**Solid-State NMR Studies of a New Ionic Conductor: Na-doped SrSiO3**

Chien, P.-H. (Florida State U., Chemistry & Biochemistry); Jee, Y. (U. of South Carolina, Mechanical Engineering); Hung, I., Gan, Z. (NHMFL); Huang, K. (U. of South Carolina, Mechanical Engineering); Hu, Y.-Y. (Florida State U., Chemistry & Biochemistry)

**Introduction**

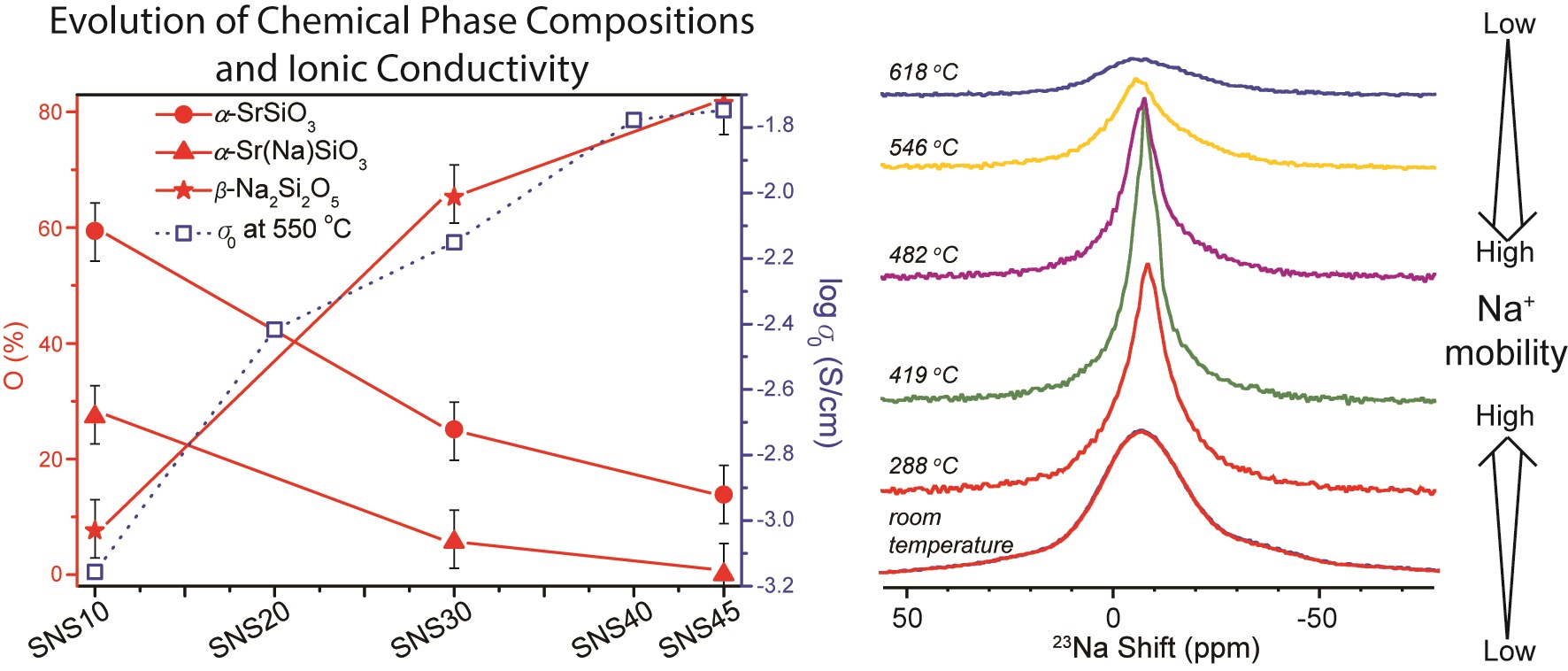
Solid-state electrolytes play a pivotal role in solid-oxide fuel cells (SOFCs), batteries, and ion exchange membranes. Recently, a novel ionic conductor, Sr1–xNaxSiO3–0.5x (SNS), has been proposed as a suitable solid-state oxide-ion electrolyte for SOFCs.1 The ionic conductivity of SNS with an apparent composition of Sr0.55Na0.45SiO2.78 (x=0.45, SNS45) was found to be the highest among all chemically stable solid oxide-ion electrolytes 1 at intermediate temperatures (σ0 ≈ 0.01 S/cm at 500 oC). The origin of this high ionic conductivity in SNS has been the topic of major debates since the birth of SNS in 2013. In this abstract, high-resolution and high-temperature solid-state 29Si, 23Na, and 17O NMR studies of SNS samples reveal that SNS is a Na-ion conductor rather than an oxide conductor as proposed before.

**Experimental**

29Si NMR spectra were acquired on a Bruker DRX-300 spectrometer at a Larmor frequency of 59.6 MHz using a Bruker 4-mm MAS probe spinning at 10 kHz. 23Na and 17O NMR spectra were acquired on a Bruker DRX-830 spectrometer with a home-built 3.2-mm low-*γ* and high-sensitivity MAS probe spinning at 18 kHz at the Larmor frequency of 219.6 MHz for 23Na and 112.6 MHz for 17O. A rotor-synchronized spin-echo pulse sequence was employed for all experiments. The MQMAS spectrum of 17O-enriched SNS45 was collected using a shifted-echo sequence using a home-built 4-mm single channel probe with a spinning speed of 10 kHz.

**Results and Discussion**

29Si, 23Na, and 17O NMR showed that the amount of the *α*-SrSiO3 phase decreased gradually as Na-doping level was increased. The expected phase with Na-doped into the *α*-SrSiO3 structure, i.e., Sr(Na)SiO3, peaked at 10% Na doping, but vanished gradually with more Na doped. Also, *β*-Na2Si2O5 became the dominated phase with > 20% Na content. Sr(Na)SiO3 and *β*-Na2Si2O5 were spatially separated and large *C*Qs shown in 23Na and 17O NMR indicate disordered structural properties of the *β*-Na2Si2O5 phase. Structural fusion of silicate framework was suggested by gradually decreased ratio of non-bridging oxygen to bridging oxygen observed in 17O NMR. Most importantly, variable high-temperature 23Na and 17O MAS NMR show changes in 23Na ion dynamics with temperature but no significant motions were observed of oxide ions.



**Figure 1** Phase evolutions correlated with ionic conductivity and ion dynamics.

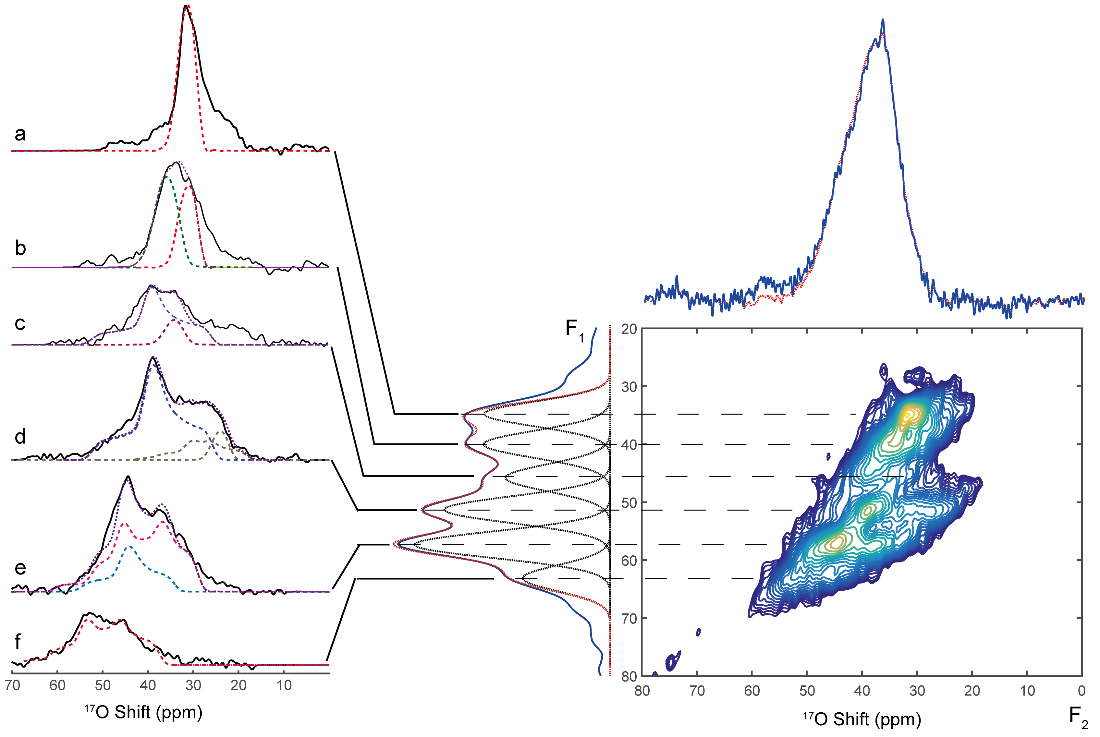


Figure 2 MQMAS 17O NMR of Sr0.55Na0.45SiO2.78

**Conclusions**

Phase evolutions and ion dynamics of SNS samples with varying Na doping contents have been investigated using advanced solid-state NMR techniques. 29Si, 23Na, and 17O NMR spectra indicate amorphous *β*-Na2Si2O5 phase dominates in SNS after Na-doping level reaches 20% and beyond. Variable high-temperature NMR results clearly showed that Na ion motions changed as the temperature increased to about 400oC as seen by narrowed spectral linewidth whereas no oxide ion motions were shown.

**Acknowledgements**

Hu and Chien acknowledge support from the National Science Foundation under Grant No. 1508404. Huang acknowledges ARPA-E, U.S. DOE for support under Award number DE-AR0000492. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida.

**References**

[1] Singh, P., *et al*., J. Am. Chem. Soc., **135**, 10149-10154 (2013).