Raman spectroscopy study of manganese oxides: Tunnel structures

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ABSTRACT

Raman spectra were collected for an extensive set of well-characterized tunnel-structure Mn oxide mineral species employing a range of data collection conditions. Using various laser wavelengths, such as 785, 633, and 532 nm at low power levels (30–500 µW), as well as the comprehensive database of standard spectra presented here, it is generally possible to distinguish and identify the various tunnel structure Mn oxide minerals. The Raman mode relative intensities can vary significantly as a function of crystal orientation relative to the incident laser light polarization direction as well as 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. For the hollandite-group minerals, the frequency of the Raman mode near 630 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 Supplemental Materials¹), 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.

Keywords: Manganese oxide, Raman spectroscopy, todorokite, hollandite

INTRODUCTION

Manganese oxide/hydroxide minerals are found in a wide variety of natural settings; they are important components of many soils and sediments and are commonly found as coatings on rocks and nodules, as well as oxidation products of Mn-rich deposits. These phases can precipitate from solution as the result of macro- or microscale changes in redox conditions, pH, or composition; additionally, studies during the past few decades have demonstrated that many Mn oxides in our environment likely form as a result of biologically mediated processes (Tebo et al. 2004; Santelli et al. 2011). Mn oxide minerals are chemically active, readily participating in redox and cation-exchange reactions. They also adsorb a large variety of metal cations, even if present in small quantities, because they commonly occur as fine-grained coatings with large surface areas. As a consequence of these properties, Mn oxides can control the metal concentrations in water associated with soils and sediments (Le Goff et al. 1996; Post 1999; 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).

Natural Mn oxides are ubiquitous and reactive, and as a result, there is a large body of research devoted to investigating their structures and reactivities. An essential part of that work requires identification of the particular Mn oxide phases and an understanding of their behaviors to inform geochemical models for basic reactions and interactions among minerals and biological systems within the Earth’s Critical Zone. Additionally, many Mn oxides are essential materials used in batteries, catalysts, molecular sieves, and numerous other industrial applications (Ghodbane et al. 2009; Li et al. 2012; Nam et al. 2015). These phases are also of interest to archaeologists because of their roles in pigments, ceramics, and as age-dating tools for certain sites and artifacts (Caggiani and Colomban 2011). As a consequence of these uses and interests, characterizing Mn oxide structures and their properties under various conditions is critical.

Studies of Mn oxides are challenged by the sheer number of these species; there are more than 30 known Mn oxide/hydroxide minerals that commonly are fine-grained, poorly crystalline, and occur in the color palette of gray to brown to black, and consequently are difficult to distinguish visually in the field or in hand specimens. This great diversity of Mn oxide minerals in natural systems is in part because Mn occurs in three oxidation states (+4, +3, and +2), and because the MnO₆ octahedral building blocks can share edges, corners, or faces to construct a large variety of tunnel and layer structures (Fig. 1). Natural samples 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) patterns exhibit broad peaks from multiple disordered phases, making basic phase identification difficult or impossible. Consequently, many researchers employ other methods in addition to XRD to characterize natural Mn oxides, 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