# Processing of steatite ceramic with a low dielectric constant and low dielectric losses

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**Abstract:** Steatite ceramic was processed from natural raw materials talc, clay and dolomite. They were stabilised in water electrostatically and electrosterically with polyacrylic acid at pH 9. The suspensions were spray dried and the resulting powders contained granules with a mean size of 10 µm. The powders were dry-pressed and sintered at 1275 °C and 1300 °C for 2 hours. The effect of type of stabilisation and sintering temperature on the phase composition, microstructure and dielectric properties of the ceramic was studied. The X-ray powder diffraction analysis revealed that the orthorhombic protoenstatite and tetragonal cristobalite were present in all the ceramic samples. The microstructures of the samples investigated by scanning electron microscopy were homogenous with grains surrounded with a glass phase and some pores. By energy dispersive X-ray spectroscopy we identified Mg, Si, Al and O in the grains and Mg, Si, O and minor amount of Al, Ca and Fe in the glassy phase. The dielectric constant of the ceramic measured at room temperature and 1 MHz decreased from about 8 to about 5 with increasing sintering temperature from 1275 °C to 1300 °C, while the dielectric losses were between 0.001 and 0.003. The dielectric properties of the steatite ceramic were related to the chemical composition of the glassy phase. The results show that the chemical composition of the phases and the dielectric properties of the ceramic depend on the processing temperature while the type of stabilization of raw materials in water has only a minor influence on these parameters.

**Keywords:** steatite ceramic; microstructure; dielectric properties

# *Priprava steatitne keramike z nizko dielektrično konstanto in nizkimi dielektričnimi izgubami*

**Izvleček:** Steatitno keramiko smo pripravili iz naravnih surovin talka, gline in dolomita, ki smo jih stabilizirali v vodi pri pH 9 elektrostatsko in elektrosterično s poliakrilno kislino. Z razprševanjem suspenzije v laboratorijskem razpršilnem sušilniku smo dobili granulat s povprečno velikostjo granul okoli 10 µm. Iz granulata smo z enoosnim stiskanjem pripravili surovce, ki smo jih sintrali pri 1275 °C in 1300 °C 2 uri. Študirali smo vpliv tipa stabilizacije in temperature sintranja na fazno sestavo, mikrostrukturo in dielektrične lastnosti keramike. Z rentgensko praškovno analizo smo ugotovili, da vsi keramični vzorci vsebujejo ortorombsko fazo protoenstatit in tetragonalno fazo kristoblit. Mikrostruktura keramike, ki smo jo preiskali z vrstičnim elektronskim mikroskopom, je bila homogena. Sestavljena je bila iz zrn, ki jih je obdajala steklasta faza, in por. Z energijsko disperzijsko spektroskopijo rentgenskih žarkov smo v zrnih dokazali prisotnost Mg, Si, Al in O, v steklasti fazi pa smo identificirali poleg Mg, Si in O tudi sledove Al, Ca in Fe. Dielektrično konstanto (ε) in dielektrične izgube (tan δ) keramike smo izmerili pri sobni temperaturi in 1 MHz. Po sintranju pri 1275 °C je imela keramika ε 8, medtem ko je bila vrednost ε po sintranju na 1300 °C nižja, t.j., 5. Vrednoti tan δ so bile med 0.001 in 0.003. Ugotovili smo, da so dielektrične lastnosti steatitne keramike odvisne od kemijske sestave steklaste faze. Rezultati so pokazali, da so dielektrične lastnosti steatitne keramike in kemijska sestava faz keramike odvisne od pogojev priprave keramike, medtem ko ima tip stabilizacije osnovnih surovin v vodi na te parametre le manjši vpliv.

**Ključne besede:** steatitna keramika; mikrostruktura; dielektrične lastnosti

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## 1 Introduction

Steatite ceramic is alumosilicate that contains approximately 60 % of $SiO_2$, 30 % of $MgO$, 5 % of $Al_2O_3$ and low amounts of oxides such as $K_2O$, $Na_2O$, $CaO$, $Fe_2O_3$ and $TiO_2$ originated from impure raw materials. It is char-acterized by a flexural strength between 110 and 165 MPa, an electrical resistivity of about $10^{11}$ Ωm at room temperature, a dielectric constant between 5.5 and 7.5 and dielectric losses of about 0.001 [1]. These charac-teristics and the ability to fabricate final products in a

wide variety of forms, make steatite ceramic attractive in many applications such as high-frequency insulators, appliance insulators, resistor cores, casings for thermostats and fuses.

Steatite ceramic is usually fabricated from natural raw materials, namely talc and clay components, that are wet ground and patterned into a green body by ceramic technologies, examples being dry pressing of spray-dried powder and extrusion or casting of the suspension. After sintering at temperatures between 1250 and 1400 $^{\circ}$C, the ceramic contains the grains of Mg-Al-Si-O that crystallise as protoensteatite and a glassy phase, whereas $SiO_2$ as crystoballite can also be present in small quantities [2,3]. Protoenstatite consists of tetrahedral chains usually of corner-shearing $SiO_4$ units that are separated by parallel chains of octahedral edge-sharing $MO_6$ units containing cations such as Mg and Al [4].

The high-temperature orthorhombic protoenstatite phase is prone to transform on cooling into clinoenstatite, a monoclinic phase [5]. The resulting unit volume change of 2.8 % may lead to formation of cracks and thus to deterioration of mechanical properties of the ceramic. The protoenstatite- clinoenstatite phase transformation is prevented when the protoenstatite grains are surrounded by the glassy phase and when the grains are in the micrometre range [1]. Thus, the microstructure of the steatite ceramic has to be homogeneous with micrometre-sized grains.

The microstructure and the phase composition of the steatite ceramic depend on the chemical composition and the morphology of the raw materials, as well as on the processing conditions, such as homogenisation of raw materials, consolidation, temperature and time of firing. The presence of agglomerates in the powder has a detrimental effect on the ceramic since agglomerates either persist during processing or even lead to the formation of new heterogeneities during densification [6]. Agglomerates can be eliminated from the powder by colloidal processing [7]. By controlling the interparticle forces using polyelectrolytes such as ammonium polyacrylate the talc was effectively dispersed in water [8]. After spray-drying and sintering the steatite ceramic was dense and homogeneous.

Electrical properties of steatite ceramics are mostly related to the amount and the composition of the glassy phase [1]. It was shown that the presence of alkalis in the glassy phase increases the electrical conductivity and dielectric losses, while the presence of alkaline earth oxides results in low-loss steatite ceramics [1,9].

In this work we processed the steatite ceramic from talc and clay components stabilized in water electrostatically and electrosterically by polyacrylic acid, respectively. The suspensions were spray-dried and the resulting powder was pressed into powder compacts. They were sintered at 1275 $^{\circ}$C and 1300 $^{\circ}$C, respectively. The aim of this work was to relate the dielectric permittivity and the dielectric losses of the resulting ceramic to the phase composition, the microstructure and the chemical composition of the phases.

## 2 Experimental

Talc, clay and dolomite were dispersed in water (Milli Q) without any additive and with polyacrylic acid (PAA, Aldrich) in the amount of 0.3 wt. % per g of the powder. The suspensions had the solid/water mass ratio 33/67. During the mixing of the suspensions with a magnetic stirrer for 2 hours, 0.2 wt. % of polyvinyl alcohol (PVA, Alfa Aesar) and 0.8 wt. % of polyethylene glycol (PEG, Aldrich) were added. Then the suspensions with pH 9 were homogenized in a planetary ball mill (Retsch) for 2 hours at 200 min$^{-1}$.

The suspensions were spray-dried in a laboratory spray drier (Buechi B-290) in air at 190 $^{\circ}$C and 7.5 bar. Powder compacts were prepared from granulated powders. The powders were placed in a steel mold with a diameter of 12 mm and uniaxially pressed at 100 MPa. The samples were then sintered at 1275 $^{\circ}$C and 1300 $^{\circ}$C, respectively, for 2 h with heating and cooling rates of 5 $^{\circ}$C/min. The ceramics prepared from the powder without PAA, sintered at 1275 $^{\circ}$C and 1300 $^{\circ}$C, were denoted S1275 and S1300, respectively. The ceramics prepared from the powder with PAA, sintered at 1275 $^{\circ}$C and 1300 $^{\circ}$C, were denoted SA1275 and SA1300, respectively.

The geometrical density of the ceramic samples was calculated from the mass and dimensions of the pellets.

The ceramics were analyzed by X-ray powder diffraction (XRD) at room temperature using a diffractometer (PANalytical, X'Pert PRO MPD, The Netherlands). The data were collected in the 2 $\theta$ range from 20 $^{\circ}$ to 50 $^{\circ}$ in steps of 0.034 $^{\circ}$, with an integration time of 100 s. The phases were identified by software X-Pert High Score using the PDF-2 database [10].

The particle size distribution of the powders was measured using a static light-scattering particle size analyser (Microtrac S3500).

For the microstructural analysis the scanning electron microscope (SEM, JSM-5800 JEOL, Japan) equipped with energy dispersive spectroscopy (EDXS, Tracor-Northern) was used. For standardless analysis, the Tracor SQ standardless analysis program, using multiple least-squares analysis and a ZAF matrix correction procedure, was used. The samples were analyzed using an accelerating voltage of 20 kV and a spectra acquisition time of 100 s. The oxygen content in the samples was obtained by difference and is considered in the matrix correction calculations. The estimated error for EDXS analysis is up to 10 % for major elements and up to 30 % for minor elements.

For dielectric investigations, the gold paste (ESL 8884 G) was screen-printed on top- and bottom- surfaces of the samples having a diameter of 11 mm and a thickness of 3 mm. The paste was fired at 900 °C for 10 minutes. The dielectric constant ($\varepsilon$) and dielectric losses (tan δ) were measured at room temperature and frequency of 1 MHz with a Novocontrol Alpha High Resolution Dielectric Analyzer. The amplitude of the probing AC electric signal was 1 V.

## 3 Results and discussion

The morphology of the spray-dried powders prepared from suspension without any PAA (denoted G) and with PAA (denoted G PAA) is shown in Figure 1 a and b, respectively,

The morphology of both powders was similar. The granules were roughly spherically shaped with sizes between a few and about 20 µm. The mean granule size $d_{v50}$ measured by the particle size analyzer was 10 µm and 9.9 µm for G and G PAA, respectively. The $d_{v90}$ for both powders was 20 µm.

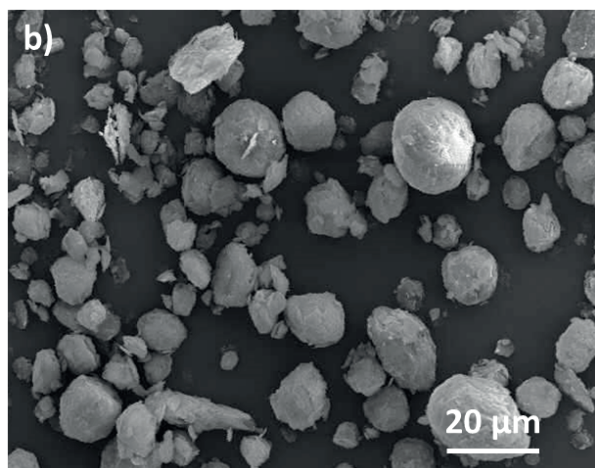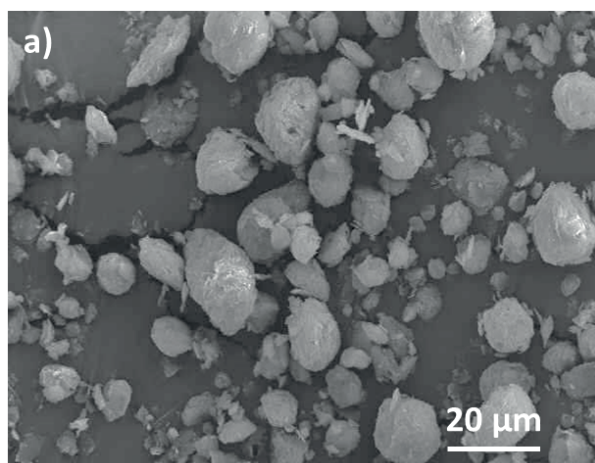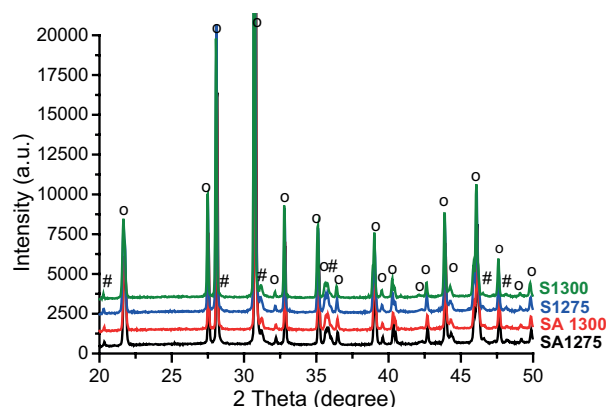The XRD spectra of the SA1275, SA1300, S1275 and S1300 ceramic samples are shown in Figure 2.



**Figure 2:** Diffraction spectra of S1275, S1300, SA1275 and SA1300 steatite ceramic. o-protoenstatite, #-cristobalite

All the spectra were similar with the diffraction peaks that corresponded to the orthorhombic protoenstatite phase (PDF 76-1806) and the tetragonal $SiO_2$ (crystobalite, PDF 76-0941). The main phase was protoenstatite, while the $SiO_2$ was present in a low quantity. The relatively high background of the spectra indicated that the ceramic contained also some amorphous phase. The intensity of the diffraction peaks and the background were comparable for all the samples, therefore we assume that the amounts of the phases in all the samples were similar.

The cell parameters of the protoenstatite in the S1275, S1300, SA1275 and SA1300 steatite ceramics are shown in Table 1.



**Figure 1:** SEM image of the spray-dried powder prepared from the suspension a) without any PAA (G) and b) with PAA (G PAA)

**Table 1:** Cell parameters of protoenstatite MgSiO$_3$ in the S1275, S1300, SA1275 and SA1300 steatite ceramic

|         | a [nm]    | b [nm]    | c [nm]    |
|---------|-----------|-----------|-----------|
| SA 1275 | 0.9246(1) | 0.8746(2) | 0.5319(1) |
| SA 1300 | 0.9251(1) | 0.8750(1) | 0.5322(1) |
| S 1275  | 0.9247(1) | 0.8745(2) | 0.5319(1) |
| S 1300  | 0.9250(1) | 0.8750(2) | 0.5321(1) |

The cell parameters of the protoenstatite phase in ceramics prepared from the granulated powder without PAA and with PAA depended on the processing temperature and were similar for the samples sintered at 1275 °C (compare S1275 and SA1275) and 1300 °C (compare S1300 and SA1300), respectively. They were in agreement with the protoenstatite unit cell reported in literature [11]. The cell parameters of the protoenstatite sintered at 1300 °C were larger than those of the sample sintered at 1275 °C.

The microstructures of the SA1275, SA1300, S1275, and S1300 ceramic samples are shown in Figure 3. The microstructure of all the samples contains a bright phase (denoted S) and a dark, glassy phase (denoted LP) in addition to pores (P) which is in agreement with the literature [1]. Pores with sizes up to about ten micrometers are homogeneously distributed in the microstructure. The geometrical density of the ceramic was similar for all the samples, 2.77 ± 0.01 g/cm$^3$.

It is evident that the grains of the bright phase (S) are distributed in the dark, glassy phase The size of the grains ranged from submicrometre to about 5 μm. In some grains we observed cracks. By SEM/EDXS analysis we confirmed that some of the grains with the cracks were SiO$_2$-rich. It is known that crystaoballite can transform during cooling to quartz with corresponding change in unit cell volume that leads to the formation of intragranular cracks [12]. With XRD analysis we confirmed the presence of cristobalite phase in all ceramic
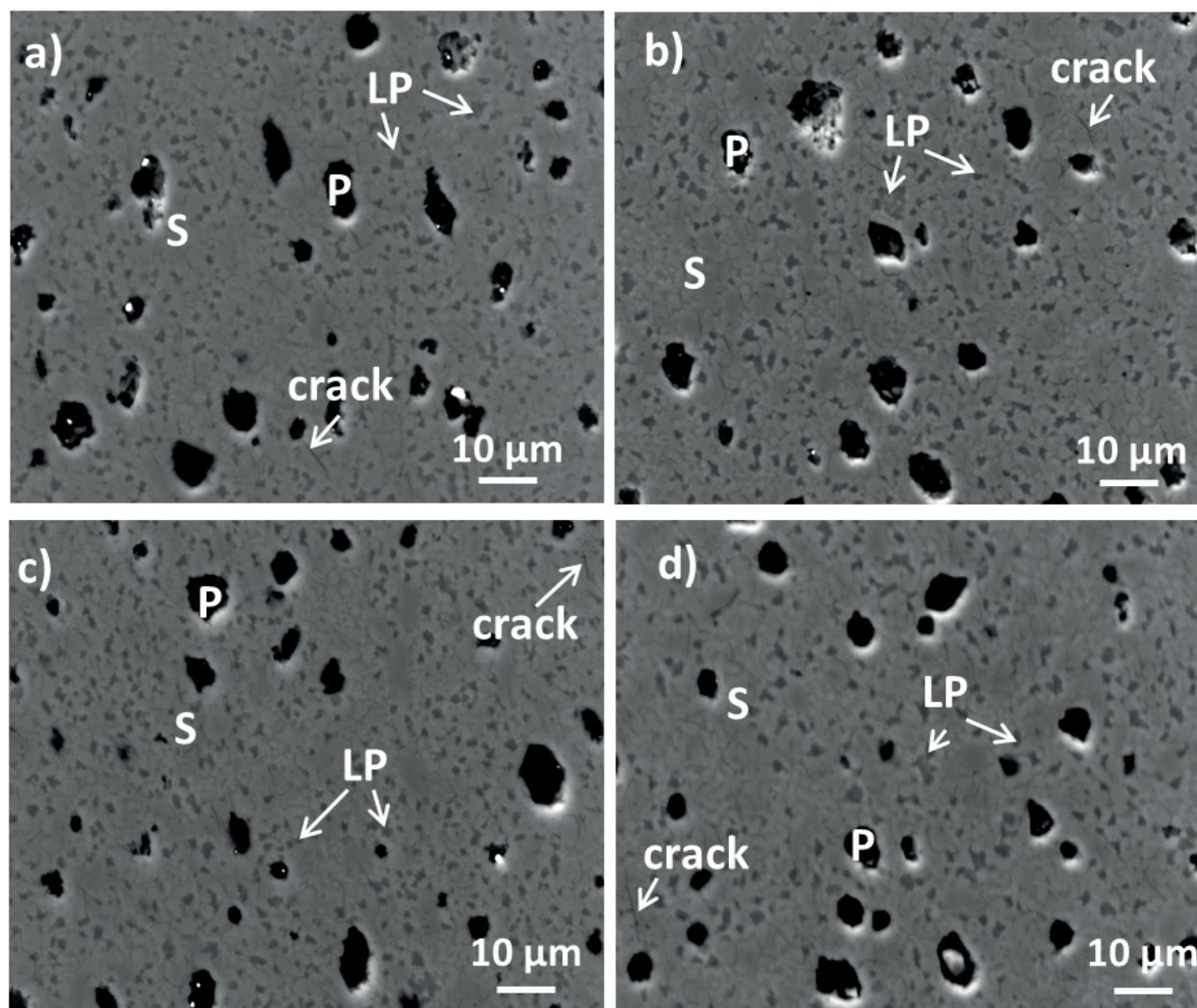


**Figure 3:** Microstructure of ceramic samples a) SA1275; b) SA 1300; c) S1275; d) S1300.
S = bright phase (steatite), LP = dark phase, P: pores.

samples. The characteristic quartz (101) diffraction peak with the highest intensity at 2 Theta of 26.2 ° was not detected in any of the samples. It is possible that the amount of quartz was below the detection limit of XRD analysis, which is about 2 wt. %. The formation of cracks could also be a consequence of protoenstatite to clinoenstatite phase transformation during cooling and corresponding difference in the unit cell volume [2,13]. However we have not detected any monoclinic clinoenstatite phase by XRD. The characteristic clinoenstatite (-2 2 1) diffraction peak with the highest intensity at 2 Theta of 29.75 ° (PDF 75-1406) was not detected in any of the samples (see Figure 2). It is possible that the amount to clinoenstatite was below the detection limit of XRD analysis.

We performed the EDXS analysis of the bright phase (S) and the dark phase (LP) in all the samples. We found out that the composition of the selected phase in the ceramic prepared from the granulated powder without PAA and with PAA was similar, but it varied with the processing temperature. The results of the analysis of the samples SA1275 and SA1300 are presented in Table 2.

**Table 2:** The composition of the dark (LP) and bright (S) phases in the samples SA1275 and SA1300.

| | SA 1275 | | SA 1300 | |
|---|---|---|---|---|
| | LP [wt. %] | S [wt. %] | LP [wt. %] | S [wt. %] |
| MgO | 14.4 ± 0.7 | 29.6 ± 1.5 | 12.8 ± 0.6 | 31.1 ± 1.5 |
| $Al_2O_3$ | 3.6 ± 0.3 | 3.6 ± 0.3 | 3.9 ± 0.6 | 2.8 ± 0.4 |
| $SiO_2$ | 79.3 ± 4 | 64.4 ± 3 | 80.4 ± 4 | 63.9 ± 3 |
| CaO | 1.9 ± 0.3 | 1.3 ± 0.2 | 2.1 ± 0.3 | 1.3 ± 0.2 |
| $Fe_2O_3$ | 0.80 ± 0.12 | 1.10 ± 0.16 | 0.80 ± 0.10 | 0.90 ± 0.13 |

In the dark and in the bright phases we identified the following elements: Mg, Al, Si, Ca, Fe and O. Concerning the sample sintered at 1275 °C, it is evident that the bright phase (S) contained about 65 % of $SiO_2$, about 30 % of MgO, 3.6 % of $Al_2O_3$, 1.3 % of CaO and about 1 % of $Fe_2O_3$ (all in wt. %). The ratio between $SiO_2$, MgO and $Al_2O_3$ corresponded well to that of steatite. On the basis of XRD and EDXS analyses we concluded that the bright phase crystallized in the orthorhombic structure and contained Si-Mg-Al-O protoensteatite phase with minor amounts of Ca and Fe. The presence of CaO and $Fe_2O_3$ is related to impurities originated from the natural raw materials.

The dark phase (LP) contained a higher amount of $SiO_2$, about 80 % and a lower amount of MgO, about 14 %, while the amounts of $Al_2O_3$, CaO and $Fe_2O_3$ were similar.

The chemical composition of the bright phase slightly changed after sintering at 1300 °C. The amount of MgO increased, while the amounts of $Al_2O_3$ and $SiO_2$ decreased. A higher amount of $Mg^{2+}$ with ionic radius r = 0.072 nm [14] and a lower amount of $Si^{4+}$ (r = 0.026 nm) [12] and $Al^{3+}$ (r = 0.039 nm) [12] may result in larger unit cell at 1300 °C which is consistent with the calculated lattice parameters of the protoenstatite (Table 1).

The dark phase (LP) contained in a sample sintered at 1300 °C less MgO and more $SiO_2$, while the amounts of $Al_2O_3$, CaO and $Fe_2O_3$ were similar to that in sample sintered at 1275 °C.

The dielectric constant ε and the dielectric losses of the S1275, S1300, SA1275 and SA1300 samples measured at room temperature are presented in Table 3.

**Table 3:** Dielectric constant ε and the dielectric losses tan δ of the S1275, S1300, SA1275 and SA1300

| | ε (1 MHz) | tan δ (1 MHz) |
|---|---|---|
| SA1275 | 8.42 | 0.002 |
| SA1300 | 5.5 | 0.003 |
| S1275 | 7.74 | 0.001 |
| S1300 | 4.6 | 0.002 |

The dielectric constants of the samples sintered at 1275 °C were higher than of those sintered at 1300 °C. This could be related to the chemical composition of the steatite ceramic which depends on the processing temperature.

The dielectric constant of the steatite $MgSiO_3$ with the density of 93 % is 6.2 [15]. The dielectric constants of MgO and $Al_2O_3$ are similar, 9.8 and 10, respectively, while the dielectric constant of $SiO_2$ is 4. It was reported that the properties of the steatite ceramic depend mostly on the composition of the glassy phase [1]. From the results it is evident that at 1300 °C the liquid phase contained more $SiO_2$ and less MgO than at 1275 °C. A higher amount of $SiO_2$ with a low dielectric constant and a low amount of MgO with a high dielectric constant decreased the dielectric constant of the glassy phase. Consequently the dielectric constant of the steatite ceramic processed at 1300 °C was lower than that at 1275 °C.

## 4 Conclusions

Aqueous suspensions of talc/clay/dolomite mixtures stabilized electrostatically and electrosterically with polyacrylic acid at pH 9 have been prepared in a solid load of 33 wt. %. After spray-drying the powder contained spherically shaped granules with sizes between a few and about 20 μm. The powder compacts were

sintered at 1275 °C and 1300 °C. The microstructures of all the steatite ceramics were homogeneous and contained protoenstatite grains surrounded with a glassy phase together with a low amount of crystobalite and some pores.

The dielectric constant was about 5 and about 8 for the ceramics sintered at 1300 °C and 1275 °C, respectively, while the dielectric losses were between 0.001 and 0.003. The values of the dielectric constant were related to the chemical composition of the glassy phase that contained more $SiO_2$, less MgO and similar amounts of $Al_2O_3$, CaO and $Fe_2O_3$ after sintering at 1300 °C. A higher amount of $SiO_2$ with the dielectric constant of about 4 and a lower amount of MgO with the dielectric constant of about 10 contributed to a lower dielectric constant of the steatite ceramics.

## 5 Acknowledgments

## 6 References

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