

Structural and Chemical Incorporation of ReO_4^- and TcO_4^- in Borosilicate Glasses

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Abstract

Sodium borosilicate glasses containing various concentrations of rhenium or technetium were fabricated, and their vibrational spectra studied using a Raman microscope. Spectra were interpreted with reference to new high resolution measurements of alkali pertechnetates and perrhenates NaReO_4 , KReO_4 , NaTcO_4 , and KTcO_4 . At low concentrations of ReO_4^- or TcO_4^- , glass spectra show weak peaks superimposed on a dominant spectrum of glass characteristic of silicate and borate network vibrations. At high concentrations, sharp peaks characteristic of crystal field splitting and C_{4h} symmetry dominate the spectra of glasses, indicating alkali nearby tetrahedral Re or Tc. Often peaks indicative of both the K and Na pertechnetates/ perrhenates are evident in the Raman spectrum, with the latter being favored at high additions of the source chemical, since Na is more prevalent in the glass and ion exchange takes place. These results have significance to immobilization of nuclear waste containing radioactive ^{99}Tc in glass for ultimate disposal.

1 Introduction

A priority goal of the United States Department of Energy (U.S. DOE) is to dispose of nuclear wastes accumulated in large underground tanks at the Hanford Nuclear Reservation in eastern Washington State, USA.^[1] 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 low activity wastes (LAW) and to isolate high-activity wastes in vitrified forms (glass) for long term disposal. Included in the inventory of highly radioactive wastes is large volumes of ^{99}Tc ($\sim 9 \times 10^2$ TBq or $\sim 2.5 \times 10^4$ Ci or ~ 1500 kg).^[2]

This paper describes the structure of glasses and crystalline salt compounds obtained when KReO_4 and KTcO_4 were added to sodium alumino-borosilicate simulated nuclear waste glass (LAW) in order to study the impact of ^{99}Tc on the properties and performance of highly radioactive glass formulations for long-term storage. Raman microscopy was used here, for the first time, to probe local environments in the glass structure and study the crystallization behavior previously observed on the surface of the glass.^[3;4] The pertechnetate ion (TcO_4^-) is the dominant form of the metal in the oxidizing environment of the waste tanks. Preliminarily, perrhenate (ReO_4^-) was used as a non-radioactive surrogate for pertechnetate to probe the effects of the ion on the coordinated silicate, borate, and aluminate networks. Later, $^{99}\text{TcO}_4^-$ 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 due to their known differences in oxidation-reduction potential.^[5;6]

The chemical and structural incorporation of ReO_4^- in alumino-borosilicate glasses were previously measured by conventional Raman spectroscopy, X-ray absorption near edge structure (XANES) spectroscopy, nuclear magnetic resonance spectrometry (NMR) 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] We present here data from high spatial- and high spectral-resolution Raman microscopy which probed the very local structure of the glasses as well as crystalline phases on the surface and in the bulk of the glasses.^[3] These measurements may guide glass formulations to provide better long term durability of ⁹⁹Tc containing alumino-borosilicate 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 never been presented before, and no comparison of the spectra of these four compounds has been offered. We present exemplar spectra and vibrational assignments of peaks from these model species and compare them to peaks from alumino-borosilicate glasses containing rhenium and technetium.

Raman spectra contain structural information about the local coordinating environments within glasses, particularly around the network forming silicate, borate, and aluminate species. The influence of incorporating alkaline and alkaline earth metals in these glasses is inferred from their effects on the coordinating environments of the network forming ions. Raman spectra were examined for evidence of perturbations of the alumino-borosilicate network by alkali cations and ReO₄⁻ or TcO₄⁻ ions added at varying concentrations to the baseline glass composition (see Table 1).

The coordinated environment of rhenium in solution and in crystalline salts has been a subject of study for many years. Beintema^[9] and Fonteyne^[10] proposed octahedral coordination for rhenium in solution, although Beintema found tetrahedral coordination in crystalline alkali perrhenates. Classen and Zielen^[11] measured the infrared and Raman spectra of dilute solutions of perrhenate and used the numerical methods of Heath and Linnett^[12] to determine that perrhenate (ReO₄⁻) 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^[13-16] as well as in the alkali salts KReO₄^[17-19] and NaReO₄.^[18; 19] Rhenium has remained of interest due to its use as a surface catalyst for a variety of organic syntheses.^[20]

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 (TcO₄⁻) in solution.^[14; 15; 17; 21-23] However, there have been few reports of the Raman spectrum of KTcO₄^[16; 17; 24] and none, to our knowledge, of NaTcO₄. McKeown and co-workers^[21] 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 due to the local presence of a particular alkali species.

2 Experimental

Glasses containing varying concentrations of rhenium and technetium were prepared according to the methods of McCloy and co-workers^[25] and the nominal composition without Re or Tc is shown in Table 1. 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 samples at higher concentrations contained crystalline inclusions of Re salts in the bulk and/or on the surface.^[3] Glasses examined here with Raman microscopy were those above the solubility limit of Re - namely target values 4000 ppm Re, 6415 ppm Re, 6415 ppm Re (no sulfate, balance of composition renormalized), and 10,000 ppm Re. Target concentrations of technetium in glass varied from 500 to 6000 ppm Tc by mass, some made under slightly reducing conditions. The solubility of Tc by mass was determined to be ~2000 ppm Tc for the LAW glass as prepared, and ~3000 ppm Tc for the same glass under slightly reducing conditions.^[8] The oxidation states of Tc varied among the glasses in the proportions of Tc(VII) (i.e., TcO₄⁻) and Tc(IV), while the oxidation state for Re in glass was always Re(VII) (i.e., ReO₄⁻).^[4; 8] Glasses examined here with confocal Raman microscopy include: 1000, 2000, 3000 and 4000 ppm target Tc concentrations obtained by adding KTcO₄ to LAW glass frit.

Reagent-grade NaReO_4 (Alfa Aesar) and KReO_4 (Alfa Aesar) were obtained for standards. NaTcO_4 and KTcO_4 were obtained as follows, with detailed procedures previously described.^[81] Solid, crystalline KTcO_4 was prepared from ammonium pertechnetate (NH_4TcO_4 , obtained from Oak Ridge National Laboratory). The NH_4TcO_4 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 re-oxidize the technetium to pertechnetate and to decompose the excess peroxide. The solution was evaporated to recrystallize phase pure NH_4TcO_4 as colorless crystals which were washed with dry ethanol to remove water, then dried. Freshly recrystallized, dry NH_4TcO_4 was weighed then dissolved in water, and a carefully measured stoichiometric amount of K_2CO_3 was added to the NH_4TcO_4 solution. The combined solution was evaporated to a low volume to expel $(\text{NH}_4)_2\text{CO}_3$ and cause crystalline potassium pertechnetate to form. The pertechnetate product was washed with ethanol to remove water and then dried. Sub-samples of the potassium pertechnetate were assayed for total technetium by liquid scintillation and found to be pure KTcO_4 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 KTcO_4 through a sodium form cation exchanger. The solution was evaporated to crystallize NaTcO_4 . The crystalline product was dried to a free-flowing powder.

Glass samples and the crystalline precursor chemicals were encapsulated in two-piece plastic membrane boxes for spectral measurements to prevent inadvertent dispersion of the radioactive technetium. Raman spectra were collected through an optical-grade quartz window epoxied to one side of the membrane box, which covered a $\frac{3}{4}$ " circular opening cut by a lathe. Technetium-containing powders or glass chunks were funneled into the center of a small nylon washer epoxied to the inside surface of the quartz window. The washer formed a cavity for the powder which was then sealed by epoxying a second quartz window over the nylon washer. The two halves of the boxes were then fit together and sealed using tape.

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 $\sim 20\text{mW}$ of power to the sample with an approximate beam diameter of 1.2 μm . Spectra were recorded using a Peltier-cooled Horiba Synapse CCD detector. 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 $\sim 50\text{ cm}^{-1}$. The number of spectral acquisitions, count times, and the diameter of the confocal iris were varied to maximize the signal to noise ratio and to provide maximal spectroscopic resolution. Most glass spectra were acquired for 10 minutes for improved signal to noise ratios. Crystalline ReO_4^- and TcO_4^- salts only required 2 to 10 seconds of acquisition time to achieve very strong signal to noise ratios.

3 Results and Discussion

Raman analyses of crystalline NaReO_4 , KReO_4 , NaTcO_4 , and KTcO_4 provided reference spectra for comparing the ReO_4^- and TcO_4^- containing glasses. These reference spectra, shown in [Figs. S1](#) and [S2](#) (supp. inf.), reveal the stretching and bending modes of ReO_4^- and TcO_4^- , as well as external or lattice vibrations of these Na salts and K salts. These fundamental vibrations, listed in [Table 2](#) and [Table 3](#), are compared to published values of aqueous anions, alkali salts, and to the acquired Raman spectra of Re-containing and Tc-containing glasses.

Alkali perrhenates, KReO_4 ^[26] and NaReO_4 ^[20] and alkali pertechnetates, KTcO_4 ^[27] and NaTcO_4 ^[28] are all tetragonal with space group $I41/a$, possessing the scheelite structure (CaWO_4). Group theory predicts that Re and Tc in K and Na salts has local symmetry C_{4h} from lattice symmetry of S_4 from

free ion symmetry T_d [16; 18; 19; 29]. A correlation diagram illustrating the mode derivations is shown in Fig. 1.

3.1 Crystalline Phases

Comparing Raman spectra of crystalline NaReO_4 and KReO_4 shows the K salt exhibits higher frequency symmetric (ν_1) and asymmetric (ν_3-E_g) stretching modes. The symmetric (966 cm^{-1}) and the asymmetric stretch (896 cm^{-1}) are $\sim 10\text{ cm}^{-1}$ higher in KReO_4 spectra, relative to NaReO_4 (Fig. S1, supp. inf.). Given that both cations are coordinated to the same ligand, this frequency difference must be due to a cation property. This frequency difference may be attributed to the larger covalent radius (203 pm), atomic volume (45.3 cc/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 cc/mol, which is half the atomic volume of K. Literature values of average alkali metal-oxygen bond lengths are 2.829 \AA [24; 27] in KTcO_4 and 2.582 \AA in NaReO_4 . [30] 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 [31] 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. [24] The asymmetric (ν_3) stretch (B_g) is approximately the same in both ReO_4^- salts (925 cm^{-1}).

Two well-resolved bending modes occur at 350 and 337 cm^{-1} in KReO_4 , with a poorly resolved shoulder at 325 cm^{-1} . Similarly, two bending modes occur at 371 and 332 cm^{-1} in NaReO_4 . This much larger energy separation (40 cm^{-1}) of these bending modes may be attributed to ReO_4^- sharing charges with a larger number of nearest neighbor Na ions in the crystalline lattice, presenting a broader manifold of bending energies.

A significant difference exists between the Raman spectra of the crystalline pertechnetates and crystalline perrhenates. In the perrhenates the symmetric stretch (ν_1) occurs well above the two asymmetric stretching frequencies. In the pertechnetates the symmetric stretch lies between the two asymmetric stretching frequencies. In this case, the role of K^+ and Na^+ in coordination with TcO_4^- is approximately the same and the principal difference lies with the role of TcO_4^- in the complexes. This downward shifting of the pertechnetate salt vibrations suggests a significantly increased degree of covalency in both the Na and K salts, relative to the perrhenates. This increased covalency would also suggest a shorter bond length exists in the Tc-O-Tc symmetric stretch compared to the Re-O-Re symmetric stretch.

In a similar trend to the perrhenates, crystalline KTcO_4 exhibits $\sim 10\text{ cm}^{-1}$ higher stretching frequencies relative to NaTcO_4 . Again, we conclude the larger K^+ maintains a more open tetrahedral structure than Na during pertechnetate stretching. 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 frequencies. This lower band is likely a polarized bending mode as the band intensity is much stronger than the subordinate bending modes; however, we were unable to obtain polarized spectra using the confocal Raman spectrometer. Interestingly, the band separation between the subordinate bands and the stronger low frequency bend is significantly larger in NaTcO_4 (42 cm^{-1}) than KTcO_4 (21 cm^{-1}). Again, one could pose that this lower frequency band could be a symmetric bending mode with greater covalency than the asymmetric bends.

3.2 Glass network

Many Raman spectra from Re-containing and Tc-containing glasses were dominated by Si-O and Si-O-Si stretching and bending modes of the sodium-borosilicate glass matrix. Low frequency Si-O bending occurs over a range of Raman frequencies from 600 to 250 cm^{-1} .^[32] The relative intensities of silicate stretches between 1200 and 800 cm^{-1} varied between different surface sites probed by the Raman laser as exemplified in Fig. S6 (supp. inf.) for the 1000 ppm target Tc glass. Generally, bands at 1095 and 990 cm^{-1} are associated with zero (Q^4) and one (Q^3) non-bridging oxygens, respectively.^[32] The band at 919 cm^{-1} is similarly attributed to two non-bridging oxygens (Q^2)^[32] in the silicate bonding network but may also have contribution from asymmetric stretching of tetrahedral ReO_4^- .^[13-16] Raman bands of ReO_4^- and TcO_4^- were superimposed on these predominant Si vibrations of sodium-borosilicate glass matrices. Weak stretching modes of tetrahedral TcO_4^- are visible at 919 and 912 cm^{-1} in Fig. S6.

The observed band at 781 cm^{-1} is attributed to stretching and bending frequencies of tetraborate groups, containing 6-membered rings of boron with one tetrahedral BO_4^- .^[33] Fukumi et al.^[33] noted that Raman cross-sections of tetraborate and boroxyl units are not influenced by one another despite forming a continuous network in the glasses. They also state that tetraborate units, in borate glasses, are less affected by the type of alkali metal present than non-bridging oxygen band intensities in silicate glasses.

3.3 Re in glass

The symmetric stretch (ν_1) of KReO_4 in glass occurs at 966 cm^{-1} with two antisymmetric stretches (ν_3) at 896 and 925 cm^{-1} .^[17-19] The intensity of the 896 cm^{-1} band is twice that of the 925 cm^{-1} band, consistent with group theory predictions ($2 \times B_g = E_g$).^[12] The bands at 349, 337, and 330 cm^{-1} are attributed to bending vibrations of tetrahedrally coordinated ReO_4^- . The spectral splitting of the ν_2 (A_g) band at 331 cm^{-1} was predicted to give another band at 343 cm^{-1} ($\Delta\nu=12 \text{ cm}^{-1}$).^[11] We observed a splitting of the 330 cm^{-1} band, giving an additional band at 337 cm^{-1} . The bands at 337 and 349 cm^{-1} are then consistent with the predicted 12 cm^{-1} splitting but are offset to higher wavenumbers. The improved spectroscopic resolution of the confocal Raman system enabled resolution of these band splittings, not previously observed.

Repeated 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 difference spectrum due to KReO_4 , are shown in Fig. 2. The KReO_4 spectrum derived by spectral subtraction shows bands at 966, 925, 896, 349, 337, 330, and 106 cm^{-1} (as indicated in Fig. S3 supp. inf.). Nearly identical ReO_4^- vibrations were observed from the 6415 ppm Re glass (see Table 2 and supp. inf. Fig. S4). We have previously shown that the solubility of Re in these glasses is 3000 ppm,^[4] and that the 4000 ppm glass showed no evidence of crystallization in the bulk of the glass (by x-ray diffraction) 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,^[7] 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 one of sixteen spectra taken for this glass contained sharp peaks, suggesting these peaks are probably due to crystalline phases.

Several Raman peaks from the 10,000 ppm Re glass occur at nearly identical frequencies to those from 4000 and 6415 ppm Re glasses. Spectra of the 10,000 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. S5 supp. inf.). However, the bands at 956, 924, 887, and 370 cm^{-1} are consistent with NaReO_4 . We propose that at higher added Re concentration there is more ionic interaction of ReO_4^- with the elevated Na^+ concentration (21 wt. % Na_2O) of the glass matrix, tending to form NaReO_4 . The downward shifting of NaReO_4 frequencies, relative to KReO_4 frequencies, is likely due to increased covalency of Na^+ - ReO_4^- bonding.^[24] We have previously shown that the 10,000 ppm Re glass contained crystals of alkali perhenate species, both NaReO_4 and KReO_4 .^[4] Fig. 3 shows a progression of spectra collected from Re glasses with the 4000 ppm Re glass spectrum being 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.

3.4 Tc 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 target concentrations of TcO_4^- (≤ 1000 ppm Tc) yielded weak peaks superimposed on the broad bands of the glass matrix (Fig. S6, supp. inf.). 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 reducing conditions^[8]) 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 salt. 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 1000 ppm Tc glass exhibited very weak TcO_4^- bands superimposed on the glass matrix (Fig. S6, supp. inf.). Spectra from the glasses with target Tc concentrations 2000 ppm (Fig. S7, supp. inf.), 3000 ppm (Fig. S8, supp. inf.), and 4000 ppm (Fig. S9, supp. inf.) exhibited much stronger TcO_4^- stretching and bending modes, and low frequency 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.^[16; 17]

Notably, as Tc target concentrations increased from 2000 to 3000 to 4000 ppm in the oxidized glasses, there were gradual ingrowths of new stretching and bending bands. Fig. 4 shows stacked Raman spectra of a) pure crystalline KTcO_4 , b) 2000 ppm Tc, c) 3000 ppm Tc, d) 4000 ppm Tc, e) surface precipitates on 4000 ppm Tc, and f) pure crystalline NaTcO_4 . Trending from top to bottom of 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, as well as the glasses, are found in Figs. S1, S7, S8, S9 and S10 (suppl. inf.). The two reduced glasses (500 ppm Tc and 4000 ppm Tc) also exhibited similar TcO_4^- bands superimposed on the glass matrix (see Fig. S11). A separate salt phase removed from the surface of the 4000 ppm Tc reduced glass was identical to crystalline NaTcO_4 (see Fig. S10).

As discussed previously regarding higher perrhenate concentrations, we infer that increasing KTcO_4 concentrations in glasses makes higher TcO_4^- concentrations available for ionic interaction with very high Na concentrations (21 wt. % Na_2O) in the glass matrix during melting. This inference necessitates at least partial equilibria of NaTcO_4 and KTcO_4 in the same volume of glass excited by the laser.

4 Conclusions

The perrhenate glasses exhibited consistent Raman frequencies for stretching and bending modes at the 4000, 6415 and 10,000 ppm Re concentrations (Table 2). 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 exists 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 KTcO_4 . However, there exists a significant degree of heterogeneity at the surface of the glasses as indicated by widely varying intensities of TcO_4^- bands from individual glasses. The 1000 ppm Tc glass exhibited very weak KTcO_4 bands superimposed upon Si-O and Si-O-Si bands of the sodium-borosilicate matrix. Spectra from glasses with Tc concentrations of 2000 ppm, 3000 ppm, and 4000 ppm exhibited much stronger TcO_4^- stretching and bending modes, and low frequency external modes. By presenting here the first reported Raman spectra of NaTcO_4 we were able to identify 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 KTcO_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 there were no indications of intermediate vibrations in the spectra collected to date.

These results and their interpretation have strong implications for the long-term stability of Tc in nuclear waste glass formulations. Both pertechnetate and perrhenate glasses exhibit characteristic Raman bands of their precursor chemicals at intermediate concentrations in glass. The strength of TcO_4^- spectral bands strongly depends on the Tc concentrations added to the base glass formulation. Indications are that pertechnetate and perrhenate 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 KTcO_4 or KReO_4 , respectively. We observe in this study that the base glass composition has a strong effect on the equilibrium speciation of pertechnetate and perrhenate in the glass melt and consequently on long term durability in storage. We conclude that the high Na^+ concentration (20 wt. % Na_2O) in the base glass formulation easily displaces K^+ from KTcO_4 and KReO_4 through mass action at elevated TcO_4^- and ReO_4^- concentrations. It is as yet unclear whether the TcO_4^- (and ReO_4^-) species which show characteristic bands are indicative of isolated oxyanions in glass or whether they indicate nanocrystals of salt species concentrated in local areas. Resolving this question will be important for determining ultimate durability of a Tc-containing waste form. However, observed spectral features suggest that some stretching and bending vibrations of ReO_4^- and TcO_4^- complexes may be used as an indicator of relative bond strengths or bond lengths of Re-O and Tc-O bonds. Strongly covalent 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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Supplementary information

Supplementary information (supp. inf). may be found in the online version of this article including all spectra with peaks indexed by wavenumber, including NaTcO₄, KTcO₄, NaReO₄, and KReO₄ salts, and perhenate and pertechnetate glasses..

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TABLES

Table 1. LAW glass composition (in Mass%) to which KReO_4 or KTcO_4 was added

Oxide	Glass (%)
Al_2O_3	6.1
B_2O_3	10
CaO	2.07
Cr_2O_3	0.02
Fe_2O_3	5.5
K_2O	0.47
MgO	1.48
Na_2O	21
SiO_2	45.3
SO_3	0.16
TiO_2	1.4
ZnO	3.5
ZrO_2	3
SUM	100

Table 2. Assignments for Re compounds and glasses. Notations for intensities of bands in crystalline species are as follows: very strong (vs), medium (m), weak (w), very weak (vw)

Mode	ReO ₄ ⁻ (aq) [13-16]	KReO ₄ [17-19; 34; 35]	KReO ₄ (PNNL)	NaReO ₄ [18; 19; 34]	NaReO ₄ (PNNL)	4000 ppm Glass (PNNL)	6145 ppm Glass (no SO ₃) (PNNL)	10000 ppm Glass (PNNL) – position 1	10000 ppm Glass (PNNL) – position 2
v₁ – ss	971-972 (A ₁)	966-967 (A _g)	966 vs	958-968	956 vs	966	965	957	967
v₃ – as	918-920 (F2)	924-928 (B _g)	924 w	924-928	924 w	925	922	924	924
		897-900 (E _g)	896 m	887-888	887 m	896	896	887	898
v₄ – sb	333 (F2)	346-351 (B _g)	349 w	360-372	372 w	349	348	350, 371	350
v₂ – ab	331-333 (E)	334-338 (A _g)	336 w	334-335	332 w	337	338	333	336
		326-332 (B _g)	-	325	-	330			
v_T(cation) Lattice	F2	158-160* (E _g)	-	181-185*	176 vw				
		151* (B _g)	-		-				
v_L (ReO₄⁻) Lattice	F1	125-128* (A _g)	142 vw	145-156*	145 vw				
		107-114* (E _g)	108 w	131-132*	-	106	106	108	108
v_T(ReO₄⁻) Lattice	F2	65-73* (E _g)	67 vw	84-89*	83 w				
		55-59* (B _g)		77-80*					
unassigned						1002, 782, 620, 520	93, 90	390 (likely artifact)	

*denoted value in range is value at 77 K^[19]; lattice modes move to lower WN as temperature is increased. Note that Johnson^[18] and Brown^[35] disagree slightly on the mode assignments for the lattice modes of the alkali perhenates.

Table 3. Assignments for Tc compounds and glasses. Raw spectra can be found in the supplementary online information. Different glass types are oxidized (Al₂O₃ milled) and reduced (WC milled). Notations for intensities of bands in crystalline species are as follows: very strong (vs), medium (m), weak (w), very weak (vw), shoulder (sh)

Mode	TcO ₄ ⁻ (aq) [14; 15; 17; 21-23]	KTcO ₄ [16; 17; 24]	KTcO ₄ (PNNL)	NaTcO ₄ (PNNL)	“surface salt”	1000 ppm Glass (Al ₂ O ₃ mill)	2000 ppm Glass (Al ₂ O ₃ mill)	3000 ppm Glass (Al ₂ O ₃ mill)	4000 ppm Glass (Al ₂ O ₃ mill)	4000 ppm Glass (Al ₂ O ₃) surface particle	500 ppm Glass (WC mill)	4000 ppm Glass (WC mill)	BS glass (VSL) [21]
v ₁ – ss	910-912 (A ₁)	913 (A _g)	910 vs	902 vs	905 vs	911	913	904, 913	905, 912	901			915 (900–920)
v ₃ – as	904-908 (F ₂)	920 (B _g)	917 m	918 w	919 m		920	920	920	916		917	
		887 (E _g)	885 s	877 s	879 s		888	888, 878	889, 879	877		877	
v ₄ – sb	323-325 (F ₂)	327 (B _g)	327 m	322 m	326 s	328	329	324	327	323		323	325
v ₂ – ab	336 (E)	360 (A _g)	358 w	377 w	377 w		361	377	378	377		377	
		348-351 (B _g)	347 vw	363 w	365 m		350, 360	349, 366	350, 366	364		364	
v _T (cation) Lattice	F ₂		-	166 vw	162 vw			167	167	162		162	
v _L (TcO ₄ ⁻) Lattice	F ₁		138 vw	138 vw	134 w		142	140	140	135		136	
		104	102 w	98 m					98		98		
v _T (TcO ₄ ⁻) Lattice	F ₂	70	70 vw										
Un-assigned			859	849, 126 sh			999, 862, 126		851	849, 129	104, 94	849	

FIGURES

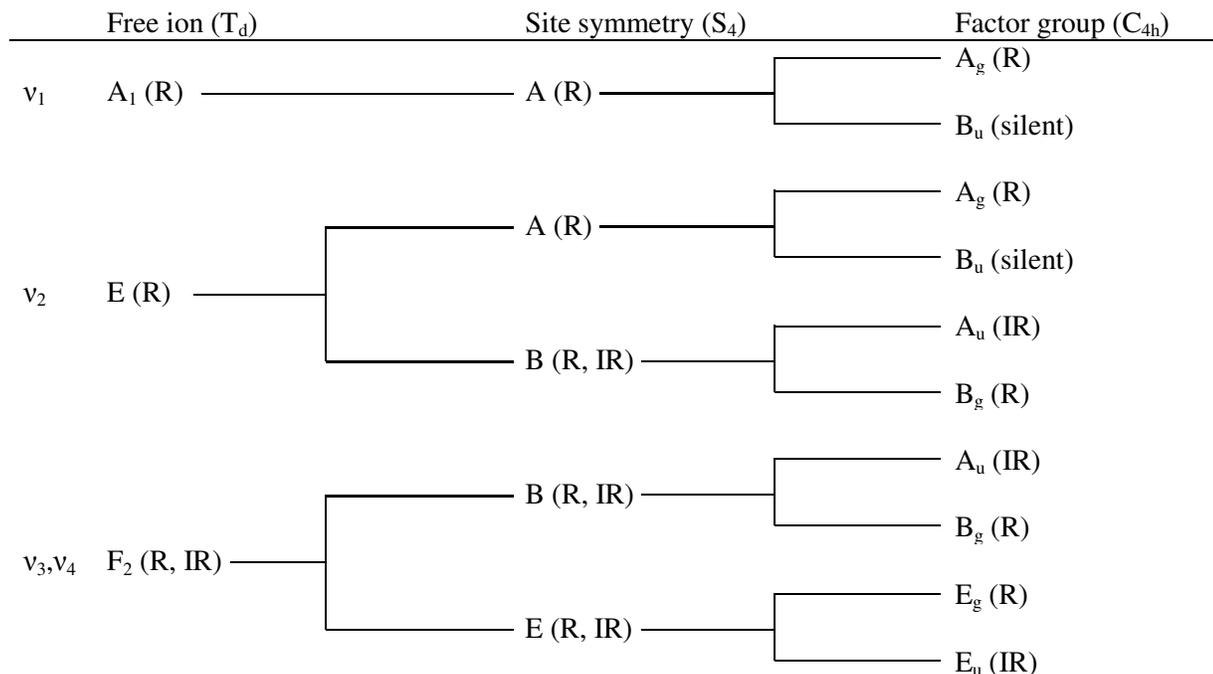


Figure 1. Group theory correlation diagram for the ReO_4^- and TcO_4^- free ion modes and their corresponding modes in alkali perrhenate and pertechnetate salts (C_{4h} symmetry). R indicates Raman-active modes and IR indicates infrared-active modes.

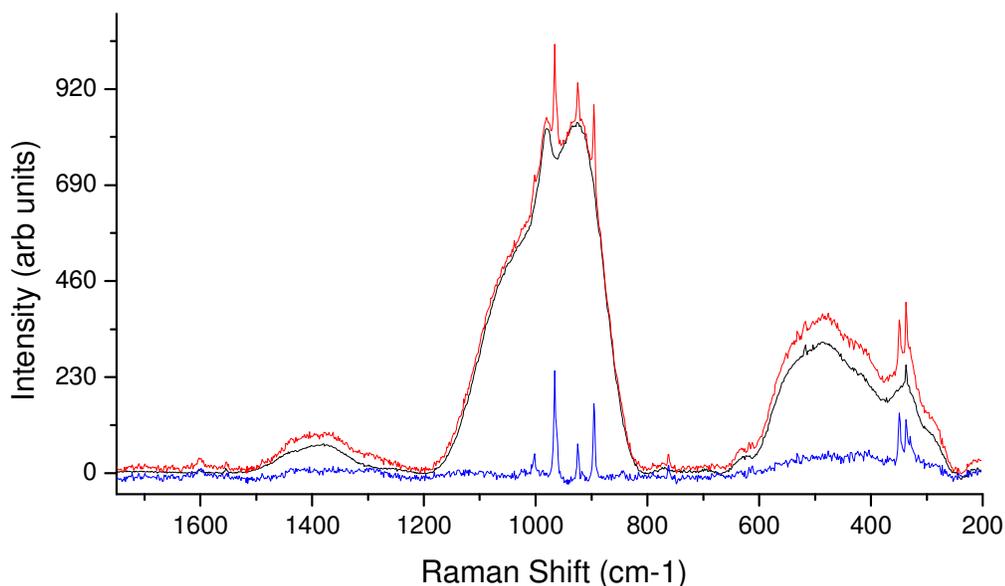


Figure 2. Raman spectra of 4,000ppm Re glass with and without ReO_4^- vibrations and derived spectrum of ReO_4^- vibrations by spectral subtraction. Peaks in derived spectrum are indexed in Fig. S3.

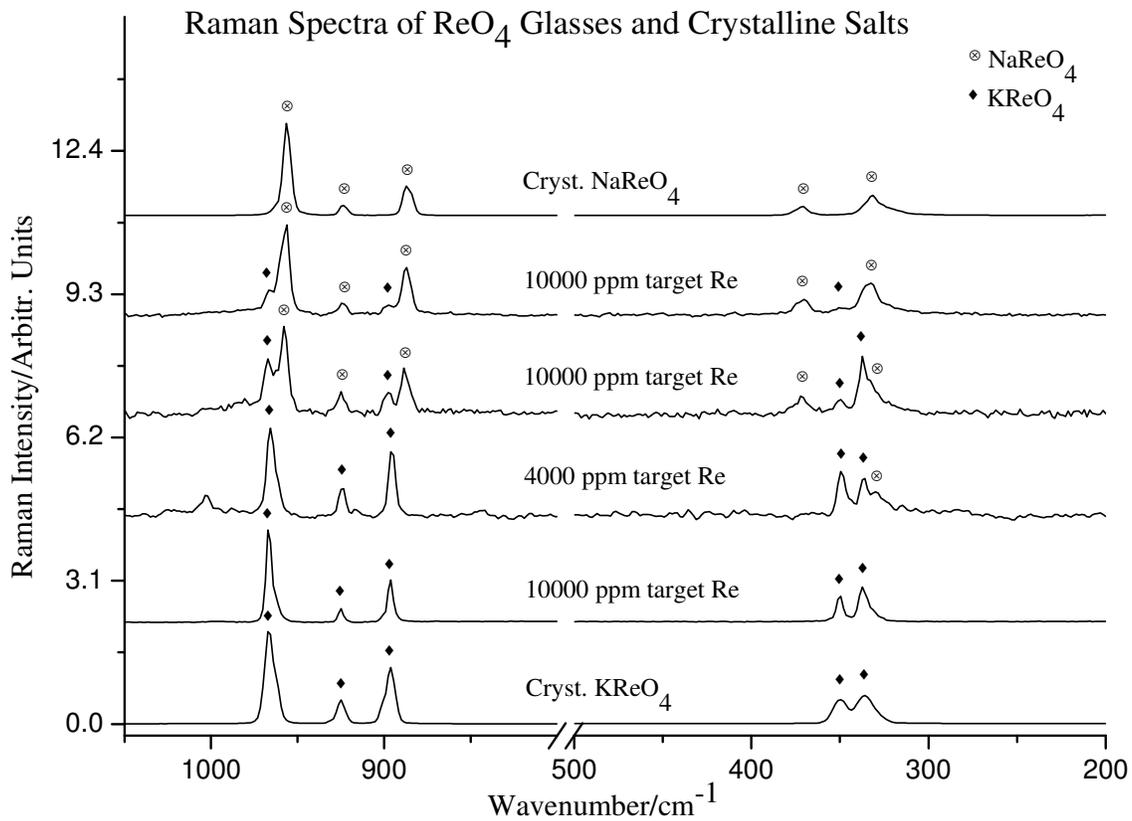


Figure 3. Raman spectra of perrhenate salts NaReO_4 and KReO_4 and perrhenate in glass. Glass spectra have “background” of pure glass signal subtracted. Raw spectra for glasses in Figs S3 and S5.

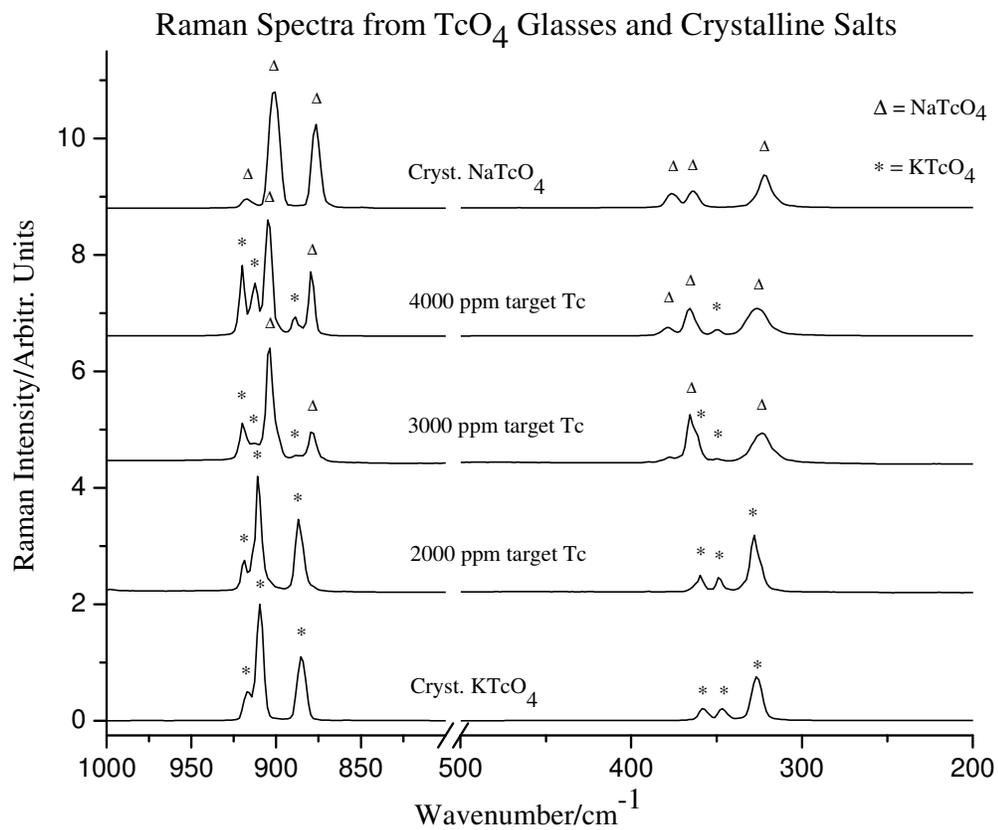


Figure 4. Raman spectra of pertechnetate salts NaTcO_4 and KTcO_4 and pertechnetate in glass. All glasses shown are oxidized glasses (Al_2O_3 milled^[81]). Raw spectra for glasses in S7, S8, and S9.

Supporting Information

Structural and Chemical Incorporation of ReO_4^- and TcO_4^- in Borosilicate Glasses

Paul L. Gassman, John S. McCloy, Chuck Z. Soderquist, and Michael J. Schweiger

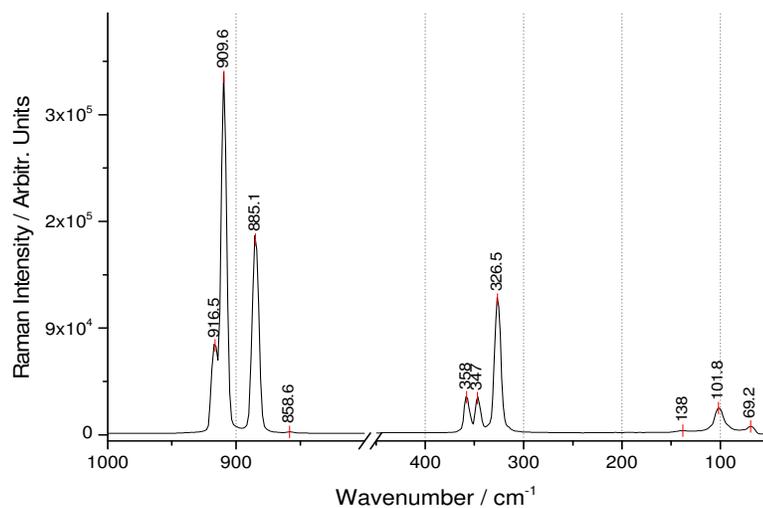
Pacific Northwest National Laboratory, Richland, WA 99352, USA

Supporting information

- 12 pages (including cover page)
- 11 figures

SUPPLEMENTAL FIGURES

Raman Spectrum of Crystalline KTcO_4



Raman Spectrum of Crystalline NaTcO_4

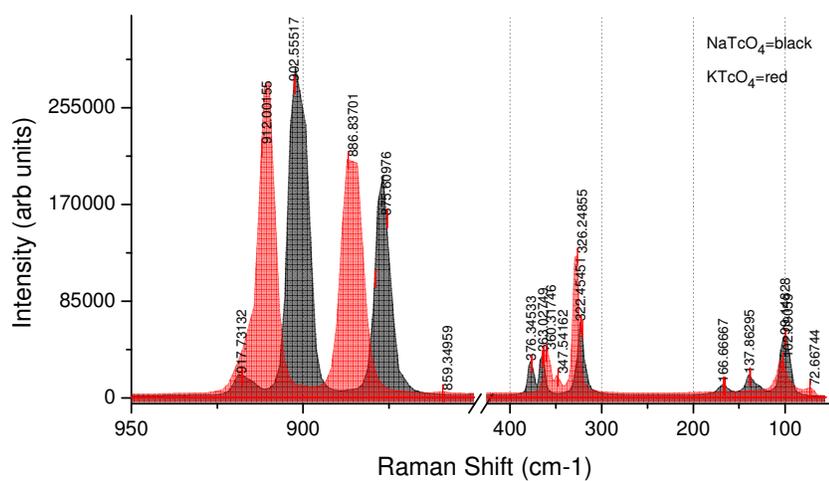
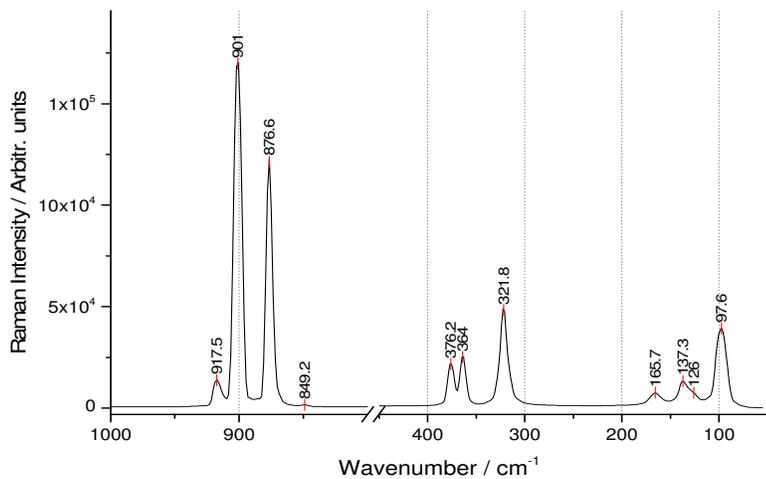
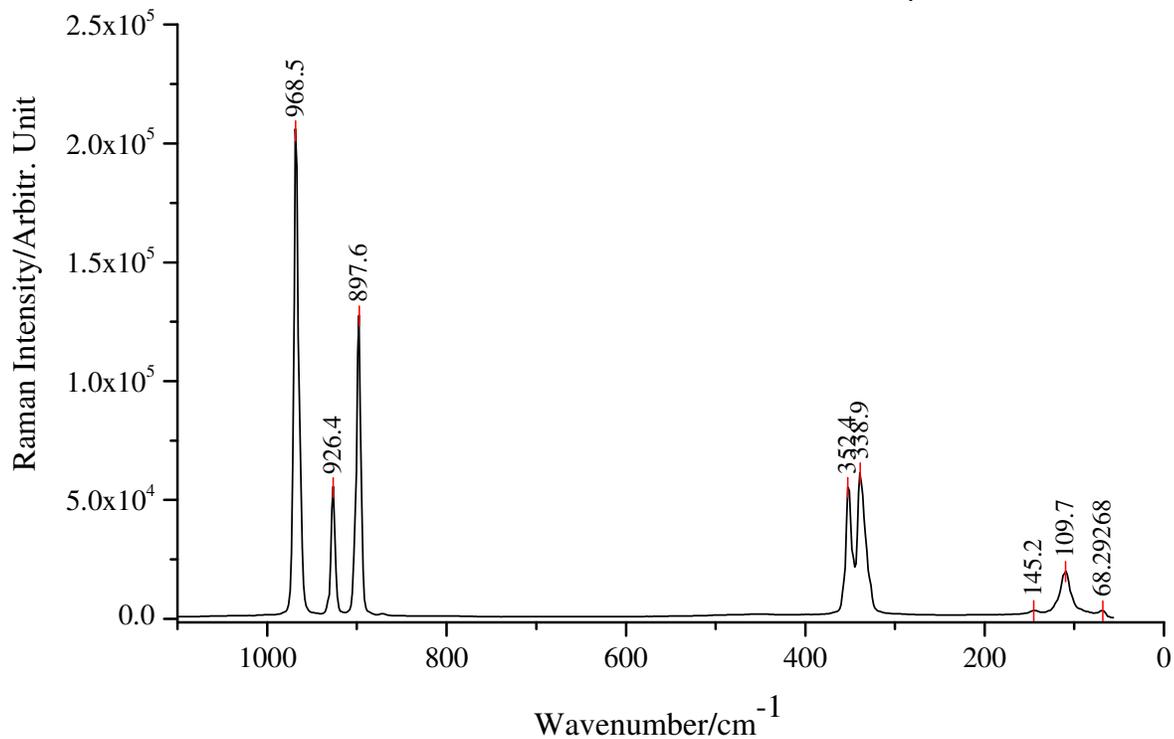


Figure S1. Raman spectra of KTcO_4 and NaTcO_4 pure compounds

Raman Spectrum of Crystalline KReO_4



Raman Spectrum of Crystalline NaReO_4

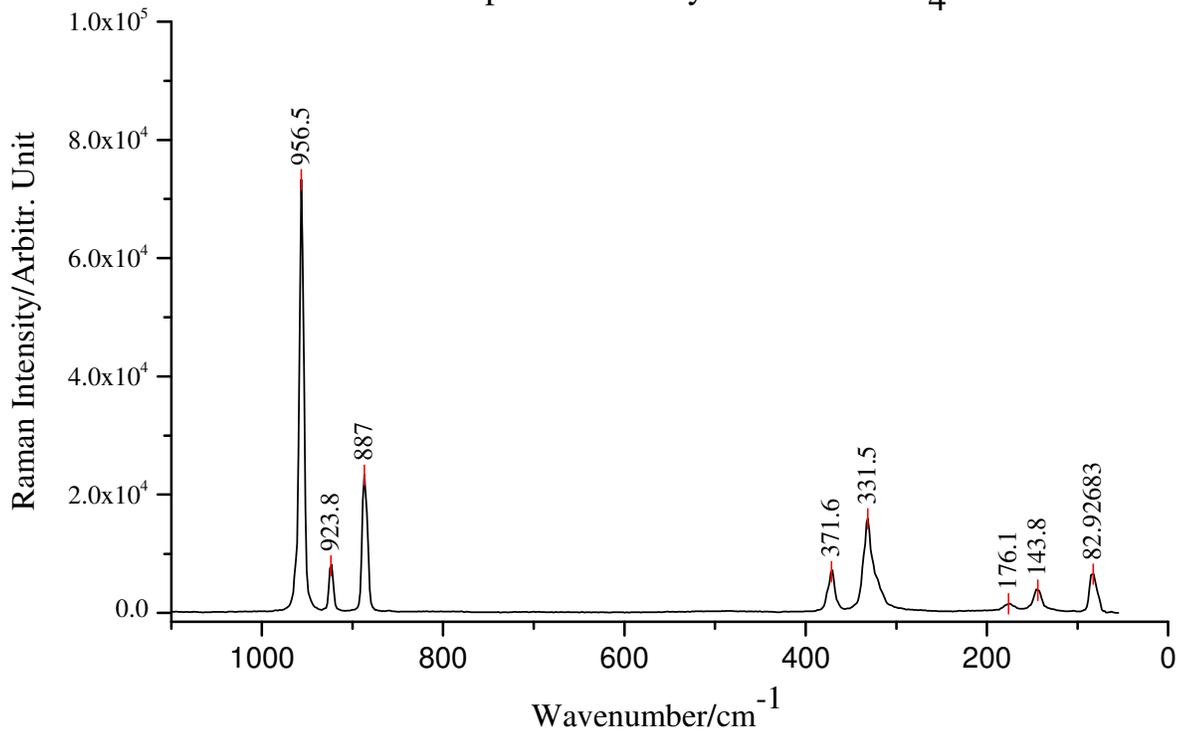


Figure S2. Raman spectra of KReO_4 and NaReO_4 pure compounds

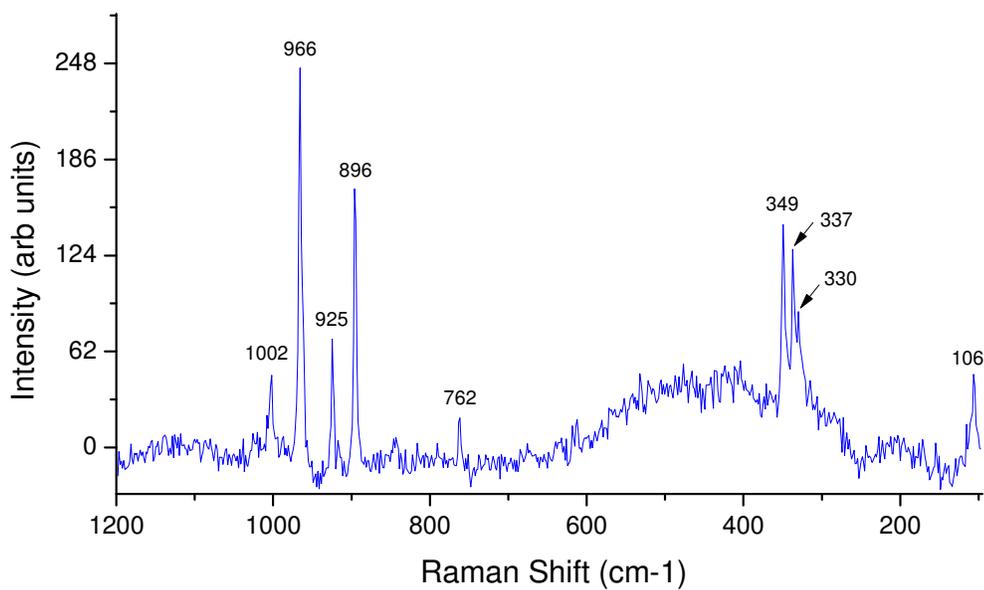
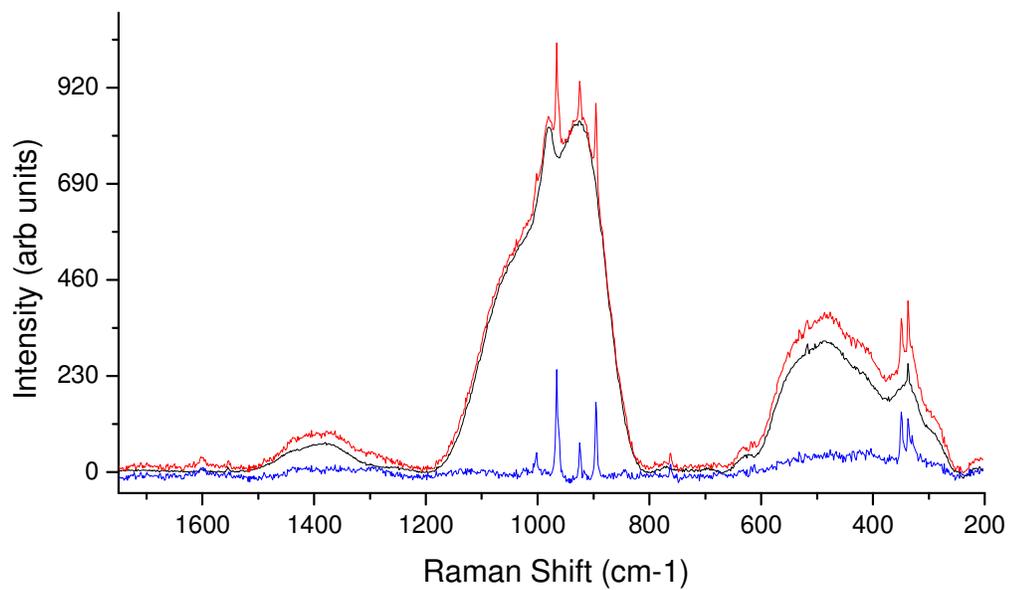


Figure S3. Raman spectra of 4,000 ppm Re glass with and without ReO_4^- vibrations and derived spectrum of ReO_4^- vibrations by spectral subtraction. This spectrum with sharp lines was obtained from an area which may have contained surface salt (see Fig. 3, main article).

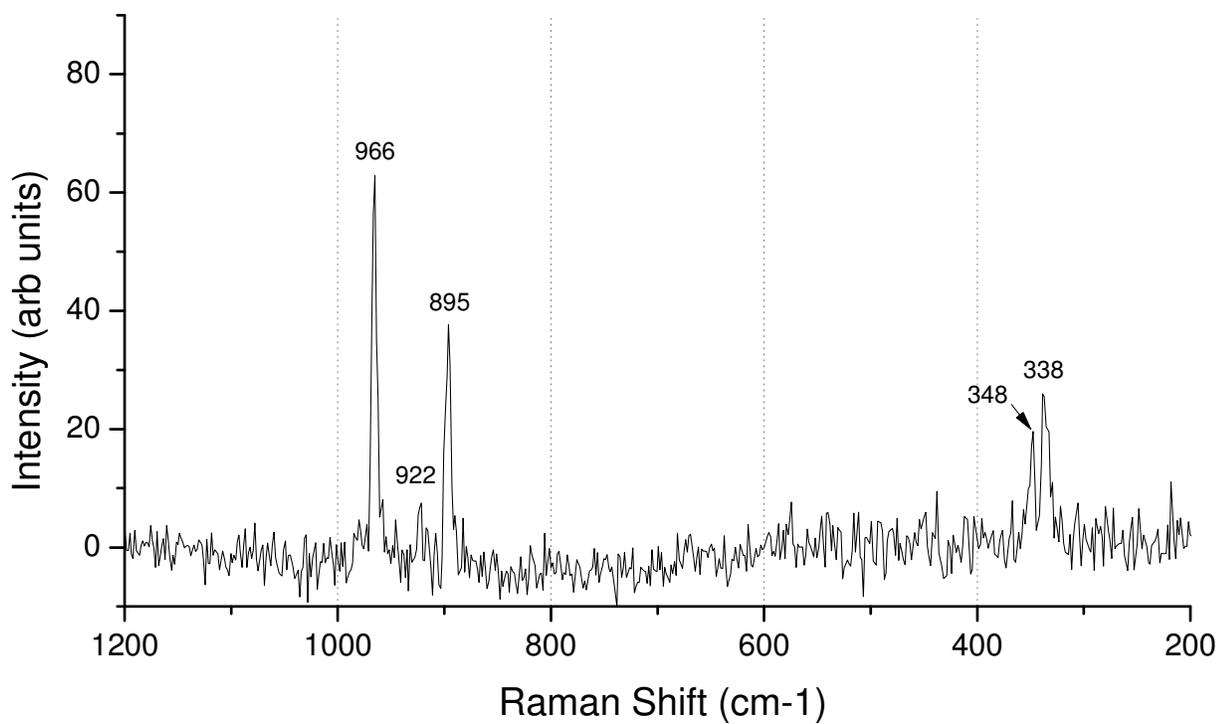
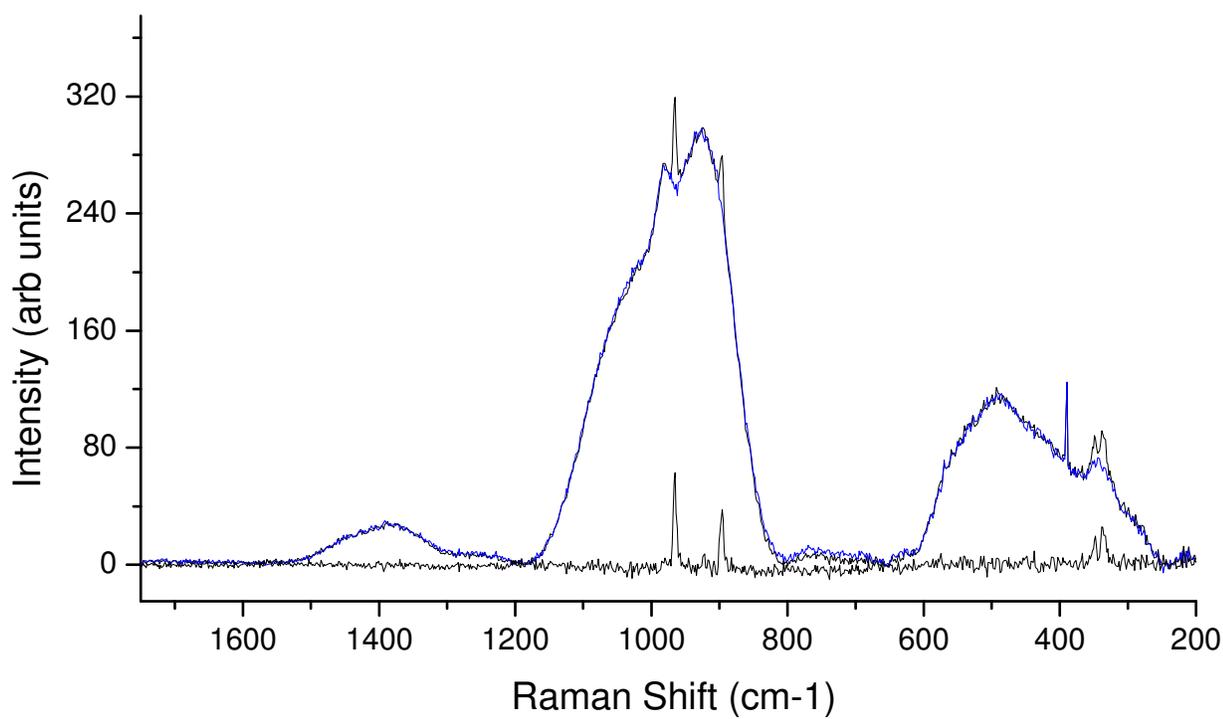


Figure S4. Raman spectra of 6,415 ppm Re (no sulfate) glass with and without ReO₄⁻ vibrations and derived spectrum of ReO₄⁻ vibrations by spectral subtraction

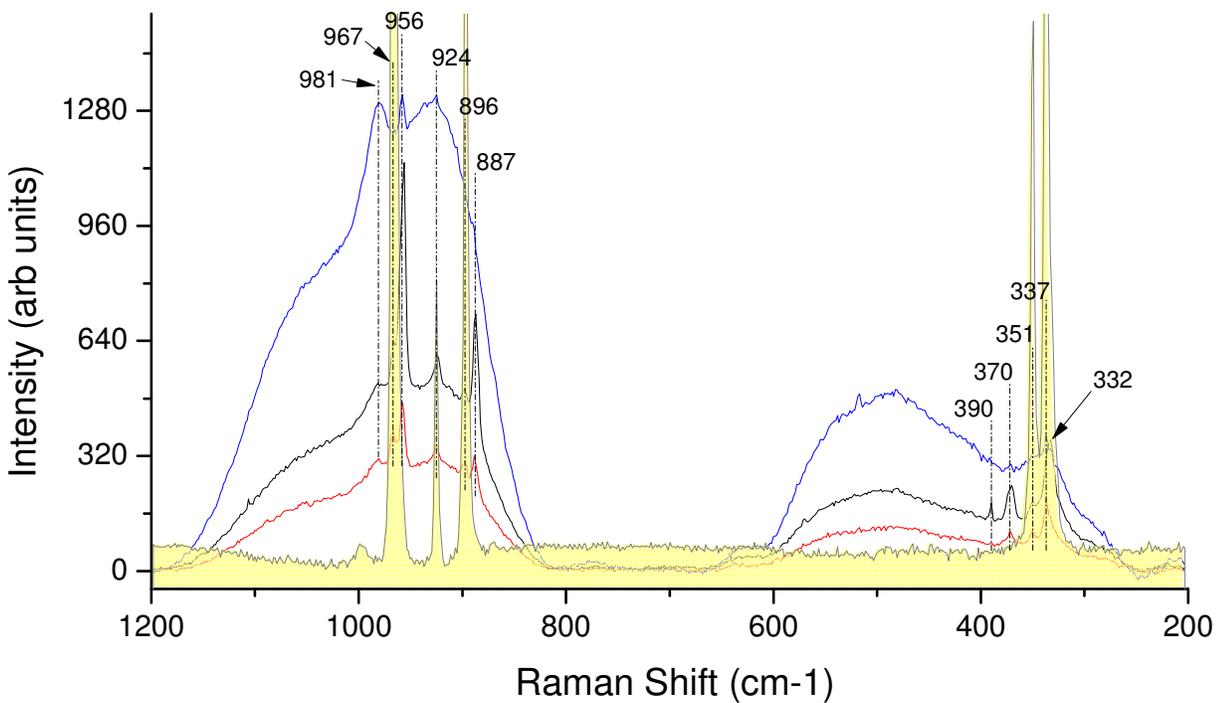
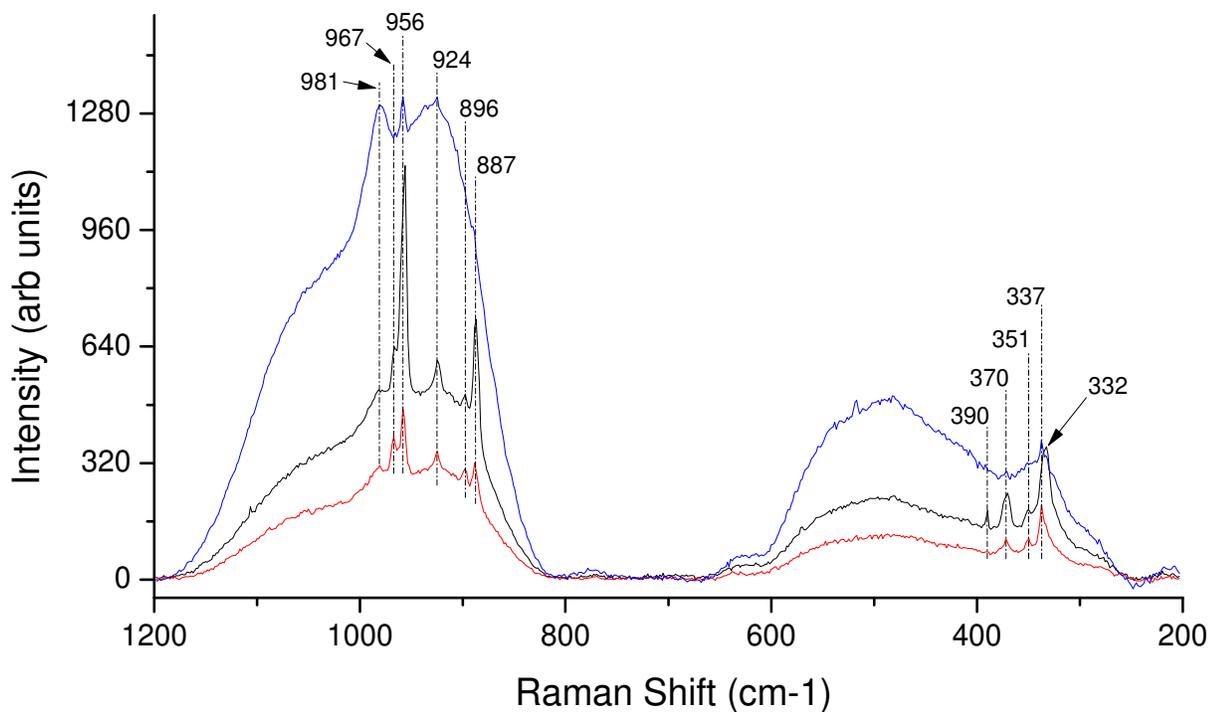


Figure S5. Raman spectra of 10,000 ppm Re glass with variable intensities of ReO_4^- vibrations. These are not derived spectra but represent some areas with strong peaks relative to glass background. Visually in the microscope these were all glass areas and not visible salt phases.

Raman Spectra from 1000ppm KTcO_4 Glass

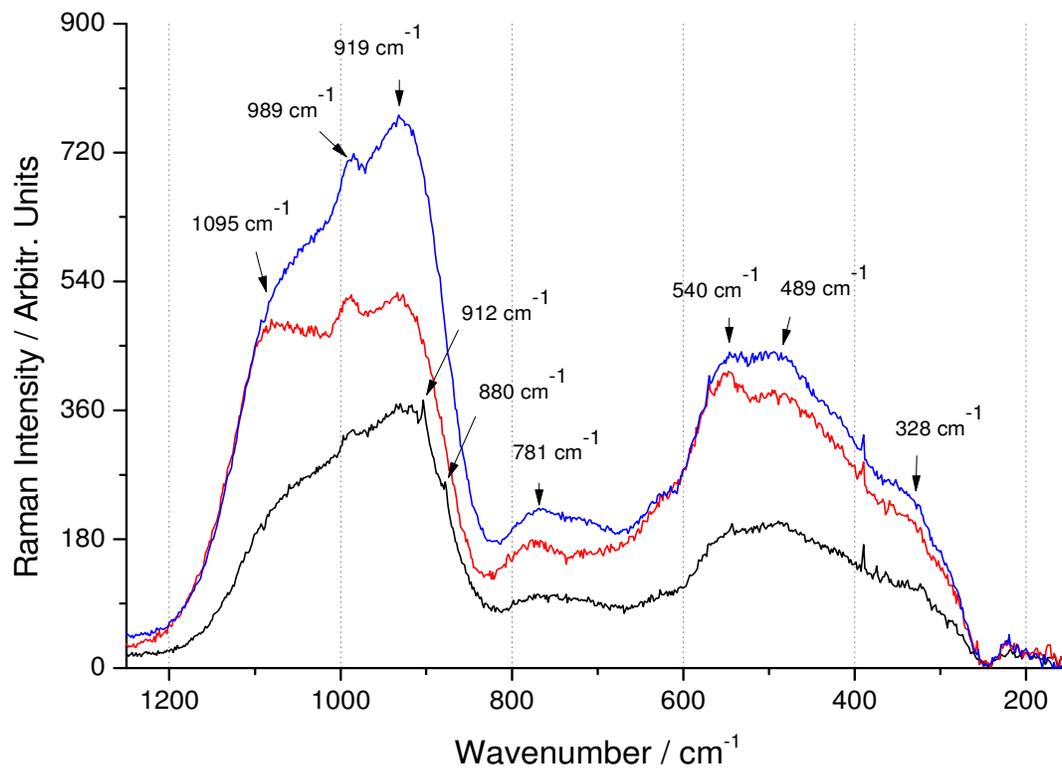
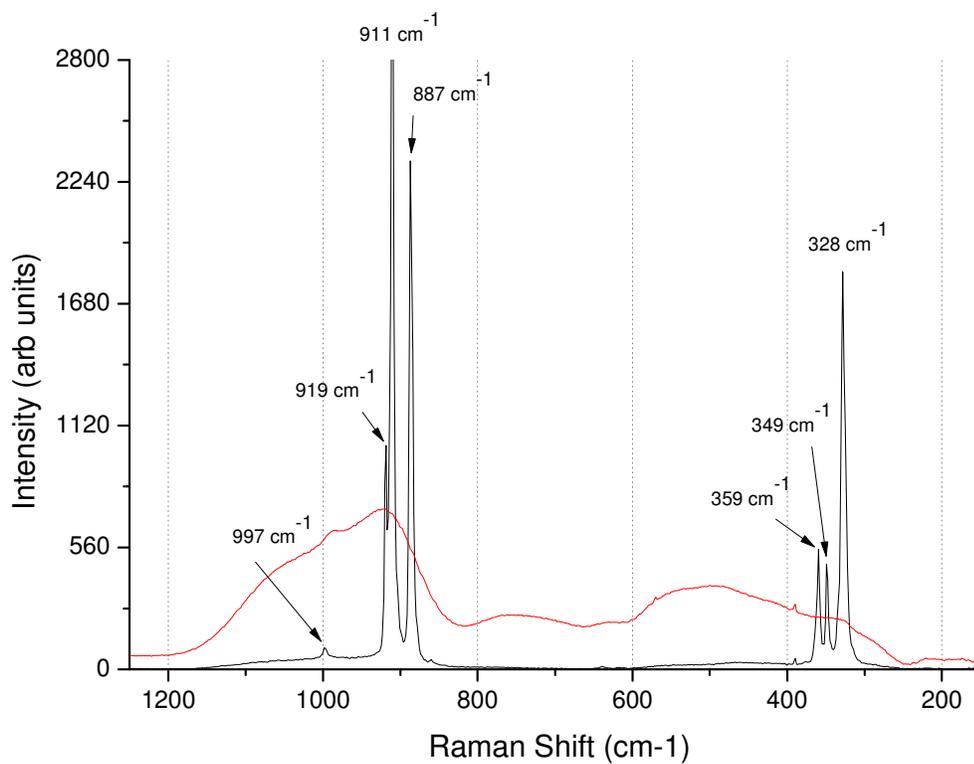


Figure S6. Various spots for the 1,000 ppm target Tc glass (Al_2O_3 milled) showing different silica speciation in local areas probed by the Raman laser. Some lines indicate TcO_4^- .



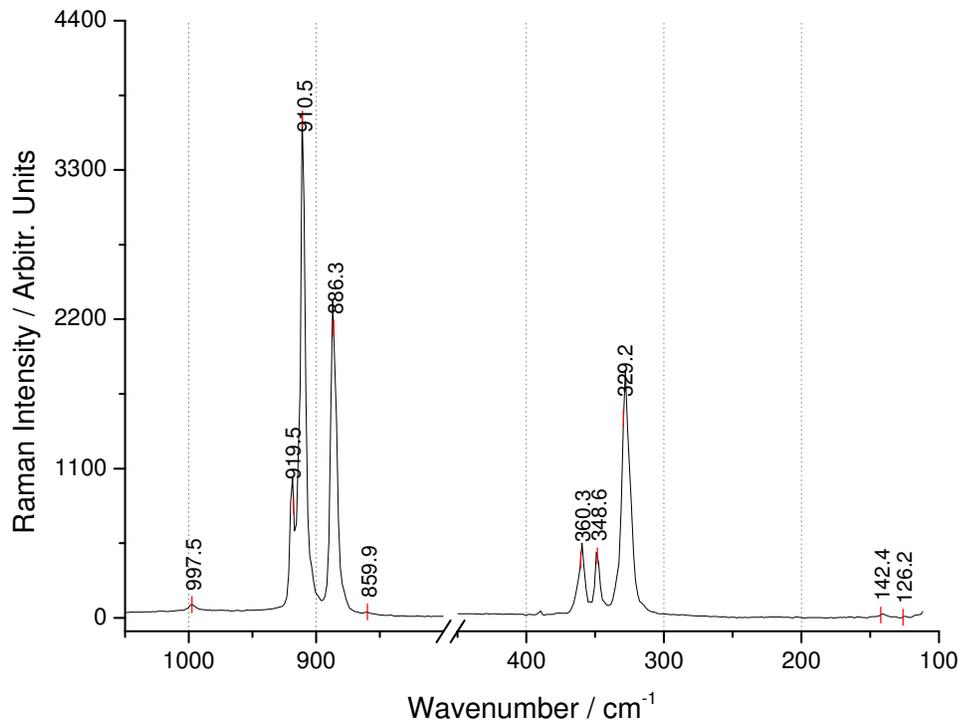
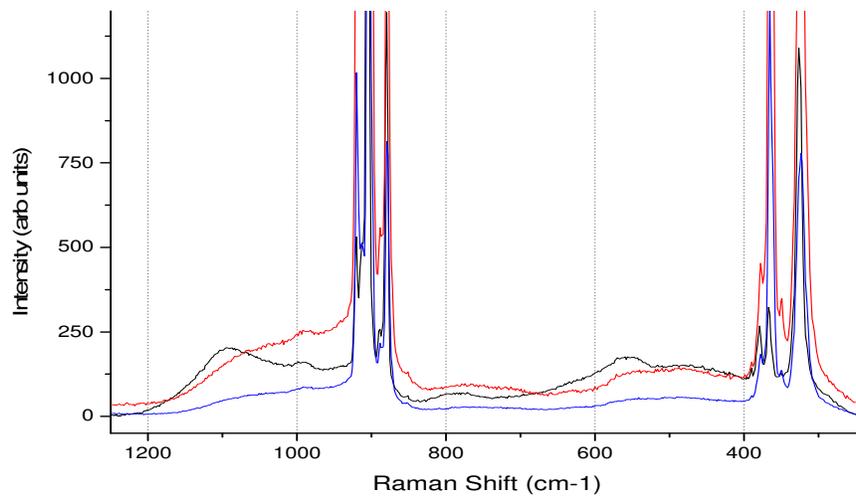
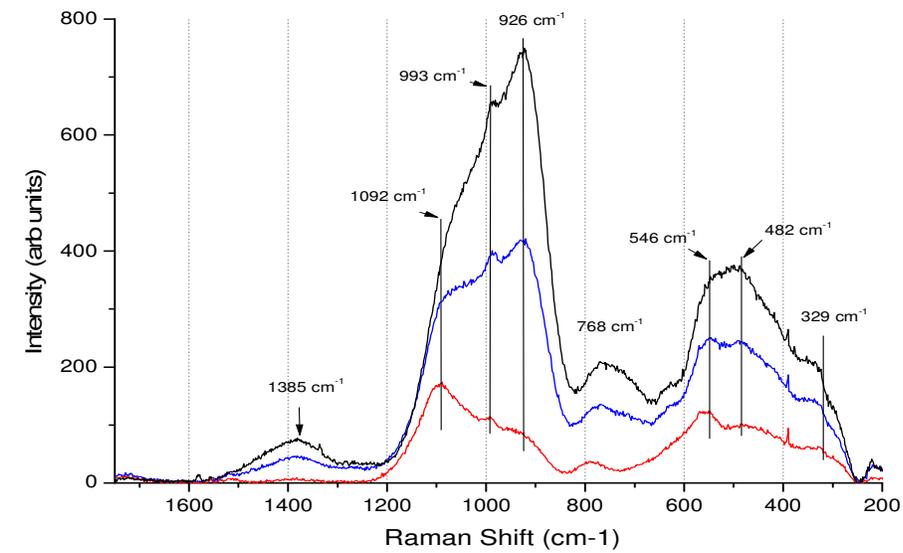


Figure S7. Raman spectra of two different sites in the 2,000 ppm target Tc glass (Al₂O₃ milled) surface



Raman Spectrum of 3000ppm KTcO₄ Glass

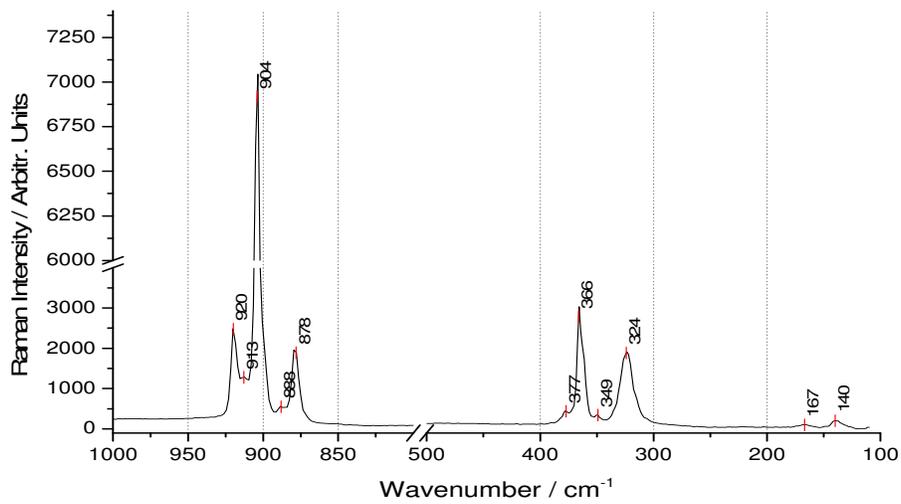
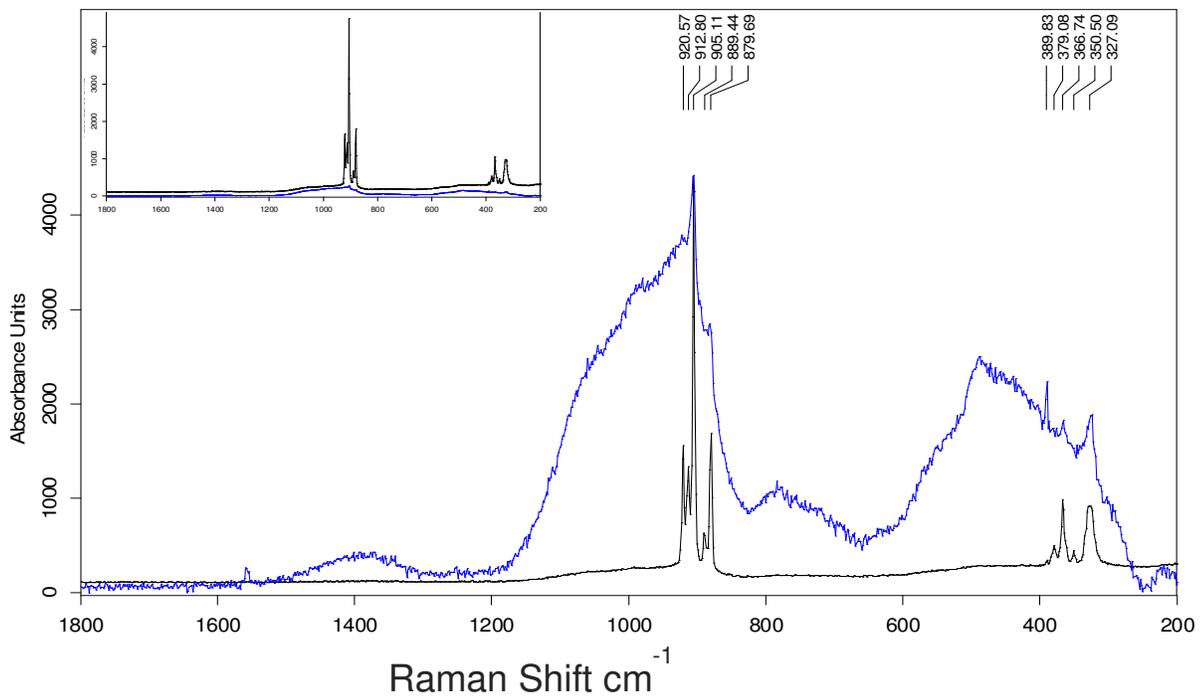


Figure S8. Raman spectra of different sites in the 3,000 ppm target Tc (Al₂O₃ milled) glass



Raman Spectrum of 4000ppm KTcO_4 Glass

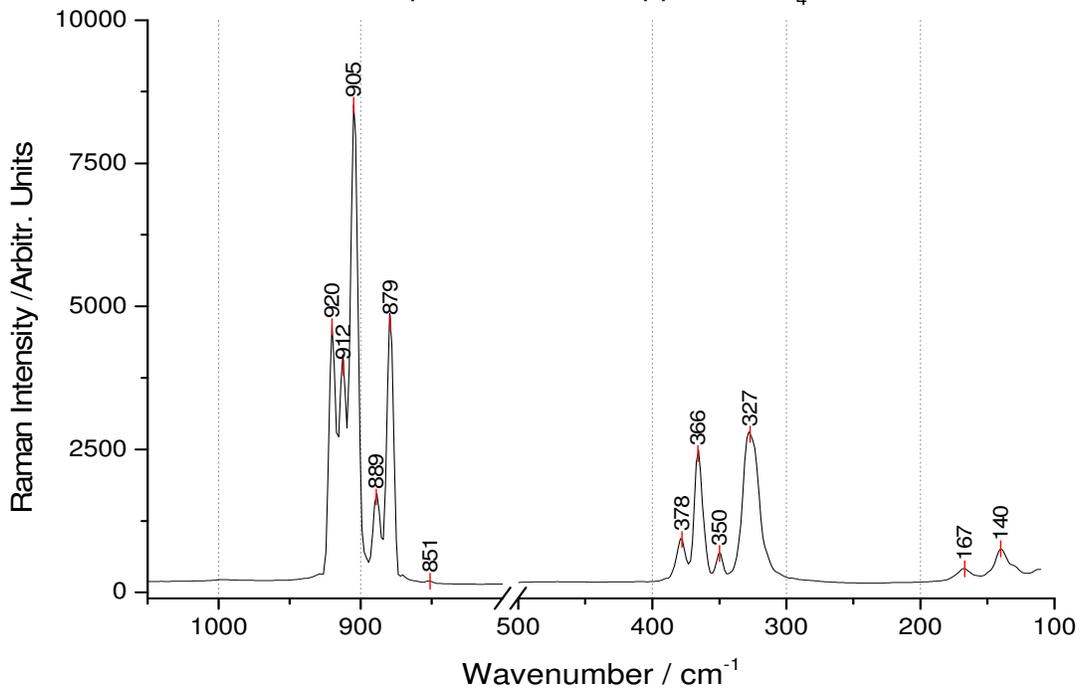


Figure S9. Raman spectra of different sites in the 4,000 ppm target Tc glass (Al_2O_3 milled). Note that this sample was investigated on the top surface as well as in a polished cross-section, and the strong peaks were evident even in the cross-sectioned sample.

Raman Spectrum of TcO_4 particles on 4000 ppm Glass (WC milled)

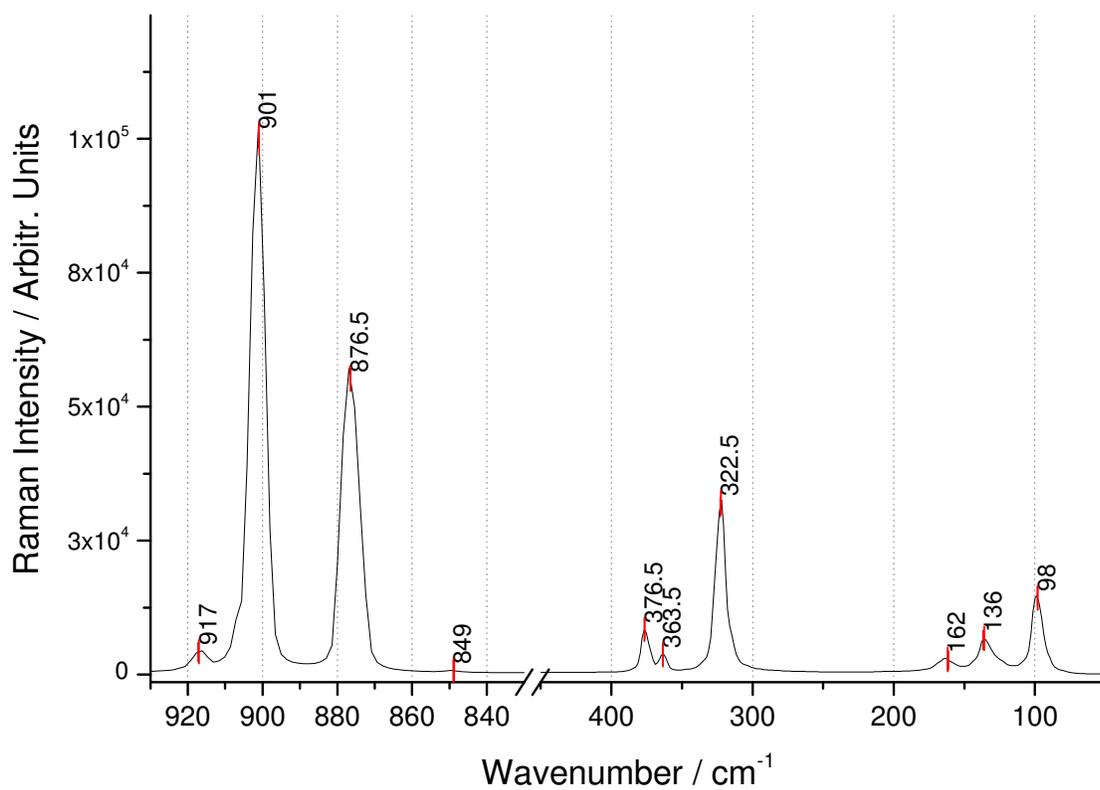
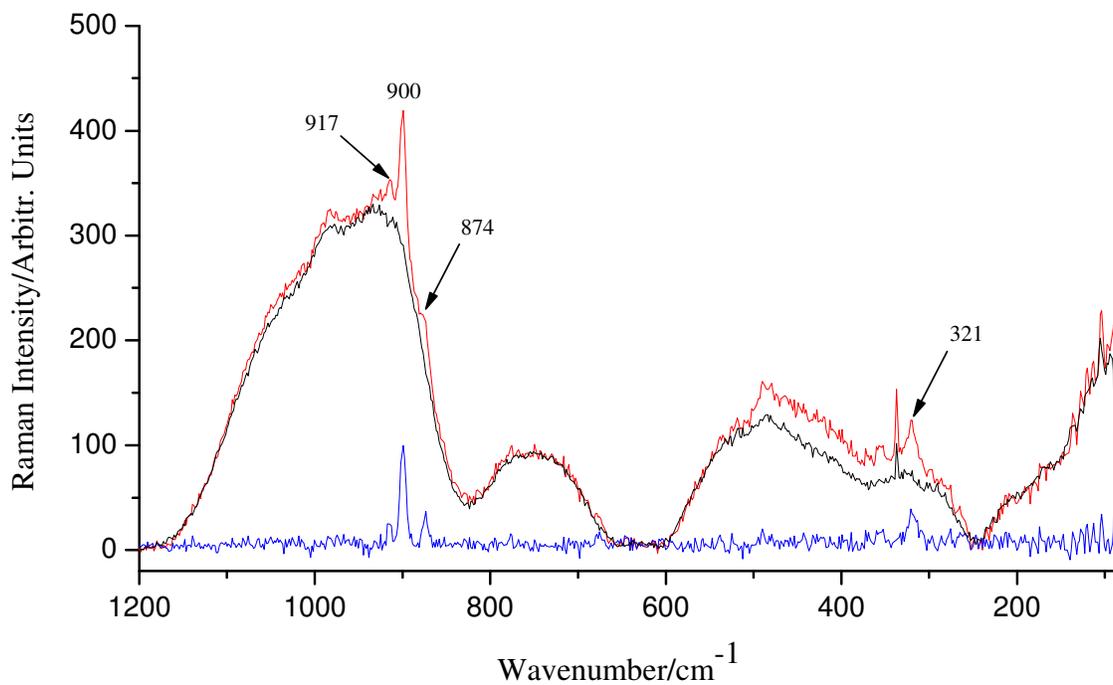


Figure S10. Raman spectra of the precipitate on the surface of the 4,000 ppm target Tc glass (WC milled). These surface particles (lower image) are consistent with NaTcO_4 .

Raman Spectra from 4000ppm KTcO₄ Glass (WC milled)



Derived Raman Spectrum from 4000ppm KTcO₄ Glass (WC milled)

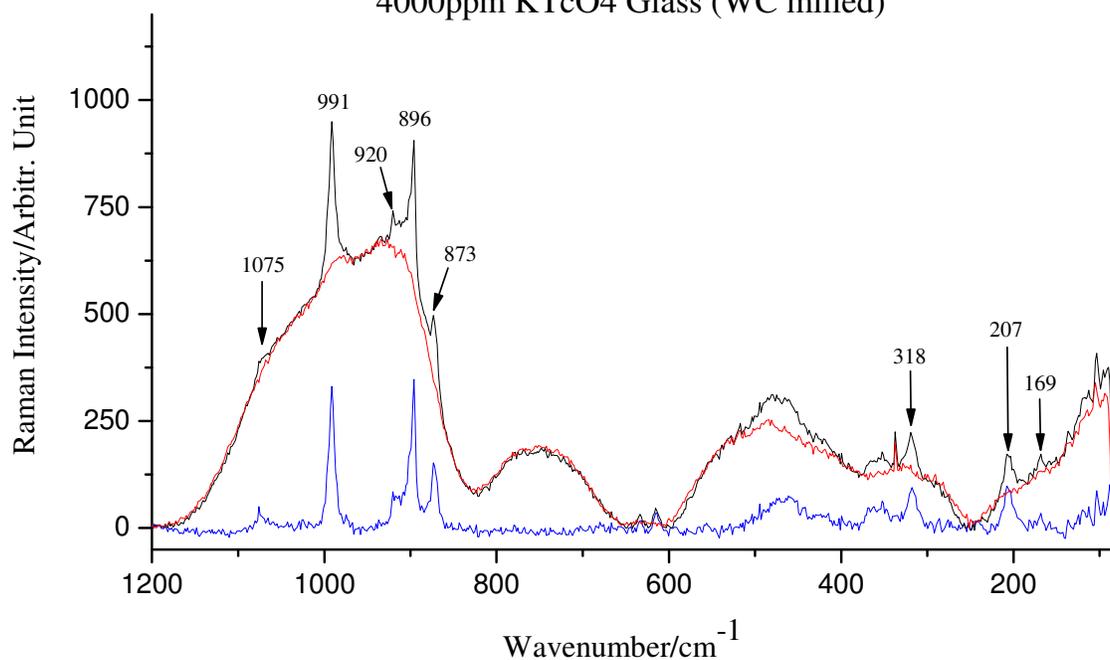


Figure S11. Raman spectra of the 4,000 ppm target Tc glass (WC milled). Top: TcO₄ peaks are more consistent with NaTcO₄ than KTcO₄. The derived spectrum is from spectral subtraction of an averaged spectrum from the strongest TcO₄ vibrations observed in 15 spectra; Bottom: blend of frequencies consistent with the 2000ppm TcO₄ Glass (Al₂O₃ milled) and some frequencies consistent with NaTcO₄.