CURIES: Compendium of uranium Raman and infrared experimental spectra

TYLER L. SPANO1,*, TRAVIS A. OLDST,†, MARSHALL MCDONNELL3, ROBERT SMITH1, JENNIFER L. NIEDZIELA1, ANDREW MISKOWIEC1, ROGER KAPSIMALIS1, AND ASHLEY E. SHIELDS1

1Nuclear Nonproliferation Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee 37830, U.S.A.
2Carnegie Museum of Natural History, 4400 Forbes Avenue, Pittsburgh, Pennsylvania 15213, U.S.A.
3Computer Science and Mathematics Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee 37830, U.S.A.

ABSTRACT

Identification of radioactive materials is a critical goal of resource exploration, basic actinide science, and nuclear forensics, and we provide here new insights toward rapid, nondestructive analysis of uranium-containing minerals and technogenic phases. Raman and infrared spectroscopic data are powerful indicators of solid-phase U(VI) coordination chemistry. In addition, U(VI) minerals exhibit high chemical and structural diversity as artifacts of geochemical processes leading to ore formation. Spectral signals of axial UO2– (U-Oyl) bond lengths and the influences of additional oxyanions on these values are well documented for uranium oxide and oxysalt minerals and technogenic phases. Additional insight regarding the underlying crystallographic structure and chemical composition of uranium materials can be extracted through a survey of all available Raman spectroscopic data for these phases. To this end, we have developed the Compendium of Uranium Raman and Infrared Experimental Spectra (CURIES). CURIES was compiled via a thorough review of literature and databases, and for mineral species that lack measured and recorded spectra, data were obtained either from museum and academic collections or by direct syntheses. Characteristic Raman spectroscopic features for subgroups of uranyl minerals within CURIES were elucidated using multivariate statistical analyses. In addition, average spectra for groups of uranyl minerals were determined, providing insight into common spectroscopic characteristics that are indicative of the structural origins from which they arise. As of publication, 275 mineral species and technogenic phases have been entered in CURIES, and of these, 83 phases have published spectra that have been included in the CURIES database. Data collection is ongoing, and we have triaged missing data sets to assess CURIES for completion and to identify mineral groups that lack representation and should therefore be prioritized for data acquisition and inclusion in the database.

Keywords: U(VI) minerals, uranyl minerals, Raman PLSR, Raman PCA, mineral spectroscopy

INTRODUCTION

A long-standing question in mineralogy is how to relate observed spectroscopic features more closely to the underlying crystal structure from which they originate. In addition, accurate identification of uranium-bearing compounds remains a significant challenge in the fields of nuclear forensics (Lin et al. 2013; Palacios and Taylor 2000; Pointurier and Marie 2010), environmental remediation (Amme et al. 2002; Christensen et al. 2004; Faulques et al. 2015b), and resource exploration (Beiswenger et al. 2018; Stefaniak et al. 2008). Although vibrational spectroscopic signatures are well documented as powerful indicators of physicochemical properties of nuclear materials relevant to the fuel cycle (Bonales et al. 2016b; Kirkegaard et al. 2020; Lv et al. 2016; Schwerdt et al. 2018; Spano et al. 2020; Sweet et al. 2013), and are often reported in investigations of new mineral species, existing spectroscopic analysis platforms (Laetsch and Downs 2006) rely on pattern matching between the collected spectrum and a database. Unfortunately, an exhaustive library of high-fidelity experimental spectroscopic data is not currently available for nuclear fuel cycle materials, nor have all available vibrational spectra for uranium minerals been collated. Because many naturally occurring uranium minerals possess structural and chemical similarities to technogenic fuel cycle materials, the compilation of these data into a compendium represents a transformative capability toward rapid and nondestructive identification of both uranium minerals and fuel cycle materials (Forsyth et al. 1986; Guo et al. 2014; Kirkegaard et al. 2019, 2020; McNamara et al. 2002; Plášil 2014; Spano et al. 2020a).

Low-symmetry crystals and amorphous phases are commonly observed in nuclear fuel cycle materials. Similarly, poorly crystalline, or admixed mineral species are often encountered. These scenarios can lead to broadening of spectroscopic information such that simple pattern matching cannot provide additional information about the sample. Nevertheless, spectral information is retained in these amorphous, admixed, and poorly crystalline systems that can be indicative of specific structural subunits (i.e., chemical coordination environment, additional oxyanion species) (Spano et al. 2020a). By relating the local chemical