



Inorganic phosphate cement fabricated with wollastonite, barium titanate, and phosphoric acid



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ABSTRACT

Inorganic phosphate cement (PC) matrix composites with different wollastonite (CaSiO_3) and barium titanate (BaTiO_3) powder contents were manufactured in this research through a room temperature process. Wollastonite powder is used because of its low cost and good cementing properties when mixed with phosphoric acid (H_3PO_4). BaTiO_3 was selected because of its good dielectric properties and high thermochemical stability. Samples were made by mixing an aqueous acidic formulation of phosphoric acid (H_3PO_4) and mineral wollastonite (CaSiO_3) in a planetary mixing apparatus. Powder mean sizes for CaSiO_3 and BaTiO_3 were respectively 15 and 0.35 μm . The effect of the BaTiO_3 concentration on the compressive strength, density, and dielectric properties is presented. Results obtained by scanning electron microscopy (SEM) and X-ray diffraction (XRD) showed a composite with residual CaSiO_3 and BaTiO_3 powders as well as newly formed silica (SiO_2), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and monetite (CaHPO_4). BaTiO_3 additions improved the compressive strength (over 100 MPa). It is shown that as the BaTiO_3 content increased, the porosity and dissipation factor decreased and the dielectric constant increased. As a control experiment, dielectric tests were conducted over the as-received wollastonite powders. The motivation of this research is to develop phosphate cements with tailored electronic properties for new applications.

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1. Introduction

Inorganic phosphate cements (PCs) are synthesized by chemical reactions at low temperatures [1–3]. These materials have been used for multiple applications including dental and bio materials [4–8], nuclear waste solidification and encapsulation [9,10], and composites with fillers and reinforcements [11–14]. It is well known that fabrication of conventional cements and ceramics is energy-intensive as it involves high-temperature processes. Current methods also emit greenhouse gases which adversely affect the environment [15]. Conversely, the fabrication process for PCs in this research is a fully green process. This fabrication method can make use of a wide variety of raw metal oxides, which opens up possibilities to obtain diverse PC compositions with many applications. PCs are typically multiphase materials composed of residual phases (from the raw oxides used) and new crystalline and amorphous phases (from the acid-metal ions reaction).

Therefore, we have an opportunity to tailor the microstructure for diverse applications. In PCs, the inorganic resin (formed by the mix of metal oxide powder and an acidic liquid based on H_3PO_4 in this case) is very convenient for manufacturing of composites because one can add, disperse, and fully impregnate reinforcements such as particles and fibers. Despite these beneficial discoveries, PCs have been poorly explored as electronic materials [16,17].

In this research, in order to produce PCs, wollastonite powder (CaSiO_3) was mixed with a phosphoric acid formulation (H_3PO_4) in a 1.2 acid to wollastonite ratio by mass. Wollastonite powder is used because of its low cost and good cementing properties when mixed with phosphoric acid (H_3PO_4), such mixture having been fabricated and commercialized as a structural material [14]. Then, barium titanate (BaTiO_3) powders were added to the mixture, therefore mostly working as a filler material. BaTiO_3 powder was selected because of its good dielectric properties and high thermochemical stability. These components reacted to transform into a PC. The sections below will present the wollastonite-based PC with BaTiO_3 contents characterized by compression, density, and dielectric properties. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) data are shown to further understand

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the crystalline characteristics of the material. The mixing of wollastonite with the acid formulation produced a multiphase material with crystalline brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and wollastonite, BaTiO_3 phases, and amorphous silica and calcium phosphates phases [14]. This research opens up other possibilities to produce a new emerging class of electronic cement-based materials fabricated at room temperature. These new PCs could be cultivated to have phases with different, engineered properties.

The aim of this research is to develop phosphate cements suitable to be used as electronic materials while keeping their good mechanical properties, positive environmental impact, and inexpensive manufacturing processing. Since traditional cements have limitations in the amount of filler one can incorporate without affecting the hydraulic reaction and since the production process is not environmentally friendly, this new line of materials could propel the construction and building materials industry into a new era, with multifunctional materials designed for communications, structural functionality, and environmental exposure. Potential applications of the materials developed in this research include insulation firewalls for protection of power plant electrical transformers [18] and capacitors [19].

2. Experimental

PC samples were fabricated by mixing an aqueous phosphoric acid formulation (from Composites Support and Solutions, Inc.) with 75.8 wt% of H_3PO_4 , 11.0 wt% of H_2O , and 13.2 wt% $\text{ZnO} + \text{Al}_2\text{O}_3$ (oxides used as retardants for the setting time). These ZnO and Al_2O_3 powders were completely dissolved in the acid, and therefore finally present as Al and Zn ions. Wollastonite powder (M200 powder, which corresponds to 15 μm mean size, from Minera Nyco; see Table 1) was mixed with H_3PO_4 in a 1.2 acid to wollastonite mass ratio. All wollastonite powders were shipped from the manufacturer in closed containers since wollastonite is hygroscopic. All PC samples were fabricated using M200 wollastonite powder because it was found [20] that this particle size produces the longest pot life of the resin, which is very important in a real industry process; other sizes usually set too fast for real applications. However, as a reference, dielectric tests were conducted over the raw powder forms of different sizes as described below.

In addition, BaTiO_3 (99% pure, from Strem Chemicals) was added to the mixture in different concentrations (0.0, 1.0, 10.0, 20.0 and 40.0 wt% of BaTiO_3). BaTiO_3 powder corresponds approximately to a 0.3 μm mean particle size. For all samples, the 1.2 liquid (phosphoric acid formulation) to powder (wollastonite + BaTiO_3) ratio remained constant; see Table 2. Up to 40.0 wt% of BaTiO_3 was loaded in the PC; more than this concentration did not set properly. In all cases, the formulations were started by mixing wollastonite and phosphoric acid in the 1.2 acid to wollastonite weight ratio mentioned previously. Then, BaTiO_3 was added and mixed for one minute. It was expected that by adding the BaTiO_3 particles at the end, they would not interact as much with the acidic formulation in order to preserve the dielectric properties.

All raw materials were stored in a refrigerator for an hour at 3 °C in closed containers before mixing, since this increases the pot life of this inorganic resin [21,22]. The mixing process was conducted in a Planetary Centrifugal Mixer AR-250 apparatus. Then,

Table 2
Raw materials contents in the composite samples fabricated.

Sample	Powders per sample (wt%)	Acid/ Σ powders (wt%)
0%	100.0 CaSiO_3 + 0.0 BaTiO_3	120/100
1%	99.0 CaSiO_3 + 1.0 BaTiO_3	120/100
5%	95.0 CaSiO_3 + 5.0 BaTiO_3	120/100
10%	90.0 CaSiO_3 + 10.0 BaTiO_3	120/100
20%	80.0 CaSiO_3 + 20.0 BaTiO_3	120/100
40%	60.0 CaSiO_3 + 40.0 BaTiO_3	120/100

resin was poured in glass molds, each 12.7 mm in diameter and 100 mm long, for compression tests. After 1 day, samples were released and cut in cylinders 25.4 mm long. Next, samples were dried in a furnace at 50 °C for 24 h and then at 100 °C for another 24 h in order to completely dry them. Compression tests were conducted using an Instron 3382 at a crosshead speed of 1 mm/min. A set of 5 samples were tested for each composition. Strain gages were used on a few samples in order to obtain the strain–stress curve.

Microstructure was investigated using a scanning electron microscope (JEOL JSM 6700R) in high vacuum mode. X-ray diffraction (XRD) experiments were conducted using a PANanalytical X'Pert PRO diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$) at 45 kV with scanning between 10° and 80°. In all tests, samples were ground in an alumina mortar, and XRD tests were conducted at room temperature. Density tests were conducted with a Mettler Toledo balance following the buoyancy method. The dry weight (W_d), submerged weight (W_s), and saturated weight (W_{ss}) were measured. The following parameters were calculated: bulk volume ($V_b = W_{ss} - W_s$), apparent volume ($V_{app} = W_d - W_s$), open-pore volume ($V_{op} = W_{ss} - W_d$), % porosity = $(V_{op}/V_b) \times 100\%$, bulk density ($D_b = W_d/(W_{ss} - W_s)$), and apparent density ($D_a = W_d/(W_d - W_s)$). In these calculations, the density of water was taken to be 1.0 g/cm^3 . A set of 3 samples per composition was tested.

Before the dielectric tests, samples were dried in a furnace at 50 °C for 24 h and subsequently at 100 °C for 24 h. This procedure was conducted taking into account that wollastonite is hygroscopic and water content in cements can significantly modify their electronic properties. In traditional cements, water molecules in the cement paste change from free to bound water in various states of hydration or crystallization which can change the bonding state and is reflected in the dielectric properties [23].

Dielectric tests were conducted with PC samples 11.4 mm in diameter and 1.5 mm long. Three samples were tested for each composition. In order to obtain flat faces, samples were ground using silicon carbide papers of ANSI 400 grit (20.6–23.6 μm) until their faces were flat, parallel, and 1.5 mm thick. The study's frequency range was between 20 Hz and 1 MHz, and all tests were conducted at room temperature. As reference for the dielectric tests, wollastonite powder of a different size was tested as received from the manufacturer. These powders were pressed in a die at 3000 lbf. This pressure value was utilized in order to obtain samples of 11.4 mm diameter and 1.5 mm thickness. The mean particle sizes for M200, M325, M400 and M1200 wollastonite powders are 15, 10, 8 and 3.5 μm respectively (data reported by NYCO, determined with a Cilas Granulometer). The surface areas for the same powders are correspondingly 1.1, 1.3, 1.6 and 2.9 m^2/g (data reported NYCO from a Micromeritics ASAP 2420 apparatus). Tests

Table 1
Chemical composition of wollastonite powder.

Composition	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	MgO	TiO ₂	K ₂ O	Impurities
Percentage	46.25	52.00	0.25	0.40	0.025	0.50	0.025	0.15	≤0.4

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