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# Celsian formation from barium-exchanged geopolymer precursor: Thermal evolution

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### ABSTRACT

In this paper, thermal evolution, including element & phase composition and microstructure, of Ba<sup>2+</sup> exchanged K-based geopolymer precursor (BaGP) were systematically investigated during high-temperature treatment. The results proved that celsian precursor with lower residual alkaline cation content were obtained through amorphous geopolymer than traditional ion-exchanged celsian through crystallized zeolite. With the increase in temperature, weight loss of BaGP was due to evaporation of –OH groups and decomposition of BaCO<sub>3</sub>. Similar to K-based geopolymer, BaGP showed amorphous structure, and nanometer-sized celsian nuclei first crystallized from the amorphous BaGP matrix after it was treated at 900 °C. In the treatment temperature range from 1000 to 1400 °C, hexagonal celsian became the main phase. After being treated at 1400 °C, hexagonal celsian grains were clearly noticeable with extra SiO<sub>2</sub> locating between celsian grains. It was therefore concluded that geopolymer precursor technique provides an alternative route for the preparation of celsian ceramics.

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## 1. Introduction

Celsian, with stoichiometric formula of BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, is an attractive refractory and high temperature electrical material, due to its high melting point, high electrical resistance, low dielectric constant, low dielectric loss, and low thermal expansion coefficient up to about 1000 °C [1]. It was also considered as ceramic matrix to prepare advanced CMCs (ceramic matrix composites) for aerospace applications such as turbine engines. As a result, demand for this kind of material has increased dramatically in recent years. Conventional manufacturing processes for celsian include solid-state reaction method [2], sol–gel method [3–5], and ion exchange from zeolite [1,6–9]. However, solid-state reaction method requires high sintering temperatures and suffers from problems of volatiliza-

tion of SiO<sub>2</sub>, agglomeration, and furnace contamination, etc. Sol–gel techniques are disadvantageous in the use of expensive alkoxides and severe preparation condition, which results in high process costs and unsatisfactory yields. Zeolite A is very selective for the large and low hydration energy Ba<sup>2+</sup> cation. Therefore, Barium-exchanged zeolite to celsian is a promising method which is of desired starting composition, homogeneous at the atomic scale and low cost. However, all the three methods start from powders and it's difficult to get bulk celsian ceramics directly without further molding process. Geopolymer, which is similar to zeolite, provides a novel way to prepare celsian ceramics based on ion-exchange. Meanwhile, with the proper processing procedure, it is possible that geopolymer is directly converted into the final bulk celsian ceramic of interest.

Geopolymer are formed by the dissolution and polycondensation of an aluminosilicate powder in an alkaline silicate solution under hydrothermal conditions [10–13] or activated by phosphoric acid [14,15]. And it consists of an amorphous, three-dimensional network of aluminosilicate chains if cured at standard atmospheric pressures (0.1 MPa) and temperatures from 40 to 80 °C. Geopolymer exhibits properties such as formability comparable to epoxies, high temperature stability, chemical resistance and compressive

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**Table 1**  
Chemical composition of metakaolin (wt.%).

| Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | K <sub>2</sub> O | Σ   |
|--------------------------------|------------------|------------------|-----|
| 40.3                           | 59.2             | 0.5              | 100 |

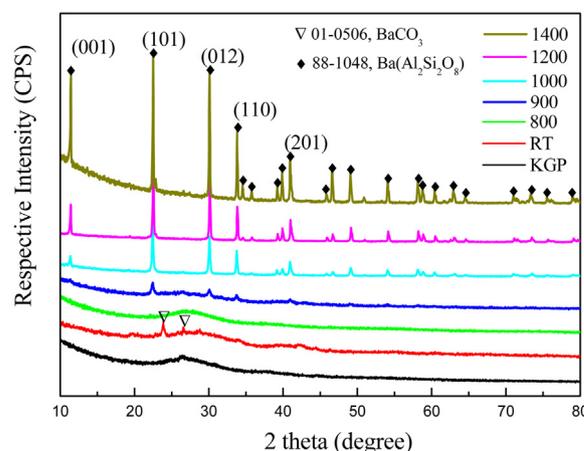
strengths superior to cement [16–20]. Positive ions (typically Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>) must be present in the framework cavities to balance the negative charge of AlO<sub>4</sub><sup>−</sup> in the geopolymer structure. Theoretically speaking, the amorphous geopolymer structure has lower bonding strength to the positive ions compared with the crystallized zeolite. Therefore, Ba exchange in geopolymer might be more thorough than that in zeolite. Meanwhile, after being cured at a temperature range from RT to 80 °C, geopolymer can obtain mechanical properties higher than Portland cement [21–24], which facilitates the in situ bulk Celsian formation after Ba exchange and proper high-temperature treatment.

This paper investigates the possibility to prepare celsian ceramic from Ba exchanged geopolymer precursor. Thermal evolution and effects of treatment temperature on the phase, element composition, and microstructure were studied.

## 2. Materials and experiments

Cation exchange operations were performed according to the following procedures. Geopolymer (KGP) with chemical composition of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 2.5, K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1 and H<sub>2</sub>O/K<sub>2</sub>O = 11 was first obtained by mechanically mixing metakaolin powder with a potassium hydroxide solution to get homogeneous slurry. Si/Al ratio in geopolymer precursor is higher than that of single-phase celsian ceramic due to the higher SiO<sub>2</sub> content in metakaolin. Chemical compositions of metakaolin were listed in Table 1. The slurry that resulted was cast into polystyrene containers (70 mm in diameter and 8 mm in height), sealed, and cured at 70 °C for 48 h. After demoulding the hardened geopolymer was further cured at 70 °C for 1 week. Then the resultant geopolymer was ground and sieved using a 200 mesh sieve, and was ready for cation exchange. 0.25 mol/L Ba<sup>2+</sup> solution was prepared by dissolving Ba(NO<sub>3</sub>)<sub>2</sub> (purity 99.5%) in the Deionized water with ultrasonic assistance. KGP was contacted overnight with the warm Ba(NO<sub>3</sub>)<sub>2</sub> solution (50 °C) with a weight solid/liquid ratio of 1/20. The solid was separated from the liquid through filtration and again contacted with the exchange solution for a total of five times. Then the Ba exchanged KGP (BaGP) was washed twice by Deionized water and dried at 300 °C for 1 h. The dried BaGP powder was then hydraulically die pressed at 5 MPa and heated to different temperatures for 2 h at 5 °C/min.

Simultaneous thermogravimetry and differential thermal analysis (TG/DTA, Netzsch STA 409, Germany) coupled with mass spectrum (Netzsch QMS 403, Germany) were carried out under Air (20 mL/min) gas flow to 1200 °C at a heating rate of 5 K/min in alumina crucibles. Element composition of KGP and BaGP were determined by X-ray fluorescence spectrometer (XRF, Panako AXIOS-PW4400, Netherlands). Phase composition was characterized by an X-ray diffractometer (XRD: Rigaku, D/MAX-2200VPC, Tokyo, Japan) with CuKα radiation at a scan rate of 4°/min. Apparent density and porosity were measured by Archimedes' method in distilled water. A scanning electron microscope (SEM: FEI Quanta 200F) was used to observe the fractographs of geopolymer samples after heat treatment. Tecnai G2 F30 and Talos F200X were used for TEM work. For BaGP samples treated at 300 and 900 °C, TEM samples were prepared by grinding them down, followed by immersion in ethanol and depositing them on holey, carbon-coated copper grids. For the ones treated at 1200 °C and 1400 °C, TEM samples were prepared by the traditional ion milling technology.

**Fig. 1.** XRD patterns of the K-based geopolymer (KGP) and Ba-exchanged KGP (BaGP) before and after being heated to a variety of temperatures.**Table 2**  
XRF results of the KGP.

| Element | Weight ratio (%) | Mole ratio (%) |
|---------|------------------|----------------|
| O       | 35.01            | 55.37          |
| Al      | 17.52            | 16.42          |
| Si      | 22.98            | 20.77          |
| K       | 24.49            | 15.89          |

## 3. Results and discussions

Fig. 1 shows the XRD patterns of the K-based geopolymer (KGP) and Ba-exchanged KGP (BaGP) before and after being heated to a variety of temperatures. Both KGP and BaGP were X-ray amorphous and had a large diffuse peak centered at 28° 2θ. However, for BaGP, a small peak at 23.8° 2θ was noted, which corresponded to BaCO<sub>3</sub> (PDF No. 01-0506). The formation of BaCO<sub>3</sub> should be ascribed to the surface efflorescence which has also been observed in the metakaolin- or fly ash-based potassium activated geopolymer. The surface efflorescence was caused by the reaction between residual Ba(NO<sub>3</sub>)<sub>2</sub> in geopolymer surface and CO<sub>2</sub> from the air, with product of BaCO<sub>3</sub>. After being treated at 800 °C, the X-ray pattern for BaGP became amorphous with the disappearance of BaCO<sub>3</sub>, indicating BaCO<sub>3</sub> decomposition at temperature lower than 800 °C. When the sample was treated at 900 °C, although it kept predominately X-Ray amorphous, the major reflections for celsian (88–1048, BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) first appeared at 22.41, 30.08 and 33.82° 2θ, corresponding to the (101), (012) and (110) reflections in hexagonal celsian, respectively. On heating to 1000 °C, these peaks grew in intensity and celsian become the major phase (space group I41/a), while the amorphous phase decreased significantly, indicating celsian crystallized from the amorphous BaGP precursor. With treatment temperature further increasing to 1100 °C, 1200 °C and 1400 °C, except for the stronger peak intensity, there was no obvious difference with sample treated at 1000 °C. Using Ba-exchanged KGP precursor, only a pure celsian phase was observed in the X-ray pattern regardless of the treatment temperature over the range of 1000–1400 °C.

Element compositions of KGP and BaGP after being treated at 300 °C were determined by XRF, as shown in Tables 2 and 3. In the geopolymer system, K<sup>+</sup> played the role of balancing the negative charge of [AlO<sub>4</sub>]<sup>−</sup> [25,26]. Therefore, mole content of K should be equal to that of Al to get a relative stable charge-balanced state. While, in the Ba<sup>2+</sup> ion-exchanged geopolymer structure, mole content of Ba<sup>2+</sup> would be half of that of K<sup>+</sup> due to their different positive charge, which were consistent with the results as shown in Tables 2 and 3. According to their different element composi-

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