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Original Article

# Hierarchical micro-nanostructured albite-based glass-ceramic for high dielectric strength insulators

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## ABSTRACT

A novel glass-ceramic material based on albite type Na-rich feldspar has been synthesized by conventional ceramic process. High crystallinity, > 94% Vol.% is obtained by fast sintering which allows energy saving processing. Albite is the main crystalline phase and tetragonal $SiO_2$ is a secondary phase. Electrical properties were examined by complex impedance, DC measurements, and dielectric breakdown test. Dielectric characterization shows a non-Debye type dielectric behavior with low dielectric constant, 4.6 at 1 MHz, low dielectric losses, ($\sim 10^{-3}$ at 1 MHz, and a large dielectric strength, ~60 kV/mm), that it is the largest value reported in ceramic insulators. Those dielectric properties are attained by the low glassy phase content in the samples and their unique micro-nanostructure. All these properties make this novel material a very promising candidate in the market of ceramic electrical insulator, highlighting for high-voltage applications.

## 1. Introduction

Electrical insulators are materials which block the flow of electric current. These materials are used in electrical equipment as insulators or insulation being their function to support or to separate electrical conductors without allowing current through themselves. The uses of it have increased in the last years because of the technology demand.

A kind of electrical insulators widely used currently is ceramic electrical insulators which are used in many microelectronic devices. Multifold insulator applications form part of automotive and aerospace sector, or home appliances. Ceramic insulators are also used for high-voltage applications, they are being one of the most important pieces used in power transmission as well as distribution lines between others [1–3]. The properties required for an insulator in this field of application are high resistivity, high dielectric strength, a low loss factor, good mechanical properties and dissipation of heat. One of the main limitations of these materials, mainly in high-voltage applications, is their dielectric breakdown, which prompts the loss of insulating properties and mechanical degradation of the material.

Dielectric strength for high-tension electrical insulation is currently limited to 30 kV/mm [4]. Only natural mica insulators provide larger dielectric strength values. Dielectric breakdown is related to scattering process and charge trapping in specific areas of the insulator material. Defects are considered as sites where polarizability is modified and where charge and energy localisation can occur. In ceramics, such defects can be porosity, crystallographic defects, lattice distortions, impurities, grain boundaries or interfaces with secondary phases [5]. Dielectric breakdown is strongly determined by micro-structure, playing the interfaces an important role since they are favourable places to charge trapping. Porosity and grain size are also some important variables to take into account [6]. It is reported in previous works that a low porosity and low grain size improve the breakdown resistance [7]. The amount of glassy phase presented in the glass-ceramic also affects the dielectric material behaviour, mainly the dielectric losses. High dielectric losses are registered in most of the glasses, so that, lower dielectric losses are expected in glass-free ceramics [8].

Albite ($NaAlSi_3O_8$) is the sodic end-member of plagioclase and alkali feldspar-group minerals. Albite may be found with an ordered or disordered structure. The ordered structure is known as low albite, which belongs to the triclinic pinacoidal crystal system. It framework consists of rings of four tetrahedron, where each tetrahedron is centered by a $Si^{4+}$ or an $Al^{3+}$. Each oxygen atom is located at the corners of the tetrahedron and links two tetrahedron which are usually labeled as T1o, T1m, T2o and T2m. The completely disorder triclinic albite is known as high albite. Disordered albite undergoes a triclinic to monoclinic phase transition at about 980 °C, where the complete order is lost. In that case, albite framework is formed by two tetrahedral sites, i.e T1 and T2 [9,10]. Previous studies about the dielectric behavior and the conduction mechanism of feldspars at high temperature and high pressure showed an insulator behavior and suggested an ionic conduction as the

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dominant conduction mechanism [11–13].

In the last years, development of nanotechnology and nanoscience have allowed the improvement and creation of new materials with unique properties [3]. In this work, we have synthesized an albite-based glass-ceramic by fast firing processes that take ~55 min for the whole sintering cycle. The so obtained glass-ceramic possesses low porosity and a low glassy phase content, which is an important novelty regarding to standard dielectric materials such as glass ceramics, steatites or dielectric porcelains among others [4,14,15]. The unique micro-nanostructure of the albite-based glass-ceramic provide a high breakdown strength that is larger than that of the standard material used in this area [16]. All of these peculiar characteristics will favour numerous processes of phonon, photon and electron scattering in the material, achieving a low thermal conductivity, a high reflection of UV and IR radiation [17] and a good insulator behavior.

The present paper shows the results of an extensive study made on the dielectric properties of this micro-nanostructured albite, such as dielectric strength, dielectric constant, loss factor, complex electric modulus and DC/AC conductivity, trying to elucidate the influence of the microstructure in the dielectric behavior observed which can be of interest in the field of ceramic insulators.

## 2. Experimental procedure

### 2.1. Sample preparation

The glass ceramic was prepared by a conventional ceramic process followed in the tile industry [18,19]. The precursors used were kaolin (MOLCASA), with a particle size ($D_{50}$) of 5.34 μm, and frit in a weight proportion of 90/10, respectively. The frit, produced by Vidres S.A., was previously melted at 1500 °C (previously warmed at 900 °C and then directly brought under the dwell temperature) and water quenched [20]. The starting raw materials used for the preparation of this frit were potassium feldspar, quartz, dolomite, calcium carbonate, sodium feldspar, calcined alumina, strontium carbonate and zircon flour. The material composition expressed in terms of equivalent oxides is shown in Table 1. Homogenization of precursors was done by milling in an alumina ball mill for 20 min with 37 wt% of water [21]. The material prepared was dried at 60 °C for 24 h and the powder obtained was sieved through a sieve of 100 μm, achieving a particle size ($D_{50}$) of this material with a monomodal distribution centered at 6.72 μm. Green discs were pressed uniaxially at 39.2 MPa with different diameters accordingly to the characterization test specifications: samples of ~60 mm of diameter for dielectric constant and dielectric losses measurement at room temperature; and samples of ~10 mm for the rest of measurements. Then, samples were sintered in an industrial type furnace at 1220 °C for 6 min with a 30 °C min$^{-1}$ heating rate, spending the sintering cycle only 55 min in being completed. This thermal cycle was chosen attending to the results obtained from the heating microscopy carried out to identify the sintering temperature of the samples. Different thermal treatments were evaluated in the range of 1000 °C–1250 °C, according to data obtained from Hot Stage Microscopy (varying the holding time and temperature). This single set of conditions was carefully chosen to adapt them to an industrial production process and to minimize porosity in the samples in order to improve mechanical behavior and dielectric strength (see Fig. S1a in section S1 of Supplementary information).

**Table 1**
Composition of the glass-ceramic expressed as equivalent oxides. The minor components are all included in other.

| *Oxides wt %* | *$SiO_2$* | *$ZrO_2$* | *SrO* | *$Na_2O$* | $K_2O$ | *$Al_2O_3$* | *ZnO* | *CaO* | Other |
|---|---|---|---|---|---|---|---|---|---|
| Frit | 54,67 | 1,24 | 7,20 | 214 | 1,44 | 22,63 | 1,27 | 7,73 | 1,68 |
| Kaolin | 55,49 | | | | 1,21 | 42,48 | | 0,17 | 0,65 |

### 2.2. Characterization

Microstructural characterization was studied by means of Field Emission Scanning Electron Microscopy (FESEM) using a Hitachi S-4700. Metalographically polished samples were chemically etched with 5 vol% of HF with the aim of removing the glass phase to reveal the microstructure. The total porosity was evaluated by an image analyzer system Leika Qwin from micrographs of representative polished surfaces. In addition, the crystalline phases formed were identified by using X-ray diffraction (XRD) technique in a diffractometer Bruker D8 Advance with Cu Kα radiation, 40 kV and 40 mA. The identification of the crystalline phases was realized by comparison with the corresponding JCPDS cards, and the glassy phase content was obtained through the integration of the areas corresponding to the glassy and crystalline phases. In addition, the crystalline phase was calculated by the diffraction software Bruker's Diffrac.Eva which takes into account integrated intensities of the amorphous and crystalline contribution. Thermal characterization was carried out by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Netzsch STA 409/C) up to 1000 °C with a heating rate of 10 °C/min in air atmosphere. Hot Stage Microscopy (Axel Hesse Instruments, Germany), was carried out from RT to 1500 °C in air atmosphere with a heating rate of 30 °C/min on a platinum substrate.

Dielectric measurements were carried out by an impedance analyzer (HP4294A, Agilent Technologies Inc., Santa Clara, CA). The frequency range was from 100 Hz to 10 MHz for dielectric constant and dielectric losses measurements at room temperature, for measurements of these magnitudes up to 800 °C using a 2 °C-min heating-cooling rate, for impedance measurements and for electric modulus. Arc obtained by Nyquist plot only were defined from 370 °C to 570 °C due to the resolution of the measurements and for this reason only arcs in this range appear plotted. The analysis of each circuits was carried out through Zplot software, based on the equations of circuits in the maximum of the arcs (ωRC = 1). DC and AC conductivity was measured by the same impedance analyzer from 30 °C to 750 °C. The measures were repeated in three samples in order to obtain an average, reducing the errors and assuring the reproducibility of the measures.

Finally, dielectric strength was evaluated by using a HV DC Power Supply 60 kV and 2.5 mA (Hipotronic, Brewster, NY) and following UNE-En iso standard no. 600,672 where > 10 disks, one face of which includes a hemispherical recess of 10°. Both sides of the disks were silver painted followed by thermal treatment at 750 °C. Samples were dried at 120 °C 2 h and then cooled down to Room Temperature in a desiccator. The discs were immersed into a dielectric medium (silicone oil).

## 3. Results and discussion

### 3.1. Microstructural characterization

Fig. 1a shows the XRD pattern of fast sintered glass-ceramic. The main phase identified in the glass-ceramic corresponds to albite feldspar. Albite is the major phase formed in our glass-ceramic when the material is sintered, although the frit only has a 2% of $Na_2O$. The addition of SrO plays a crucial role in the crystallization of albite phase, since SrO is a lattice disruptor which favours the formation of this sodium aluminosilicate after devitrification process [22]. The (131) and (1–31) reflections show the symmetry of the feldspar. In monoclinic albite only the (131) reflection appears in the XRD pattern. However, in triclinic albite, a splitting of this peak takes place. Inset of Fig. 1a shows the (1–31) and (131) reflections located at 30.1° and 31.2° 2θ, respectively, which agrees with literature data, JCPDS Card no. 01-084-0752 [23]. These data indicate the symmetry of the triclinic albite, that is, the most ordered Na-rich feldspar. In addition, $SiO_2$ crystalline phase appears in low concentrations. The broad band located between 15° and 35° 2θ allows us to estimate the glassy phase content present in the