Raman spectroscopic investigation of selected natural uranyl sulfate minerals

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ABSTRACT

Uranyl sulfates are important constituents of uranium ores and represent a significant fraction of U(VI) minerals discovered in recent years owing to their propensity to form in mine tailings and legacy sites related to uranium exploration. Recently, we surveyed all published Raman spectra for uranium minerals and found significantly less easily accessible data available for uranyl sulfates relative to other groups of uranium minerals (Spano et al. 2023). In that work, we described average spectra for groups of uranyl minerals to understand common vibrational spectroscopic features attributable to similarities in oxyanion chemistry among U(VI) minerals, but only data for three uranyl sulfate minerals were included in the study. The present work reports on Raman spectra collected for 18 additional uranyl sulfate minerals. To better understand underlying structural and chemical features that give rise to spectroscopic observables, we relate differences in structural topology, charge-balancing cations, and locality of origin to features observed in the Raman spectra of selected natural uranyl sulfates.

Keywords: Uranyl sulfates, Raman spectroscopy, U(VI) minerals

INTRODUCTION

Accurate, nondestructive identification of uranium-bearing compounds is of critical interest in the fields of nuclear forensics, environmental remediation, and resource exploration. Uranyl sulfate minerals are important constituents of uranium ore deposits, occurring as weathering products via oxidation-hydration alteration of primary uranium oxides such as uraninite (Plášil 2014). The propensity for uranyl sulfate occurrences is due in part to the interaction of decomposing primary sulfide phases, resulting in low-pH, aqueous complexes of UO22+ and SO42− (Finch and Murakami 1999; Krivovichev and Plášil 2013). Analogously, sulfuric acid is commonly employed during uranium extraction and milling operations (Seidel 1981; Sharifironizi et al. 2016), resulting in a diverse population of technogenic uranyl sulfate phases (Guettaf et al. 2009; Ling et al. 2010).

Systematic descriptions of both naturally occurring (Burns et al. 2003; Finch and Murakami 1999; Gurzhiy and Plášil 2019; Krivovichev and Plášil 2013; Tyumentseva et al. 2019) and technogenic (Kohlgruber et al. 2022; Smith et al. 2018; Tyumentseva et al. 2019) uranyl sulfate species are provided elsewhere. Briefly, uranyl sulfate minerals are composed of U(VI) in pentagonal bipyramidal coordination, further linked through edge- and vertex-shared SO4 tetrahedra, forming a topologically diverse group of minerals. Currently, 46 uranyl sulfate minerals are recognized by the International Mineralogical Association, making sulfates the most numerous group of uranyl minerals. Linkages between U(VI) and S(VI) polyhedra are typically monodentate with few exceptions (Burns et al. 2003; Gurzhiy and Plášil 2019). Uranyl sulfate minerals predominantly form sheet-like 2-D structures; however, some are known to crystallize with infinite chain topologies, and few structures with isolated clusters of polyhedra are reported. In addition to classification based on structure type, uranyl sulfates may also be categorized by relations between their overall bond topologies with previously described species (Burns 2005; Lussier et al. 2016). Gurzhiy and Plášil (Gurzhiy and Plášil 2019) describe eight categories of structural topologies in which uranyl sulfate minerals may be grouped, including the zipperite (Burns et al. 2003), leydetite (Plášil et al. 2013b), phosphuranylite (Demartin et al. 1991), and mathesiusite (Plášil et al. 2014c) topologies, as well as isolated clusters, chains of polyhedra, dense chains of polyhedra, and rare layers (Gurzhiy and Plášil 2019).

To elucidate the relationships between structural attributes and observable spectroscopic features, here we discuss in detail the Raman spectra of uranyl sulfate minerals and the underlying crystallographic features from which they originate. This work focuses on mineral species possessing the zipperite, mathesiusite, and phosphuranylite anion topologies and members of the uranyl sulfates that are composed of isolated clusters, chains of polyhedra, and dense chains of polyhedra, as delineated by Gurzhiy and Plášil (2019). First, common features are examined in the spectra of all uranyl sulfate minerals, and then we discuss average spectra calculated for groups of uranyl sulfate minerals based on structure type (and anion topology). As a means toward understanding potential crystal-chemical influences that charge-balancing cations may have on observable spectroscopic features, we examine differences between the spectra of individual mineral species belonging to a given structural group. Finally, we explore...