$SrCO_3$) L*	3160	0.014
1.5 wt.% (LiF·$SrCO_3$)	3256	0.058
2 wt.% (LiF·$BaCO_3$)	2260	0.031
1.5 wt.% (LiF·$BaCO_3$)	2505	0.066
1.5 wt.% (LiF·$CaCO_3$)	2940	0.029

L*: laminates.

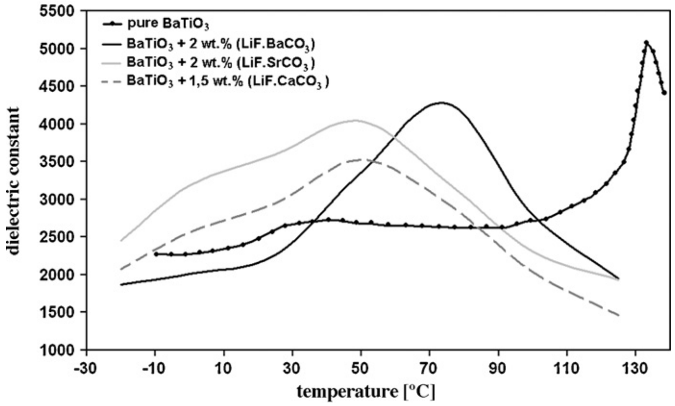

Fig. 9. Temperature dependence of the dielectric constant in the temperature range from −20 °C to 125 °C for pure and doped $BaTiO_3$.

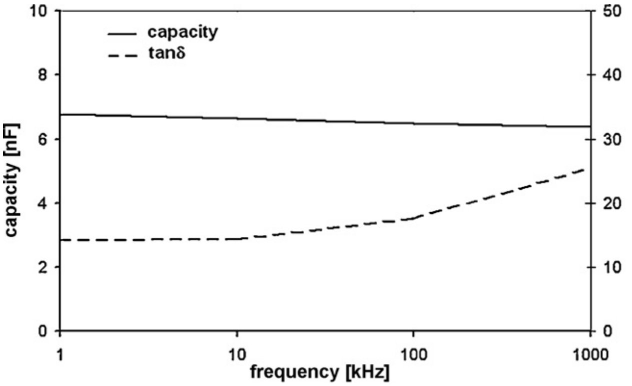

Fig. 11. Frequency dependence of capacity and dielectric loss for LiF·$SrCO_3$ doped $BaTiO_3$ laminates at room temperature.

titanate structure is comparatively higher due to the compatible size and charge with barium. Therefore LiF·$SrCO_3$ doped BT ceramics show the highest densification and the highest room temperature dielectric constant.

The capacitance variation over the temperature range from −20 °C to 125 °C for LiF·$SrCO_3$ containing BT is relatively small both for laminates and powder compacts as shown in Fig. 10. The lower temperature dependence of capacity for LiF·$SrCO_3$ containing BT is due to the formation of a core-shell structure in a fine-grained microstructure of this material after sintering at 900 °C as shown in SEM and TEM results. The laminates of LiF·$SrCO_3$ containing BT could be fully densified at a sintering temperature of 860 °C, and exhibit a high dielectric constant and a low dielectric loss as shown in Table 2.

Fig. 11 shows the effect of frequency on the capacity and dielectric loss for LiF·$SrCO_3$ doped BT capacitor materials. The capacity decreases slightly over the investigated frequency range (10^3–10^6 Hz), while the dielectric loss increases slowly.

The dielectric strength is an important parameter for high-voltage capacitors. The dielectric strength of pure and 2 wt.% LiF·$SrCO_3$ containing BT compacts with a thickness of about 300 μm are 5 ± 0.6 kV/mm and 7 ± 0.8 kV/mm, respectively. No deterioration of dielectric strength due to the sintering additives was observed. It is well known that the dielectric breakdown phenomenon of dielectrics is structure-sensitive, and breakdown strength values scatter widely according to the characteristics of the microstructure and thickness of dielectric materials.[10,11] The smaller the sample thickness, the greater the chance that some samples contain no pronounced defects such as large pores, which deteriorate the dielectric strength. Thin capacitor tapes are normally relevant for the future applications, therefore the dielectric strength was also measured on thin capacitor tapes. The dielectric strength of LiF·$SrCO_3$ containing BT for tapes with a thickness of about 80 μm is 31 ± 3 kV/mm. As expected the dielectric strength of thin tapes is much higher than powder compacts of the same material. That is because of more homogeneous microstructure and smaller thickness of tapes compared to powder compacts.

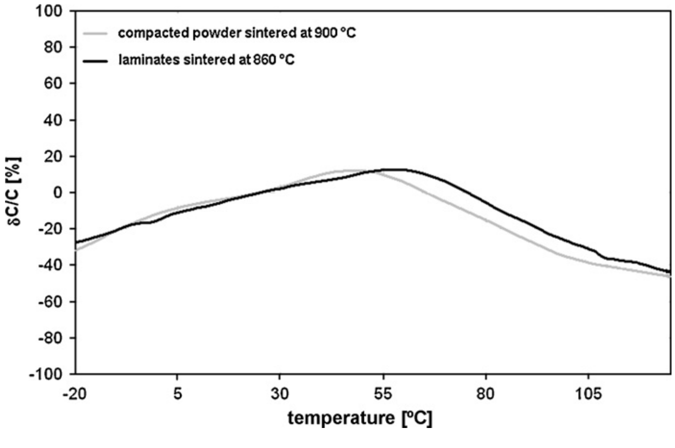

Fig. 10. Capacitance variation in the temperature range from −20 °C to 125 °C of 2 wt.% LiF·$SrCO_3$ doped $BaTiO_3$ powders for laminates and compacted powder.

4. Conclusions

The influence of different LiF-containing additives on the densification behaviour and dielectric characteristics of $BaTiO_3$ was investigated. An addition of 2 wt.% LiF·$SrCO_3$ to $BaTiO_3$ lowered the sintering temperature and allowed a co-sintering with silver electrodes. Excellent densification (more than 98% theoretical density) without any interfacial reaction between the dielectric layer and the Ag-electrode was obtained in laminates. No deterioration of dielectric parameters due to the sintering additives was observed. The dielectric parameters of 2 wt.% LiF·$SrCO_3$ doped BT laminates are $\varepsilon_r = 3160$, $\tan\delta = 0.014$ ($f = 1$ kHz, $T = 25$ °C) and dielectric strength 31 ± 3 kV/mm (for about 80 μm tapes). The barium titanate ceramics obtained by addition of LiF·$SrCO_3$ turned out to be promising for integration of buried capacitors in multilayer LTCC applications.

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