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Feature article

Comparative study of dielectric properties of geopolymer matrices using different dielectric powders

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ABSTRACT

Due to their interesting properties, geopolymers have found various applications in different domains. The evaluation of the dielectric properties of a geopolymer matrix for RF applications is innovative. In this context, this paper focuses, first, on the evaluation of the suitability of a geopolymer matrix with dielectric materials, and then on the improvement of the real permittivity value of the obtained material. For this purpose, the precursors either dielectric powder or aluminosilicate powder were first characterized. Then, the feasibility of the geopolymer matrix was investigated. Based on the feasibility test, it was shown that these kinds of materials can be successfully filled with various types of dielectric materials, such as ZrO_2, $BaTiO_3$ and Y_2O_3. Moreover, the optimized parameters of the synthesis process, which included a small amount of water in the formulation, were 20 °C for the synthesis temperature, 85% for the humidity level and 7 days for the setting time. The measurement of the dielectric properties evidenced, first, that the real part of the relative permittivity strongly depends on the formulation and storage process. Then, the incorporation of a high percentage of $BaTiO_3$ (60%) induced an increase in the real part of the permittivity value and a decrease in the loss tangent. Finally, the mixing law of Maxwell-Garnet was applied to compare the theoretical and measured values of the permittivity. It was deduced that the small difference detected at low percentages whatever the dielectric materials can be explained by the preponderant effect of the geopolymer matrix compared to ZrO_2 or $BaTiO_3$, it seems that the mixing law well functioned with $BaTiO_3$ than ZrO_2. This is in accordance with the better dielectric properties for samples containing $BaTiO_3$.

1. Introduction

During the past decade, considerable research efforts [1] have been directed toward the development of volumetric antennas and their dimensions due to the wide range of their potential applications in many fields of electronics and communications. Some of these applications, such as detection, location and identification of buried items, require the use of antennas operating over a wide frequency band with low frequencies in the spectrum (a few hundred of MHz). In this frequency range, for radar applications for example, the volumetric antennas need to have compatible dimensions and weights to portable systems that can be moved by human strength. The NETTUN project [2] showed that the use of resin can decrease the antenna size, but the exothermic reaction mixture used for creating the resin caused damage to the connectors of the antenna; hence, the idea to search other potential materials with high dielectric permittivity properties is being pursued [3]. Generally, the dielectric materials mainly used are zirconia (ZrO_2), barium titanate ($BaTiO_3$) and yttrium (Y_2O_3) thanks to their high permittivity values [4]. In recent years, much attention has been paid to (ZrO_2) because of its various applications in materials such as solid electrolytes, structural ceramics and optical functional materials [5]. Zirconia ceramics, for example, have attractive properties, such as high strength and fracture toughness for COMS applications. [6] The very good chemical stability and mechanical and thermal properties of barium titanate enable its use in many applications that use its various features, such as the sensitivity of its permittivity to the temperature, frequency range or an external constraint [7]. Y_2O_3 compound was used in various ceramics due to the increase of the dielectric loss in Si_3N_4 ceramic substrate [8] as well as to

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be a promising microwave absorber with satisfactory mechanical properties in Short carbon-fiber (C_{sf}) reinforced alumina ceramics with $MgO–Y_2O_3$ fabricated by pressure less sintering at 1500 °C for 2 h [9].

Today, it is becoming increasingly important to develop materials that are safe and environmentally friendly. New materials such geopolymers are currently being designed. The term geopolymer is generically used to describe an amorphous alkali aluminosilicate that is also commonly used as inorganic polymer [10], in which alkaline activators such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate and potassium silicate are added to activate aluminosilicate materials, such as metakaolin [11,12]. Their formation produces an amorphous three-dimensional geopolymer network by the polycondensation reaction. Based on their structure, this new generation of materials may exhibit good mechanical, chemical and thermal properties, making them a promising alternative for a variety of applications, such as insulated packaging materials at high temperatures and in the aviation industry [13,14]. However, such materials have rarely been used as dielectric materials and few investigations have been conducted on their physical properties. Due to being sinter-free, simple to manufacture and low cost, geopolymers should suit for a variety of electronic applications [15]. Therefore, a study of the dielectric properties of these materials would to be interesting considering that the dielectric properties combine two different contributions: the water and the solid phases in the pore [16]. In this context, some authors [17] synthesized alkali-activated materials, such as fly ash geopolymer pastes, based on sodium silicate and studied their dielectric properties within a frequency range of 100 Hz–10 MHz. It was revealed that, the permittivity value depended on the frequency range and the liquid alkali solution to fly ash ratios (L/FA ratio). However, the real permittivity value decreased with increasing frequency. The dielectric performance of alkali activated slag cement paste was also investigated in the frequency range of 1–1000 MHz [18]. The experimental results showed that the dielectric properties of the hardened paste were mostly influenced by the fraction of free water in the paste or absorbed water from the ambient. Li et al. [18] highlighted that the temperature and the relative humidity of the environment were the key factors for free water adsorption. The cement-based materials may be applied in humidity sensitive materials or for making dielectric materials. Since, it has been proven that there is a relationship between the dielectric properties and chemical composition of the constituents of a geopolymer (alkaline solutions for example). An investigation of the microwave dielectric property measurements [19] of twelve laboratory synthetic water glass samples within the X band (8.2–12.4 GHz) showed an exponential decay in the loss factor as a function of the increasing silica- to- alkali ratio, suggesting a correlation with the increase in the bound water of the samples and the decrease in the fluid ionic concentration.

In addition to the synthesis of geopolymer mortars with fibers [20], the possibility to find geopolymers that also contain non-aluminosilicate additives was demonstrated. Phair et al. [21] proved that the successful incorporation of zirconia highlighted the multicomposite capabilities of the geopolymeric matrixes. Thus, incorporating additional or filler materials into geopolymers is necessary for a variety of structural and mechanical improvements. However, the study underscored the effect of incorporating non-aluminosilicate additives on the compressive strength and did not evaluate its influence on the dielectric properties.

The main objective of this study is to evaluate the suitability of geopolymers as dielectric matrixes and to determine their dielectric properties. To achieve this objective, geopolymer formulations containing different dielectric material oxide rates will be synthesized in various experimental conditions. Then, the mixture will be added to an alkaline solution. The samples will be kept at different temperatures while varying the moisture content and dielectric material content.

2. Experimental part

2.1. Raw materials and sample preparation

The raw materials used in this study for the various syntheses are as follows: alkali hydroxide KOH as pellets (85,97% purity), alkaline silicate solution SiK (Si/K = 1.7, K_2O = 7.6 wt.%, SiO_2 = 16.4 wt.%, H_2O = 76 wt.%), metakaolin (M) (SiO_2 = 55 wt.%, Al_2O_3 = 40 wt.%) and dielectric materials as additives: monoclinic and quadratic zirconia (99% of purity, supplied by Aldrich), barium titanate (99% of purity, supplied by Aldrich) and yttrium (99.5% of purity, supplied by Aldrich). The characteristics of the metakaolin and the dielectric materials are reported in Table 1. The alkaline activation solution is obtained by dissolving the alkali hydroxide pellets in an alkali silicate solution to obtain a Si/K ratio equal to 0.5. After stirring for 15 min at 700 rpm, the metakaolin and the dielectric material are added. The reactive mixture is consolidated at different operating conditions that are detailed later. The mixture is poured in a mold ($80*80*15\ mm^3$) and then subjected to vibration for 15 s on a vibrating table. The samples are then stored for 7 days and demolded after 24 h. The samples were synthesized at different temperatures and kept at various humidity levels.

Different formulations were synthesized from potassium silicate solution and different rates of potassium hydroxide introduced in varying proportions (Table 2). Consolidation occurred at different operating conditions. The corresponding synthesized samples were denoted as $(^{X}M_{YW})^{T(°C)}{}_{H(\%)}$, where X is the metakaolin mass (g), Y is the mass percentage of the dielectric material, W is the dielectric material used, T (°C) is the synthesis temperature, and H (%) is the storage humidity. For example, the sample $(^{12}M_{16Zr})^{20}{}_{43}$ was obtained from a potassium silicate solution while mixing 12 g of the metakaolin with 16% of zirconia. The sample was synthesized at 20 °C and kept at 43% of humidity.

2.2. Technical characterization

The particle size distribution of the raw materials was measured using a laser particle size analyzer (Mastersizer 2000). The mixture contained 1 g of dielectrical powders or aluminosiliacte source in 20 ml of water and was mixed by ultrasound to eliminate any aggregation. The measured particle sizes were in the range of 0.05–880 μm. Additionally, the concentration of the solution was not too large (obscuration <35%). Powder BET surface areas were

Table 1
Characteristics of the raw materials.

Raw materials	Relative Permittivity value (±2% @ Frequency)	D_{50} (μm)	S_{BET} ($m^2\ g^{-1}$)	ρ ($g\ cm^{-3}$)	Wettability ($\mu l\ g^{-1}$)
M	4 @1.5 GHz	10	17	2.40	570
ZrO_2	12 @ 8.9 GHz	9	6	7.42	227
$BaTiO_3$	3000 @ 9.7 GHz	<1	2	5.94	750
Y_2O_3	10.2 @ 6.5 GHz	2	2	5.00	550