

## Electronic Supplementary Information

### Sample preparation

The samples in this study were prepared via solid-state reactions. The starting materials SrCO<sub>3</sub> (99.9 %, Alfa Aesar, USA), Na<sub>2</sub>CO<sub>3</sub> (99.9 %, Fisher Scientific, USA) and SiO<sub>2</sub> (99.9 %, Alfa Aesar, USA) were first intimately mixed for 20 minutes in a high-energy mechanical mixer (8000M Mixer/Mill®, SPEX® SamplePrep, USA) in the presence of alcohol and ZrO<sub>2</sub> milling balls. The well mixed and dried powders were then pelletized at 5 MPa, followed by calcination at 800°C for 10 hours. Thus pre-calcined pellets were then broken into fine particles of 1-2 μm with a high-energy vibrational mill (Micronizing Mill, McCrone, USA). After being pelletized again at 75 MPa, the samples were finally sintered at 900°C for 10 hours with a heating and cooling rate of 2°C·min<sup>-1</sup>. In particular, we have also synthesized a crystalline Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> phase (denoted as C-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) at 840°C, a temperature lower than its melting point 848.8°C, as well as an amorphous Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (denoted as AM-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) at 900°C where Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> was melted.

### Microstructural characterization

A field emission scanning electron microscope (FE-SEM, Ultraplus, Zeiss, Germany) was employed to capture the microstructures of the samples. The chemical composition of each distinctive phase observed was further analyzed with an Energy Dispersive X-ray (EDX) spectrometer equipped with FE-SEM.

### X-ray diffraction (XRD)

The evolution of phase composition as a function of temperature (RT-600°C) was examined with a high-temperature powder X-ray diffractometer (X1 Theta-Theta, Scintag, USA) and graphite-monochromatized Cu Kα radiation (λ=1.5418 Å). The scan was performed at a rate of 1°·min<sup>-1</sup> from 2θ = 10 - 90°. In particular, the crystallization process of the AM-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> was investigated in the temperature range of 400 - 900°C with a high-temperature X-ray diffractometer (Ultima IV, Rigaku, Japan) and a scan rate of 1°·min<sup>-1</sup> over a 2θ range of 10 to 80° and pre-holding time of 10 min at each temperature. For all the high-temperature XRD studies, the heating rate was 10°C·min<sup>-1</sup>. All the spectra collected were analyzed with the JADE (Materials Data Inc., USA) to identify phase compositions.

### Thermal analysis

To understand the crystallization process of AM-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and of x=0.45 samples, differential scanning calorimetry (DSC) was also carried out with a thermal analyzer (STA 449F1, Netzsch, Germany) in the temperature range of RT-800°C with a heating/cooling rate of 5°·min<sup>-1</sup> in flowing air at 20 ml·min<sup>-1</sup>.

### Electrical conductivity measurement

The electrical conductivity of all the samples were evaluated by electrochemical impedance spectroscopy (EIS). A typical EIS symmetrical cell consisted of a pellet with a thickness of 2 mm and diameter of 13 mm and with an electrode/current collector made of silver paste (C8829, Heraeus, USA) and mesh (40935, Alfa Aesar, USA). The EIS spectra were collected with an

electrochemical station (1260/1287, Solartron Analytical, UK) in the temperature range of 400 to 650°C within a frequency range of 0.5 Hz - 1 MHz and AC amplitude of 50 mV. For the long-term conductivity study, the spectra of the  $x=0.45$  and AM- $\text{Na}_2\text{Si}_2\text{O}_5$  samples were collected at 500°C as a function of time for a total of 20 days.