Raman spectroscopy study of manganese oxides: Layer structures

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ABSTRACT

Raman spectra were collected for an extensive set of well-characterized layer-structure Mn oxide mineral species (phyllomanganates) employing a range of data collection conditions. We show that the application of various laser wavelengths, such as 785, 633, and 532 nm, at low power levels (30–500 μW) in conjunction with the comprehensive database of standard spectra presented here, makes it possible to distinguish and identify the various phyllomanganese minerals. The Raman modrelative intensities can vary significantly as a function of crystal orientation relative to the incident laser light polarization direction as well as incident laser light wavelength. Consequently, phase identification success is enhanced when using a standards database that includes multiple spectra collected for different crystal orientations and with different laser light wavelengths. The position of the highest frequency Raman mode near 630–665 cm−1 shows a strong linear correlation with the fraction of Mn3+ in the octahedral Mn sites. With the comprehensive Raman database of well-characterized Mn oxide standards provided here (and available online as Online Material1), and use of appropriate data collection conditions, micro-Raman is a powerful tool for identification and characterization of biotic and abiotic Mn oxide phases from diverse natural settings, including on other planets, as well as for laboratory and industrial materials.

Keywords: Manganese oxide, Raman spectroscopy, phyllomanganates, birnessite

INTRODUCTION

Layer-structure Mn oxide minerals, also called phyllomanganates, are found in a wide variety of geological settings and are important constituents in many soils and sediments (Post 1999). These phases can precipitate from solution as the result of macro- or micro-scale changes in redox conditions, pH, or composition; additionally, natural and laboratory Mn oxides that form by biologically mediated processes are predominantly phyllomanganates (McKeown and Post 2001; Tebo et al. 2004; Santelli et al. 2011). Phyllomanganates having a birnessite-like structure readily participate in redox and cation-exchange reactions and exhibit high adsorption capacities for various organic pollutants and toxic metallic ions (Le Goff et al. 1996; Manning et al. 2002; Feng et al. 2007; Lopano et al. 2009; Kwon et al. 2013; Fleeger et al. 2013; Shumlas et al. 2016; Kong et al. 2019). They also have been identified as promising heteronuclear compounds for water-oxidation catalysis (Sauer and Yachandra 2002; Jiao and Frei 2010; Wiechen et al. 2012; Frey et al. 2014; Feng et al. 2017). Phyllomanganates are critical battery materials and are being investigated for their applications as catalysts and cation-exchange agents, as well as for their potential to mitigate hazardous materials in the environment (Ghodbane et al. 2009; Li et al. 2012; Nam et al. 2015).

Phyllomanganates are constructed of sheets of MnO₆ octahedra. The Mn is predominantly Mn⁴⁺ but can be substituted by Mn³⁺ and vacancies, with the resulting layer charges being compensated by various interlayer cations in the different phases (Fig. 1). Most phyllomanganates also have interlayer water molecules. Natural samples commonly are fine-grained and poorly crystalline, and the particular phyllomanganese mineral phases are difficult to distinguish visually in the field or in hand specimens. They also can occur as fine-scale intergrowths of two or more phases that readily alter from one to another. In many cases, X-ray diffraction (XRD) of these phases also fails to identify them because the XRD patterns often exhibit broad peaks from multiple disordered phases, making basic phase identification difficult or impossible (Ling et al. 2020). Consequently, many researchers employ other methods in addition to XRD to characterize natural phyllomanganates, such as X-ray absorption spectroscopy (XAS), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and combined energy-dispersive X-ray spectroscopy and scanning electron microscopy (EDS-SEM). These techniques also have experimental limitations and requirements, such as special sample preparation methods, large sample sizes, or synchrotron X-ray sources.

Due to the difficulties of working with complex and typically poorly crystalline natural phyllomanganate samples, many researchers use synthetic phases that are presumed to be suitable analogs of the minerals. Offsetting the advantages of working with pure, relatively well-crystalline laboratory-produced samples is the difficulty of assessing their relevancy to natural phases or systems. Additionally, complexities and confusion introduced