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Optical and dielectric properties of nano-sized tricalcium aluminate hexahydrate (C3AH6) cement

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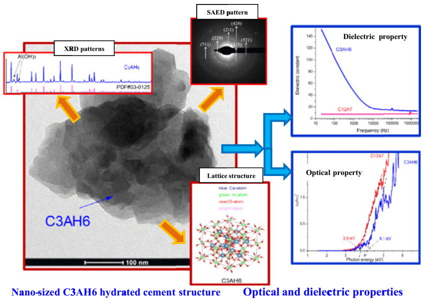
HIGHLIGHTS

- Nano-sized C3AH6 was fabricated by simple hydration process from C12A7 precursor.
- Nano-sized C3AH6 cement showed high capacitance and dielectric constant.
- C3AH6 was visible transparent materials with a direct energy gap of 4.1 eV.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study investigates the optical and dielectric properties of nano-sized C3AH6 cement hydrates. A cement product was fabricated via a simple hydration process using a derivative of a C12A7 cement precursor reacting with de-ionized water while raising the reaction temperature to 100 °C. A crystalline phase of the C3AH6 cement product was characterized and confirmed using an XRD technique. Its morphology was also evaluated using TEM and SEM techniques. It was found that nano-sized C3AH6 (in size 10–50 nm) was successfully derived via this process. This cement product was thermodynamically stable over the range of room temperature to 300 °C. The optical direct gap was 4.1 eV and the indirect energy gap was 2.45 eV. Over the range of 20 Hz to 2 MHz, the observed capacitance was 10^{-10} F–10^{-11} F and the dielectric constant varied from 20 to 150. The dielectric properties were enhanced over those of general cement compounds. This effect was due to its complex structure in which –O–H bonding appeared in the structure and the formation of nano-sized structures from this process. These results suggested that the nano-C3AH6 hydrated particles were transparent to visible light and exhibited a high frequency electrical response. This implies an important role for these cement-based materials as potential

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candidates having optical and dielectric properties appropriate for applications such as smart building materials in the form of transparent electrode windows, smart wall capacitors, triboelectric devices and supercapacitors.

1. Introduction

Recently, cement-based materials [1] have attracted significant attention owing to their very interesting optical and dielectric properties for applications as smart building materials including transparent electrode windows, smart wall capacitors, triboelectric devices, and supercapacitors. These cement-based materials are composed of Portland and calcium aluminate cements. They are abundant, low cost and easily fabricated materials. Portland cements, which are composed of phases of lime-silica minerals, are commonly used in structures, agro-industrial infrastructure and transport infrastructure [2]. Calcium aluminate cements, which consist of reactive phases of lime-alumina compounds with various geometric structures, represented by the notation, nCao-mAl_2O_3 (CnAm in cement notation), are used in construction and optical devices, among other applications [3–6]. Calcium aluminate cements, such as monocalcium aluminate [CaO-Al_2O_3 (CA)] [4] and monocalcium dialuminate [CaO-2Al_2O_3 (CA2)] are used for refractory castable and structural materials [3]. It is notable that dodecacalcium hepta-aluminate [12CaO-7Al_2O_3 (C12A7)] cement offers high performance in optical smart materials such as transparent electrodes [7], transparent conducting oxides [8], emitters [9], and electrides [10]. Hussain et al. [11], Lobo et al. [12] and Ruttanapun et al. [13] reported a direct optical energy gap for the C12A7 insulator phase of approximately 3.5 eV [12], 3.64 eV [11], and 4.2 eV [13] by computer simulation and 3.9 eV [13] by calculation. For calcium aluminate cements (CA, CA2, CA6, CA3), Hussain et al. [11] reported a direct optical energy gap of 3.85–4.62 eV using a first principles approach. Dielectric properties are related to the electrical nature of a material. Cabeza et al. [2] reported a dielectric constant for Portland cement of approximately 13 for frequencies ranging from 100 kHz to 15 MHz. Torres-Luque et al. [14] and Hussain et al. [11] reported that calcium aluminate cements (CA, CA2, C12A7) displayed dielectric constants of approximately 2–4 over a frequency range of 100 Hz–5 MHz. In another study, Smith et al. [13] worked with hydrated alumina cements and observed dielectric constants for calcium aluminate decahydrate [CaO-Al_2O_3-10H_2O (CAH10)] and tricalcium aluminate hexahydrate [3CaO-Al_2O_3-6H_2O (C3AH6)] cement hydrate in the range of 15–35 at a frequency of 1 GHz. From this, it can be concluded that the hydrated alumina cements of this type displayed dielectric constants that were higher than those of calcium aluminate cements. Using the Kramers-Kroing approach [3], the dielectric and optical properties (AC conductivity and absorption coefficient) can be related via the dielectric function consisting of the real and imaginary parts of dielectric constant. Consequently, hydrated alumina cements are promising candidates to improve optical and dielectric properties for smart building materials in applications such as smart wall capacitors, triboelectric devices and transparent electrode devices [4,15,16].

Moreover, C3AH6 cement hydrate is the focus for investigation of the optical and dielectric properties because it is a thermodynamically stable cement structure derived from calcium aluminate cement hydrate compounds at room temperature [16]. Pure C3AH6 is called katoite cement and it is a mineral in the hydrogarnet group. It has a stoichiometric formula of $Ca_3Al_2(OH)_{12}$ [17]. Its crystal structure displays a cubic unit cell in the Ia3d (2 3 0) space group. Dilnesa et al. [18] found that C3AH6 can be described by a general formula, $Ca_3A_{l2}(OH_4)_3$, with the Ca site occupied by divalent cations (Ca^{2+}), the Al site by trivalent cations (Al^{3+}) in an octahedral and a tetrahedral framework, and the 4OH^- positioned inside the tetrahedral framework. The H^+ ions were bonded to each of the four O atoms surrounding the vacant site for charge balancing. The unit cell contained six $Ca_3Al_2(OH)_{12}$ units, comprising 132 atoms (24 Ca, 16 Al, 96H and 96O). It basically formed a tree framework consisting of $Ca(OH)_8$ dodecahedra and $Al(OH)_6$ octahedral sub-structures [17,18]. The unit cell structure had a lattice constant of $a = 12.55695$ Å, and a unit cell volume $V = 1986$ Å^3. In nature, C3AH6 can form a crystalline phase at high temperatures. Literature reports [17,19,20] detailed that C3AH6 can exist as an anhydrous cement when CA reacts with water in a cement hydration process [17,19,20]. Additionally, Barnes and Bensted [21] reported that C3AH6 can be prepared using C12A7 cement as starting material that can be rapidly reacted with water at elevated temperatures above 60 °C. However, to best of our knowledge, there are no reports of an investigation into the optical and dielectric properties of C_3AH_6 cement hydrate.

This work therefore aims to investigate the optical and dielectric properties of C3AH6 cement hydrate. A C3AH6 product was synthesized via a simple hydration process using a C12A7 cement precursor reacting with water at 100 °C. The C12A7 precursor and the resulting products were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and a high-resolution TEM (HRTEM), IR spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and differential thermogravimetric analysis. Ultraviolet/visible/near-infra red (UV–VIS–NIR) spectroscopy and impedance analysis of optical and dielectric properties were done. Their optical and dielectric properties were investigated. Surface nano-scale morphology and thermodynamic stability were evaluated. The effect of nano-C3AH6 particles on dielectric properties are reported.

2. Experimental details

2.1. Chemicals

Calcium carbonate ($CaCO_3$, 99% purity), alumina powder (Al_2O_3, 99.9% purity), and ethanol (95%) were purchased from Sigma-Aldrich (USA). All chemicals were used as received without further purification.

2.2. Preparation of C12A7 cement

In this work, C12A7 cement powder was first prepared via a solid state reaction using $CaCO_3$ and Al_2O_3 as starting materials. In brief, $CaCO_3$ and Al_2O_3 powders were stoichiometrically mixed following the reaction, $12CaCO_3 + 7Al_2O_3 \rightarrow Ca_{12}Al_{14}O_{33}$ (C12A7) + $12CO_2$. The powder was mixed during ball milling with ethanol for 24 h at room temperature. This was followed by drying in an oven at 80 °C for 24 h. Then, the resulting powder was placed in an alumina crucible and sintered in an electric furnace at 1200 °C in an air atmosphere for 24 h. Finally, the obtained C12A7 cement sample was crushed into a powder for use as a precursor material to prepare C3AH6 cement-hydrates.