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Scandium Coordination in Solid Oxides and Stabilized Zirconia: ^{45}Sc NMR

Namjun Kim,*[,†] Cheng-Han Hsieh,[‡] and Jonathan F. Stebbins[†,‡]

Departments of Geological and Environmental Sciences and Materials Science and Engineering,
Stanford University, Stanford, California 94305

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^{45}Sc NMR isotropic chemical shifts and quadrupole coupling constants of several scandium-containing solid oxides have been measured. Both parameters prove to be sensitive to local structure. In particular, in these materials the ^{45}Sc isotropic chemical shift appears to be dominated by the first neighbor coordination environment, i.e., the coordination number. The difference in the isotropic shifts between six-coordinated and eight-coordinated scandium is more than 150 ppm, suggesting that this parameter may be especially useful in studying the scandium coordination in oxide materials, disordered solids in particular. Quadrupole coupling constants are sensitive to the nature of the second coordination cation, although many other structural details may play a role. The chemical shift correlation was applied to scandia-stabilized zirconia, $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$, and the mean coordination number obtained appears to be close to seven, which suggests the possibility of two scandium cations pairing with one vacancy.

Introduction

In oxides, scandium commonly forms a trivalent cation with radius and chemical properties similar to Y^{3+} and the rare-earth elements. Due to its rarity and difficulties in separation, and thus high cost, the chemical and physical properties of scandium-containing compounds are not well characterized.[1−3] Therefore, scandium-containing oxides have not been extensively used for materials applications despite their potential. However, since many materials are now synthesized and used in nanocrystalline and thin film forms, high-cost elements such as scandium may become more widely applied.

One notable example is scandia-stabilized zirconia (SSZ).[4−7] Due to their high oxide ionic conductivity and thermal stability, cubic stabilized zirconias have long been used as the solid electrolyte in devices such as solid oxide fuel cells and oxygen sensors. However, high operating temperatures, typically 800−1000 °C, are still required to obtain usefully high conductivity. Many efforts have been made to lower the operating temperature by developing new ways of fabricating materials[8,9] or new types of materials.[10,11] Here, an atomic-level understanding of conductivity is often essential. The high-temperature cubic phase of zirconia can be stabilized at room temperature by doping aliovalent cations such as Y^{3+}, Sc^{3+}, Ca^{2+}, etc.[12,13] Doping not only stabilizes the cubic phase, but also increases the number of oxygen vacancies, which results in higher conductivity. The latter depends on the dopant cations and their concentration as well as synthesis conditions and thermal history. Scandia-stabilized zirconia shows the highest conductivity among these phases, up to 2 orders of magnitude higher than commercially used yttria-stabilized zirconia (YSZ).[13−15]

Studies of scandia-stabilized zirconias have been based mainly on conductivity and structures from X-ray and neutron diffraction. In many cases, however, information only on average long-range structure and bulk properties has been reported. More detailed information, such as local coordination environments around dopant cation and oxygen ions or an atomic scale picture of oxygen motion, is not readily available. Since ionic conduction is mainly attributed to defects, i.e., oxygen vacancies in oxide ionic conductors, information on local structure is essential to understand the ionic conduction and improve performance. Solid-state NMR is well known for its potential sensitivity to the local structure including effects of dopants and defects. Because NMR is a nuclear-specific technique, it is possible to look directly at

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* To whom correspondence should be addressed. Phone: 650-723-4475. Fax: 650-725-2199. E-mail: njkim@stanford.edu.
[†] Department of Geological and Environmental Sciences.
[‡] Department of Materials Science and Engineering.

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the environment of specific ions such as scandium in scandia-stabilized zirconia. The gyromagnetic ratio of ^{45}Sc is comparable to that of ^{13}C, and the natural abundance is 100%, predicting high sensitivity: however, the former is a quadrupolar nucleus with a spin quantum number of 7/2 and a quadrupole moment of -0.22×10^{28}/m^2, leading to complications of quadrupolar broadening.[16−18] Despite the potential, few reports on solid-state ^{45}Sc NMR have appeared,[19−29] and relatively little is known about the relationship between observed NMR parameters of ^{45}Sc and local structure. We thus studied ^{45}Sc NMR for several stoichiometric, ordered scandium-containing oxides to establish the correlation between the ^{45}Sc NMR chemical shift and the scandium local coordination environment, such as coordination numbers, and applied these preliminary results to scandia-stabilized zirconia.

Experimental Section

Sc_2O_3 (99.9%, Aldrich) was used as purchased, and $ScVO_4$, $ScPO_4$, $LiScO_2$, and $NaScO_2$ were synthesized by solid-state reactions of $(NH_4)_2HPO_4$ (99.3%, J. T. Baker), V_2O_5 (99.6%, Alfa Aesar), Li_2CO_3 (99.999%, Aldrich), Na_2CO_3 (99.999%, J. T. Baker), and Sc_2O_3 (99.9%, Aldrich). Stoichiometric proportions of reactants were mixed and ground in an agate mortar. Mixtures were then pressed into 1 cm pellets and sintered. $ScPO_4$ was prepared from $(NH_4)_2HPO_4$ and Sc_2O_3 by gradual heating to 300 °C (50 °C/h), held at that temperature for 1 day, and then heated for 2 days at 1100 °C. $ScVO_4$ was made from V_2O_5 and Sc_2O_3 heated at 800 °C for 6 days with intermittent grinding and repelletizing. $LiScO_2$ was made from Li_2CO_3 and Sc_2O_3 by heating at 500 °C for 12 h and then 800 °C for 24 h. $NaScO_2$ was synthesized by heating the mixture of Na_2CO_3 and Sc_2O_3 at 835 °C for 12 h with a gradual temperature increase (~50 °C/h) followed by pelletizing and sintering at 1400 °C for 1 day.

Eight percent scandia-stabilized zirconia, $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$, was synthesized by a Pechini-type sol−gel method.[30] Appropriate amounts of Sc_2O_3 and $ZrO(NO_3)_2 \cdot xH_2O$ were dissolved in concentrated nitric acid and water, respectively, at 70−80 °C and mixed together after complete dissolution. The overall cation concentration in this solution was approximately 0.5 M. Citric acid and ethylene glycol were mixed in an approximate 1:2 ratio. The nitrate solution was then added to a citric acid−ethylene glycol mixture (molar ratio of metal cation to citric acid approximately 1:3) with vigorous stirring. The resulting mixture was then heated at temperatures gradually increasing to 150 °C for 1−2 h with stirring until it became a gel. The gel was calcined in a porcelain crucible at temperatures gradually increasing from 200 to 600 °C and then held overnight to remove residual water and organic compounds. The resulting white powders were further sintered in platinum crucibles at 1400 °C for 12 h. X-ray diffraction patterns for all compounds were collected with a Rigaku Geigerflex X-ray diffractometer and compared with ICDD (The International Centre for Diffraction Data) Powder Diffraction Files to confirm phase identity and purity.

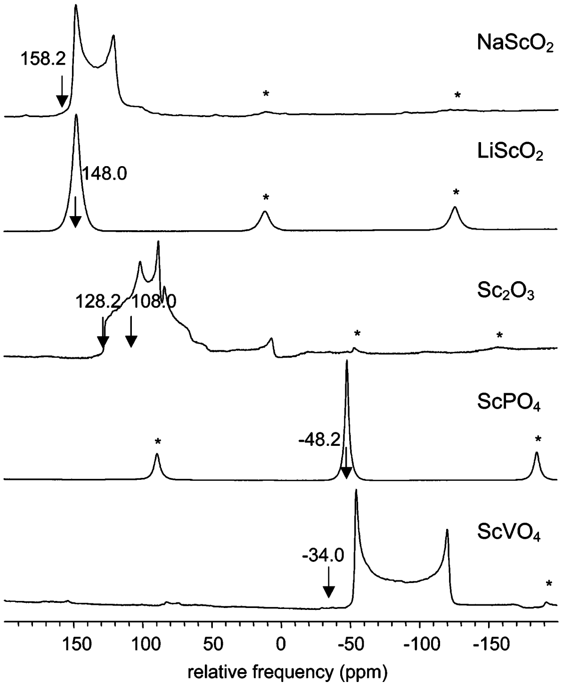

Figure 1. ^{45}Sc MAS NMR spectra of scandium compounds (as labeled) at 14.1 T. Isotropic chemical shifts are marked with arrows, and sidebands are marked with asterisks.

^{45}Sc NMR experiments were carried out with Varian Infinity Plus 400, Unity/Inova 600, and Unity/Inova 800 spectrometers at Larmor frequencies of 97.11, 145.70, and 194.29 MHz, respectively, using 3.2 mm Varian/Chemagnetics "T3" type MAS probes. One-dimensional ^{45}Sc MAS NMR spectra were obtained using a single-pulse experiment with a typical pulse width of approximately 0.25 μs, which was $\pi/24$ for the liquid reference, and spinning speeds of 20 kHz. The chemical shifts were referenced to $ScCl_3$ aqueous solution at 0 ppm.

Results

^{45}Sc NMR of Model Compounds. Figure 1 shows ^{45}Sc NMR spectra of Sc_2O_3, $LiScO_2$, $NaScO_2$, $ScPO_4$, and $ScVO_4$. All five compounds are well-ordered crystalline solids. Each has a single scandium crystallographic site, except Sc_2O_3, which has two.

Sc_2O_3 is cubic; the two, six-coordinated, Sc^{3+} sites (Sc1, Sc2) have a ratio of 1:3.[31] Sc1 lies on the $C3$ axis (Table 1) with equal bond distances to six oxygens, while Sc2 is a much more distorted octahedron. The spectrum has a broad composite peak that appears to be two overlapped resonances with typical second-order quadrupolar line shapes. C_Q and

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Table 1. Structures, Isotropic Chemical Shifts, C_Q, and η of Scandium Compounds

compounds	space group	symmetry	sites	CN	isotropic shift (ppm)[a]	C_Q[a] (MHz)	η[a]
Sc_2O_3	*Ia*3	cubic	2	6	Sc1 108.0 ± 0.2	23.4 ± 0.1	≤0.02
					Sc2 128.2 ± 0.2	15.3 ± 0.1	0.63 ± 0.01
$LiScO_2$	*I*41/*amd*	tetragonal	1	6	148.0 ± 0.6[b]	1.6 ± 0.8[b]	
$NaScO_2$	*R*-3*m*	rhombohedral	1	6	158.2 ± 0.4	14.2 ± 0.1	≤0.07
$ScPO_4$	*I*41/*amd*	tetragonal	1	8	−48.2[c]		
$ScVO_4$	*I*41/*amd*	tetragonal	1	8	−34.0 ± 0.5	21.6 ± 0.1	≤0.03

[a] Isotropic chemical shifts, C_Q's, and η's of Sc_2O_3, $NaScO_2$, and $ScVO_4$ were obtained by simulating the second-order quadrupolar line shape using WSolids.[32] [b] Isotropic chemical shift and C_Q of $LiScO_2$ were estimated using second-order quadrupolar induced shifts at 9.4 and 18.8 T, and η is arbitrarily chosen as 0.7. The uncertainty in C_Q includes the 15% total range when η is varied from 0 to 1. [c] Peak maximum at 14.1 T.

η of Sc_2O_3 were determined by simulating second-order quadrupolar line shapes of central transitions using WSolids,[32] using the 18.8 T data, and confirmed with 14.1 T data. C_Q's, η's, and isotropic shifts are listed in Table 1 and agree well with those previously reported.[26,27]

The Sc1 site proved to be more shielded than the Sc2 site (108.0 vs 128.2 ppm). C_Q's of both sites are relatively large, and the C_Q of Sc1 (23.4 MHz) is larger than that of Sc2 (15.3 MHz). η for the Sc1 site is close to zero, as required by its point symmetry, while η of the Sc2 site is 0.63. The relative intensity of the two is approximately 1:3, confirming their assignments to Sc1 and Sc2, respectively.

$LiScO_2$ is tetragonal and has one six-coordinated scandium site.[33] The line width is narrow compared to Sc_2O_3, indicating a small C_Q that was estimated to be 1.6 MHz from the quadrupolar induced shift (QIS) obtained from the spectra at 9.4 and 18.8 T (arbitrarily assuming that η is 0.7). The isotropic chemical shift estimated from the QIS is 148.0 ppm.

$NaScO_2$ has rhombohedral symmetry, which can be considered as distorted tetragonal similar to tetragonal $LiScO_2$, and has one scandium site which is six coordinated.[34] The isotropic shift, C_Q, and η are derived from the second-order quadrupole line shape at 14.1 T. The estimated isotropic shift of 158.2 ppm indicates an even more deshielded scandium site, compared to $LiScO_2$. η of Sc in $NaScO_2$ is close to zero. Although the structures are quite similar, the line width of $NaScO_2$ is much larger than that of $LiScO_2$ because of its greater C_Q.

$ScPO_4$ and $ScVO_4$ have the same tetragonal symmetry group, and their Sc sites are coordinated by eight oxygens.[35,36] ^{45}Sc NMR of $ScPO_4$ shows a sharp single resonance, while $ScVO_4$ has a broad second-order quadrupolar line shape as in $NaScO_2$. The isotropic chemical shift, C_Q, and η of $ScVO_4$ were also estimated by simulating the line shape. For $ScPO_4$, C_Q was not estimated due to a small C_Q thus small QIS; its peak maximum at 14.1 T is −48.2 ppm. The eight-coordinated Sc sites in these phases thus have much lower chemical shifts than the six-coordinated sites in the other compounds studied here.

^{45}Sc NMR of 8% Scandia-Stabilized Zirconia. Figure 2 shows the ^{45}Sc MAS NMR spectra of 8% scandia-stabilized zirconia collected at 14.1 and 18.8 T. Each spectrum shows a broad line shape with a low-frequency tail that is probably dominated by quadrupolar broadening, which is a common feature in disordered materials with a wide distribution of C_Q's. The higher field spectrum shows much narrower peak, consistent with quadrupolar broadening. Broadening due to distributions in a chemical shift, however, is also expected in disordered solids such as stabilized zirconias.

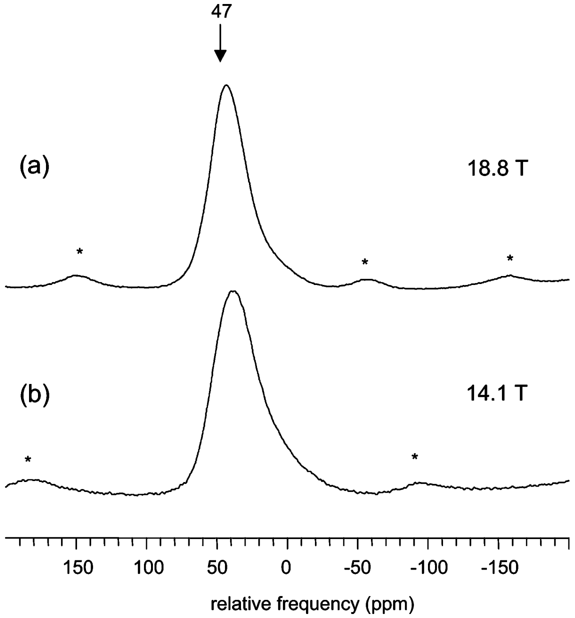

Figure 2. ^{45}Sc MAS NMR spectra of 8% scandia-stabilized zirconia at 14.1 and 18.8 T. Mean isotropic chemical shift is marked with an arrow, and sidebands are marked with asterisks.

The contribution (in Hz) from the chemical shift distribution is proportional to the applied field, while that from the second-order quadrupole broadening is inversely proportional to the field. The two contributions can be determined by analyzing data from two different fields, as proven to be especially useful in disordered solids.[37,38] Line widths were analyzed using the following equations[38]

$$\mathrm{fwhm}_1^{\,2} = W_q^{\,2} + W_{csd}^{\,2}$$

$$\mathrm{fwhm}_2^{\,2} = \left(\frac{B_1}{B_2}\right)^2 W_q^{\,2} + \left(\frac{B_2}{B_1}\right)^2 W_{csd}^{\,2} \qquad (1)$$

where fwhm_1 and fwhm_2 are full widths at half-maxima at

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Table 2. Estimated Mean Isotropic Chemical Shift, C_Q, W_q, and W_{csd} of 8% Scandia-Stabilized Zirconia

δ_{cg} (ppm)		mean δ_{iso} (ppm)	mean $C_Q{}^a$ (MHz)	line width (kHz)		W_q (ppm)	W_{csd} (ppm)
14.1 T	18.8 T			14.1 T	18.8 T	14.1 T	14.1 T
33	39	47 ± 5	10 ± 2	5.7	6.0	29 ± 4	26 ± 3

[a] Mean isotropic shift and C_Q were estimated from quadrupole-induced shift at 14.1 and 18.8 T when η is arbitrarily chosen as 0.7.

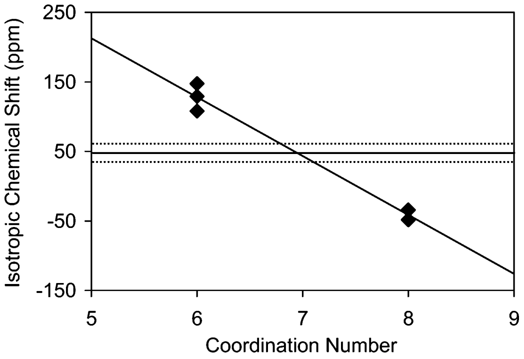

Figure 3. Plot of ^{45}Sc isotropic chemical shift vs the coordination number of scandium cation based on four model compounds. The mean isotropic chemical shift of 8% scandia-stabilized zirconia is marked as a solid line, and the range between the two dotted lines represents the full width at half-maximum of the chemical shift distribution (26 ppm).

the lower and higher magnetic fields, respectively. W_q is the contribution to the peak width from the second-order quadrupolar effect, W_{csd} is that from the distribution of chemical shifts, and B_1 and B_2 are the strengths of the lower and higher magnetic fields, respectively. W_q and W_{csd} derived from spectra at 14.1 and 18.8 T are given in Table 2.

The mean quadrupole coupling constant (C_Q) and the mean isotropic shift (δ_{iso}) were also estimated by plotting the centers of gravity (δ_{cg}) of the spectra from 14.1 and 18.8 T versus the inverse of the resonance frequency (ν_0) using the following equation[38]

$$\delta_{cg} = \delta_{iso} - \frac{10^6}{40}\frac{C_Q{}^2(3+\eta^2)}{\nu_0{}^2 I^2(2I-1)^2}\left(I(I+1)-\frac{3}{4}\right) \tag{2}$$

where I is a nuclear spin quantum number (7/2 for ^{45}Sc).

The estimated mean isotropic chemical shift of 8% scandia-stabilized zirconia is approximately 47 ppm with a mean C_Q of approximately 10 MHz when η is arbitrarily assumed to be 0.7 and may vary by up to 8% depending on the value of η ($0 \leq \eta \leq 1$). The estimated contribution to the peak width (fwhm) from the distribution of chemical shifts is about 26 ppm.

Discussion

NMR Parameters and Local Structures around Scandium. Isotropic chemical shifts show the most obvious correlation with local structure among the ^{45}Sc NMR parameters and are spread over a wide range from −48 to 158 ppm. This parameter may thus be most useful in characterizing unknown structures. The isotropic chemical shift clearly depends on the Sc^{3+} coordination number. It lies in the range between 108.0 and 158.2 ppm for six-coordinated Sc^{3+} in $LiScO_2$, $NaScO_2$, and Sc_2O_3, while eight-coordinated Sc^{3+} in $ScPO_4$ and $ScVO_4$ show chemical shifts of −48.2 and −34.0 ppm (Figure 3). Chemical shifts for seven-coordinated sites should lie roughly halfway between these two ranges.

A similar trend of decreasing chemical shift with increasing coordination number can be found in NMR data for many other cations NMR such as ^{11}B, ^{23}Na, ^{25}Mg, ^{27}Al, and ^{29}Si NMR.[39] As coordination number increases, the ionic character of the cation generally increases. There is also less paramagnetic shift to higher frequency when the electronic distribution is more symmetric, i.e., more ionic. Therefore, as coordination number increases, lower resonant frequencies are observed.[18]

This correlation is consistent with several ^{45}Sc chemical shifts previously reported, e.g., scandium coordinated by six oxygens in scandium fluorophosphates.[28] However, the relationship appears to be valid only for simple inorganic oxide compounds in which all the coordinating anions are oxygen without any influence of protons or organic functional groups. For example, when Sc^{3+} is coordinated by one or more fluorine anions,[28] the chemical shift range is shifted by about 100 ppm to lower frequency. A similar deviation from the trend was also found in compounds that have scandium coordinated to six $[HPO_4]^{2-}$ ligands.[27] Since scandiums coordinated to $[PO_4]^{3-}$ in $ScPO_4$ and scandium fluorophosphates are consistent with the empirical trend, these deviations are probably due to the strong influence of the protons in $[HPO_4]^{2-}$ ligands.

Apart from this overall general correlation, there is still a significant difference in ^{45}Sc chemical shifts among the compounds that have the same coordination number. This indicates that ^{45}Sc isotropic shifts are also quite sensitive to other structural differences such as bond angles and bond distances, although it may not be easy to pin down what the dominating factors are. However, chemical shifts do not appear to be very sensitive to the second neighbor cation. When the structures are similar, the difference in isotropic shift is not large, as seen by comparing $LiScO_2$ (148.0 ppm) and $NaScO_2$ (158.2 ppm) or $ScPO_4$ (−34.0 ppm) and $ScVO_4$ (−48.2 ppm).

Unlike isotropic shifts, C_Q's appears to be very sensitive to second neighbor cations since there is a significant difference in C_Q values even when the structures are similar. A larger C_Q may be related to a second neighbor cation's larger radius when the structure is otherwise similar as in $NaScO_2$ and $LiScO_2$ or $ScVO_4$ and $ScPO_4$. However, there could be many other factors affecting the C_Q, and there is not enough data to draw any conclusions at this time. Asymmetry parameters for sites in several compounds are zero, which is consistent with the point symmetry. For Sc_2O_3, η of zero for the Sc1 site is consistent with the axial symmetry of the site, which is on the C_3 axis. On the other hand, η of the Sc2 site is 0.63 since the site has distorted

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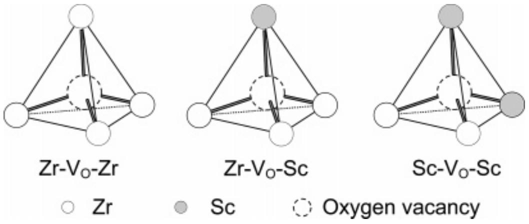

Figure 4. Models of the associations between cations and vacancies in stabilized zirconia: (a) vacancy is next to zirconium cation, (b) vacancy is next to one dopant cation, and (c) vacancy is next to two dopant cations.

octahedral symmetry. Scandium in $ScVO_4$ lies on a 4-fold inversion axis $\bar{4}$ in the tetragonal structure: $NaScO_2$ is rhombohedral, and scandium is not on the symmetry axis. The fact that η is close to zero for both $ScVO_4$ and $NaScO_2$ suggests that the deviation from C_4 symmetry is very small.

Implication of ^{45}Sc NMR for Scandium Coordination in Scandia-Stabilized Zirconia. The estimated mean isotropic chemical shift of 8% scandia-stabilized zirconia is 47 ppm. This value is almost centered between the observed ranges for eight and six coordination (Figure 3), indicating that the average scandium coordination in this phase is probably close to seven.

Cations in the cubic phase of pure zirconia are coordinated by eight oxygen anions. In scandia-stabilized zirconia, however, the vacancies generated by doping of scandium (one mole of vacancy per mole of Sc_2O_3) must result in a change to lower the overall mean cation coordination. There have been many discussions concerning the association of dopants and vacancies and the location of the vacancies in stabilized zirconia.[40−43] The vacancies can be located next to zero, one, or two dopant cations as shown in Figure 4. It is generally believed that the vacancies are likely to be located next to zirconium cations when the dopant cations are much larger, while the vacancies tend to be located next to dopant cations when the dopants are smaller.

If R is the ratio of oxygen vacancies to total oxygen and if both scandium cations and vacancies are distributed randomly in a structure, the average coordination number of all the cations should be approximately $8 \times (2 - R/2) = 7.7$. However, Sc^{3+} cations and oxygen vacancies may tend to associate to help local charge balance. The average scandium coordination number in the extreme case, when all vacancies are associated with scandium cations and cation−vacancy pairs are isolated, will be close to 7.5 because one vacancy is generated by two scandium cations. Therefore, to have a coordination number smaller than 7.5, as the isotropic chemical shift suggests, there could be ordering beyond a simple isolated vacancy−cation association. One obvious possibility is that two scandium cations pair with one vacancy so that more than one-half of the scandium cations have adjacent vacancies. Since dopant scandium cations and oxygen vacancies exist in a 2:1 ratio in the structure, the association of two scandium cations with one oxygen vacancy may be thermodynamically favorable.

It is also possible that there could be scandium-rich regions resulting from low-temperature disequilibrium, although in such a case a coordination number of six would seem more likely. To check this possibility, the 8% scandia-stabilized zirconia sample was heated for 5 days at 1600 °C, where significant cation diffusion should occur. No significant change in peak position was observed after this heat treatment. Therefore, the possibility of disequilibrium segregation is small.

It has been reported that the tendency to form a defect cluster with two dopants and one vacancy is strong.[44] This trimer cluster was also suggested to form for stabilized zirconia with small dopant cations based on X-ray absorption data.[41] However, the suggested low scandium coordination number is surprising since the association energy between dopant scandium cations is known to be relatively low.[43] The isotropic shifts vary up to ∼50 ppm among the compounds with the same coordination number, which makes determination of the exact range for each coordination number imprecise. Thus, the relationship should be applied with care, and studies for more model compounds would be useful.

Conclusions

The relationship between ^{45}Sc NMR parameters and scandium local structure has been investigated for five scandium-containing crystalline compounds Sc_2O_3, $ScPO_4$, $ScVO_4$, $LiScO_2$, and $NaScO_2$.

A clear correlation has been found between Sc^{3+} coordination numbers and the isotropic chemical shifts. As coordination number increases, isotropic chemical shifts decrease, which is the same trend found for many other cations in oxide materials. The difference between six- and eight-coordinated scandium is more than 100 ppm, which indicates that ^{45}Sc NMR will be potentially very useful to study scandium local structure. While the isotropic shift is strongly affected by first neighbor coordination environments and relatively insensitive to second neighbor cations, the quadrupole interaction appears to be sensitive to the nature of the second neighbor cations, although it is not yet clear what aspects of the structure control the size of the quadrupolar interaction.

Investigation of scandium-stabilized zirconia with ^{45}Sc MAS NMR has shown that the average scandium coordination number may be close to seven, which implies that ordering of two scandium cations together with one vacancy may be common.

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