Bright	at%	ratio	
O K	59.14	-	-
Na K	1.18	6.8	42.3
Sr L	16.1	93.2	
Si K	23.58	-	57.7

Dark	at%	ratio	
O K	60.79	-	-
Na K	18.73	99.8	47.8
Sr L	0.03	0.2	
Si K	20.45	-	52.2

The Na-SrSiO$_3$ is a mixture of lightly Na-doped SrSiO$_3$ and amorphous Na$_2$Si$_2$O$_5$

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On the Cause of Conductivity Degradation in Sodium Strontium Silicate Ionic Conductor

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Here we present strong experimental evidence that elucidates the fundamental cause for the conductivity degradation observed in Na-SrSiO$_3$ ionic conductor.

Recent reports by Singh *et al.* on a new family of ionic conductors bearing a generic formula of Sr$_{1-x}$A$_x$MO$_{3-0.5x}$ (A = K or Na and M = Si or Ge) have sparked a heated debate on the nature of ionic conduction [1, 2]. Singh *et al.* originally postulated from high-temperature neutron diffraction data that the oxygen vacancies were created through Sr-site doping by Na and became mobile at a temperature >400°C, thus leading to oxide-ion conduction [3]. While the oxide-ion conduction mechanism in Sr$_{0.7}$K$_{0.3}$SiO$_{2.85}$ was partially supported by NMR and neutron diffraction data provided by Xu *et al.* [4], others instead argued that this material was essentially a mixture of a crystalline phase and amorphous phase [5-9]. A critical work by Bayliss *et al.* showed from an experimental and theoretical perspective that substitution of Na or K into Sr sites is an energetically unfavourable process [5, 6]. A subsequent oxygen isotope exchange and SIMS measurement on the Sr$_{0.8}$K$_{0.2}$Si$_{0.5}$Ge$_{0.5}$O$_{2.9}$ sample indicated a very low oxygen-ion diffusivity [5]. By using NMR, Evans *et al.* further identified that the crystalline and amorphous phases in the Sr$_{1-x}$Na$_x$SiO$_{3-0.5x}$ were SrSiO$_3$ and Na$_2$Si$_2$O$_5$, respectively. It was also found that the conductivity increased with the amount of amorphous phase Na$_2$Si$_2$O$_5$ present in the sample, which was also proportional to the Na-content [7]. Similarly, Tealdi *et al.* and Fernández-Palacios *et al.* confirmed that the amorphous Na$_2$Si$_2$O$_5$ phase was responsible for the ionic conduction [8, 9].

Among these mechanistic studies on ionic conduction, Bayliss *et al.* [6] first reported the conductivity degradation phenomenon in a Sr$_{1-x}$Na$_x$SiO$_{3-0.5x}$ (x=0.45) sample although the causes for the degradation were not specifically discussed in the paper. We have also observed a similar conductivity degradation behaviour of the

same composition in our recent independent study. Herein we present a strong evidence that unambiguously elucidates the fundamental cause for the degradation. The x=0.45 was particularly selected since it has been the most studied composition.
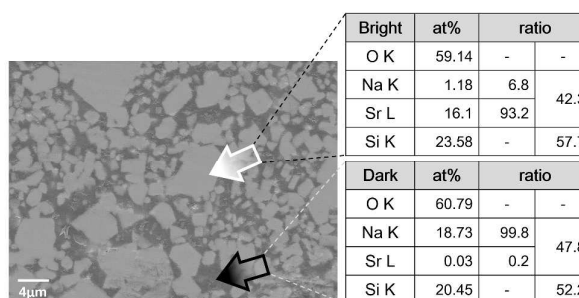

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O K	59.14	-	-
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Fig. 1 SEM image and EDX analysis of the x=0.45 sample

The two-phase nature of the x=0.45 sample as reported by other researchers is confirmed by Fig.1; there are clearly a liquid-like dark phase mixed with a crystalline-like bright phase in the SEM image. The EDX analysis indicates that the dark phase has an average chemical composition of Na:Si≈1:1 with a very low concentration of Sr, implying a likely Na$_2$Si$_2$O$_5$ composition. By contrast, the bright phase has a very low concentration of Na (~6.8 at%), but a high and similar concentration of Sr and Si, suggesting that SrSiO$_3$ with a minor doping by Na be the composition. While prepared as x=0.45, it is evident that the majority of Na did not enter Sr-sites as expected, but segregated out to form molten Na$_2$Si$_2$O$_5$ (T$_m$=848.8°C) at the synthesis temperature of 900°C. These findings are generally consistent with those reported by Bayliss, [5, 6], Ivana [7] and Tealdi [8].

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The Arrhenius plot of conductivity of the x=0.45 sample is shown in Fig.2 (a), which also includes those measured from the amorphous and crystalline $Na_2Si_2O_5$ samples for comparison. One distinctive feature is the curve bend-over for the x=0.45 and amorphous $Na_2Si_2O_5$ (AM-$Na_2Si_2O_5$) samples, although the bend-over occurs at different temperatures: 600°C for the x=0.45 sample and 500°C for the AM-$Na_2Si_2O_5$. By contrast, the crystalline $Na_2Si_2O_5$ (C-$Na_2Si_2O_5$) sample did not show any bend-over. The bend-over behaviour is later determined to originate from the time-dependence of conductivity of these two samples; the evidence is given in Fig.2 (b). Nevertheless, one important information gained from Fig.1 (a) is that the AM-$Na_2Si_2O_5$ has a higher intrinsic conductivity than the x=0.45 and C-$Na_2Si_2O_5$ samples and C-$Na_2Si_2O_5$ is an electrical insulator.
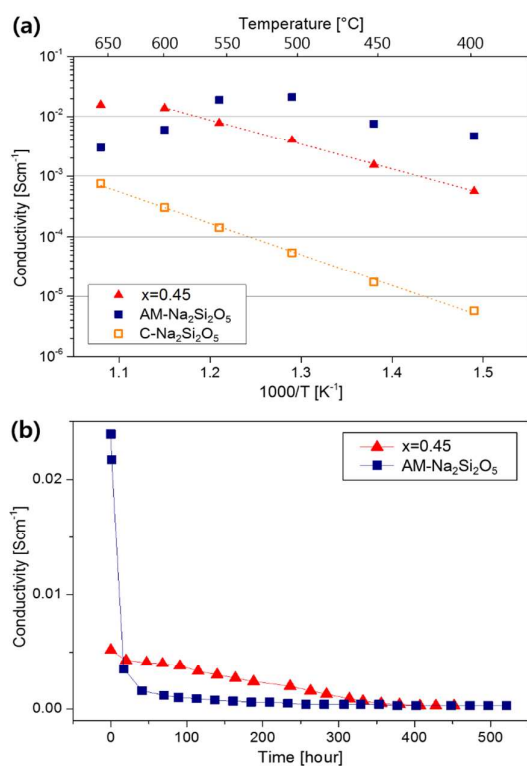

Fig. 2 (a) Arrhenius plot and (b) time-dependent plot of conductivity for the x=0.45, AM- and C- $Na_2Si_2O_5$ samples, respectively.

The time dependence of the conductivity for the x=0.45 and AM-$Na_2Si_2O_5$ samples measured at 500°C and in air is shown in Fig.2 (b). It is evident that the conductivity of the x=0.45 sample exhibits a steady-state degradation over a period of 450 hours. In contrast, the initially high conductivity of the AM-$Na_2Si_2O_5$ experiences a sharp drop in the first 24 hours, followed by a gradual stabilization to a value close to the x=0.45 sample. The resemblance in the final conductivity between the two samples signals that the original conducting and final less-conducting phases are similar in chemical

composition, *viz.* amorphous and crystalline $Na_2Si_2O_5$, respectively; the latter phase transition will be further discussed in the following.

One reasonable hypothesis that can explain the above results is that the original high-conductivity AM-$Na_2Si_2O_5$ gradually crystalizes into the low-conductivity C-$Na_2Si_2O_5$ at elevated temperatures. To prove this hypothesis, we conducted a high-temperature XRD study. Fig.3 shows the phase evolution of the x=0.45 and AM-$Na_2Si_2O_5$ samples. The crystalline phase in the x=0.45 sample can be indexed into a $SrSiO_3$ phase (PDF No. 36-0018, c2/c, space group (15)) as reported by Singh *et al.* [1-3]. More importantly, Fig.3 (a) indicates that the x=0.45 sample precipitates out a new phase RC-$Na_2Si_2O_5$, a polymorph of $Na_2Si_2O_5$ (PDF No. 19-1233), at 600°C. In comparison, the pure AM-$Na_2Si_2O_5$ also crystalizes into the RC-$Na_2Si_2O_5$ phase at lower 550°C, further proving that the crystallization of AM-$Na_2Si_2O_5$ is a thermodynamically favourable process; the RC-$Na_2Si_2O_5$ is a more stable phase at elevated temperatures.

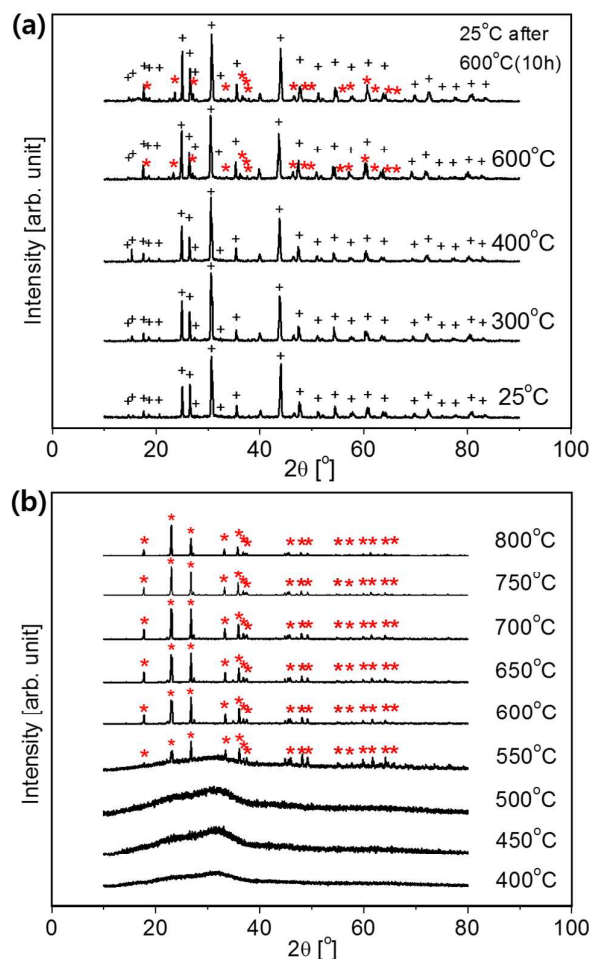**Fig. 3** Phase evolution of the x=0.45 (a) and AM-$Na_2Si_2O_5$ (b) samples with temperature. ("*" in red: RC-$Na_2Si_2O_5$, "+": $SrSiO_3$)

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The crystallization of amorphous $Na_2Si_2O_5$ is further supported by an independent DSC study. Fig.4 shows a DSC diagram measured from the AM-$Na_2Si_2O_5$ and x=0.45 samples. Ignoring the desorption-related peaks at T<400°C, exothermic heat flows corresponding to the crystallization start at ~ 490°C and peak at 550 and 650°C for the AM-$Na_2Si_2O_5$ and x=0.45 samples, respectively. These glass-to-ceramic transition temperatures match well those indicated by HT-XRD spectra shown in Fig.3, implying that the nature of these thermal peaks are related to the crystallization process. The disappearance of thermal peaks during cooling suggests that the crystallization process is irreversible and C-$Na_2Si_2O_5$ is a thermodynamically more stable phase. The smaller magnitude of heat flow for the x=0.45 sample (dotted line) is due to less amount of the AM-$Na_2Si_2O_5$ in the material.
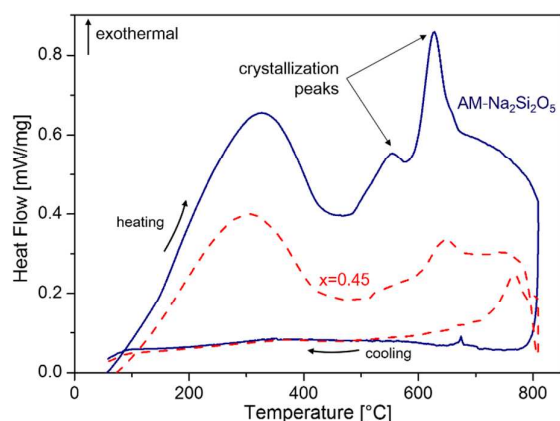

Fig. 4 DSC diagram measured from the AM-$Na_2Si_2O_5$ and x=0.45 samples in air

In conclusion, the present study has again confirmed that the $Sr_{1-x}Na_xSiO_{3-0.5x}$ system is a two-phase material consisting of a crystalline $SrSiO_3$ phase with minor Na-doping and amorphous $Na_2Si_2O_5$ phase. An independent conductivity study showed that the AM-$Na_2Si_2O_5$ is a highly conductive ionic conductor. While the nature of ionic conduction in terms of O^{2-} *vs* Na^+ has not been fully understood at the present time, this study explicitly shows that the AM-$Na_2Si_2O_5$ is a thermodynamically unstable phase at elevated temperatures, transforming into a crystalline form that is an electrical insulator. It is the amorphous-to-crystalline phase transformation in the highly conductive AM-$Na_2Si_2O_5$ at elevated temperatures that causes the conductivity degradation observed.

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