

Optical phonons, OH vibrations, and structural modifications of phlogopite at high temperatures: An in-situ infrared spectroscopic study

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ABSTRACT

The thermal behavior of optical phonons and OH vibrations of phlogopite (a trioctahedral mica) was examined at temperatures up to 1000 K using in situ infrared spectroscopy. The results showed that with increasing temperature, O–K bands in phlogopite exhibited a relatively strong variation in frequency in a manner similar to those in muscovite. The work revealed that different types of OH bands (fundamentals and combinations) have very different thermal behavior or temperature dependence, and their absorption coefficients are commonly not constant on heating. OH combination bands that are associated with summation processes of multi-phonon interactions commonly show a decrease in their intensities on heating, but in contrast combination bands due to difference processes generally exhibit an increase. This means that temperature dependencies of their absorption coefficients need to be considered when using the Beer-Lambert law to determine or estimate OH contents or hydrogen concentrations at high temperatures. The results showed a structural anomaly associated with a discontinuity in the temperature derivative of the wavenumber of Al–O and Si–O vibrations and O–H stretching near 600 K. However, framework-related phonon modes in the FIR and MIR regions do not suggest a break of the original monoclinic structural symmetry in the investigated temperature region. The complex changes are attributed to temperature-induced alteration of local configuration involving TO₄ tetrahedra and a possible change of the orientation of OH dipoles, in addition to a previously reported distortion of MO₆ octahedra. Increasing temperature to 1000 K also causes partial dehydroxylation, as evidenced by the disappearance of the OH band near 3623 cm⁻¹ and the decrease in OH band height and area of other OH bands. The study did not record the formation of H₂O inside phlogopite as a result of partial dehydroxylation. The work offers new data and findings that have important implications in understanding the complex structural modifications and the behavior of phonon modes and the thermal stability of hydroxyls on approaching the dehydroxylation, as well as the way hydrogen is released from micas at high temperatures. Our data also show that phlogopite becomes less transparent with increasing temperature suggesting a change of radiative properties and ability to transmit heat, which could be of interest for modeling thermal-transmission in crustal rocks.

Keywords: Phlogopite, infrared spectra, high temperature, phonon modes, OH, dehydroxylation, phase transition