

Solid-State NMR Studies of Oxide Ion Conducting Ceramics for Enhanced Fuel Cell Performance

Investigators

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Abstract

Over the past year, we have made considerable progress in the overall goal of this project, which is to improve our understanding of the local atomic structure and dynamics of oxide ion conducting ceramics of potential use in solid oxide fuel cells. Our primary experimental tools continue to be solid-state NMR spectroscopy and impedance measurements. We completed a study that developed a first empirical correlation between NMR chemical shifts for ^{45}Sc and local structure in oxide materials, and applied this to estimate the mean coordination number of Sc in scandium-doped zirconia, which is the best known conductor in this class of materials. Considerable ordering of oxygen vacancies is implied by our results, which have been published in *Chemistry of Materials*. In a second major effort, we synthesized a variety of other zirconia ceramics, doped with other cations and exchanged with ^{17}O to allow NMR spectroscopy on this key nuclide. The ^{17}O proved useful at constraining the extent of ordering at room temperature, and *in-situ*, high temperature, high-resolution NMR provided direct information on the average rates of exchange of oxide ions among different sites in the material. We compared these results to complex impedance spectroscopy to better understand what components of the dynamics are sampled by the two methods; this work has been submitted for publication in *Solid State Ionics*. We have also made some preliminary studies of ^{17}O and ^{89}Y NMR of yttria-doped bismuth oxide, also a well-known ionic conductor. Finally, we have nearly completed a major effort on yttrium-doped cerium oxide, again using both nuclides and spectra collected both at ambient and high temperature. In this system, we can, for the first time, quantify oxide sites with varying numbers of Ce and Y neighbors, and quantify the number of Y cations with zero, one, and two oxygen vacancy neighbors, providing a remarkably detailed picture of the local structure of this potentially important material.

Introduction

The purpose of this project is to develop new understanding of the atomic-scale structure and dynamics of oxide ion conducting ceramic materials that are at the heart of solid oxide fuel cells ("SOFC's"), with the aim of more effectively optimizing their performance, lowering operating temperatures, size, and costs. Given the high efficiencies of fuel cells and their likely central role in future hydrogen-based fuel systems, SOFC's may eventually play an important part in the GCEP mission of reducing total CO_2 emissions to the atmosphere.

An especially powerful experimental tool, which has received only limited application to such materials, is high-resolution, solid-state Nuclear Magnetic Resonance spectroscopy (NMR). We are using NMR to characterize the structure of oxide ion

conductors, in particular the nature of the order or disorder among dopant cations, which is difficult or impossible to obtain by other methods. We are studying the effects of composition, temperature, and processing conditions on this structure, including new thin film materials being developed in a related program by the group of Professor Fritz Prinz. We are also using the unique capability of NMR to detect the dynamics of ion motion with *in situ*, high temperature experiments. We have related both types of results to state-of-the-art electrical conductivity measurements, also in collaboration with the Prinz group. The combination of these approaches should lead to more fundamental understanding of the mechanism of ionic conduction in SOFC materials and hence provide new tools for engineering their properties.

This report summarizes the background and motivation for this project as presented in our previous reports, and describes the considerable progress made in the last 12 months of the project.

Background

Fuel cells, which directly convert the energy released by fuel oxidation to electricity, have been studied for decades as power sources that are cleaner and more efficient than conventional combustion-based systems. In most designs, the primary reaction involved is the oxidation of hydrogen by oxygen. In systems under development for use in the existing fossil fuel-based energy systems, the H₂ reactant is generally produced by “reforming” of gaseous hydrocarbons. In the short term, therefore, growing use of high-efficiency fuel cell-containing systems will contribute to net reductions in the rate of CO₂ emissions to the atmosphere primarily by lowering the amount of hydrocarbons that must be oxidized per unit of energy produced. In the longer term, however, movement towards a hydrogen-based fuel economy will be greatly facilitated by advanced fuel cell technology, which is ideally suited to the direct utilization of H₂.

Most commonly used types of fuel cells are designed around gas-impermeable solid barriers that separate the H₂-rich fuel gas from the O₂-rich oxidant, but which allow rapid transfer of either H⁺ or O²⁻ by ionic conduction. The latter process uses oxide anionic conducting electrolytes, most typically yttrium-stabilized zirconia or “YSZ”. The potential efficiencies of SOFC’s, especially when combined with cogeneration systems to fully utilize the byproduct heat, their modularity and unit size flexibility, and their environmental advantages (low SO₂, NO_x, and particulate emissions), have lead to major government and industry research and development efforts and the beginnings of installation of multi-megawatt commercial systems in distributed generation applications.

Typical SOFC’s must be operated at the relatively high temperatures (600 to 1000 °C) where electrolyte conductivity is sufficient to reduce resistive energy losses to acceptable values. Although high temperatures have the advantage of rapid redox reaction kinetics, and the ability to reform hydrocarbon fuels internally, they may limit the use of SOFC’s in applications that are critical to restructuring global energy systems, in particular to powering automobiles. (Note however that existing SOFC technologies are already being tested for powering long-range buses and trucks.) Other types of fuel cells that operate at

lower temperatures have thus been developed, for example those involving proton-conducting electrolyte membranes (“PEM” cells). Further advances in SOFC’s for some such applications will depend in part on increasing oxide membrane conductivity, by designing new materials and/or by developing new methods of fabricating much thinner electrolyte layers and integrating them into robust, miniaturizable fuel cell systems with fast warm-up times. The latter was one of the goals of another recent GCEP project, lead by Professor Prinz.

The general principles of oxide ion conduction in ceramics have long been understood: O^{2-} ions diffuse through the crystal lattice at a rate that depends primarily on the concentration, distribution, and mobility of anion vacancies in the structure. Vacancies are most commonly introduced by creating solid solutions with cations (“aliovalent”) having formal valences that are reduced from that of the host phase. A lack of information about atomic-scale structure and dynamics of these materials has hindered full development of predictive models of their properties. In particular, most oxide conductors have complex but poorly-characterized degrees of cation and/or vacancy disorder that may vary with composition, temperature, and even the partial pressure of O_2 . The extent and type of ordering can have major effects on conductivity. However, commonly-applied analytical techniques have been of limited utility in directly characterizing and quantifying such disorder. X-ray and neutron diffraction, for example, reveal the structure averaged over long range, and only indirectly characterize the energetically often more significant short-range order/disorder.

Methods of observing atomic-scale mechanisms of dynamics (the hopping from site to site that controls diffusivity and conductivity) are even more limited, and for the most part rely on modeling of bulk property data collected over ranges of temperature, composition, and external conditions. Information about preferred structural pathways for ion migration, about frequencies of ion exchange among locally different types of sites, and about mobility of populations of ions in energetically distinct sites can in general thus be only inferred. Over the last twenty years, solid state nuclear magnetic resonance (NMR) has developed into a powerful new method for elucidating the short-range structure of disordered oxide materials [1]. Even more uniquely, NMR can sometimes directly sample ion dynamics at the microsecond to second time scales required to characterize diffusion in disordered crystalline systems [2,3,4].

NMR provides information primarily about local structure around isotopes of specific elements in crystalline, amorphous, or liquid materials. Spectra are thus primarily controlled by the number and spatial distribution of first and second atomic neighbors. In many cases it is this short- to intermediate-range structure that has the greatest energetic importance in controlling disorder and ion mobility. Among spectroscopic methods, NMR is unusual in that the strength of the observed signal in a properly designed experiment is directly proportional to the concentration of atoms in a given structural environment, providing an often unique approach to quantitatively measuring site occupancies and hence the ordering state.

The common (and structurally predominant) element in all of these materials is of course oxygen. However, the only NMR-active stable isotope of oxygen, ^{17}O , has a natural abundance of only 0.035%. Isotopic enrichment by up to >1,000 times is usually needed to observe high-quality spectra. Such enrichment is not inexpensive, but is feasible. Because of the great potential of this approach for obtaining structural and dynamical information on a wide range of oxide ceramics, we have emphasized it in our research. A few studies of this kind on oxide ion conductors have been made using low-resolution, high temperature ^{17}O NMR of yttria-doped ceria [5], zirconia [6, 7] and barium indate [8]. Recent breakthroughs in high-resolution ^{17}O NMR at elevated temperatures on materials such as bismuth vanadates, by the group of Clare Grey at SUNY Stonybrook, have demonstrated that this approach can be very revealing of the rates and pathways for oxide ion diffusion [9].

Several important dopant cations in SOFC's also have abundant isotopes that can also yield NMR spectra that potentially provide important additional constraints on both structure and dynamics, in particular ^{45}Sc and ^{89}Y . Only a few studies of these nuclides in any oxide material have been reported, and these were all done at ambient temperature [10-19].

Experimental approaches that we are taking are described below, so that they may be illustrated by our recent results. All NMR spectra shown use the "magic angle spinning" (MAS) technique, in which samples are spun at very high rates (here, 5 to 20 kHz) to eliminate some types of line broadening that result from orientation-dependent interactions. Data were collected at external fields of 9.4, 14.1, and 18.8 Tesla in labs at Stanford. The first two are maintained by the P.I., the third is part of the Stanford Magnetic Resonance Laboratory, run by Professor J. Puglisi of the Medical School. We have acquired a specially-built, high temperature MAS NMR probe capable of operating to over 700 °C (Doty Scientific, Inc.). Only a handful of such instruments are in use, worldwide. Our group pioneered in the application of an early version of this technology to ionically conductive oxides [20].

Results

Materials synthesis

As described in more detail in previous reports and publications, we have synthesized most of our samples in our own laboratory, using modified "Pechini" (aqueous phase/gel) methods as well as high temperature sintering of oxide powders. We characterized all samples by powder x-ray diffraction to determine phase purity and the long-range average crystal structure and symmetry. Samples prepared and studied to date include a variety of "stabilized" zirconias, doped with ranges in concentration of Sc_2O_3 , Y_2O_3 , CaO , and MgO , and combinations of these oxides. Because of the utility of the ^{45}Sc nuclide in NMR studies, and the observation that Sc-doped oxides often have excellent oxide ion conductivities, we have synthesized Sc-doped versions of fluorite-structured $\text{Y}_2\text{Zr}_2\text{O}_7$, the related pyrochlore-structured $\text{Y}_2\text{Ti}_2\text{O}_7$, and several Sc-doped variations of the perovskite phase CaZrO_3 . The latter is of interest as a possible protonic conductor when vacancies are associated with H^+ ions.

For study both by ^{17}O and ^{89}Y NMR, we have synthesized and characterized isotopically-enriched samples of Y-doped CeO_2 [21, 22], of widespread interest as a possible SOFC material, as well as Y-doped Bi_2O_3 [23-25]. For ^{17}O NMR, we have developed methods for ^{17}O enrichment from a gas source of the isotope. We have also synthesized a number of ordered, crystalline model compounds needed to help relate observed NMR spectra to local structural parameters such as cation coordination number, particularly a series of Sc-containing oxide phases to better interpret ^{45}Sc spectra.

Sc-45 NMR, Sc-stabilized ZrO_2

100% of natural Sc is ^{45}Sc , an isotope with nuclear spin = 7/2 and a conveniently high NMR resonant (Larmor) frequency, similar to those of other commonly studied nuclides such as ^{13}C and ^{27}Al . However, only a few solid-state NMR studies of this nuclide have been published [11, 14, 18, 19]. To learn about technologically interesting scandium-doped zirconias (which have the best conductivities in this class of materials), we thus developed optimized experimental methods for this nuclide, collected data for a number of ordered “model compounds” (Figure 1) and derived the first empirical correlations between local structure and NMR observables for ^{45}Sc (Figure 3). It is clear that this approach holds real promise: there is a well-defined correlation between the number of oxygens coordinating the Sc cation and the isotropic chemical shift.

^{45}Sc NMR peaks for SSZ samples lie between the values for six- and eight-coordination, suggesting a mean Sc coordination of about seven (Figures 2, 3). This is surprisingly low, suggesting some ordering of oxygen vacancies. These results were recently published in *Chemistry of Materials*. Our high temperature NMR data (to 400 °C) also indicate a slight increase in the average coordination number of the Sc as oxygen vacancies become more randomly distributed at higher temperature. We note that these

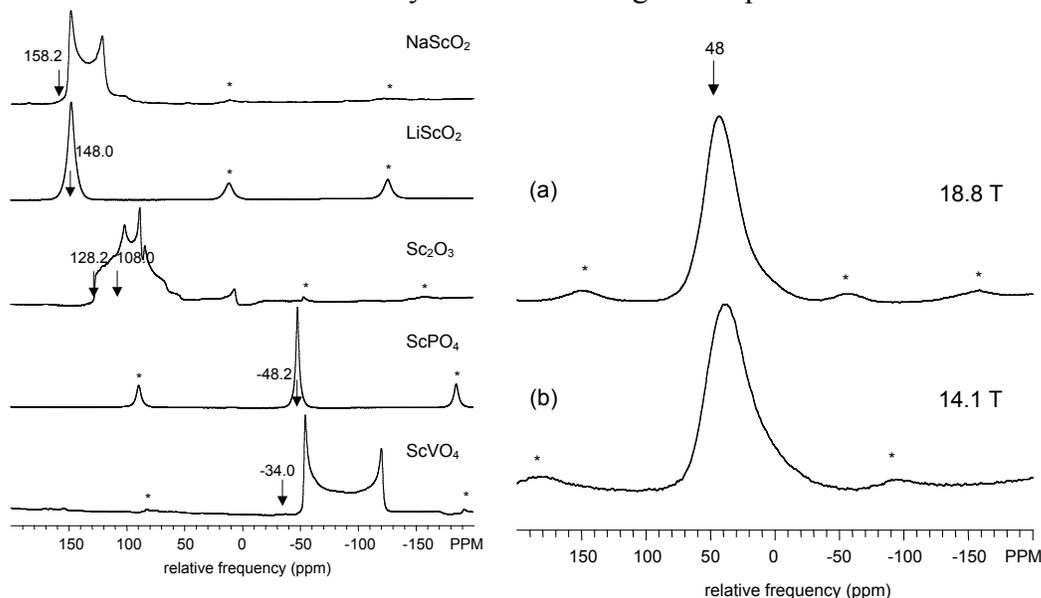


Figure 1. (left) ^{45}Sc MAS NMR spectra at 14.1 Tesla of scandium compounds as labeled. Arrows show isotropic chemical shifts.

Figure 2. (right) ^{45}Sc MAS NMR spectra of 8% Y_2O_3 stabilized zirconia at fields as labeled. “*” show spinning sidebands.

structural changes apparently are rapidly reversible on cooling, highlighting the importance of these unique, *in situ* spectroscopic studies.

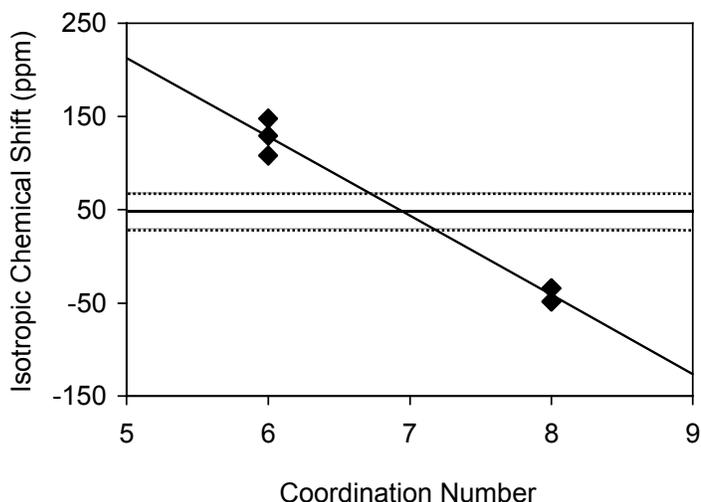


Figure 3. Isotropic chemical shifts for ^{45}Sc in model compounds (diamonds), vs. observed values for Sc-doped zirconia (horizontal lines).

Oxygen site exchange in zirconia

In our previous GCEP report and in a manuscript recently submitted for publication in *Solid State Ionics*, we describe in detail our results from ambient temperature and high-temperature ^{17}O MAS NMR studies of zirconias doped with Sc, Y, Ca and Mg, in both monoclinic and cubic phases. There we describe the progress made in using this approach to characterizing the ordering state and the oxide ion exchange dynamics, as functions of the charge and size of the dopant cations. The high T MAS NMR is made possible by the acquisition of a specially-built NMR probe from Doty Scientific, Inc., capable of remarkable performance to temperatures over 700 °C.

Part of this effort involved simulation of the high temperature spectra for a Ca-stabilized zirconia, which shows partial resolution of the NMR signals for oxide ion sites with varying neighbors of Ca and Zr neighbors (Figure 4). While this modeling does not attempt to reproduce the real, low temperature peak widths caused by local disorder in bond distances, it does allow us to estimate the mean frequencies of exchange of the oxide ions among the various sites. These frequencies can then be combined with a simple random-walk model to predict the ionic conductivity (Figure 5). When compared with the conductivities measured by Dr. Hong Huang in the group of Professor Prinz, there is good agreement in the mid-temperature range (near to 400 °C), but diverge at higher and lower temperatures because of a lower estimated mean activation energy. It is apparent that the NMR is not sampling the oxide ion hopping in exactly the same way as do measurements of through-going diffusion as recorded by conductivity. Our discussions of these differences have led to new considerations about the symmetry of “forward” vs. “backward” ionic jumps that may suggest new experimental and theoretical directions.

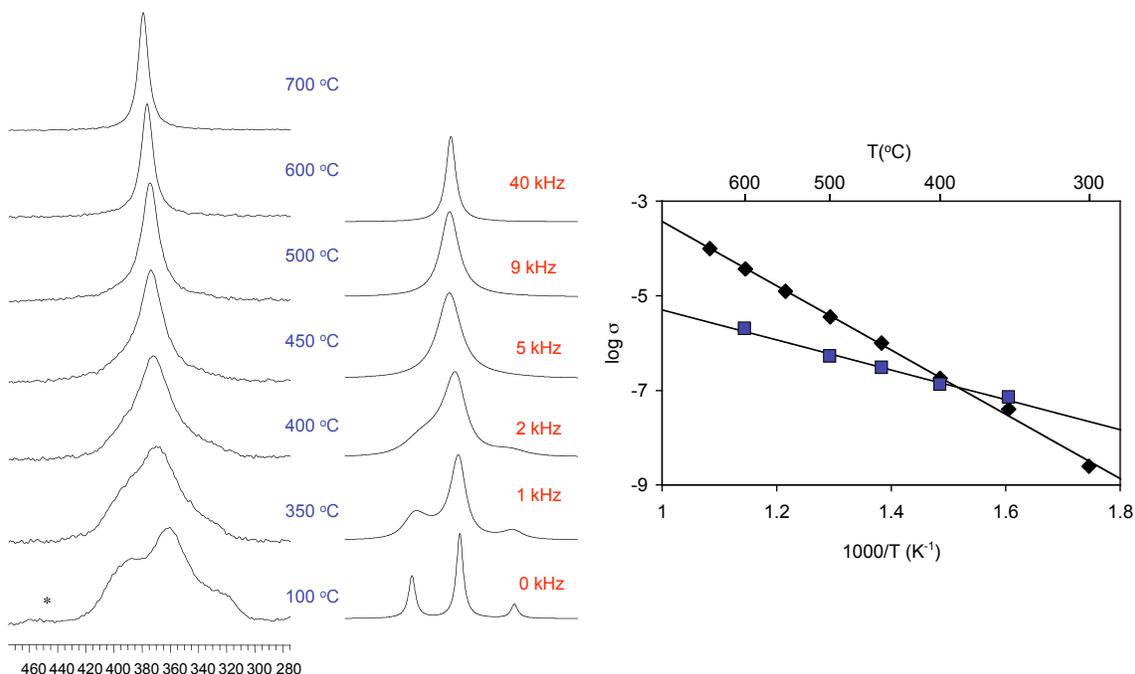


Figure 4. (left) High-temperature ^{17}O MAS NMR spectra of 15% CaO-doped zirconia, with simulations of peak shapes. Temperatures are shown in blue, exchange frequencies in red.

Figure 5. (right) Conductivities estimated from NMR exchange frequencies (black diamonds) vs. those measured by impedance spectroscopy (blue squares).

Yttrium-doped ceria

Yttrium-doped cerium oxide, like stabilized zirconias, has a cubic, fluorite structure and excellent oxide ion conductivity [21, 22]. Although reduction of the Ce^{4+} by H_2 may be a problem in high-T SOFC's, ceria-based materials may be important as lower operating temperatures are obtained. Y-doped ceria has been the subject of several ^{17}O NMR studies, including in-situ high T work, but all with low spectral resolution. Our first results using high-resolution ^{17}O NMR are thus quite dramatic. Pure CeO_2 has the very narrow, single peak expected for the cubic phase. As more Y_2O_3 is added, at least two other peaks appear at lower chemical shifts, due to the development of oxygen sites with one or two Y neighbors, the remainder being Ce.

^{89}Y is another potentially favorable NMR nuclide for studies of oxides [12-14], but only occasionally has this method been successfully applied to Y-doped oxide ion conductors, including YSZ [15-17]. Because its nuclear spin is 1/2 and it has a wide chemical shift range, ^{89}Y NMR studies can potentially accurately quantify the proportions of Y^{3+} with varying oxygen coordination numbers in oxides, with in turn is closely linked to the extent of disorder in the distribution of cations and of oxygen vacancies. Results for this nuclide on a series of yttria-doped ceria (YDC) are thus also quite striking: peaks for eight-coordinated Y (the ideal value in a vacancy-free structure), and for seven- and six-coordinated Y are clearly resolved. Integration of peak areas readily determines the proportions of each. Both the ^{17}O and ^{89}Y NMR indicate significant ordering of vacancies, as Y coordinations are considerably lower than for a random distribution.

In-situ, high temperature ^{17}O MAS NMR of a YDC sample clearly shows the initial broadening and then narrowing expected as oxide ions begin to move rapidly through the lattice; this is apparent even at temperatures below 200 °C where we are able to use a conventional NMR probe with much higher sample spinning rate than can be obtained with the “high T” MAS probe (20 vs. 5 kHz). These results are currently being analyzed and written up for publication.

Yttrium-doped bismuth oxide

Yttria-doped bismuth oxide (Bi_2O_3 , YDB) is another material of considerable potential interest for SOFC's, with a demonstrated high oxide ion conductivity [23-25]. Although volatility and Bi^{3+} reduction can be a problem at high temperatures as commonly used in SOFC's, these materials may become more important in thin film systems that can operate at lower T. The long-range average structure of YDB is known to have the cubic fluorite geometry, but with one vacancy for every two cations, which are all trivalent. Unlike in YSZ, the trivalent “stabilizing” cation in YDB does not enhance conductivity by increasing the vacancy content; its major role is to maintain the stability of the disordered, high T cubic phase at lower temperatures, an effect common with YSZ.

We have synthesized a number of different Y-doped bismuth oxides and enriched them in ^{17}O . The previous GCEP report describes the marked effects of composition on these spectra; high temperature results again reveal the beginning of motional narrowing as oxide ions begin to mobilize. (These data were collected with a “conventional” probe to 240 °C only, as the spinning rate of the “high T” probe is insufficient to yield good results for these relatively broad spectra.)

As for the Y-doped ceria, the ^{89}Y spectra for a range of compositions of YDB are especially informative. Samples with 15 to 35 % Y_2O_3 have single peaks all centered at about 270 ppm, which is close to the peak identified as six-coordinated Y in Y-doped ceria and in previous reports on Y_2O_3 [12, 16]. This indicates that most of the Y is six-coordinated, indicating that vacancies are paired adjacent to the Y^{3+} cations.

Progress

We can not yet predict in detail the specific consequences of this project for reduction in global CO_2 emissions. However, its most important overall goal is to provide the mechanistic understanding of fundamental processes in fuel cells that is needed to optimize their performance sufficiently to allow them to take their role as key elements in future hydrogen-based energy systems. If such systems do indeed become a major part of a global, reduced- CO_2 energy economy as is being explored by GCEP and many other research efforts, then the impact of our studies may be quite significant.

Future Plans

In the remaining months of this project, we plan to complete a number of high temperature NMR studies of several of the phases described above, particularly the YDC, in order to acquire a more complete picture of cationic and anionic mobility. We are also working on experiments to determine temperature effects on the ordering state of these

phases, which will be important to understand the effects of synthesis procedures, and of annealing during actual use in SOFC's, which can have dramatic effects on conductivities. We also plan to complete the writing up of our results for journal publication.

Publications, conference presentations, and reports

1. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Scandium coordination in solid oxides and stabilized zirconia: ^{45}Sc NMR. *Chem. Mat.* **18**, 3855-3859 (2006)
2. Hsieh, C.-H. Solid-state NMR and x-ray studies of local coordination environment in the $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ system. *M.S. Report, Dept. of Materials Science and Engineering, Stanford University.*
3. Kim, N., Hsieh, C.-H., Huang, H., Prinz, F.B. & Stebbins, J.F. High temperature ^{17}O MAS NMR study of calcia, magnesia, scandia and yttria stabilized zirconia. *Sol. State Ionics*, submitted
4. Kim, N. & Stebbins, J.F. Cation coordination and vacancy ordering in yttrium-doped ceria: ^{17}O and ^{89}Y NMR, in preparation
5. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Studies of local structures and dynamics of stabilized zirconia solid electrolytes using solid state NMR (abstract). *Am. Ceram. Soc., 30th Int. Conf. Adv. Ceram. Mat.* (2006)
6. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Local structure and motion in stabilized zirconia: ^{45}Sc and ^{17}O NMR studies (abstract). *47th Exp. NMR Conf.* (2006)
7. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Local structure and motion in fluorite oxide ionic conductors: high temperature ^{17}O MAS NMR studies (abstract). *Mat. Res. Soc. Fall Mtg.* (2006)
8. Huang, H., Hsieh, C.-H., Kim, N., Stebbins, J.F. & Prinz, F. Structure, local environment, and ionic conduction in scandia stabilized zirconia (abstract). *16th Int. Conf. Sol. St. Ionics* (2007)

References

1. MacKenzie, K. J. D. & Smith, M.E. *Multinuclear Solid-State NMR of Inorganic Materials* (Pergamon, New York, 2002).
2. Stebbins, J.F., Magnesium site exchange in forsterite: a direct measurement by high temperature ^{25}Mg nuclear magnetic resonance spectroscopy, *Am. Mineral.*, **81**, 1315-1320 (1997)
3. Stebbins, J.F., Dynamics in Ceramics, *Science*, **297**, 1285-1286 (2002)
4. Xu, Z. & Stebbins, J.F. Cation dynamics and diffusion in lithium orthosilicate: two-dimensional lithium-6 NMR., *Science*, **270**, 1332-1334 (1995)
5. Fuda, K., Kishio, K., Yamauchi, S. & Fueki, K. Study of vacancy motion in Y_2O_3 - doped CeO_2 by ^{17}O NMR technique, *Phys. Chem. Solids*, **10**, 1141-1146 (1985)
6. Adler, S.B., Michaels, J.N. & Reimer, J.A. A compact, high temperature nuclear magnetic resonance probe for use in a narrow-bore superconducting magnet, *Rev. Sci. Inst.*, **61**, 3368-3371 (1990)
7. Viehhaus, T., Bolse, T. & Müller, K. Oxygen ion dynamics in yttria-stabilized zirconia as evaluated by solid-state ^{17}O NMR spectroscopy. *Sol. St. Ionics*, **177**, 3063-3068 (2006)
8. Adler, S.B., Reimer, J.A., Baltisberger, J. & Werner, U. Chemical structure and oxygen dynamics in $\text{Ba}_2\text{In}_2\text{O}_5$, *J. Am. Chem. Soc.*, **116**, 675-681 (1994)
9. Kim, N. & Grey, C.P. Probing oxygen motion in disordered anionic conductors with ^{17}O and ^{55}V NMR spectroscopy, *Science*, **297**, 1317-1320 (2002)
10. Pike, K.J., Malde, R.P., Ashbrook, S.E., McManus, J. & Wimperis, S. Multiple-quantum MAS NMR of quadrupolar nuclei, Do five-, seven-, and nine-quantum experiments yield higher resolution than the three-quantum experiment, *Sol. St. NMR*, **16**, 203-215 (2000)
11. Tien, C., Charnaya, E.V., Sun, S.Y., Wu, R.R., Ivanov, S.N. & Khananov, E.N. ^{27}Al and ^{45}Sc NMR studies of the $\text{Y}_3\text{Sc}_x\text{Al}_{5-x}\text{O}_{12}$ mixed garnets, *Phys. Stat. Sol. (b)*, **233**, 222-229 (2002)
12. Florian, P., Massiot, D., Humbert, G. & Coutures, J.P. Etudes par RMN de ^{17}O et ^{89}Y des formes C et B de l'oxyde d'yttrium Y_2O_3 , *C. R. Acad. Sci. Paris IIb*, **320**, 99-104 (1995)
13. Grey, C.P., Smith, M.E., Cheetham, A.K., Dobson, R. & Dupree, R. Y-89 MAS NMR study of rare-earth pyrochlores: paramagnetic shifts in the solid state, *J. Am. Chem. Soc.*, **112**, 4670-4680 (1990)

14. Thompson, A.R. & Oldfield, E. Solid-state scandium-45, yttrium-89, and lanthanum-139 nuclear magnetic resonance spectroscopy, *J. Am. Chem. Soc., Chem. Comm.*, **1987**, 27-29 (1987)
15. Kawata, K., Maekawa, H., Nemoto, T. & Yamamura, T. Local structure analysis of YSZ by Y-89 MAS-NMR. *Sol. St. Ionics*, **177**, 1687-1690 (2006)
16. Battle, P.D., Montez, B. & Oldfield, E. The characterization of anion-vacancy ordering in the oxide ion conductor $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x$ by ^{89}Y N.M.R. spectroscopy. *J. Chem. Soc., Chem. Commun.*, **1988**, 584-585 (1988)
17. Ashbrook, S.E., Whittle, K.R., Lumpkin, G.R. & Farnan, I. ^{89}Y Magic-angle spinning NMR of $\text{Y}_2\text{Ti}_{2-x}\text{Sn}_x\text{O}_7$ pyrochlores. *J. Chem. Phys. B*, **110**, 10358-10364 (2006)
18. Riou, D., Fayon, F. & Massiot, D. Hydrothermal synthesis, structure determination, and solid state NMR study of the first organically templated scandium phosphate. *Chem. Mat.*, **14**, 2416-2420 (2002)
19. Rossini, A.J. & Schurko, R.W. Experimental and theoretical studies of ^{45}Sc NMR interactions in solids. *J. Am. Chem. Soc.* **128**, 10391-10402 (2006)
20. Stebbins, J.F., Farnan, I., Williams, E.H. & Roux, J. Magic angle spinning NMR observation of sodium site exchange in nepheline at 500°C . *Phys. Chem. Minerals*, **16**, 763-766 (1989)
21. Mogensen, M., Sammes, N.M. & Toppsett, G.A. Physical, chemical and electrochemical properties of pure and doped ceria. *Sol. St. Ionics*, **12**, 63-94 (2000)
22. Wang, D.Y., Park, D.S., Griffith, J. & Nowick, A.S. Oxygen-ion conductivity and defect interactions in yttria-doped ceria. *Sol. St. Ionics*, **2**, 95-105 (1981)
23. Shuk, P., Wiemhöfer, H.-D., Guth, U. & Göpel, W. Oxide ion conducting ceramics based on Bi_2O_3 . *Sol. St. Ionics*, **89**, 179-196 (1996)
24. Takehashi, T., Iwahara, H. & Arao, T. High oxide ion conduction in sintered oxides of the system $\text{Bi}_2\text{O}_3\text{-Y}_2\text{O}_3$. *J. Appl. Electrochem.* **5**, 187-195 (1975)
25. Jaiswal, A. & Wachsman, E.D. Direct current bias studies on $(\text{Bi}_2\text{O}_3)_{0.8}(\text{Er}_2\text{O}_3)_{0.2}$ and $\text{Ag-}(\text{Bi}_2\text{O}_3)_{0.8}(\text{Er}_2\text{O}_3)_{0.2}$ cermet electrode. *Sol. St. Ionics*, **177**, 677-685 (2006)

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