Sodium borosilicate glasses containing rhenium or technetium were fabricated and their vibrational spectra studied using confocal Raman microscopy. Glass spectra were interpreted relative to new high-resolution spectra of pure crystalline NaReO4, KReO4, NaTcO4, and KTcO4 salts. Spectra of perrhenate and pertechnetate glasses exhibited sharp Raman bands, characteristic of crystalline salt species, superimposed on spectral features of the borosilicate matrix. At low concentrations of added KReO4 or KtCo4, the characteristic pertechnetate and perrhenate features are weak, whereas at high additions, sharp peaks from crystal field-splitting and C3v symmetry dominate glass spectra, clearly indicating ReO4 and TcO4 is locally coordinated with K and/or Na. Peaks indicative of both K and Na salts are evident in many Raman spectra, with the Na form being favored at high concentrations of the source chemicals, where more K is available for ion exchange with Na⁺ from the base glass. The observed ion exchange likely occurred within depolymerized channels where nonbridging oxygens create segregation from the glass network in regions containing anions such as ReO4⁻ and TcO4⁻ as well as excess alkali cations. Although this anion exchange provides evidence of chemical mixing in the glass, it does not prove the added salts were homogeneously incorporated in the glass. The susceptibility to ion exchange from the base glasses indicates that long-term immobilization of Tc in borosilicate glass must account for excess charge compensating alkali cations in melt glass formulations. Published 2014. This article is a U. S. Government work and is in the public domain in the USA.

Additional supporting information may be found in the online version of this article at the publisher’s web site.

Keywords: perrhenate; pertechnetate; borosilicate; confocal Raman; technetium

Introduction

A priority goal of the US Department of Energy (US DOE) is to dispose of nuclear wastes accumulated in large underground tanks at the Hanford Nuclear Reservation in eastern WA, USA. These nuclear wastes date from the Manhattan Project of World War II and from plutonium production during the Cold War. The DOE plans to separate highly radioactive wastes from the oxidizing environment of the waste tanks. Preliminarily, perrhenate (ReO4⁻) and TcO4⁻ are added to the glass in order to study the impact of 99Tc on the properties and performance of highly radioactive glass formulations for long-term storage. Raman microscopy was used here to probe local environments in the glass structure and to study the crystallization behavior previously observed on the surface of the LAW glass.3,4 The pertechnetate ion (TcO4⁻) is the dominant form of Tc metal in the oxidizing environment of the waste tanks. Preliminarily, perrhenate (ReO4⁻) was used as a nonradioactive surrogate for pertechnetate to probe the effects of the ion on the coordinated silicate, borate, and aluminate networks. Later, 99TcO4⁻ was used for direct measurement of its structural and chemical effects on the borosilicate glass networks. It was expected that incorporation of Tc and Re in glasses would be somewhat different because of known differences in oxidation-reduction potential.3,6 The incorporation of ReO4⁻ in aluminoborosilicate glasses was previously measured by conventional Raman spectroscopy, X-ray absorption near edge structure spectroscopy, nuclear magnetic resonance spectrometry, and X-ray diffraction (XRD) analysis.4,7 A subset of these measurements were performed on analogous Tc-containing glasses, and results are presented elsewhere.8

This work presents data from high spatial-resolution and high spectral-resolution Raman microscopy, which probed the local structure within the glasses as well as crystalline phases on the bulk glasses. These measurements may guide glass formulations to provide better long-term durability of 99Tc-containing aluminoborosilicate glasses, specifically by providing insight into the local environment around pertechnetate species. As part of this effort, new high-resolution Raman spectra were obtained from pure alkali perrhenate and pertechnetate salts: NaReO4, KReO4, NaTcO4, and KtCo4. To our knowledge, the full Raman spectrum of NaTcO4 has not been published in the past. Here we describe Raman spectra of perrhenate and pertechnetate glasses to help guide glass formulations to achieve better durability of 99Tc in glasses.

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never been presented before (a partial spectrum was provided in 9), and no comparison of the spectra of these four compounds has been offered. Presented here are exemplar spectra and vibrational assignments of peaks from these model species and comparisons to peaks from alumino-borosilicate glasses containing KReO₄ and KTCO₄. Raman spectra were analyzed for evidence of perturbations of the alumino-borosilicate networks after adding KReO₄ or KTCO₄ at varying concentrations to the LAW glass. The LAW glass has the following composition by weight: 61% Al₂O₃, 10% B₂O₃, 2.07% CaO, 0.02% Cr₂O₃, 5.5% Fe₂O₃, 0.47% K₂O, 1.48% MgO, 21% Na₂O, 45.3% SiO₂, 0.16% SO₃, 1.4% TiO₂, 3.5% ZnO, and 3% ZrO₂.

The coordinated environment of rhenium in solution and in crystalline salts has been a subject of study for many years. Beintema[10] and Fonteyn[11] proposed octahedral coordination for rhenium in solution, although Beintema found tetrahedral coordination in crystalline alkali perrhenates. Claassen and Zielen[12] measured the infrared and Raman spectra of dilute solutions of perrhenate and used the numerical methods of Heath and Linnett[13] to determine that perrhenate (ReO₄²⁻) exists in tetrahedral coordination in both solutions and in crystalline solids. Since this time, a few authors have revisited the vibrations of perrhenate in solution[14–17] as well as in the alkali salts KReO₄[18–20] and NaReO₄[19,20]. Rhenium has remained of interest because of its use as a surface catalyst for a variety of organic syntheses.[21]

Similarly, technetium has remained of interest since its discovery, because of its role in nuclear processes and concern over its long-term environmental disposal. Several studies have been made of the Raman spectra of pertechnetate (TcO₄³⁻) in solution. However, there have been few reports of the Raman spectrum of KTCO₄[17,18,25] and only one of NaTcO₄.[17] McKeown and coworkers[22] are the only ones to report Raman spectra of technetium in glass. They describe pertechnetate in glass as being similar to the free-ion vibration but shifted up to 20 wavenumbers because of the local presence of a particular alkali species.

**Experimental**

Glasses containing varying concentrations of rhenium and technetium were prepared according to the methods of McCloy and coworkers[26] by melting glass frits of the composition above at 1000 °C for 2 h in sealed silica tubes with potassium salts of Re or Tc oxide. Target concentrations of rhenium in glass varied from 100 to 10 000 ppm Re by mass. The solubility of Re in glass was previously determined to be ~3000 ppm Re,[4] so target concentrations in glasses varied from 500 to 6000 ppm Tc, with counts times, and the diameter of the confocal iris were varied to achieve very strong signal-to-noise ratios. Similarly, technetium has remained of interest since its discovery because of its role in nuclear processes and concern over its long-term environmental disposal. Several studies have been made of the Raman spectra of pertechnetate (TcO₄³⁻) in solution. However, there have been few reports of the Raman spectrum of KTCO₄[17,18,25] and only one of NaTcO₄.[17] McKeown and coworkers[22] are the only ones to report Raman spectra of technetium in glass. They describe pertechnetate in glass as being similar to the free-ion vibration but shifted up to 20 wavenumbers because of the local presence of a particular alkali species.

**Experimental**

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Reagent-grade NaReO₃ and KReO₃ (Alfa Aesar) were obtained for standards. NaTcO₃ and KTCO₃ were obtained as follows, with detailed procedures described elsewhere.[8] Solid, crystalline KTCO₃ was prepared from ammonium pertechnetate (NH₄H₂TcO₄, obtained from Oak Ridge National Laboratory). The NH₄H₂TcO₄ was partially decomposed from its own beta radiation and so was recrystallized by dissolving in a solution of ammonium hydroxide and hydrogen peroxide and then heated to reoxidize the technetium to pertechnetate and to decompose the excess peroxide. The solution was evaporated to recrystallize phase pure NH₄H₂TcO₄ as colorless crystals, which were washed with dry ethanol to remove water, then dried. Freshly recrystallized, dry NH₄H₂TcO₄ was weighed then dissolved in water, and a carefully measured stoichiometric amount of K₂CO₃ was added to the NH₄H₂TcO₄ solution. The combined solution was evaporated to a low volume to expel (NH₄)₂CO₃ and cause crystalline potassium pertechnetate to form. The pertechnetate product was washed with ethanol to remove water and then dried. Subsamples of the potassium pertechnetate were assayed for total technetium by liquid scintillation and found to be pure KTCO₃ within analytical uncertainty. The product was free-flowing, white crystalline powder, a little finer than table salt. Sodium pertechnetate was prepared from potassium pertechnetate by passing an aqueous solution of KTCO₃ through a sodium form cation exchanger. The solution was evaporated to crystallize NaTcO₄. The crystalline product was dried to a free-flowing powder.

Glasses and crystalline materials were analyzed using a Horiba high-resolution confocal inverted-stage microscopic Raman spectrometer (LabRam HR8000) with 600 grooves/mm diffraction gratings, using a Nikon Eclipse Ti microscope. Laser excitation at 532 nm was provided by a Quantum Laser MPC-3000, which delivered ~20 mW of power to samples with an approximate spot diameter of 1 μm on the samples. Spectra were recorded using a Peltier-cooled Horiba Synapse charge-coupled device (CCD) detector with a 1024 × 256 pixel array. The spectrometer was calibrated using the line positions of a Hg pen lamp, and the spectral resolution of the system, as described, was 1.8 cm⁻¹/pixel with a laser spot size of 1.1 μm. The spectrometer was preliminarily centered at 1000 cm⁻¹ Raman shift from the 532 nm laser excitation, precluding measurement of some external (skeletal) modes. The spectrometer position was changed to 950 cm⁻¹ to capture these low wavenumber peaks, allowing data collection from 1750 to ~50 cm⁻¹. The number of spectral acquisitions, count times, and the diameter of the confocal iris were varied to maximize the signal-to-noise ratio of spectra. Most glass spectra were acquired for 10 min for improved signal-to-noise ratios. Crystalline ReO₃ and TcO₄ salts only required 2–10 s of acquisition time to achieve very strong signal-to-noise ratios.
**Results and discussion**

Raman analyses of crystalline NaReO_4, KReO_4, NaTcO_4, and KTcO_4 provided reference spectra for comparing ReO_4\(^-\) and TcO_4\(^-\) containing glasses. These reference spectra shown in Figs 1 and 2 reveal stretching and bending modes of perrhenates and pertechnetates, as well as external or lattice vibrations of these Na and K salts. Spectra from the crystalline solids did not require any spectral manipulations to provide very strong and well-resolved Raman bands. Fundamental vibrations, listed in Table 1 and Table 2, are compared with published values of aqueous anions, alkali salts, and to the acquired Raman spectra of Re-containing and Tc-containing glasses. Spectra from glasses containing low concentrations of KReO_4 and KTcO_4 were baseline corrected (‘rubberband’ correction) to provide consistent spectral resolution and band positions. Derived spectra were obtained by spectrally subtracting baseline LAW glass spectra from spectra of KReO_4 and KTcO_4 containing glasses. Spectral subtractions were sometimes aided by adjusting spectral amplitudes using a multiplicative constant. A spectral artifact observed in several glass spectra at 390 cm\(^-1\) was attributed to poor spectral filtering of a plasma line from the HeNe laser. A few glass spectra contain weak peaks, which have not been resolvable to Raman vibrations from Tc and Re. These bands have been included in the bottom of Tables 1 and 2 as unassigned vibrations.

**Crystalline phases**

Alkali perrhenates, KReO_4\(^-\)[28] and NaReO_4\(^-\)[21] and alkali pertechnetates, KTcO_4\(^-\)[29] and NaTcO_4\(^-\)[30] are all tetragonal with space group I\(4'h\), possessing the Scheelite structure (CaWO_4). Group theory predicts that Re and Tc in K and Na salts has local symmetry \(C_{4v}\) from lattice symmetry of \(S_4\) from free-ion symmetry \(T_d\)[17,19,20,31]. A correlation diagram illustrating the mode derivations is shown in Fig. 3.

Comparing Raman spectra of crystalline NaReO_4 and KReO_4 shows the K salt exhibits higher symmetric (\(\nu_1\)) and antisymmetric (\(\nu_3-E_g\)) stretching modes. The symmetric (969 cm\(^-1\)) and the antisymmetric stretch (898 cm\(^-1\)) are \(\sim 10\) cm\(^-1\) higher in KReO_4 spectra, relative to NaReO_4 (Fig. 1). Given that both cations are coordinated to the same ligand, this spectral difference must be due to an intrinsic property of the cation. This difference may be attributed to the larger covalent radius (203 pm), atomic volume (45.3 cm\(^3\)/mol), or K-O bond length of K relative to Na (and Na-O). Sodium has a covalent radius of 154 pm and an atomic volume of 23.7 cm\(^3\)/mol, which is roughly half the atomic volume of K. Literature values of average alkali metal–oxygen bond lengths are 2.829 Å\[^{25,29}\] in KTcO_4 and 2.582 Å in NaReO_4\[^{32}\]. If the larger atomic or covalent radii or longer bond length of K (as K-O) is responsible for the higher vibrational mode in KReO_4, then there should be fewer K+ coordinated per ReO_4\(^-\). Fewer coordinating K+ per ReO_4\(^-\), relative to the number of coordinating Na+ per ReO_4\(^-\), is consistent with observations by Gafurov and Aliev\[^{33}\] that ‘the number of the complexing ions becomes smaller with enlargement of the ionic radius of the cation’ in alkali metal salts. Alternatively, one could pose that the degree of covalency experienced by each ReO_4\(^-\) is higher in NaReO_4 (and possibly NaTcO_4) because there are more Na–O nearest neighbors sharing charge with the ligand. This increased covalency could shift NaReO_4 modes to lower wavenumbers\[^{25}\]. The antisymmetric (\(\nu_3\)) stretch (\(\nu_3\)) is approximately the same in both ReO_4\(^-\) salts (925 cm\(^-1\)).
### Table 1. Raman assignments of pure Re compounds and glasses

<table>
<thead>
<tr>
<th>Mode</th>
<th>ReO₄ (aq) [14–17]</th>
<th>KReO₄ [18–20,52,53]</th>
<th>KReO₄ (PNNL)</th>
<th>NaReO₄ (PNNL)</th>
<th>NaReO₄ (PNNL)</th>
<th>4000 ppm glass (PNNL)</th>
<th>6145 ppm glass (no SO₃) (PNNL)</th>
<th>10000 ppm glass position 1 (PNNL)</th>
<th>10000 ppm glass position 2 (PNNL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁-sym stretch</td>
<td>971–972 (A₁)</td>
<td>966–967 (A₀)</td>
<td>969 vs</td>
<td>958–968</td>
<td>957 vs</td>
<td>966</td>
<td>965</td>
<td>957</td>
<td>967</td>
</tr>
<tr>
<td>ν₂-antisym stretch</td>
<td>918–920 (F₂)</td>
<td>924–928 (B₁g)</td>
<td>926 w</td>
<td>924–928</td>
<td>924 w</td>
<td>925</td>
<td>922</td>
<td>924</td>
<td>924</td>
</tr>
<tr>
<td>ν₃-sym bend</td>
<td>333 (F₂)</td>
<td>346–351 (B₁g)</td>
<td>352 w</td>
<td>360–372</td>
<td>372 w</td>
<td>349</td>
<td>348</td>
<td>350, 371</td>
<td>350</td>
</tr>
<tr>
<td>ν₄-antisym bend</td>
<td>331–333 (E)</td>
<td>334–338 (A₁g)</td>
<td>339 w</td>
<td>334–335</td>
<td>332 w</td>
<td>337</td>
<td>338</td>
<td>333</td>
<td>336</td>
</tr>
<tr>
<td>νMESS (cation) lattice F₂</td>
<td>158–160* (Eₗ)</td>
<td>151* (B₁g)</td>
<td>—</td>
<td>181–185*</td>
<td>176 w</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ν₅ (ReO₄) lattice F₁</td>
<td>125–128* (A₁g)</td>
<td>142 w</td>
<td>145–156*</td>
<td>144 w</td>
<td>—</td>
<td>106</td>
<td>106</td>
<td>108</td>
<td>108</td>
</tr>
<tr>
<td>ν₆(ReO₄) lattice F₂</td>
<td>65–73* (Eₗ)</td>
<td>67 w</td>
<td>84–89*</td>
<td>83 w</td>
<td>77–80*</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Unassigned: 1002, 762, 620, 520, 93, 90, 390 (artifact)

Raw spectra can be found online in the Supporting Information. Columns denoted [Pacific Northwest National Laboratory (PNNL)] are measurements from this current work. For new crystalline measurements, the relative strength of peaks is indicated by vw (very weak), w (weak), m (medium), and vs (very strong).

* Denoted value in range is value at 77 K [20]; lattice modes move to lower wavenumber as temperature is increased. Note that Johnson [19] and Brown [53] disagree slightly on the mode assignments for lattice modes of the alkali perrhenates.

### Table 2. Raman assignments of pure Tc compounds and glasses

<table>
<thead>
<tr>
<th>Mode</th>
<th>TcO₄ (aq) [15,16,18–24]</th>
<th>KTCO₄ [17,18,25]</th>
<th>KTCO₄ (PNNL)</th>
<th>NaTcO₄ (PNNL)</th>
<th>Surface salt</th>
<th>1000 ppm glass</th>
<th>2000 ppm glass</th>
<th>3000 ppm glass</th>
<th>4000 ppm glass</th>
<th>4000 ppm particle</th>
<th>BS glass [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁-sym stretch</td>
<td>910–912 (A₁)</td>
<td>913 (A₀)</td>
<td>910 vs</td>
<td>902 vs</td>
<td>905 vs</td>
<td>911</td>
<td>913</td>
<td>904, 913</td>
<td>905, 912</td>
<td>901</td>
<td>1018</td>
</tr>
<tr>
<td>ν₂-antisym stretch</td>
<td>904–908 (F₂)</td>
<td>920 (B₁g)</td>
<td>917 m</td>
<td>918 w</td>
<td>919 m</td>
<td>920</td>
<td>920</td>
<td>920</td>
<td>920</td>
<td>916</td>
<td>916</td>
</tr>
<tr>
<td>ν₃-sym bend</td>
<td>323–325 (F₂)</td>
<td>327 (B₁g)</td>
<td>327 m</td>
<td>322 m</td>
<td>326 s</td>
<td>328</td>
<td>329</td>
<td>324</td>
<td>327</td>
<td>323</td>
<td>325</td>
</tr>
<tr>
<td>ν₄-antisym bend</td>
<td>336 (E)</td>
<td>360 (A₁g)</td>
<td>358 w</td>
<td>377 w</td>
<td>377 w</td>
<td>361</td>
<td>377</td>
<td>378</td>
<td>377</td>
<td>377</td>
<td>—</td>
</tr>
<tr>
<td>νMESS (cation) lattice F₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>ν₅ (TcO₄) lattice F₁</td>
<td>104</td>
<td>102 w</td>
<td>98 m</td>
<td>167</td>
<td>167</td>
<td>167</td>
<td>167</td>
<td>167</td>
<td>167</td>
<td>162</td>
<td>162</td>
</tr>
<tr>
<td>ν₆(TcO₄) lattice F₂</td>
<td>70</td>
<td>70 w</td>
<td>859</td>
<td>849, 126 sh</td>
<td>999, 862, 126</td>
<td>851</td>
<td>849, 129</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Unassigned: 859, 849, 126 sh

Raw spectra can be found online in the Supporting Information. Columns denoted [Pacific Northwest National Laboratory (PNNL)] are measurements from this current work. For new crystalline measurements, the relative strength of peaks is indicated by vw (very weak), w (weak), m (medium), vs (very strong), and sh(shoulder).
Two well-resolved bending modes occur at 352 and 339 cm$^{-1}$ in KReO$_4$, with a poorly resolved shoulder at 325 cm$^{-1}$. Similarly, two bending modes occur at 372 and 332 cm$^{-1}$ in NaReO$_4$. This larger energy separation (40 cm$^{-1}$) from NaReO$_4$ indicates a greater difference in oscillator strengths of these bending modes relative to KReO$_4$. This larger difference in oscillator strengths may indicate that Na$^+$ has two distinctly different bond lengths or bond angles amongst nearest neighbor Na$^+$ in the crystalline lattice.

A significant difference exists between the Raman spectra of the crystalline pertechnetates and crystalline perrhenates. In the perrhenates, the symmetric stretch ($v_1$) occurs well above the two antisymmetric stretching bands. In the pertechnetates, the symmetric stretch lies between the two antisymmetric stretching bands (Fig. 2). In this case, the role of K$^+$ and Na$^+$ in coordination with ReO$_4$ and TeO$_4$ is approximately the same, and the principal difference lies with the role of TeO$_4$ in these complexes. This downward shifting of the pertechnetate salt vibrations suggests a significantly increased degree of covalency of pertechnetate in both the Na and K salts, relative to the perrhenates. Increased covalency is consistent with the shorter Tc-O bond length seen in KTaO$_3$ (1.724 Å) versus the Re-O bond length of KReO$_4$ (1.733 Å).

In a similar trend to the perrhenates, crystalline KTaO$_3$ exhibits $\sim$10 cm$^{-1}$ higher stretching bands relative to NaTaO$_3$, with the exception of the antisymmetric ($v_3$) stretch (B$_1g$) at $\sim$917 cm$^{-1}$. Once again, it is concluded that the larger K$^+$ maintains a more open tetrahedral structure than Na during perrhenate stretching (Fig. 2). The pertechnetates also express three bending modes instead of two as observed in the perrhenates. Two subordinate bending modes occur with approximately a 10 cm$^{-1}$ difference between them, along with a stronger band offset to lower wavenumbers. This lower band is likely a polarized bending mode as the band intensity is much stronger than the subordinate bending modes; however, the confocal Raman spectrometer was not configurable to collect polarized spectra. Interestingly, the band separation between the subordinate bands and the stronger bend is significantly larger in NaTaO$_3$ (42 cm$^{-1}$) than KTaO$_3$ (21 cm$^{-1}$). Again, one could pose that this lower wavenumber band could be a symmetric bending mode with greater covalency than the antisymmetric bends.

### Table 3. Group theory correlation diagram for ReO$_4$ and TeO$_4$ free-ion modes and corresponding modes in alkali perrhenate and pertechnetate salts (C$_{4v}$ symmetry). R indicates a Raman-active mode and IR indicates an infrared-active mode.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Free ion (T$_d$)</th>
<th>Site symmetry (S$_a$)</th>
<th>Factor group (C$_{4v}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>A$_1$ (R)</td>
<td>A (R)</td>
<td>A$_1$ (R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B$_1$ (silent)</td>
</tr>
<tr>
<td>$v_2$</td>
<td>E (R)</td>
<td>A (R)</td>
<td>A$_1$ (R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B$_1$ (silent)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B (R, IR)</td>
<td>A$_1$ (IR)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R$_1$ (R)</td>
</tr>
<tr>
<td>$v_3$,$v_4$</td>
<td>F$_2$ (R, IR)</td>
<td></td>
<td>E$_g$ (R)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Glass network

Raman spectra from the borosilicate matrix of Re-containing and Tc-containing glasses exhibited two broad envelopes, one containing primarily Si–O–Si bending modes (650–250 cm$^{-1}$) and the second Si–O–Si stretching modes (1200–800 cm$^{-1}$). Generally, the strong bands in the Si–O–Si stretching region correlate to an increasing number of bridging oxygens (BOs) per SiO$_4$ with increasing wavenumbers. However, some variability exists in the reported frequencies of these bands. McMillan described band frequencies for Na and K borosilicates as near 1110, 950–930, 900, and 850 cm$^{-1}$ with successively greater degrees of silicate polymerization with increasing wavenumber. These bands are conventionally described as Q$^1$, Q$^2$, Q$^3$, Q$^4$, with 0, 1, 2, and 3 nonbridging oxygens (NBOs) per silicate unit, respectively. The 850 cm$^{-1}$ band was said to first appear at 40 mol% of alkali oxide (M$_2$O = Li$_2$O, Na$_2$O, K$_2$O) and increased in intensity with increasing M$_2$O addition. The 990 cm$^{-1}$ band was described in the succeeding text was likely promoted from the 950–930 cm$^{-1}$ range because of the high molar percentage of silica (50% SiO$_2$). Parkinson et al. identified four Si–O–Si stretches at 1150, 1065, 970, and 925 cm$^{-1}$ from Cs$_2$O-borosilicate glasses and correlated them to Q$^4$(B), Q$^3$, Q$^2$, and Q$^1$, respectively. In this nomenclature, Q$^4$(B) species are fully coordinated tetrahedral Si predominantly bonded to two Si and two B next nearest neighbors. The high-frequency band identified at 1150 cm$^{-1}$ occurs only as a weak shoulder in spectra and decreases in intensity with decreasing silica content.

In this study, the relative intensities of silicate stretches between 1200 and 800 cm$^{-1}$ varied between different surface sites probed by the Raman laser as exemplified by spectra from the 1000 ppm Tc glass (Fig. S1(a), Supporting Information). Three different spectra yield varying band intensities from Si–O–Si stretching at 1095 (Q$^4$), 990 (Q$^3$), and 920 (Q$^2$) cm$^{-1}$. These bands, attributed to Si–O–Si stretching in the silicate banding network, also have some contribution from antisymmetric and symmetric stretching of tetrahedral TcO$_4$ visible at 919, 880, and 912 cm$^{-1}$ (Fig. S1(a), Supporting Information). The strength of the TcO$_4$ contributions to glass spectra increased with increasing Tc additions (Fig. S1(b), Fig. S2(a, b), Supporting Information). A salt removed from the surface of the 4000 ppm Tc glass is shown in Fig. S1(a), Supporting Information. Three bands are correlated to Q$^4$(B), Q$^3$, and Q$^2$, respectively. In this nomenclature, Q$^4$(B) species are fully coordinated tetrahedral Si predominantly bonded to two Si and two B next nearest neighbors. The high-frequency band identified at 1150 cm$^{-1}$ occurs only as a weak shoulder in spectra and decreases in intensity with decreasing silica content.

The Si–O–Si bending modes are broad and poorly resolved, showing weak peaks at $\sim$570, 540, 490, 437, and 330 cm$^{-1}$. These modes significantly overlap and provide little useful information regarding the coordinating environments in the borosilicate matrix. Generally, these poorly resolved bands resemble silicate glasses containing high molar percentages of alkali oxides (M$_2$O) with weak unresolved bands at 590, 560, and 520 cm$^{-1}$. McMillan notes that bands at 610–590 and 560–520 cm$^{-1}$ are not simply derived from the 500 and 600 cm$^{-1}$ bands of vitreous silica, but are new bands introduced with addition of metal oxide. At high molar additions of Na$_2$O (20%) to silicate glasses, Raman bands were
observed at 530, 495, and 450 cm\(^{-1}\) by Furukawa and White.\[^{27}\] Sharma et al.\[^{35}\] in their analyses of SiO\(_2\) glass attributed a band at 430 cm\(^{-1}\) to vibrations of six-membered rings of SiO\(_2\) and a band at 490 cm\(^{-1}\) to vibrationally isolated symmetric stretching of Si–O–Si from four-membered rings of SiO\(_2\) tetrahedra.

A singular broad band exists between the stretching and bending regions discussed earlier. This weak band at 781 cm\(^{-1}\) may be due to silicon vibrating against its tetrahedral oxygen cage, the silicon moving symmetrically with respect to the bridging oxygen.\[^{36}\]

A weak and poorly resolved band at 770 cm\(^{-1}\), observed in glass spectra, has been attributed to vibrations of six-membered borate rings with one or two [BO\(_2\)]\(^−\) units.\[^{27}\] Another weak and broad band ~630 cm\(^{-1}\) may be due to short-range ordering by B or possibly SiO\(_3\) chain units. This band was attributed to Na\(_3\)B\(_3\)O\(_6\) from crystallized Na\(_2\)O 0.5·SiO\(_2\) 0.5·B\(_2\)O\(_3\) glass.\[^{27}\] Lastly, a weak high-frequency mode at ~1400 cm\(^{-1}\) is attributed to antisymmetric stretching of trigonally coordinated boron (BO\(_3\))\(^−\) within the borosilicate lattice. Trigonal boron also has a Raman-active vibration \(\nu_2(E^1)\) at 545 cm\(^{-1}\), which may be contributing to the band observed at 540 cm\(^{-1}\) discussed earlier.

**Rhenium in glass**

The symmetric stretch \(\nu_1\) of KReO\(_4\) in glass occurs at 966 cm\(^{-1}\) with two antisymmetry stretches \(\nu_2, \nu_3\) at 896 and 925 cm\(^{-1}\).\[^{18–20}\]

The intensity of the 896 cm\(^{-1}\) band is twice that of the 925 cm\(^{-1}\) band, consistent with group theory predictions \((2 \times B_3 = E_g)^{[13]}\) for the weak bands at 349, 337, and 330 cm\(^{-1}\) are attributed to bending vibrations of tetrahedrally coordinated ReO\(_4\). Spectral splitting of the \(\nu_2\) \((A_2)\) band at 331 cm\(^{-1}\) was predicted to give another band at 343 cm\(^{-1}\) \((\Delta \nu=12 \text{ cm}^{-1})\), because of tetrahedral distortion.\[^{12}\] This 343 cm\(^{-1}\) degenerate band was not observed in Re glass spectra; however, the observed bands agreed well with those of crystalline KReO\(_4\).

Repetitive spectral collection from 4000 and 6415 ppm Re glasses yielded very few spectra with evidence of ReO\(_4\). Two Raman spectra from the 4000 ppm Re glass, with a derived spectrum showing KReO\(_4\) bands, are shown in Fig. S4 (Supporting Information). The KReO\(_4\) spectrum derived by spectral subtraction shows bands at 966, 925, 896, 349, 337, 330, and 106 cm\(^{-1}\) (Fig. S4, Supporting Information). Nearly identical KReO\(_4\) vibrations were observed from the 6415 ppm Re glass (Table 1 and Fig. S5, Supporting Information). The solubility of Re in these glasses has been shown to be 3000 ppm,\[^{41}\] and the 4000 ppm glass has shown no evidence of crystallization in the bulk glass (by XRD) and no visual evidence of salt formation on the surface.\[^{7}\] Unlike bulk Raman spectroscopy, which showed no evidence of crystallinity on the 4000 ppm Re glass,\[^{23}\] the Raman microscopy suggested KReO\(_4\) crystals, and optical microscopy confirmed the presence of white crystals decorating cracks in the glass produced by cooling. As the glass cooled in the ampoule, thermal stresses caused it to crack, while the salt was still molten, and it was pulled into the cracks where it crystallized. However, only 1 of 16 spectra taken for this glass contained sharp peaks, suggesting that these peaks are probably due to crystalline phases.

Several Raman peaks from the 10000 ppm Re glass are nearly identical to those from 4000 to 6415 ppm Re glasses. Spectra of the 10000 ppm Re glass show ReO\(_4\) vibrations of varying intensity superimposed on broad Si–O and O–Si–O stretching between 1200 and 800 cm\(^{-1}\) (Fig. S6, Supporting Information). However, the bands at 956, 924, 887, and 370 cm\(^{-1}\) are consistent with NaReO\(_4\).

It is likely that at higher added Re concentration, there is more ionic interaction of ReO\(_4\) with the elevated Na\(^+\) concentration (21 wt.% Na\(_2\)O) of the glass matrix, tending to form NaReO\(_4\). The downward shifting of NaReO\(_4\) bands, relative to KReO\(_4\) bands, is likely due to increased covalency of Na\(^+\)–ReO\(_4\) bonding.\[^{25}\] The 10 000 ppm Re glass has been shown to contain crystals of alkali perrhenate species of both NaReO\(_4\) and KReO\(_4\). The upper panel of Fig. 4 shows a progression of Raman spectra from crystalline KReO\(_4\) (bottom) and NaReO\(_4\) (top) and 10 000, 4000, and 10 000 ppm Re glasses (derived spectra). The 4000 and lowest 10 000 ppm Re glass spectra were the most similar to KReO\(_4\). However, the 10 000 ppm Re glass exhibits Raman peaks of KReO\(_4\), NaReO\(_4\), or both, depending on the subsampling of the glass.

**Technetium in glass**

Raman spectra from Tc-containing glasses showed varying band intensities from TcO\(_4\), similar to that variability previously described for the perrhenates. Low concentrations of TcO\(_4\) (≤1000 ppm Tc) yielded weak peaks superimposed on the broad bands of the glass matrix (Fig. S1(a), Supporting Information). There was also significant heterogeneity in the observed spectra at different locations on the same glass surface, particularly if the surface was from the top of the melt. Above the TcO\(_4\) solubility limit (2000 ppm for glass as prepared and 3000 ppm for glass under slightly reducing conditions\[^{26}\]), the glass surface was covered with crystalline pertechnetate salt when cooled to room temperature. Fractures formed in the glass during later stages of cooling were sometimes in-filled by still molten pertechnetate.
silt. In some cases, pertechnetate salts collected in surface pores of the cooled glass and, in other cases, formed well-shaped crystals, suggesting vapor phase deposition. Care was taken to obtain spectra from glass surfaces visibly free of crystalline precipitates, unless of specific interest.

Generally, as Tc concentrations in glasses increased, the characteristic Raman bands of TcO$_4^-$ stretching and bending became better resolved and allowed discrimination from the glass matrix. Spectra acquired from glasses containing 2000, 3000, and 4000 ppm Tc (Figs. S1(b), S2(a), S2(b), Supporting Information) exhibited much stronger TcO$_4^-$ stretching and bending modes and low wavenumber external modes. These latter modes are typically associated with vibrations in crystalline lattices but are here referring to translational and rotational vibrations of the alkaline metal to oxygen bond of the TcO$_4^-$ ion in glass.[17,18]

Notably, as Tc target concentrations increased from 2000 to 3000 to 4000 ppm in the glasses, there were gradual ingrowths of new stretching and bending bands. Figure 4 shows stacked Raman spectra of pure crystalline KTcO$_4$ (bottom) and NaTcO$_4$ (top) and 2000, 3000, and 4000 ppm Tc glasses (derived spectra). Trending from bottom to top in this figure, the stretching and bending vibrations of KTcO$_4$ as the salt and then in glasses become more consistent with crystalline NaTcO$_4$. The spectrum of the 4000 ppm glass appears to contain both KTcO$_4$ and NaTcO$_4$. Individually, indexed spectra of these salt phases are found in Fig. 2 and the glasses in Fig. S1 and Fig. S2 (Supporting Information).

Similarly to the previous discussion regarding higher perrhenate concentrations, it is likely that increasing KTeO$_4$ concentrations in glasses makes higher TcO$_4^-$ concentrations available for ionic interaction with very high Na concentrations (21 wt.% Na$_2$O) in the glass matrix during melting. This inference necessitates at least partial equilibrium of NaTcO$_4$ and KTeO$_4$ in the same volume of glass excited by the laser. The process of Na$^+$ exchanging for K$^+$ from KTeO$_4$ may have been controlled by the difference in melting points of NaTcO$_4$ and KTeO$_4$, which Vida et al. measured using calorimetry to be 378°C and 532°C, respectively. This difference in melting temperature may have limited the amount of Na that exchanged for K and predisposed the formation of KTeO$_4$ over NaTcO$_4$ during cooling.

Alkali cations above the concentration needed to compensate network forming anions are attributed to coordinating with NBOs and becoming segregated from the network forming cations and BOs in glasses. The segregation and coalescence of these excess alkali cations and NBOs into microscopic channels have been proposed as a mechanism for enhanced movement of cations in silicate glasses.[39] The observed Na$^+$ for K$^+$ exchange likely occurred within these channels in proximity to ReO$_4^-$ and TcO$_4^-$ anions distributed within the LAV glass. It is thought that many cations such as neodymium,[40] molybdenum,[41] sulfur,[42,43] and likely rhenium[44] exist as oxyanion polyhedra along with halides[44,45] in a ‘depolymerized zone’ disconnected from the glass network, which at significant concentration can form ‘percolation channels’.[46] The alternative to the assumption that the oxyanion (e.g. molybdenate) is in a depolymerized zone[41] is that it exists as isolated tetrahedra.[47] If it is assumed that Re and Tc behave in the latter way, one would expect the Raman spectrum to consist of single bending and stretching modes, such as was observed by McKeown et al.[22] in their Tc-containing glasses. If, however, for kinetic or concentration reasons, the Tc (or Re) tendency to cluster together in zones rich with alkali, one might expect the Raman spectra to be more characteristic of the crystal field-splitting because of nearby alkali, as is observed in the current work.

Although the observed Na/K anion exchange provides evidence of chemical mixing in the glass, it does not prove the added KReO$_4$ or KTeO$_4$ salts were completely melted in the glass. Therefore, it cannot be ruled out that some sharp Raman peaks from glasses may be due to crystalline KReO$_4$ or KTeO$_4$ inclusions. It is unclear whether these structures were formed from the original starting materials (i.e. were not adequately homogenized), were formed during cooling (i.e. nanostructures in low concentration, not detectable by XRD or optical microscopy), or were present in disordered ‘depolymerized zones’ at melt temperatures but crystallized on cooling. Melting points of crystalline metasilicates (K$_2$O·SiO$_2$, 976°C; Na$_2$O·SiO$_2$, 1088°C) and disilicates (K$_2$O·2SiO$_2$, 1015°C; Na$_2$O·2SiO$_2$, 874°C) are significantly lower than that of crystalline SiO$_2$ (1723°C).[48,49] Brawer and White[50] suggest from this melting data that the Si–O networks are not ‘grossly altered’ when metasilicates and disilicates melt and that only the alkali-NBO bonds are broken on melting. They go on to propose that ‘in passing from the crystal to the melt the Si–O network becomes disordered without significantly altering its short-range order and general topological structure’.[50] The argument for incomplete homogenization of the glass comes from observations by Ebert et al.[51] that glasses, similar to those considered here but containing 1500 ppm Tc as NaTcO$_4$, showed inclusions by scanning electron microscopy when melted at 1100°C but not when melted at 1200°C. Similarly, McKeown et al.[22] melted 1580 ppm Tc glass at 1250°C compared with the 1000°C used for the glasses investigated here.

Conclusions

Spectra of perrhenate and pertechnetate glasses exhibited sharp Raman bands, characteristic of crystalline salt species, superimposed on spectral features of the borosilicate matrix. The perrhenate glasses exhibited consistent Raman stretching and bending modes at the 4000, 6415, and 10,000 ppm Re concentrations. With the exception of the 10 000 ppm Re glass, all Raman bands were consistent with crystalline KReO$_4$. The 10 000 ppm Re glass exhibited bands consistent with both crystalline KReO$_4$ and crystalline NaReO$_4$. At this higher concentration, there exist two populations of ReO$_4^-$, one associated with Na$^+$ and another associated with K$^+$. The weaker external modes (translational, rotational) observed in the crystalline solids were only observed in one spectrum of the 4000 ppm Re glass (106 cm$^{-1}$) and a few of the 10 000 ppm Re glass spectra (146 and 108 cm$^{-1}$).

Raman spectra of the pertechnetate glasses showed gradually increasing TcO$_4^-$ band intensities consistent with increasing addition of KTeO$_4$. However, there exists a significant degree of heterogeneity in the glasses as indicated by widely varying intensities of TcO$_4^-$ bands from individual glasses. The 1000 ppm Tc glass exhibited very weak KTeO$_4$ bands superimposed on Si–O–Si stretching and bending vibrations. Spectra from glasses with Tc concentrations of 2000, 3000, and 4000 ppm exhibited much stronger TcO$_4^-$ stretching and bending modes and low wavenumber external modes. Acquisition of the Raman spectrum of NaTcO$_4$ enabled identification of Raman bands appearing in spectra of the 3000 and 4000 ppm Tc glasses as being due to formation of NaTcO$_4$ in the presence of KTeO$_4$. Therefore, there are at least two populations of TcO$_4^-$ species at higher concentrations in glass, one associated with Na$^+$ and the other associated
with $K^+$. The possibility exists that another population of TcO$_4^-$ exists in the glass that shares charges with both Na and K ions, but none were observed in the spectra. These findings are consistent with the observations by Greaves and Ngal[30] who stated ‘Once the concentration of modifying oxide exceeded the percolation threshold ($x > 0.16$, where $x$ is the mole fraction of modifying oxide), these micro-segregated regions would coalesce to form channels which in turn would offer energetically advantageous pathways for ionic transport.’

These results and their interpretation have strong implications for the long-term stability of Tc in nuclear waste glass formulations. Both pertechnetate and perhenate glasses exhibit characteristic Raman bands of their precursor chemicals at intermediate concentrations in glass. Indications are that pertechnetate and perhenate glasses contain a continuum of anionic complexes associated with $K^+$ or Na$^+$ concentrations in the melt, and their relative abundances are controlled by the concentrations of added K$_2$CO$_3$ or KReO$_4$, respectively. It appears the high Na$^+$ concentration (21 wt.% Na$_2$O) in the base glass easily displaces $K^+$ through mass action at elevated K$_2$CO$_3$ and KReO$_4$ concentrations. Indeed, Vida[38] noted that the alkali cation in the Tc salt strongly influences the degree of Tc retention in borosilicate glasses, as both NaTcO$_4$ and K$_2$CO$_3$TcO$_4$ were better retained in the glass relative to CsTcO$_4$.

The base glass composition also has a strong effect on the equilibrium speciation of pertechnetate and perhenate in the glass melt and consequently on long-term durability in storage. It seems likely that the sharp TcO$_4^-$ and ReO$_4^-$ bands are due to crystalline or nanocrystalline species, not visible under light microscopy. Resolving the identity of these species will be important for determining the ultimate durability of a Tc-containing glass. Indications are that pertechnetate and ReO$_4^-$ complexes may be used as an indicator of relative bond strengths or bond lengths of Re–O and Tc–O bonds. Strongly cohesive bonding of the pertechnetate anion to alkali metals in the glass suggests better long-term chemical stability of the resulting mixture. Subsequent glass formulations will need to address apparent heterogeneities in individual glasses to ensure more homogeneous mixing.

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References

Raman analysis of perrhenate and pertechnetate


Supporting information

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