$Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$ and Their Solid Solutions: ^{45}Sc, ^{17}O, and ^{27}Al MAS NMR Results at Ambient and High Temperature

Namjun Kim* and Jonathan F. Stebbins

Department of Geological and Environmental Sciences, Stanford University,
Stanford California 94305-2115

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The mobilities of trivalent ions are generally considered to be low in solid oxides and thus trivalent ionic conductors are rare. $Sc_2(WO_4)_3$ and related compounds have been described as Sc^{3+} ionic conductors. However, there has not been conclusive experimental evidence whether Sc^{3+} is the major or the only mobile species. Here, we report ^{45}Sc, ^{17}O, and ^{27}Al MAS NMR studies at ambient and high temperature of $Sc_2(WO_4)_3$-type compounds including $Sc_2(WO_4)_3$, $Sc_2(MoO_4)_3$ (scandium tungstate and scandium molybdate), and their solid solutions, as well as aluminum-doped $Sc_2(WO_4)_3$. ^{45}Sc MAS NMR spectra at ambient temperature of the $Sc_2(WO_4)_3-Sc_2(MoO_4)_3$ binary are consistent with random mixing of W^{6+} and Mo^{6+} on tetrahedral sites. ^{17}O spectra show that the details of the end-member short-range structure are preserved throughout this solid solution, indicating that lattice distortion is minimized by the close similarity of the radii of the hexavalent cations. Al^{3+} substitutes only into the octahedral sites. At high temperatures (600−700 °C), only the ^{17}O high spectra show noticeable line shape changes, whereas ^{45}Sc high-temperature spectra maintain a constant peak width and shift in position only, suggesting that the oxide anion may be a more mobile species but not excluding the possibility of a minor number of mobile scandium ions. ^{17}O high-temperature NMR data also suggest that oxide ions bonded to molybdenum ions may be more mobile than those in tungstate groups.

1. Introduction

Ionic motion in solid oxides plays an essential role in many technological applications including electrolytes in solid state ionic devices such as fuel cells and sensors. In most ionic conductors, the mobile ions are mono- or divalent, such as Na^+, Li^+, Ag^+, F^-, and O^{2-}. However, trivalent ions are generally expected to be poor conducting species and trivalent ionic conductors are thus rare.

$Sc_2(WO_4)_3$ and related compounds have been known as Sc^{3+} cationic conductors, and similar compounds such as $Sc_2(MoO_4)_3$ and rare earth tungstates and molybdates have been studied.[1−8] However, very little is known about how the scandium ions migrate in such materials. In particular, $Sc_2(WO_4)_3$-type compounds do not have any extrinsic vacancies or extrinsic interstitials, as are normally introduced into other well-known conductive oxides by doping with aliovalent ions, which makes it difficult to predict the ion hopping mechanism. There is no conclusive evidence that Sc^{3+} is the only mobile species responsible for the ionic conduction, and a computer simulation study suggested the possibility of oxygen or scandium interstitial ions.[7]

There have been some efforts to improve the conductivity of these materials by making solid solutions. For example, $Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$ are known to form solid solutions over the entire mixing range.[6] W^{6+} and Mo^{6+} presumably substitute for each other in the tetrahedral sites: they have the same charge and similar ionic radii and the two end members are isostructural.[9,10] However, the ionic conductivity is found to increase linearly with the Mo^{6+} content, and pure $Sc_2(MoO_4)_3$, not one of the intermediate compositions, shows the highest conductivity in the binary.[6] The effects of dopant ions such as Al^{3+} in $Sc_2(WO_4)_3$ have been studied as well.[3]

The $Sc_2(WO_4)_3$ structure is particularly simple, making it amenable to determination of effects of cation substitution on local vs long-range ordering, a problem that often remains ambiguous if only diffraction data are available. The trivalent cations occupy symmetrical octahedra that are corner-shared with the tetrahedra formed by the smaller, hexavalent cations, creating a three-dimension network with no interstitial or "charge-balancing" cations as in, for example, zeolite or garnet structures. $Sc_2(MoO_4)_3$ and related materials are also known to have negative thermal expansions, with unit cell volumes decreasing when temperature is increased.[11] All

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* Corresponding author. Tel: (650) 723-4475. Fax: (650) 725-2199. E-mail: njkim@stanford.edu.

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oxygens in the structure are two-coordinated by one octahedral and one tetrahedral cation.

High-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy is highly sensitive to first- and second-neighbor coordination environments and has been widely used to probe the local structure of disordered crystalline materials. NMR is also well-known as capable of detecting and quantifying chemical exchange processes via one-dimensional line shape analysis or two-dimensional exchange spectroscopy. Many solid systems that have considerable ion mobility have been studied using solid-state NMR including Li^+, Na^+, F^-, and O^{2-} conductors.[12−17]

In this report, ^{45}Sc, ^{17}O, and ^{27}Al magic angle spinning (MAS) NMR spectroscopy are utilized to observe local environments around scandium, oxygen, and aluminum ions in $Sc_2(WO_4)_3$−$Sc_2(MoO_4)_3$ solid solutions and in Al-substituted $Sc_2(WO_4)_3$. ^{17}O (spin = 5/2) MAS NMR has been used widely to study many crystalline and amorphous oxide materials: its chemical shift spans more than 1000 ppm and is known to be very sensitive to the coordinating cations and coordination environments.[18] In some systems, there are well-established relationships between ^{17}O chemical shifts and bond angle and distance, especially for the oxides containing aluminum and silicon; the ^{17}O NMR spectra of transition metal oxides have also been extensively studied.[18−21] Despite high natural abundance and Larmor frequency, ^{45}Sc (spin = 7/2) NMR has not been widely applied, and only recently has received growing attention because of the potential application of scandium compounds in many fields. The relationships between ^{45}Sc NMR parameters and structure is beginning to be established and successfully applied.[22−24]

2. Experimental Section

$Sc_2(WO_4)_3$, $Sc_2(MoO_4)_3$, and their solid solutions $Sc_2(W_xMo_{1-x}O_4)_3$ (x = 0.25, 0.5, and 0.75) were synthesized from Sc_2O_3, WO_3, and MoO_3 by solid-state reaction. The end-member tungstate was produced by mixing and grinding the reagents in an agate mortar and heating the mixture at 1000 °C for 12 h and 1200 °C for 12 h.[6] The mixture was then pressed into a pellet and sintered at 1400 °C for 12 h. To prepare $Sc_2(MoO_4)_3$ and the solid solutions, stoichiometric amounts of Sc_2O_3, WO_3, and MoO_3 were ground together and heated them at 700 °C for 12 h and 1100 °C for 12 h. The mixtures were pelletized and sintered at 1100 °C for 12 h. A doped tungstate of nominal composition $(Al_{0.1}Sc_{0.9})_2(WO_4)_3$ was produced by similar methods. The resulting compounds were confirmed by powder X-ray diffraction to be single phases; ^{27}Al NMR (see below) showed that the Al-doped tungstate contained some unreacted α-alumina. Samples for ^{17}O NMR were isotopically enriched by heating in sealed silica glass tubes with 40% ^{17}O oxygen gas at 600 °C for 12 h.

All ambient temperature spectra were collected using 3.2 mm Varian/Chemagnetics "T3" type MAS probes and sample spinning rates of about 20 kHz. ^{45}Sc NMR experiments were carried out with Varian Infinity Plus 400 (9.4 T), Unity/Inova 600 and 800 (14.1 and 18.8 T) spectrometers at 97.11, 145.70, and 194.29 MHz, respectively. 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 standard. A small pulse width was used to ensure that the intensities are quantitative. The chemical shifts were referenced to a 0.02 M $ScCl_3$ aqueous solution at 0 ppm, which is known to be more dilute than the range of concentrations where the chemical shift depends significantly on composition.[25] ^{17}O NMR data were collected at 9.4 and 14.1 T (54.19 and 81.31 MHz). A typical pulse width was 0.3 μs, equivalent to a $\pi/18$ rf tip angle for the liquid standard, and chemical shifts were referenced to ^{17}O-enriched water at 0 ppm. ^{27}Al NMR data were collected at 14.1 T (156.26 MHz). The pulse width was 0.2 μs, equivalent to a $\pi/18$ rf tip angle for the liquid standard; the reference was 0.1 M $Al(NO_3)_3$ aqueous solution at 0 ppm.

In situ, high-temperature MAS NMR experiments to 700 °C were performed at 9.4 T with a probe with 7 mm Si_3N_4 rotors (Doty Scientific, Inc.), at a spinning rate of 4 kHz.[25] Typical pulse widths were 0.69 μs ($\pi/18$ rf tip angle) for ^{17}O NMR and 0.50 μs ($\pi/18$ rf tip angle) for ^{45}Sc.

3. Results and Discussion

3.1. ^{45}Sc and ^{17}O NMR Spectra of the End Members. Figure 1 show the ^{45}Sc MAS NMR spectra of $Sc_2(WO_4)_3$, $Sc_2(MoO_4)_3$, and their solid solutions, collected at 14.1 and 18.8 T. The spectra of the two end members show single, narrow resonances with peak maxima and widths given in Table 1. The resonances do not show any noticeable second-order quadrupolar line shapes, indicating values of C_q (quadrupolar coupling constant) are small.[18,26] From the slight changes with external field we estimate that the C_q values are about 3.6 ± 1 MHz; the isotropic chemical shifts are about 1 ppm higher than the peak maxima at 18.8 T. The shift is about 5 ppm higher in the tungstate than in the molybdate. Because Sc^{3+} ions occupy octahedral sites in both end members (and the solid solutions), this difference is small compared to the shifts of >100 ppm caused by changes in coordination number,[22] but does indicate that the cations in the second coordination shell have some effect. Such effects, as well as those of other structural differences (e.g., coordination number of oxide ions) can be larger, as suggested by the much higher chemical shifts for octahedral Sc^{3+} in compounds such as alkali scandates and scandium oxide.[24]

The ^{17}O NMR spectrum of $Sc_2(WO_4)_3$ (Figure 3) shows three partially resolved resonances around 455 ppm, while

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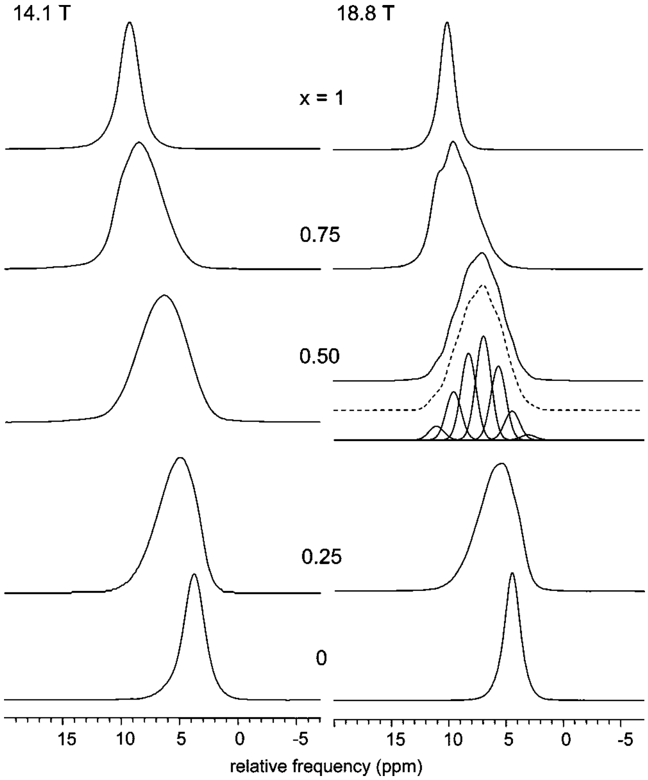

Figure 1. ^{45}Sc MAS NMR spectra of $Sc_2(W_xMo_{1-x}O_4)_3$ solid solutions at 14.1 and 18.8 T as labeled. Fitted components and their sum are shown with solid line and dashed line, respectively, below the spectrum for $x = 0.5$ at 18.8 T.

that for $Sc_2(MoO_4)_3$ has a similar pattern, shifted up to about 560 ppm. Because each oxygen is coordinated to only one Sc^{3+} and one W^{6+} or Mo^{6+} cation, this rather large difference is likely to be due to the effects of the latter on the local electronic structure, despite the close similarity of the tabulated ionic radii (0.041 nm for $^{[4]}W^{6+}$ and 0.042 nm $^{[4]}Mo^{6+}$)[27] and that cation−oxygen first-shell distances are within 1%.[9,10] As is common for transition metal oxides, each component peak is narrow (about 5 ppm fwhm), with no evident quadrupolar line shape. C_q values less than about 2 MHz are thus indicated.

The overall shapes of the three overlapping components are similar in the molybdate and tungstate, suggesting intensity ratios of 1:2:2 in both if Gaussian peak shapes are assumed. However, because there are six crystallographically distinct oxygen sites in the structure,[9,10] it is not straightforward to assign the resonances: peak overlap and the possibility of non-Gaussian line shapes caused by minor second-order quadrupolar broadening mean that decomposition of the spectra into six equal-area components is nonunique. These differences in chemical shifts may be primarily due to differences in the bond angles, which has an especially wide range in these structures, for example the Sc−O−W angle varies from 142 to 176° on the basis of 300 K powder neutron diffraction data.[11] The separations between the components are slightly smaller for the tungstate than for the molybdate, while line widths are similar, so the resolution is slightly better for the latter. In both the end-members and the solid solutions, the oxygen coordinated by W appears to undergo spin−lattice relaxation slightly faster than that coordinated by Mo. The relaxation times were not measured but the Sc−O−W peaks were fully relaxed with a long series of $\pi/18$ excitation pulses with a 1 s delay, whereas the Sc−O−Mo peaks were fully relaxed with the same excitation pulses and a 5 s delay. The spectra in Figure 2 were all collected with 1 s pulse delays to enhance signal-to-noise ratio.

3.2. $Sc_2(WO_4)_3$−$Sc(MoO_4)_3$ Solid Solutions: ^{45}Sc and ^{17}O NMR.

From crystallographic studies and the known similarity of the ionic radii of W^{6+} and Mo^{6+}, $Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$ are thought to be miscible in all compositions and thus to form a continuous solid solution. For example, unit-cell parameters have been observed to change continuously and linearly with composition for samples along the binary that were synthesized by the same methods used here.[6] However, little direct evidence has appeared about the true, short-range structure and extent of cation order/disorder, as opposed to information from diffraction results on long-range structure.

In the ^{45}Sc NMR spectra of the solid solutions (Figures 1 and 2), the peak centroids (centers of gravity) change gradually from 3.7 ppm in $Sc_2(WO_4)_3$ to 9.3 ppm in $Sc_2(MoO_4)_3$. The peak widths, which in the mixed crystals are controlled primarily by distributions in chemical shifts, are greatest at the 50% composition. The even lower second order quadrupolar broadening at 18.8 T compared with 14.1 T yields slightly better resolution and the clear indication of multiple component peaks within the overall line shapes (Figure 2). Each ScO_6 octahedron in these structures is corner-shared with six WO_4 and/or MoO_4 tetrahedra, leading to seven locally different Sc^{3+} environments. Changes in the ratio of W and Mo among these first neighbor cations are expected to have the largest effect on the ^{45}Sc chemical shift. We have thus fitted the line shapes for the spectra of the solid solutions with seven Gaussian subpeaks, assuming that their positions and widths are constant, the latter being set at 300 Hz based on the end-member values of 290 and 310 Hz. A typical result for the 18.8 T data is shown in Figure 1; comparisons with the proportions expected from a completely random distribution of Mo^{6+} and W^{6+} in the tetrahedral sites are shown in Table 2. Given the simplified assumptions and uncertainties of the fitting process, the agreement with the random model is good, suggesting that the tungsten and molybdenum are homogeneously mixed in the solid solutions.

Such a direct confirmation of short-range random cation mixing is unusual. In another particularly clear recent example, based on high-resolution ^{19}F NMR of CaF_2−SrF_2 solid solutions, well-resolved peaks for F^- with varying numbers of Ca^{2+} and Sr^{2+} neighbors were quantified.[28] As observed here, the peaks for the end-member-like components (e.g., Ca−F_6, Sc−$[OW]_6$) are shifted slightly from those of the pure end-member phases, suggesting longer-range effects of the solid solution on chemical shifts. A similar example was found in an ^{89}Y NMR study of

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Table 1. Results from ^{45}Sc MAS NMR Spectra of $Sc_2(W_xMo_{1-x}O_4)_3$ Solid Solutions for the Peak Centers of Gravity (δ_{cg}) and Full Widths at Half Maxima in Hertz

		9.4 T		14.1 T		18.8 T	
composition x	T (°C)	δ_{cg} (± 0.2)	fwhm	δ_{cg} (± 0.2)	fwhm	δ_{cg} (± 0.2)	fwhm
1	25			9.3	290 ± 10	10.1	290 ± 10
0.75	25			8.2	620 ± 30	9.4	760 ± 30
0.50	25			6.3	710 ± 30	7.3	880 ± 30
0.25	25	3.7	430 ± 10	5.2	590 ± 30	5.9	780 ± 30
0.25	100	4.5	430 ± 10				
0.25	300	6.6	430 ± 10				
0.25	500	9.2	430 ± 10				
0.25	700	12.2	430 ± 10				
0	25			3.7	310 ± 10	4.5	310 ± 10

$Y_2Ti_2O_7-Y_2Sn_2O_7$ solid solutions, in which it was shown that the distribution of Ti and Sn in second coordination shell of Y is homogeneous.[29]

The ^{17}O MAS NMR spectra collected for the $Sc_2(WO_4)_3-Sc_2(MoO_4)_3$ solid solutions are shown in Figure 2. The "triplet" peak shapes for the pure end members are retained in the intermediate compositions, with little or no change in position or shape. Although the data shown were collected with a pulse delay of 1 s to enhance signal-to-noise ratio and hence are not fully relaxed, correction for the differential relaxation noted above for the end members yields proportions of Sc−O−W and Sc−O−Mo oxygens that agree well with those expected from composition.

The constancy in the NMR response of the two types of oxygen (those with Mo vs those with W neighbors) is striking: the spectra are almost exactly what would be expected for a bulk mechanical mixture of the end members, not a homogeneous solid solution. The latter is, however, confirmed by the ^{45}Sc NMR, and suggested by published XRD data on materials prepared by nearly identical methods.[6]

The implication of this finding is clear: the short-range structure, i.e. the sets of Sc−O−(Mo,W) bond angles that give the characteristic "triplet" line shape for the ^{17}O, is nearly identical in the solutions and the pure phases. The presence of a Mo^{6+} vs a W^{6+} first neighbor has the same effect on the ^{17}O chemical shift in the solid solutions as in the end members, and second-neighbor cation effects (e.g., proportions of Mo vs W linked to the other oxygens in a given ScO_6 octahedron) on ^{17}O chemical shifts are negligible. All of these observations are consistent with local structures in the solid solutions that are undistorted relative to those of the end members. The near-identity of the true short-range structure, as sampled by NMR, to that of the average long-

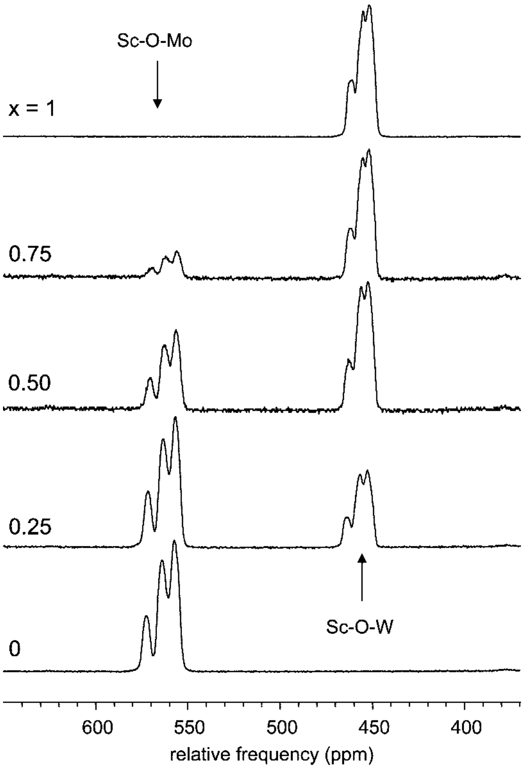

Figure 2. ^{17}O MAS NMR spectra of $Sc_2(W_xMo_{1-x}O_4)_3$ solid solutions at 14.1 T with a pulse delay of 1 s.

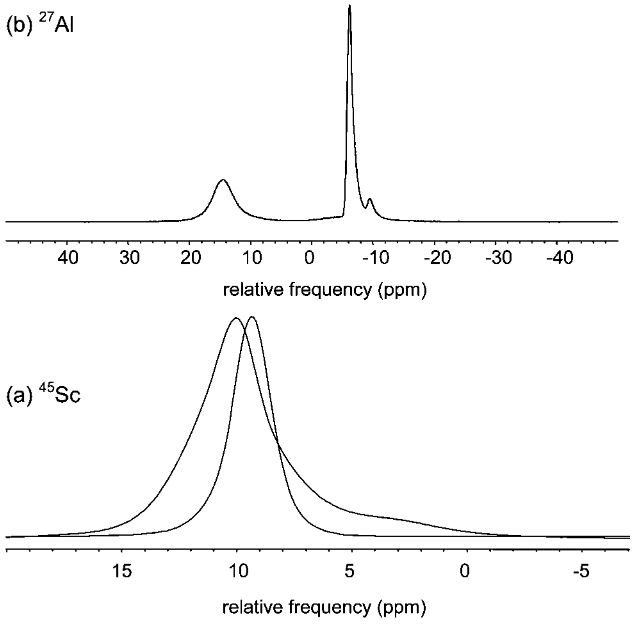

Figure 3. (a) ^{45}Sc MAS NMR spectrum of $(Al_{0.1}Sc_{0.9})_2(WO_4)_3$ (nominal composition) at 14.1 T; narrower spectrum is that for pure $Sc_2(WO_4)_3$ (b) ^{27}Al MAS NMR spectrum at 14.1 T.

Table 2. Results of Fits of ^{45}Sc NMR Spectra for $Sc_2(W_xMo_{1-x}O_4)_3$ Solid Solutions (18.8 T) with Peaks Representing from 6 W and 0 Mo neighbors (6W) to 0 W and 6 Mo neighbors (0W)[a]

composition, x	6W	5W	4W	3W	2W	1W	0W
0.75	27	34	24	10	3	1	1
	18	36	30	13	3	0	0
0.5	4	14	24	28	20	9	1
	2	9	23	31	23	9	2
0.25	1	3	11	23	32	26	4
	0	0	3	13	30	36	18

[a] For each composition, the fitted component areas, in %, are given in the first line, those for a random distribution in the second line.

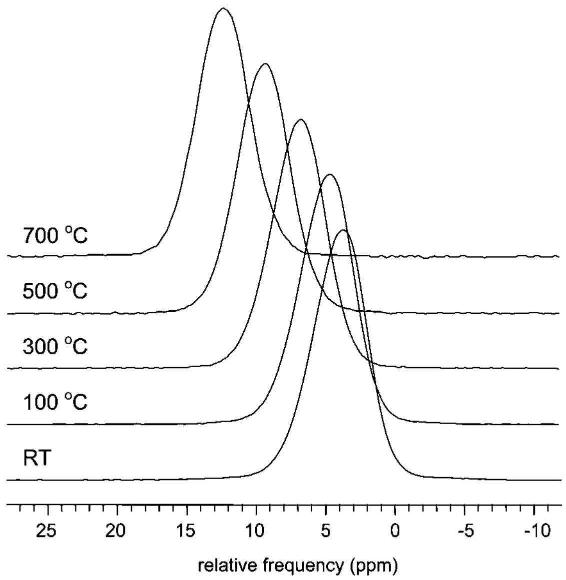

Figure 4. High-temperature ^{45}Sc MAS NMR spectra of Sc$_2$(W$_{0.25}$Mo$_{0.75}$O$_4$)$_3$ at 9.4 T with a sample spinning rate of 4 kHz.

range structure as determined by diffraction is unusual and presumably can occur only when substituent cations are as close in size as are W^{6+} and Mo^{6+}.

3.3. Effect of Al Doping on Structure: ^{45}Sc and ^{27}Al NMR. The ^{45}Sc MAS NMR spectrum of Al-doped scandium tungstate with nominal composition (Al$_{0.1}$Sc$_{0.9}$)$_2$(WO$_4$)$_3$ is much broader than that of pure Sc$_2$(WO$_4$)$_3$ (Figure 4). Because the substituent Al^{3+} cations are in octahedral sites that are two cations away from the Sc^{3+} (see below), their effect on the ^{45}Sc chemical shifts and C_q's is likely to be through distortions of the lattice and perturbations in local bond angles and distances, and not by direct electronic effects. In any case, these effects clearly produce a distribution of Sc sites with varying local geometries, leading to the broadened peak. Unlike the case of the W/Mo substitution, such distortions are expected from the large differences in radii between octahedral Al and Sc (0.053 vs 0.073 nm).[27]

The ^{27}Al MAS NMR spectrum of this material shows three obvious, narrow resonances centered at 14.6, −6.2, and −9.5 ppm and a minor, broad feature centered at about −4 ppm (Figure 4), all due to Al^{3+} in octahedral sites. No signals at higher chemical shifts that could be due to four- or five-coordinated Al were observed. The first of these is the same in position, shape, and width (600 Hz fwhm) as that reported for α-Al$_2$O$_3$ at this field[30] and represents unreacted alumina. The major peak at −6.2 ppm is even narrower: its width permits a maximum C_q of only about 1.5 MHz, and thus an isotropic chemical shift only up to about 0.6 ppm higher than the observed peak maximum. This peak is presumably from Al dissolved in the Sc$_2$(WO$_4$)$_3$ host phase and thus having all W^{6+} first cation neighbors. Its very negative chemical shift is among the lowest reported for octahedral Al in oxides, although values for the four Al sites in Al$_2$(MoO$_4$)$_3$ are even lower, −10.3 to −13.4 ppm.[31] Small, highly charged ligands such as Mo^{6+}, Ti^{4+}, and P^{5+} are indeed known to lower chemical shifts for ^{27}Al in oxides,[18,30] presumably by contributing to longer, more ionic, Al−O bonds for a given polyhedral geometry. The other, smaller resonances in the Al-doped tungstate may result from second-neighbor effects or other consequences of cation disorder.

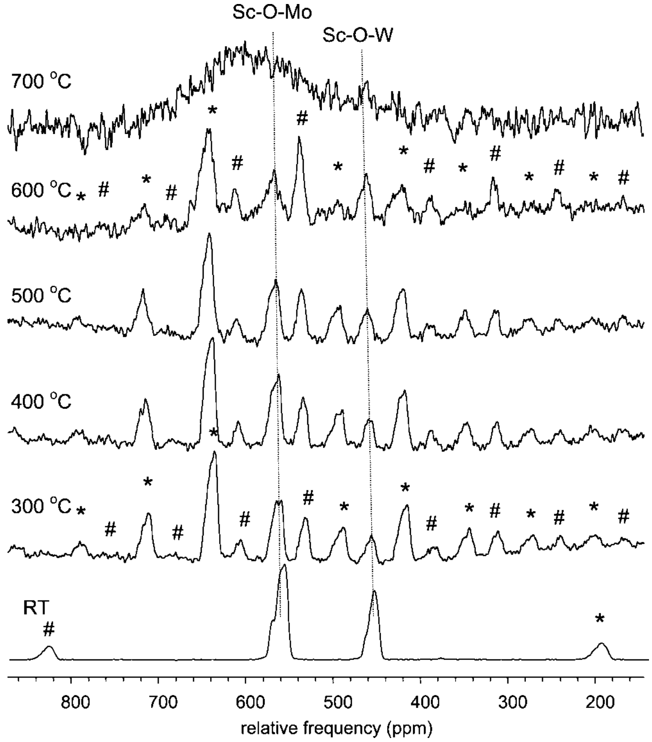

Figure 5. High-temperature ^{17}O high MAS NMR spectra of Sc$_2$(W$_{0.25}$Mo$_{0.75}$O$_4$)$_3$ at 9.4 T with a sample spinning rate of 4 kHz. The room-temperature spectrum is shown for comparison and was collected with a spinning rate of 20 kHz. Central peaks are marked with dotted lines; spinning sidebands for the Sc−O−Mo sites are labeled with * and those for the Sc−O−W sites with #.

3.4. High-Temperature ^{45}Sc and ^{17}O NMR. Solid solutions of Sc$_2$(WO$_4$)$_3$ and Sc$_2$(MoO$_4$)$_3$ have been known as trivalent ionic conductors but different mechanisms for conduction have been suggested. For example, AC and DC conductivity measurements (DC polarization) and electrolysis studies have supported ionic conduction dominated by Sc^{3+} migration.[5,32] ^{45}Sc and ^{17}O high temperature MAS NMR experiments were therefore performed up to 700 °C for a representative solid solution, Sc$_2$(W$_{0.25}$Mo$_{0.75}$O$_4$)$_3$. Because the conductivity is known to increase with Mo/W ratio,[6] this composition was expected to show relatively high ionic mobility, as well as having multiple types of Sc^{3+} and O^{2-} sites with varying numbers of W and Mo neighbors and thus distinct NMR signatures.

In the ^{45}Sc high-temperature MAS spectra of Sc$_2$(W$_{0.25}$Mo$_{0.75}$O$_4$)$_3$, the chemical shift moves systematically to higher frequency as temperature is increased (Figure 5), but no significant change in line shape was observed. The line width (fwhm) is approximately 430 Hz at room temperature and in all high-T spectra. It is thus likely that exchange of Sc^{3+} ions among sites with different proportions of Mo and W neighbors (i.e., typical adjacent octahedral sites

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in a random solid solution) occurs on average at a frequency well below 430 Hz even at 700 °C.

The cation jump frequency required for a given bulk conductivity can be roughly estimated from the following equation based on a 3-dimensional random walk model

$$f = \frac{6k_B T\sigma}{nq^2r^2} \qquad (1)$$

where n is the number of charge carriers per unit volume, q is their charge, r is the jump distance, k_B is the Boltzmann constant, T is the temperature, and f is the jump frequency. If the charge carrier is assumed to be only Sc^{3+} ions and thus the total number per unit volume of this cation is used for n, the distance between two adjacent scandium sites (0.6 nm) is appropriate for the jump distance. For a predicted conductivity comparable to that measured at 600 °C[6] of about 1×10^{-4} Scm^{-1}, the mean jump frequency should be greater than 1 MHz. This seems to be inconsistent with the observed lack of chemical exchange in the ^{45}Sc spectra, even at a frequency scale of a few 100 Hz.

Because ^{45}Sc is a quadrupolar nuclide, there is some chance that NMR signals could be missed for a relatively small number of Sc^{3+} ions in highly distorted sites (e.g., interstitial defects) with large quadrupolar coupling constants and hence very broad peaks, although we note that signals from sites with C_q's as large as 23 MHz have readily been observed in ordered Sc-containing oxide crystals.[22] However, rapid exchange of Sc^{3+} from "normal" crystallographic sites with such defect sites would be expected to lead to obvious line shape changes.

The observed progressive shift of the ^{45}Sc peak to higher frequency at higher temperature, given the lack of change in line shape, is probably the result of an increase in the chemical shift. This positive correlation is typical of cations such as Pb^{2+} in $Pb(NO_3)_2$,[33,34] and Mg^{2+} in MgO.[35] Although such effects are not well-understood, theoretical calculations have shown that static models accounting only for the changes in atomic positions due to thermal expansion can predict the wrong sign of the temperature effect, and that the dynamic effects of vibrations on electron distributions must be accounted for.[36]

Figure 5 shows ^{17}O MAS NMR spectra acquired up to 700 °C. At the relatively low sample spinning rate used, wide, asymmetric manifolds of spinning sidebands are seen, which are probably related primarily to the chemical shift anisotropy (CSA). The CSA parameters were derived by the Herzfeld-Berger method[37] using nine sidebands with an assumption that the contribution from the quadrupolar interaction is negligible.[38] The span ($\Omega = \delta_{33} - \delta_{11}$) estimated for the 300 °C spectrum is about 420 ppm and the skew ($\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$) is about 0.7, where the three components in CSA are denoted as δ_{11}, δ_{22}, and δ_{33}.

Although no significant line shape change was seen in the ^{45}Sc high temperature NMR spectra, the ^{17}O spectra do show interesting changes, beginning at 600 °C. At this temperature the Sc−O−Mo peak at 560 ppm, and its accompanying spinning sidebands, begin to broaden. This suggests that oxide ion exchange among adjacent sites, or among "normal" sites and interstitials, partially averaging the CSA, is beginning to be observable at this temperature, implying motion at a frequency comparable to the sideband spacing or a few kHz. The lack of obvious broadening of the Sc−O−W oxygens at 600 °C indicates that these sites may exchange somewhat more slowly. By 700 °C, the entire CSA pattern has merged into a single very broad peak, suggesting exchange at roughly the 10 kHz time scale that involves both types of oxygens.

Equation 1 can also be to used roughly estimate the mean ion jump frequency if oxide ion motion dominated the conductivity, again giving about 1 MHz at 600 °C. As for Sc^{3+}, this is still more than 2 orders of magnitude higher than the O^{2-} exchange frequency suggested by the NMR at this temperature. Although modeling of ^{17}O chemical exchange in high-temperature, high-resolution NMR spectra of oxide ion conductors can give results that are somewhat discrepant with conductivity measurements, apparently because somewhat different aspects of the dynamics may be sampled,[39] the results on $Sc_2(W_{0.25}Mo_{0.75}O_4)_3$, suggest that neither simple exchange of Sc^{3+} among all octahedral sites, nor of O^{2-} among the normal, crystallographic oxide ion sites, can explain measured conductivities if the latter are indeed characteristic of the bulk material. The NMR data also suggest a considerably greater mobility of the anion than of the cation. Conductivity dominated by interstitial ions that do not exchange rapidly with those in the bulk structure, or on grain boundaries, may be implied.

Conclusions

$Sc_2(WO_4)_3$, $Sc_2(MoO_4)_3$ and their solid solutions were studied using ^{45}Sc and ^{17}O MAS NMR at ambient to high temperature to investigate the extent of short-range disorder and the dynamics, in particular whether the scandium ion is indeed the main mobile species. The latter has seemed unlikely because trivalent ions generally diffuse relatively slowly due to their high charge.

Ambient temperature ^{45}Sc MAS NMR of compounds across the tungstate−molybdate join show gradual changes in chemical shifts and line widths, whereas ^{17}O MAS NMR spectra have resonances that remain at positions similar to those in the two end members. This results suggest that $Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$ form homogeneous solid solutions with little or no distortion or change in the local, short-range structure as W substitutes for Mo.

^{45}Sc MAS NMR line shapes change very little with temperature all the way up to 700 °C, although they shift systematically to higher frequency. Apparently, most of the scandium ions in the bulk material are not mobile enough to be the major source of the ionic conductivity, although we cannot completely rule out some role for such ions in

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grain boundary or interstitial sites. Above about 500 °C, ^{17}O MAS spectra do show noticeable changes in line shape, suggesting that oxide ions may be a major mobile species, or at least one of the mobile species. ^{17}O high-temperature NMR also shows that oxygens near to molybdenum ions may be more mobile than those near to tungsten ions.

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