

## Synthesis of hexacelsian barium aluminosilicate by film boiling chemical vapour process

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### Abstract

An original oxide/oxide ceramic-matrix composite containing mullite-based fibers and a barium aluminosilicate matrix has been synthesized by the film boiling chemical vapour infiltration process. Alkoxides were used as liquid precursors for aluminum, silicon and barium oxides. The structure and microstructure of the oxide matrix were characterized by Scanning Electron Microscopy, Energy Dispersive Spectroscopy and X-ray diffraction. Apart from small residual mullite and amorphous phase amounts, the oxide matrix is composed of the hexacelsian phase, conferring to the material interesting perspectives for high-temperature electromagnetic and structural applications.

**Keywords:** *film-boiling process, hexacelsian barium aluminosilicate (BAS), ceramic matrix composite (CMC), oxide/oxide composite*

### 1. Introduction

Ceramic-matrix composites (CMCs) are potential candidates for high-temperature applications because of their refractory character combined to non-brittle mechanical behavior and excellent chemical stability [1]. For fibers and matrices, oxides are generally considered as adequate for lesser temperatures as compared to non-oxide compounds like carbides, nitrides, borides, though they have a superior resistance to high-temperature degradation in an oxidative ambient. However, there is still a great potential for developing highly refractory oxides as matrices in CMCs. Moreover, in some applications, some electromagnetic properties may be required that only oxides can achieve. In this respect, barium aluminosilicate (BAS,  $\text{BaAl}_2\text{Si}_2\text{O}_8$ ), especially in its hexacelsian allotropic form, is especially attractive. It is a highly refractory glass ceramic and has a dielectric constant of 7 [1]-[11].

BAS has different polymorphic forms: paracelsian, monoclinic (celsian) hexacelsian (hexagonal- $\alpha$ ) and orthorhombic (hexagonal- $\beta$ ) [4]-[7];[12]-[14]. The paracelsian and the monoclinic are the two phases of BAS that exist in their natural state. The first is the less common of the two. In question, its instability under atmospheric pressure [7],[8], [13]. The monoclinic phase is the most studied. It is stable up to 1590°C [13], [17]. Its low coefficient of thermal expansion ( $2.29 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ), coupled with a relative permittivity of 6.55, make it an ideal candidate in the fields of electronics and electromagnetism [6],[9], [14]. The hexacelsian (hexagonal- $\alpha$ ) and orthorhombic (hexagonal- $\beta$ )

phases are the two synthetic polymorphs of BAS [2]. The hexacelsian phase is stable between 1590°C and 1760°C. This thermal stability as well as a relative permittivity similar to the monoclinic phase makes it a suitable material for applications in the fields of electronics and very high temperature electromagnetism [15]. Its coefficient of thermal expansion is higher than that of the monoclinic phase ( $8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ) [16]. Below 300°C, the hexacelsian phase very sluggishly and reversibly transformed into the orthorhombic phase [2]; [17]. During this transformation, the crystal lattice changes only very slightly [1], [10]. This causes a volume expansion greater than 0.3%, including the formation of stresses and cracks within the material [1], [6]. However, for some specific applications, at very high temperature (in the range 1600°C and 1700°C), the use of the hexacelsian form is required. It is interesting for applications in the fields of electronics and electromagnetism at very high temperature, for electromagnetic windows, radome or thermal insulation [2], [18]-[21].

The use of BAS as a matrix in CMCs dates back to N. P. Bansal's works [22]-[26], which mostly considered SiC fibers as reinforcements; SiC whiskers or platelets also have been used [27], [28]. Later on, Si<sub>3</sub>N<sub>4</sub>-whiskers reinforced BAS composites have been developed [29],[30]. More recently, carbon-fiber reinforced BAS composites were synthesized with Si<sub>3</sub>N<sub>4</sub> as an interphase around the fibers prepared [31]-[34]. Few works have been done on oxide/oxide composites. BAS/BAS composite has been prepared, apparently with only the celsian phase [18]. A patent reports the synthesis of alumina-short fiber reinforced BAS composites by sintering [35]. Oxide woven preform reinforced BAS composites have never been synthesized.

Experimentally, the hexacelsian phase is the first synthesized in most processes such as sol-gel process and powders sintering [8], [36]-[38]. Under 1590°C, it is converted to the celsian phase, although it can metastably exist below 1590°C due to the sluggishness of the hexacelsian to celsian transformation [29]. To avoid this transformation and stabilize the hexacelsian phase after processing, usual techniques are excluded. One has to use a process that ensures a fast thermal decrease after synthesis, or that directly leads to the preparation of this phase at relatively low temperatures.

In this work, we have therefore considered a fast, out-of-equilibrium process to investigate its potential to synthesize a stabilized hexacelsian phase of BAS as the matrix of an all-oxide CMC.

The film boiling chemical vapour infiltration process [39] is already used to synthesize ceramic-matrix composites [40]-[45]. This technology can be compared to the cold-wall thermal CVD (Chemical Vapour Deposition) process, but the main difference comes from the fact that the substrate, in contact with the heating device, is maintained very close to the boiling precursor. A high thermal gradient is generated between the hot substrate and the surrounding fluid, which maintains a gaseous state close to it - from which the "film-boiling" name arises. When the substrate is porous, as is the case for fiber-reinforced CMC preforms, the infiltration occurs from the inside to the outside, ensuring an optimal infiltration as compared to the more classical isothermal, isobaric chemical vapour infiltration (I-CVI) [46], and a much faster infiltration rate [43]-[45], [47]. Another advantage of this non-conventional process is that the residence time of the precursor gases is small before deposition

occurs. Initially designed for the infiltration of pyrolytic carbon from liquid hydrocarbons, the process has been extended to organosilanes for SiC matrix infiltration [48]. Pushing forward this idea, alkoxides can be considered in this process as liquid precursors for oxide deposits; this is classical in plain CVD, eg TEOS is routinely used for silica deposition [49]-[52].

Here, we perform film-boiling chemical vapour infiltration of a mixture of liquid alkoxides which contains all necessary species to synthesize BAS in a woven preform made of Nextel™312 alumina-boria-silica fibers. The aim of our study is to prepare a fully oxide CMC of which the matrix consists of the hexacelsian phase. In this paper, we first describe the experimental apparatus, then we report several characterization results confirming the composition and phase of the matrix.

## 2. Experimental procedure

The experimental device is represented in Fig. 1. It composed of two general parts: the reactor and a gas condenser. The reactor is a boro-silica tube 46 mm in diameter. It can contained up to 200mL of liquid precursor. The heating system, a cylindrical carbon resistor (Mersen® 2020 graphite,  $\phi=3\text{mm}$ ,  $L=70\text{mm}$ ), is placed at the center of the reactor. The resistor is inserted into a Nextel™312 preform (3M™ Nextel™ AS-40 Sleevng). **The preform is fixed on the resistor using a carbon based cement (Fig. 2). It is a tubular oxide preform. This flexible braided sleeving (3M®) has an internal diameter of 1.6 mm and a thickness around 600  $\mu\text{m}$ .**

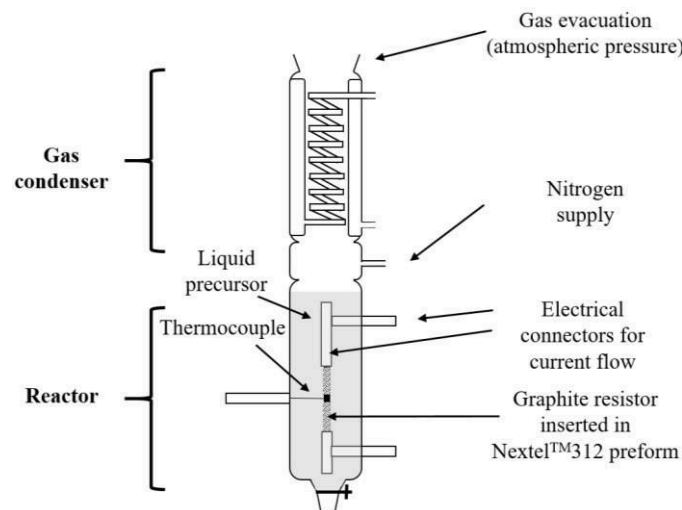


Fig. 1: Experimental setup

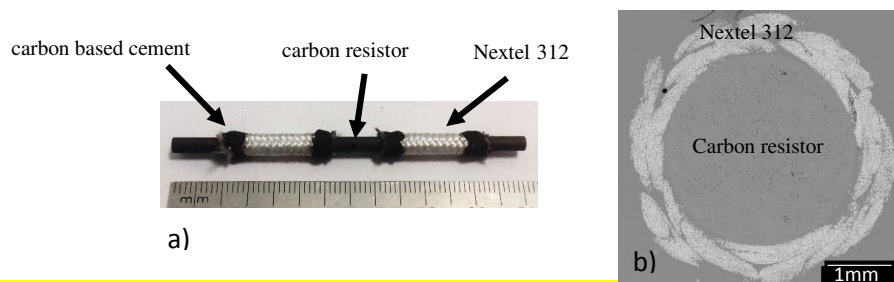


Fig. 2: a) The resistor with the tubular Nextel preform and b) microscope image of the resistor and the preform

Some openings have been created to connect the resistor to an electrical power supply outside the system and for thermal monitoring.

The condenser above the reactor is cooled with a 0°C ethylene glycol exchanger. Indeed, condensing vapours avoids an excessive loss of precursor. The reactor is maintained under atmospheric pressure. During the process, the graphite heater is held in the liquid precursor to avoid oxidation. For safety, a nitrogen supply is inserted between the reactor and the condenser to minimize oxidation.

The liquid precursor is a mixture of three alkoxydes: the silicon source is tetraethyl orthosilicate (TEOS,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , Sigma Aldrich, reagent grade, 98%), the aluminium source is aluminum-tri-sec-butoxide (ATSB,  $\text{Al}(\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{O})_3$ , Sigma Aldrich, 97%) and the barium source is barium isopropoxide, 20% w/v in isopropanol (BIP,  $\text{Ba}(\text{OCH}_2(\text{CH}_3))_2$ , Alfa Aesar). Molar mixture proportion is 65 TEOS / 30 ATSB / 5 BIP.

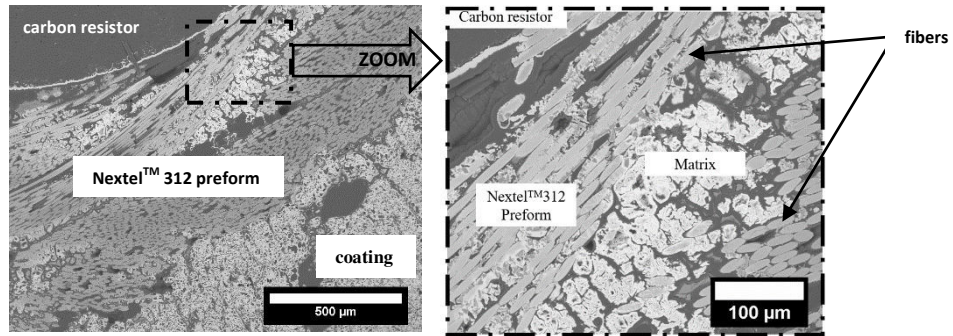
The resistor temperature is controlled by a thermocouple, which has been directly inserted in its middle, in a hole of 1mm of diameter. During the process, the experimental parameters are time and generator intensity for Joule Effect. A progressive increase of intensity from 50 A to 66 A, 0.3A/min, is ordered. This increase is equivalent to a temperature increase inside the carbon resistor from 300°C to 1250°C. The processing time was less than an hour.

Scanning Electron Microscopy (SEM, FEI 400 FEG) was used to characterize the microstructure of the final composite. Matrix composition was determined by Energy Dispersive Spectroscopy (EDS EDAX, 15kV) and X-ray diffraction (XRD, Bruker D8 Advance). XRD patterns were compared with the PDF-2 database cards from the ICDD database (International Centre for Diffraction Data).

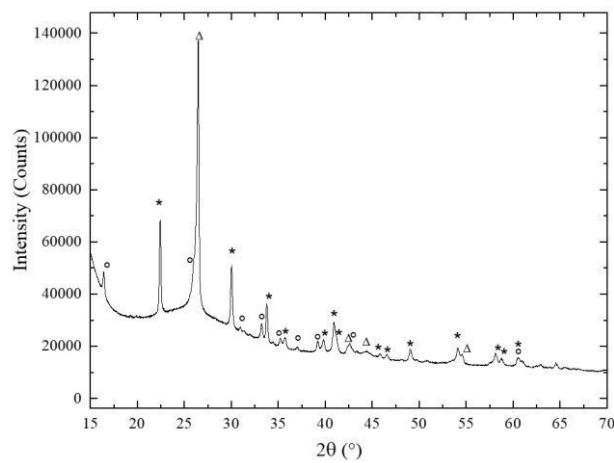
### 3. Results and discussion

The Nextel™312 preform is partially densified after process, as shown in Fig. 3 Inside the preform, near the heating system, the matrix is composed of  $58\%_{\text{at}}\text{O} \pm 2$  ;  $16\%_{\text{at}}\text{Al} \pm 2$  ;  $17\%_{\text{at}}\text{Si} \pm 1$  ;  $8\%_{\text{at}}\text{Ba} \pm 1$  according to an EDS analysis. This composition is close to composition of BAS,  $\text{BaAl}_2\text{Si}_2\text{O}_8$ . A thick coating is observed all around the composite. Its composition is heterogeneous and with Ba, Al, Si and O in varying proportions.

An XRD analysis of the sample indicates the presence of hexacelsian BAS and mullite ( $\text{Al}_{2.32}\text{Si}_{0.68}\text{O}_{4.84}$ ) (see Fig. 4). The hexacelsian peaks are higher than the mullite peaks, indicating that the latter phase is present in relatively smaller amounts. The graphite of the carbon resistor is also detected. No characteristic peak of any other phase of BAS is visible; on the other hand, broad background variations indicate the presence of amorphous phases.



**Fig. 3: SEM micrographs of composite infiltrated by the film boiling chemical vapour infiltration process from a 65 TEOS / 30 ATSB / 5 BIP liquid precursor source**



*Fig. 4: XRD diffractogram of the sample synthesized by film boiling chemical vapour infiltration process from alkoxides mixture; ICCD database peaks are:*

*○: Mullite (04-016-1588); \*: Hexacelsian BAS (01-072-7502); Δ: Graphite (00-012-0212)*

We conclude that a hexacelsian BAS matrix has been successfully infiltrated. The fibrous preform has played the role of a filter layer which homogenized the gaseous phase before its rapid deposition. The hexacelsian is located inside the preform and near the heating resistor. It is assumed that it is the hottest place in the sample because of the thermal insulation property of the oxide fiber preform. The time needed for the gas mixture to reach the hot parts of the preform is short, so that few or no parasitic reactions occur in addition to simple ligand loss reactions like  $\text{TEOS} \rightarrow \text{Si}(\text{OCH}_2\text{CH}_3)_3 + \text{OCH}_2\text{CH}_3$ . The hexacelsian phase being kinetically favored, it is deposited first; however, the temperature being relatively low (less than  $1300^\circ\text{C}$ ), the kinetic rate of its transformation to celsian is very slow; accordingly, after completion of the process run, this transformation has not taken place.

#### 4. Conclusions

We have achieved for the first time the synthesis of an all-oxide CMC with an oxide woven preform and a hexacelsian BAS matrix by the film-boiling chemical vapour infiltration process. A

precursor mixture of three liquid alkoxides leads to partially crystallized system with hexacelsian BAS, with some residual mullite. The strong gradients present in the process and its moderate processing temperature allowed the synthesis of metastable phases and led to a rapid densification. In order to optimize the material composition, further studies are required, in particular variations of the liquid precursor mixture composition.

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