

TIME-RESOLVED RAMAN AND LUMINESCENCE SPECTROSCOPY OF FELDSPARS AT HIGH TEMPERATURES RELEVANT TO VENUS EXPLORATION. M. J. Egan¹, P. D. Barnett¹, A. K. Misra¹, T. E. Acosta-Maeda¹, S. K. Sharma¹, and M. N. Abedin², ¹Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii at Mānoa, Honolulu, HI 96822, USA; ²NASA Langley Research Center, Hampton, VA 23681, USA. sksharma@soest.hawaii.edu

Introduction: Raman spectroscopy (RS) has been proposed as a candidate analysis system for missions to Mars, and more recently as a potential mineralogical analysis system to Venus. This technique has several distinct advantages over other spectroscopic techniques that have been used on past missions. For planetary applications, the sharpness of Raman spectral features of minerals allows for less ambiguous detection, especially in the presence of mixtures [1]. On Venus, application of Vis-NIR spectroscopy is hampered by the presence of the thick CO₂-rich Venusian atmosphere, and measurements can only be made near a 1 μm window in that type of atmosphere [2, 3]. Small portable remote Raman systems, which are suitable for planetary rovers and landers, have been shown to be effective in identifying hydrous and anhydrous minerals, glasses of mineral compositions, ices and atmospheric molecular species [4-7].

In recent years, we have evaluated time-resolved (TR) Raman spectroscopic detection of minerals in an environment with temperatures similar to those found on Venus [8]. Although the pressure of the Venusian atmosphere (91 atm) has not been taken into account in these experiments, it has been demonstrated that the 91 atm pressure will not affect Raman analytical capability. Time-resolved Raman spectroscopy with pulsed 532 nm laser has been shown to be an effective technique for high-temperature Raman spectroscopy [9]. Previous work showed that high temperatures can have a strong effect on the position and bandwidth of Raman vibrational modes in minerals [9-10]. In this work, we have investigated the Raman spectra of a number of well characterized feldspars as well as observed fast luminescence, which appears at high-temperatures when the sample is exposed to 532 nm pulse laser.

Samples: Three feldspar samples were purchased from Ward's Natural Science Establishment, Inc., Rochester, New York. Electron microprobe analysis of sample #1, Microcline Crystallize Crystal Peak Colorado, USA, revealed its composition to be Ab_{5.48}An_{0.03}Or_{94.43}, where Ab = NaAlSi₃O₈, An = CaAl₂Si₂O₈ and Or = KAlSi₃O₈. The composition of sample #2 listed as Orthoclase crystal contains a major plagioclase phase Ab_{76.09}An_{21.18}Or_{2.78} and a minor phase Ab_{5.49}An_{0.3}Or_{94.22}.

Experimental: The feldspar samples were illuminated by a 532 nm laser, generated from a diode pumped frequency-doubled laser (Viron, Big Sky la-

ser, 20 Hz, 6 ns pulse width). The laser beam's diameter was enlarged by a 5x beam expander (not shown in Fig. 1). Following the beam expander, the properties of the laser beam were further manipulated by a simple aperture to ensure that the feldspars received 0.5 mJ/pulse of 532 nm light and that the laser spot size was 2 mm in diameter.

Mineral samples were heated to high temperature in a furnace (Fig. 1). The furnace is heated with a Pt-10% Rh wire that can achieve a maximum temperature of 1400 K. The mineral is placed inside the furnace close to the center of a ceramic tube, and the 532 nm pulsed laser beam was slightly defocused with a 150 mm focal length (F/6) planoconvex lens in oblique illumination unto the sample (Fig. 1). The scattered

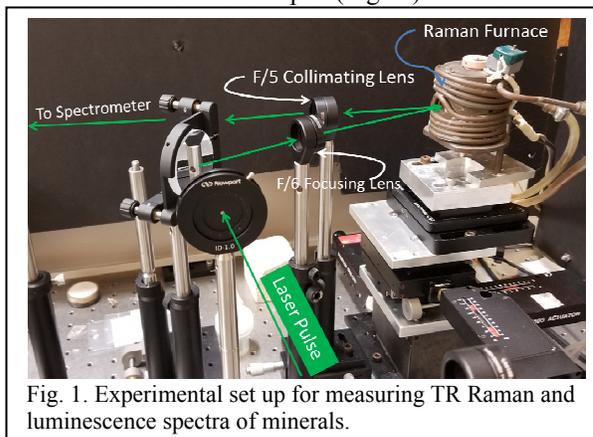


Fig. 1. Experimental set up for measuring TR Raman and luminescence spectra of minerals.

light was collected with a 25 mm diameter and 125 mm focal length (F/5) planoconvex collecting lens (Fig. 1). The collected parallel beam was analyzed with a Kaiser Optics HoloSpec spectrometer equipped with a 532 nm edge filter and focusing lens. A time-gated intensified CCD camera from Princeton instrument was used to measure the laser-induced luminescence and Raman spectra of feldspars.

Results: Figure 2 show the combined Raman and luminescence spectra of microcline #1 as a function of temperature. The intensity of luminescence background goes up and reaches maximum at 473 K. On further heating of the sample, the luminescence background decrease and at 773 K it appears below the room temperature luminescence background. Note that the 773 K spectrum has been upshifted by +40 and the 286 K spectra has been down shifted by -50 for the sake of clarity.

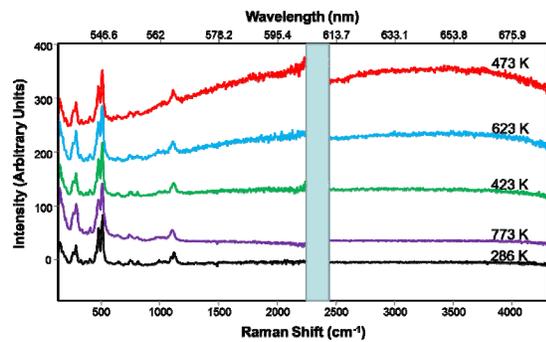


Figure 2. Time resolved Raman and luminescence spectra of microcline #1 as a function of temperature. The curves have been vertically displaced for clarity.

Figure 3 shows the TR Raman spectra of microcline #1 as a function of temperature in the range 173-1300 cm^{-1} . It is evident from Fig. 3 that the Raman spectra of microcline can be measured to 773 K. With increasing temperature, the Raman lines of microcline increase in width and shift toward lower wavenumbers. The presence of four-membered rings of TO_4 ($\text{T} = \text{Si}, \text{Al}$) tetrahedra in the feldspar group of mineral results in two or three Raman peaks lying between 450 and 515 cm^{-1} , the strongest of which falls within the narrow region of 505 to 515 cm^{-1} [11, 12]. The degree of Al/Si disorder is reflected in the position of high frequency (950-1200 cm^{-1}) antisymmetric stretching of bridging oxygen ($\nu_{\text{as}}(\text{T-O-T})$). The spectra in Fig. 3 show the presence of well-defined ν_{as} bands at 1105, 1124 and 1139 cm^{-1} .

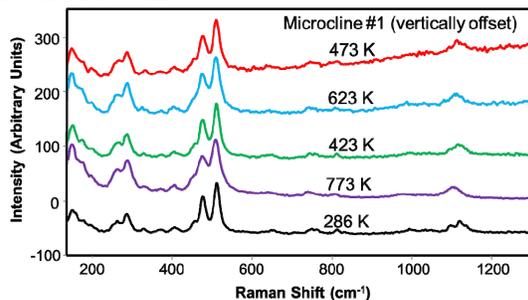


Figure 3. TR Raman spectra of microcline #1 as a function of temperature. The spectra are vertically off set as following: 473 K by +150, 623 K by +50, 423 K by +50, 773 K by +0 and 286 K by -75.

Figure 4 shows the combine TR Raman and luminescence spectra of orthoclase #2 sample. The behavior of the thermally induced luminescence is similar to that of microcline #1. Figure 5 shows the Raman spectra of orthoclase #2 in the range 175-1300 cm^{-1} . Orthoclase #2 has a major and minor phase. It appears that the minor phase being measured has the composition of $\text{Ab}_{5.49}\text{An}_{0.3}\text{Or}_{94.22}$. The presence of broad and weak ν_{as} bands in the 900-1200 cm^{-1} region indicates that

this is the high temperature phase containing significant Si/Al disorder.

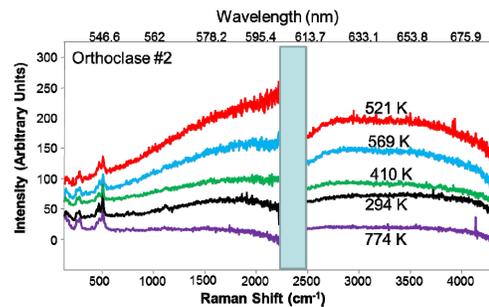


Figure 4. Time resolved Raman and luminescence spectra of orthoclase #2 as a function of temperature. The curves have been vertically displaced for clarity.

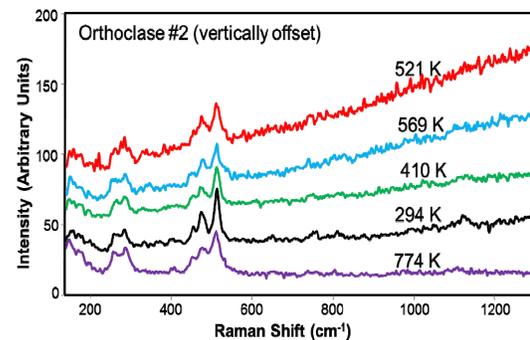


Figure 5. TR Raman spectra of orthoclase #2 as a function of temperature. The spectra are vertically off set as following: 521 K by +0, 569 K by +0, 410 K by +25, 294 K by +15 and 774 K by +0.

Conclusion: We have demonstrated that good quality TR Raman spectra of feldspar minerals can be measured at temperatures relevant to Venus exploration. The observed thermoluminescence decreases sharply on heating the sample above 473 K, and will not pose any difficulty in making measurements on the ~ 735 K surface of Venus.

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