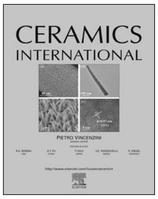
ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Influence of different bonding and fluxing agents on the sintering behavior and dielectric properties of steatite ceramic materials

Anja Terzić[a,*], Nina Obradović[b], Jovica Stojanović[c], Vladimir Pavlović[b], Ljubiša Andrić[c], Dragan Olćan[d], Antonije Đorđević[d]

[a] Institute for Testing of Materials IMS, Vojvode Mišića Bl. 43, 11000 Belgrade, Serbia
[b] Institute of Technical Sciences, Serbian Academy of Sciences and Arts, Knez Mihailova St. 35, 11000 Belgrade, Serbia
[c] Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey 86, 11000 Belgrade, Serbia
[d] School of Electrical Engineering, University of Belgrade, Kralja Aleksandra Bl. 73, 11000 Belgrade, Serbia

ARTICLE INFO

Keywords:
A. Sintering
B. Electron microscopy
B. Microstructure-final
B. X-ray methods
C. Dielectric properties
D. MgO
E. Insulators

ABSTRACT

The focus of the study was on providing insights into interconnections between sintering and development of the crystalline microstructure, and consequently variations in dielectric behavior of four steatites fabricated from a low-cost raw material, i.e. talc. The changes, induced by the alternations of the binders (bentonite, kaolin clay) and fluxing agents ($BaCO_3$, feldspar), were monitored in the temperature range 1000° to 1250 °C in which complete densification and re-crystallization of the investigated structures were accomplished. The critical points in the synthesis of steatite materials were assessed by instrumental analyses. Crystallinity changes and mineral phase transition during sintering were monitored by X-ray diffraction technique. Microstructural visualization of the samples and the spatial arrangements of individual chemical elements were achieved via scanning electron microscopy accompanied with EDS mapping. The thermal stability was observed on the green mixtures using differential thermal and thermo gravimetric analyses. Electrical measurements recorded variations of the dielectric constant (ε_r) and loss tangent (tan δ) as a function of the sintering temperature. The investigation highlighted critical design points, as well as the optimal combinations of the raw materials for production of the steatite ceramics for advanced electrical engineering applications.

1. Introduction

Depending on choice of raw materials, the ceramic is indexed as either "triaxial", which, besides clayey base and flux, comprises quartz or alumina, or "dielectric" that primarily rests on magnesium silicate [1–3]. The materials from the first group generally prevail in the construction field as they are predominantly being used for manufacturing of the stoneware, while the second group includes high-temperature resistant products that are mainly employed in electrical engineering. The magnesium silicate materials are produced via standard ceramic processing schemes (e.g. dry pressing, extrusion, casting, semi-wet pressing) and fabricated or sintered into a variety of forms [4,5]. The steatite ceramics is, besides cordierite, the main represent of "dielectric" materials with trademarks such as high mechanical strength, good electrical properties, low dielectric loss, and excellent resistance to high temperatures [6,7]. Also, steatite is appraised as a cost-effective alumina replacement, because it satisfies the performance requirements of alumina, yet its production is more economical due the facilitated forming and lower temperature of sintering [1]. Such predispositions are classifying this type of material for applications in field of electrical and electronic engineering: electrical insulation, regulator bases, switches and plug parts, sockets bases for halogen bulbs, heating element holders, NH-fuses, element formers and casings for thermostats, interlocking insulating beads, etc. [7–11]. Apart from the use in electrotechnics, the steatite ceramic is employed in medicine as a material for dental implants and artificial bones due to high hardness and bending resistance, and good biocompatibility [12–14].

Mineral enstatite is natural equivalent of the inorganic material with chemical formula: $Mg_3(Si_4O_{10})(OH)_2$ [15,16]. The mineral shows 3.21 g cm^{-3} theoretical density, a melting point at 1557 °C, and an orthorhombic crystal lattice with silica-tetrahedra chains connected by two symmetrical octahedral Mg^{2+} sites [6,15–18]. The steatite ceramics can be manufactured completely from economic natural raw materials, as its mineral base for the synthesis generally comprises the talc mineral mixture for the calcination procedure (80–90%), plastic

---

[*] Corresponding author.
E-mail address: anja.terzic@institutims.rs (A. Terzić).

http://dx.doi.org/10.1016/j.ceramint.2017.07.024
Received 12 April 2017; Received in revised form 20 June 2017; Accepted 3 July 2017

Please cite this article as: Terzic, A., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.07.024

clay as a bonding agent (5–10%) and a melting agent (5–10%). This mixture of raw materials is fired at temperatures up to 1400 °C depending on the selected sintering procedure [1,4–6]. The final structure of steatite is formed though crystallization of mineral phases, as well as their fusion and dissolution during the vitrification. By the time the sintering process reaches the end, the steatite comprises about 70% of crystalline $MgSiO_3$ (i.e. protoenstatite) and about 30% of glassy phase [11]. The flux (e.g., BaO, $BaCO_3$, ZnO, feldspar) enables and controls the formation of amorphous matter during the sintering, and influences mechanical and dielectric properties of the material [1,5,18–20]. The microstructure development and the sintering behavior of the steatite, therefore, depend on the ratio of formed crystalline and liquid phases, as well as on the amount of present pores. A vitreous phase surrounds the crystals merging them together [11,19]. Two most commonly used fluxes in the industrial ceramics are feldspar and barium carbonate. Feldspar, due to the presence of alkaline ions, may lead to the ceramic with lower performances, including increased dielectric losses, while barium carbonate usually produces better dielectric properties [19–21]. The dielectric properties of a steatite product are also strongly dependent on the temperature range and/or cycling assigned for the given synthesis procedure, largely because enstatite undergoes a complex series of polymorphic transitions [10,17]. Namely, steatite occurs in four magnesium metasilicate polymorphic forms: enstatite, protoenstatite, clinoenstatite, and high-temperature clinoenstatite [4,11,17,22–25]. At normal ambient conditions, enstatite appears as a low temperature polymorph – clinoenstatite (i.e., low clinoenstatite) in monoclinic symmetry, or as orthoenstatite in orthorhombic symmetry. At elevated temperatures (up to 1000 °C) crystals undergo a transition into an intermediate structure: e.g., the low clinoenstatite inverts reversibly to the high clinoenstatite [21,22]. The thermodynamically stable crystals of protoenstatite initially appear above 985 °C. The well-ordered and fully stable protoenstatite is usually obtained upon heating up to 1300 °C [21,22]. At lower temperatures, the crystals within the ceramic body are stabilized by the vitreous phase. When crystals are not properly stabilized, protoenstatite transforms to the room temperature polymorph - clinoenstatite. The volume changes that occur during this transition lead to formation of cracks and deterioration of dielectric properties of the material [21,22].

Even though there are numerous literature reports on the production of various types of dielectric ceramic materials [26–32], a very few works are dealing with low-cost fabrication of steatite [1,5,6,19,20]. This study provides insight into dielectric behavior of steatite that is prepared from natural raw materials (talc, $BaCO_3$, feldspar, bentonite, kaolin) and sintered at four temperatures: 1000°, 1100°, 1200° and 1250 °C. The focus of the experiment was on altering of the bonding and fluxing agents in order to reduce the temperature of sintering as the most common route to obtain cost effective production of steatite ceramics. The interconnections between sintering procedure, microstructural and crystalline development, and dielectric properties of four steatite types were established. The aim of the study is to detect the critical points in the design of steatite, to make improvements in its synthesis in order to satisfy the increasing demands of the dielectric material performances, and finally to assess the materials suitability for advanced engineering applications.

2. Materials and methods

Table 1
Chemical compositions of applied raw materials and steatite mixtures S1-4.

Oxide, %	Feldspar	Talc	Bentonite	Kaolin	S1	S2	S3	S4
SiO_2	70.15	50.75	68.48	70.83	58.6	69.7	55.8	56.9
K_2O	4.82	–	0.42	0.07	0.5	0.3	0.1	0.01
Na_2O	6.27	–	0.23	0.64	0.65	0.40	0.65	0.05
Fe_2O_3	0.11	0.42	2.42	0.11	0.65	0.65	0.65	0.62
CaO	0.76	0.56	2.10	0.72	0.57	0.57	0.57	0.78
MgO	0.13	25.3	2.28	–	25.8	25.2	25.1	25.1
Al_2O_3	17.47	0.03	17.20	20.12	5.2	6.2	4.7	6.3
TiO_2	–	–	–	0.23	–	0.02	–	0.02
LoI	0.29	22.94	6.87	7.46	8.03	6.96	12.43	10.22

Four steatite mixtures, marked as S1, S2, S3, and S4, were prepared for the experiment. All steatite materials were based on talc from *Bela Stena* deposit in Serbia. Talc comprised 80% of total mixture mass. Bentonite (*Jelenkovac* deposit, *Vranjska Banja*, Serbia) was applied as a bonding agent, in 10 wt% quantity, in the S1 and S3 mixtures. Kaolin clay (*Crna Dolina* deposit, *Prijedor*, Bosnia and Herzegovina) was used as binder (10 wt%) in the S2 and S4 mixtures. The fluxing agents, used in 10 wt% quantities, were: feldspar (*Bujanovac* deposit, Serbia) in S1 and S2 mixtures and barium carbonate ($BaCO_3$, 99+ %, synthetic, Acros Organics, India) in S3 and S4 mixtures. The chemical compositions of raw materials and starting steatite mixtures (S1–4) are given in Table 1. The chemical analysis was performed by means of the X-ray fluorescence method on an ED 2000 XRF spectrophotometer (Oxford Instruments, UK). Representative samples (100 g) were pulverized in a laboratory vibratory mill prior to the testing. The chemical composition of $BaCO_3$ was provided by the manufacturer: Ba = 77%; and CO_2 = 22.3%. The loss on ignition (LoI) was determined as a weight difference between 20° and 1000 °C.

An ultra-centrifugal mill (ZM-1, Retsch, Germany) was used for the micronization of green steatite powders. The mill has a 300 ml working element which comprises a high-alloyed stainless steel rotor (∅100 mm, 600 W) and a variable mesh size ring sieves. The sieve with a 120 µm mesh size and trapezoid holes was used. The rotor velocity was adjusted at 20.000 rpm. The milling period was set at 30 min.

Upon micronization, the binder-free S1–4 powders were pressed into cylindrical tablets using uniaxial double compression on a 40 mm diameter tool in a laboratory hydraulic press (4000 kg cm^{-2}). Thus prepared samples were submitted to the sintering procedure. The same sintering regime was applied on all four steatite mixtures. The samples were fired at four different temperatures – 1000°, 1100°, 1200°, and 1250 °C, in a CWF 1300 laboratory furnace (Carbolite, UK). Sintering was conducted under a 10 °C/min heating rate. The samples were kept at the maximal projected sintering temperature for 60 min and extracted only when the furnace was completely cooled down.

Mineralogical analyses were performed on the pulverized sintered steatite samples by means of the X-ray powder diffraction technique (XRD). The XRD patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube. The instrument operates at 40 kV voltage and 30 mA current. It is equipped with a slanted graphite monochromator and a scintillation counter. The intensities of the diffracted CuKα X-ray emission (λ = 1.54178 Å) were measured at the ambient temperature in the intervals 0.02°2θ in the 2θ Bragg angle range from 4 do 65°2θ, counting for 0.5 s. The slits for the steering of the primary and diffracted beams were fixed at 1° and 0.1 mm.

Differential thermal (DTA) and thermo-gravimetric (TGA) analyses were carried out in a static air flow with an automatic thermal analyzing system Setsys, SETARAM Instrumentation, Caluire, France. The steatite green powdery mixtures (approx. 30 mg) were loosely packed into an alumina holder and thermally treated at a constant heating rate of 10 °C/min in the temperature range between 25 °C and 1100 °C in air flow, in an alumina pan.

The microstructure of the steatite samples S1–4 sintered at 1000 °C and 1250 °C was studied on a scanning electron microscope (JEOL, JSM-6390 LV). Parts of sintered tablets, whose surface was not polished prior to the imaging, were used in the analysis. The samples were covered with an Au film to improve the conductivity during recording. Energy-dispersive X-ray spectroscopic (EDS) analysis was conducted at the selected points on the S1–4 samples.

The dielectric properties of the samples S1–4 were characterized by