

CHARACTERIZING SILICATE GLASSES WITH VIBRATIONAL SPECTROSCOPY Xiaohui Fu^{1,2}, Alian Wang², and Michael J. Krawczynski². ¹National Astronomical Observatories, Chinese Academy of Sciences, Beijing 10012, China (fuxh@bao.ac.cn), ² Dept. Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, 63130, USA.

Introduction: Amorphous silicates are common in extraterrestrial materials. They are found in the matrix of carbonaceous chondrites and other primitive meteorite [1]. Tagish Lake is an excellent example whose TEM and XRD analyses found evidence for poorly crystalline phyllosilicate-like species [2], and Raman spectroscopy studies revealed amorphous silicates with variable degrees of polymerization [3]. On Mars, CheMin instrument discovered amorphous phases in all analyzed samples, and poorly crystalline smectite in mudstone samples [4].

Despite the lack of periodicity and long-range order, silicate glasses and melts retain a characteristic short-range order structure [5]. The polymerization degrees of silicate glasses/melts affect their chemical, physical and thermal properties [6]. Laser Raman spectroscopy has been used to study the structure of melts of a variety of chemistry and polymerization degrees for terrestrial applications [7-8].

Raman spectroscopy was proposed as a powerful technique for planetary surface exploration since 1995[9]. Three Raman systems have been selected as scientific payloads for *in situ* and/or stand-off sensing by NASA's Mars 2020 and ESA's 2018 ExoMars rover missions. To determine the polymerization degree and crystallinity of silicate glasses at the surface of Mars within the geological context will help us understand their formation processes and the preservation conditions.

In this study, we synthesized silicate glasses in a range of NBO/T ratios (from 0 to 4), and then characterized the different degrees of polymerizations using Raman and Mid-IR spectroscopy. On the basis of these experiments, we developed a calibration curve to semi-quantify polymerization degree of silicate glasses, which was validated using natural silicates glasses.

Experiments: Silicate glasses were synthesized from pure oxides in a range of NBO/T ratios (from 0 to 4). The starting material is a homogenized mixture prepared with appropriate quantities of high purity reagent-grade oxides. Depending on the composition of mixed oxides, the selected temperature for each experiment fell in a range from 1260 to 1520 °C. Experimental durations varied from 2.5 to 5 hours. The synthesized molten silicate was quenched into liquid N₂ or DI. The resulting glass bead was crushed and pieces were mounted in epoxy and polished for further analysis. Homogeneity of glass was checked using optical and electron microscopy.

A HoloLab 5000-532 laser Raman spectrometer was used to obtain Raman spectra of the samples from 150 to 4300 cm⁻¹. A 20x microscopic objective was used to focus the laser beam (6 μm in diameter) of 532 nm wavelength onto the sample and to collect the Raman photons produced by the sample. Each measurement typically uses 20 s exposure time and 2 times accumulations which are stacked to get a Raman spectrum with good signal/noise ratio. For each type of silicate glass, over 100 spots were analyzed on chips that were 0.5-1.0-mm in size that were free of bubbles and microcrystals.

A Nicolet Nexus 670 (FTIR) spectrometer was used to make Mid-IR ATR (attenuated total reflectance) measurements of silicate glasses. Spectral data were collected over the wavelength range of 2.5-25 μm at 4 cm⁻¹ spectral resolution. For each sample, 128 scans (collected over 2.5 min) were averaged to produce each final spectrum.

We analyzed the major element compositions by quantitative wavelength-dispersive spectroscopy electron-probe microanalysis (EPMA) using a JEOL 8200 electron microprobe. An accelerating voltage of 15 kV, a beam current of 20 nA, and a defocused beam (10 μm spot size). The ratio NBO/T, non-bridging oxygens per tetrahedron, is widely used as a measure of polymerization degree of silicate glasses/melts. The NBO/T of each silicate glass was calculated on the basis of obtained chemical compositions using the method in [6].

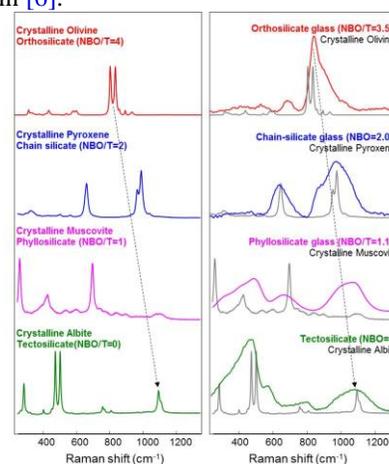


Fig.1 Raman spectra of crystalline silicate and synthetic silicate glasses

Results and discussions: Raman spectra of silicate glasses can be clearly divided into three main characteristic regions (Fig.1). The high-frequency en-

velope (HF, 850-1100 cm^{-1}) is assigned to Si-O_{nb} (O_{nb} =non-bridging oxygen) stretching vibration [8]. The low-frequency region (LF) in the range of 400-600 cm^{-1} is a complex mixed vibrational mode of the $\text{Si-O}_b\text{-Si}$ bond (O_b =bridging oxygen), the breathing vibration of four- to six-member rings, and symmetric stretch of bridging oxygen in $\text{T-O}_b\text{-T}$ ($\text{T}=\text{Si, Al}$) linkages. The middle-frequency Raman band (MF) near 650-750 cm^{-1} is a straightforward indication of $\text{Si-O}_b\text{-Si}$ bonds that exist in chain-, ring-, and phyllosilicates.

Fig.1 compares Raman spectra of crystalline and glassy silicates. We found that: (1) Crystalline and glassy silicate of similar NBO/T share very similar peak positions, while silicate glasses have much broader peaks; (2) Positions of Raman peak(s) in HF shift to higher wavenumber with increasing polymerization degree; (3) The intensity ratio of $\text{Si-O}_b\text{-Si}$ to Si-O_{nb} peaks increases following the increasing degree of polymerization in both crystalline phases and silicate glasses.

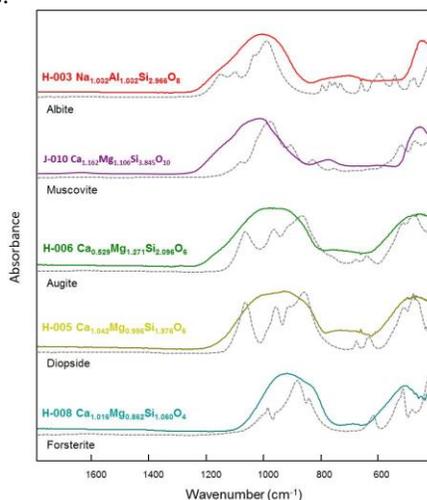


Fig.2 MIR spectra of crystalline silicate and synthetic silicate glasses

MIR-ATR spectra of silicate glasses are shown in Fig.2. Silicate minerals have two diagnostic spectral features: Christiansen Feature (CF) and Reststrahlen Band (RB). The CF occurs near 1250 cm^{-1} , expressing as a minimum in reflectance or a maximum in emission. The CF position is related to silicate polymerization degree, occurring at higher wavenumbers for tectosilicate and lower wavenumbers for orthosilicate. CF position downshift to shorter wavenumbers with decreasing polymerization in silicate glasses is consistent with what is observed in crystalline silicates. The centers of RBs occur near 1000 cm^{-1} and gradually migrate to low wavenumbers when the glasses get polymerized.

RBs are the results of strong Si-O asymmetric stretching vibration. RBs positions of silicate glasses general-

ly match with the ν_3 asymmetric vibrational peaks of crystalline silicates with similar degree of polymerization. However, all sharp sub-peaks observed in crystalline silicates, are totally lost in the glasses. This is because silicate glasses only conserve the short-range order and lack the long-range order that gives rise to symmetry and anisotropy in crystals [10]. Silicate glasses are therefore both isotropic and have broad and smooth infrared spectral features.

We built the relationship between Raman peak area ratio and the parameter NBO/T of silicate glass. For each type of synthetic glass, 40 representative Raman spectra have been selected. We used curve fitting to obtain the integrated peak areas of three Raman peaks in each spectrum, then calculated the Raman peak area ratio, $A_{\text{LF+MF}}/A_{\text{HF}}$. Fig.3 shows the correlation between NBO/T and peak area ratio. This calibration curve has been verified using natural glass samples (an obsidian sample, Hawaii basaltic glass, Apollo 14 brown glass and Apollo 16 green glass).

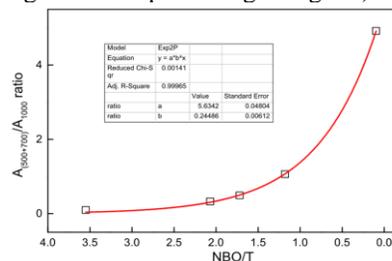


Fig.3 The relationship between NBO/T and band area ratio, $A_{\text{LF+MF}}/A_{\text{HF}}$.

Conclusions: Compared with crystalline silicates, amorphous silicates are isotropic. Their Raman and mid-IR spectra are characterized by broad spectral peaks/bands, with similar central positions. With increasing degree of polymerization, there is a weakening and a position shift of the Raman peak near 1000 cm^{-1} (Si-O_{nb} stretching mode), and the strengthening of broad Raman peaks near 500 cm^{-1} (ring breathing mode) and 700 cm^{-1} ($\text{Si-O}_b\text{-Si}$ mode). We found that the polymerization degree of silicate glasses could be semi-quantified by Raman peak area ratio using the established calibration curve.

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