Mid-infrared emission spectroscopy of sulfate and sulfate-bearing minerals

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ABSTRACT

Mid-infrared thermal emission spectra were acquired and are presented for 37 different sulfate minerals representing Strunz classes 6/A-D as well as a few other miscellaneous sulfate-bearing minerals (Strunz class 3/C and 8/J). Sulfate vibrational modes are assigned to each spectrum; also assigned are the modes of component OH, H2O, and carbonate where applicable. A discussion also is presented regarding the effect of hydration state on the emissivity spectra; dehydration of the Ca-sulfate mineral series (e.g., gypsum-bassanite-anhydrite), as well as the Mg-sulfate series, causes the high-frequency edge of the sulfate ν1 band to shift to a larger wavenumber.

Keywords: Mid-infrared, vibrational, spectroscopy, emissivity, emission, sulfate, spectra

INTRODUCTION

Approximately 370 sulfate-mineral species are known to exist in nature (Hawthorne et al. 2000). Sulfate minerals are found in a variety of geologic settings, including volcanic, hydrothermal, evaporitic, and chemical-weathering environments. Some sulfate species are specific to single formational chemical environments, but others can form in several. Sulfates are formed in the presence of water of varying acidities and temperatures. In high-temperature volcanic and hydrothermal settings, metal-sulfate salts are common around active crater lakes, fumaroles, and hot springs, and may form volcanic aerosol particles. In low-temperature evaporite settings, preserved textural relationships (precipitation fabrics) between the sulfates and other salts can provide information regarding the precipitation sequence and mineral chemistry, thereby providing insight into the chemistry of the (sometimes ancient) surface waters. Chemical weathering can produce sulfate minerals that are entrained in soil or as crusts (or efflorescence) on host materials.

Sulfate minerals may be distinguished using thermal infrared (mid-infrared) spectroscopy. Early mid-infrared spectroscopic studies have shown that the aqueous sulfate anion (SO₄²⁻) produces four infrared absorption features at ~1105, ~983, ~611, and ~450 cm⁻¹ (corresponding to the asymmetric stretch, ν3; symmetric stretch, ν1; asymmetric bend, ν2; symmetric bend, ν3, respectively) (Nakamoto 1986; also see Herzberg 1945; Hug 1997) of which only ν1 and ν3 are infrared active. These vibrations are modified when the sulfate anion is present within a solid-state medium, such as a mineral with a repeating molecular order, resulting in the potential appearance of all four sulfate vibrational modes in the spectrum.

The objective of this study is to present and discuss the mid-infrared emissivity spectra of a variety of sulfate-bearing minerals. A large suite of spectra are included to discuss the emissivity variations that arise over the mid-infrared wavelengths due to differences in chemistry, including hydration state of the samples. The results of this study will aid the interpretation of thermal-infrared spectral data acquired in laboratories and those data acquired remotely of the Earth and other planetary bodies. The results of this study will be particularly relevant to the remote study of Mars, on which sulfate bedrock and sulfate-rich soils have been identified (e.g., Squyres et al. 2004; Squyres and Knoll 2005), and for which mid-infrared spectral data are plentiful (e.g., Christensen et al. 2001, 2003, 2004). Remote identification of specific sulfate minerals on Earth or elsewhere would enable the geologic setting in which the mineral formed to be determined. The spectra presented in this work are available through the Arizona State University Thermal Emission Spectral Library (http://speclib.asu.edu).

SAMPLE DESCRIPTIONS

For this study, 62 sulfate-bearing mineral samples were studied, representing 37 different minerals (Table 1) that are reasonably common, available, and stable. These include the samples: afghanite, alanite, anglesite, anhydrite, antlerite, aphythitalte (glasierite), apjohnite, barite, bassanite (hemihydrate), bloedite (blodite), brochantite, burkeite, celestine (celestite), coquimbite/paracoquimbite, credite, ferricopiapite, glauberite, gypsum, hanksite, hexahydrite, jarosite, kainite, kieserite, linarite, minamite, natrojarosite, pickeringite, plumbojarosite, polyhalite, potassium alum (potash alum; kalinite), rozenite, serpierite, sulfohalite, szomolnokite, thalmasite, thenardite, and zincobotryogen.

To confirm the mineralogic identification, all of the samples were analyzed by powder X-ray diffraction (XRD). The samples range in physical state from hand samples that are well-crystalline and dense, to less dense hand samples that are consolidated crystallites, to coatings, to loose particulate samples (powders) (Table 1).

EXPERIMENTAL METHODS

The samples in this study were analyzed in thermal emission at ambient pressure using the Mars Space Flight Facility at Arizona State University. The spectrometer used is a modified Nicolet Nexus 670 E.S.P. FT-IR interferometer attached to an external glove box containing a temperature-stabilized sample chamber (maintained with circulating water behind the chamber wall). This spectrometer is equipped with a thermoelectrically stabilized DTGS detector and a CdI beam splitter.