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Electron densities over Si and O atoms of tetrahedra and their impact on Raman stretching frequencies and Si-NBO force constants

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ABSTRACT

Systematics of Si—O Raman stretching frequencies in the range 800–1200 cm^{-1}, and Si 2p and O 1s XPS binding energies (BE) are examined for a large number of alkali and alkaline earth silicate glasses, melts, and crystals. Several relationships in the Raman and X-ray Photoelectron spectral (XPS) data lead to new insights concerning charge delocalization over Si tetrahedra and to recognition of controls on both Raman stretching frequencies, and Si 2p and O 1s XPS chemical shifts. The Raman stretching frequencies of the five Q species and the Si 2p and O 1s XPS chemical shifts, vary linearly with the alkali and alkaline-earth content of glasses over the range 0–50 mol% counter oxide (M_2O or MO). The relationships demonstrate that the frequencies and chemical shifts are controlled by the same property, the valence band electron densities on the atoms of silicate tetrahedra. Specifically, where M-O ion interactions are strongly ionic, the *number* of NBO's attached to the central Si atom most affects the electron density of Si and O in tetrahedra, and is the major control on Raman symmetric stretching frequencies. Also, the Raman stretching frequency of individual Q species are effectively independent of the mass of the alkali counter cation (M═Na, K, Rb, Cs).

Addition of alkali oxides to vitreous SiO_2 produces Si 2p and O 1s XPS chemical shifts. The magnitude of the chemical shifts increase with counter oxide abundance through transfer of valence 's' electrons from alkali atoms to NBO of tetrahedra. The negative charge acquired by the NBO is redistributed (delocalized) over all atoms of the tetrahedron via Si—O bonds thereby increasing valence band electron densities over the constituent Si and O atoms. The greater the number of NBOs associated with a tetrahedron the greater the enhancement of electron density on all atoms of the tetrahedron, thus explaining the Si 2p and O 1s XPS chemical shifts. With respect to Raman spectra, the increased valence electron density causes the central Si atom to become appreciably less positive, which diminishes the strength of Coulombic interactions between Si and O atoms, and weakens Si—O force constants. In turn, the weakened force constants result in decreases to Si—O stretching frequencies. The weakening of force constants and decrease in stretching frequencies occur in a stepwise manner and relate directly to the number of NBO attached to the tetrahedra. The Si—O force constant for the Q^4 species is much larger than the force constant for the Q^0 species, causing their stretching frequencies to decrease (stepwise) from ~1200 cm^{-1} to ~850 cm^{-1}. The mathematical relationships among alkali oxide compositions, Raman stretching frequencies and XPS chemical shifts are quantified.

1. Introduction

Raman spectroscopy is used widely to investigate the structure of crystals glasses and melts (e.g., McMillan, 1984a; Mysen and Frantz, 1992, 1993; Richet et al., 1996). Individual Raman vibrational bands can be, for example, assigned to small and large rings characteristic of intermediate-range structure, to counter cation-O vibrations (M-O) and to Si—O (tetrahedral) vibrations associated with different Q^n species where Q represents the tetrahedron and 'n' the number of associated bridging oxygen atoms (Engelhardt et al., 1975; Dubessy et al., 2012; Neuville et al., 2014). In addition, the relative intensities of individual vibrational bands can be used to obtain proportions of Q species in glasses (e.g., Furukawa et al., 1981; Koroleva et al., 2013; O'Shaughnessy et al., 2016).

Symmetric stretching frequencies associated with tetrahedra of silicate glasses generally occur in the 900–1200 cm^{-1} region (McMillan, 1984a). In vitreous silica where O exists only as bridging oxygen (BO or Si-**O**-Si), there are two weak, high frequency bands observed at ~1080 and ~1200 cm^{-1} (Fig. 1a) due to BO asymmetric stretching (the T_2 and A_1 modes of the Q^4 tetrahedron, Sarnthein et al., 1997, Pasquarello et al., 1998). With the addition of alkali or alkaline earth

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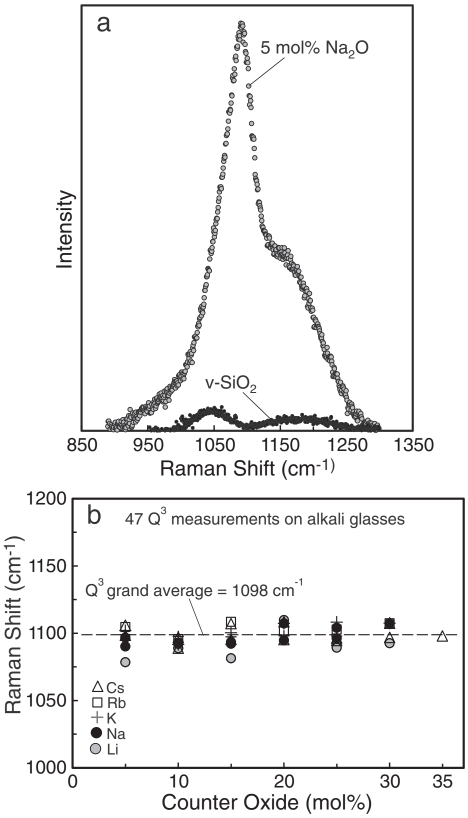

Fig. 1. (a) the black dots illustrate the high frequency portion of a Raman spectrum of vitreous silica (v-SiO$_2$) and the shaded circles represent the high frequency portion of a Raman spectrum of sodic glass containing 5 mol% Na$_2$O. The data are taken from O'Shaughnessy et al. (2016). (b) the symbols represent 47 measurements of the Q^3 species Raman frequencies of Li, Na, K, Rb and Cs glasses containing 5 to 35 mol% alkali oxide. The dashed curve represents the grand average Q^3 species frequency of all values plotted. Data plotted are derived from Matson et al. (1983) and O'Shaughnessy et al. (2016). These and other data are compiled in Table 3.

oxides to silica glass/melt, Non-Bridging Oxygen atoms (NBO or Si-**O**-M) are produced and the resulting symmetric stretch of the NBO-bearing tetrahedra are observed at different frequencies: Q^3 vibrations at ~ 1100–1050 cm^{-1}; Q^2 at ~1000–940 cm^{-1}; Q^1 at ~900 cm^{-1} and; Q^0 at ~850 cm^{-1} (McMillan, 1984a). Complications in interpretation may arise from the presence of two Q^3 or Q^4 species in some glasses and melts (cf., Brawer and White, 1975, 1977; Verweij, 1979; Furukawa et al., 1981; Matson et al., 1983; McMillan, 1984a; Mysen and Frantz, 1992; Olivier et al., 2001; Sen and Youngman, 2003; Koroleva et al., 2013).

Whereas crystals typically contain only one Q species (You et al., 2001; Richet et al., 1996), Raman spectra of binary silicate melts and glasses typically display numerous bands representing different Q species (Stebbins, 1987) and this observation gives rise to some intriguing questions which seem to have been largely unaddressed: (1) the Q^0 to Q^3 species are represented by four bands of *different frequency* but these arise from the *same* symmetric stretch of the Si tetrahedron. Why then are there four distinct vibrational frequencies?; (2) the Q^4 band undergoes an increase in intensity where alkalis or alkaline earths are added to a glass. As shown in Fig. 1a, the intensity of the 5 mol% Na$_2$O glass has an intensity *17 times* that of vitreous silica at 1200 cm^{-1}, the region where Q^4 typically contributes to the spectrum (McMillan, 1984a). Why is the Q^4 band strongly enhanced in Na-bearing glasses even though Na is not formally bonded to BO of the Q^4 species?; (3) as shown for the Q^3 peak in Fig. 1b, the frequency of individual Q species bands is effectively independent of the type of alkali oxide present and of the alkali content of the glass. Why are Q species frequencies largely independent of the mass of the alkali present *and* of its abundance? These aspects are addressed but in doing so X-ray Photoelectron spectroscopic (XPS) results are discussed and related to Raman spectral results.

2. Background and theoretical considerations

XPS measures the energy with which electrons of a specific orbital (e.g., O 1s) are bound to its nucleus (i.e., the O 1s binding energy or BE). The O 1s BE changes somewhat depending on the local environment of the atom from which the electron is derived. The changes are referred to as 'chemical shifts' and are represented by 'ΔBE' (Siegbahn et al., 1969; Carlson, 1975; Nesbitt and Bancroft, 2014; p. 21). The Si 2p$_{3/2}$ peak is, for example located at 103.7 eV for quartz and at 101.7 eV for Mg-rich olivine (Zakaznova-Herzog et al., 2005), thus the Si 2p$_{3/2}$ chemical shift is 2 eV, which results from Si being bonded to 4 BO in quartz and 4 NBO in olivine. Recent technical advances in charge compensation allow for collection of highly resolved XPS spectra of solids (e.g., Nesbitt et al., 2004), and for accurate measurement of Si 2p and O 1s peak energies of silicate crystals and glasses (Dalby et al., 2007; Nesbitt et al., 2011; Sawyer et al., 2012, 2015; Nesbitt et al., 2015a, 2015b). There also have been important advances in the interpretation of XPS spectra (e.g., Bancroft et al., 2009; Nesbitt et al., 2015a) and using high resolution XPS spectra of Na-silicate and K-silicate glass compositions we can now determine accurately Si 2p and O 1s chemical shifts (Nesbitt et al., 2011; Sawyer et al., 2012, 2015).

2.1. Valence electron (charge) density and XPS

Changes to the electron density within the valence band of an atom affects the energy with which electrons are bound to the nucleus (i.e., affects the BE). The BE of Si 2p core electrons, for example, is dependent on the shielding provided by its valence electrons (i.e., Si 3s and Si 3p orbitals). Here, *shielding* refers to the change in the nuclear charge experienced by a core orbital resulting from the effectiveness of electrons in other orbitals to neutralize the positive charge of the nucleus. Neighbouring atoms to which a central atom is bonded affect the electron density over the central atom by sharing or transferring charge via molecular orbitals. The binding energies of core orbitals of an atom consequently vary depending on its immediate chemical environment. The BE variations due to the local environment (chemical shifts or ΔBE) have been rationalized by Siegbahn et al. (1969). They considered a core orbital of an element to lie centered within a larger electrostatic sphere, where the larger sphere of mean radius r_u and of charge q_e is taken to represent the valence band. The potential (U_i) felt by the core electrons (e.g., i = Si 2p or O 1s) is given by $q_e e^2/r_u$ (a Coulombic interaction) so that the *change* in potential resulting from a change in the electronic charge of the valence band is given by (Carlson, 1975):

$$\Delta U_i = \Delta q_e e^2/r_u \tag{1}$$

where ΔU_i represents the change in potential energy resulting from a change in electronic charge (Δq_e) within the valence band. The change in potential energy (ΔU) is measured directly by XPS as ΔBE, so that ΔBE of a core photopeak 'i' (i.e., ΔBE_i or chemical shift of 'i') is proportional to ΔU_i and considering Eq. (1):

$$\Delta BE_i = k_i \Delta q_e e^2/r_u \tag{2}$$

where 'k_i' is the proportionality constant, the value of which is discussed subsequently. Carlson (1975, Table 5.7) tabulated ΔU_i for a unit change in electron charge ($\Delta q_e = 1.0$) of the valence orbitals. They are: O 2p = 31.6 eV, Na 3s = 8.8 eV, Si 3p = 13.8 eV and K 4s = 7.0 eV. Assuming that $k_i = 1.0$, the removal of one 3s electron from a Na atom, for example, should yield a Na 1s core level chemical shift of 8.8 eV. Where the electron is transferred to an O 2p valence orbital, the resulting O 1s chemical shift is 31.6/N eV where N is the number of O atoms to