Time-resolved Raman and luminescence spectroscopy of synthetic REE-doped hydroxylapatites and natural apatites

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Abstract

Using continuous and time-resolved spectroscopy, we investigate Raman and luminescence signals from synthetic hydroxylapatites doped with trivalent REE including Dy³⁺, Eu³⁺, Nd³⁺, and Sm³⁺, as well as REE in natural apatites, with laser excitations at 532 and 785 nm. We demonstrate that time-resolved spectroscopy is an efficient method to reduce luminescence from Raman spectra or, alternatively, to investigate the luminescence signals without interference from the Raman contribution. Time-resolved luminescence spectroscopy is a powerful technique for generating specific high-quality luminescence spectra for the REE emission activators in apatites by using appropriate combinations of delay and gate width for time synchronization of the laser pulse and ICCD detector. This allows the unambiguous detection and identification of the activators by avoiding overlapping of various emission signals in the luminescence spectra. This is particularly useful in the case of natural samples, which often have several activators for luminescence. In the case of synthetic REE-doped apatites, a quenching process for luminescence due to activator concentration is seen for Eu³⁺ and Sm³⁺, i.e., the higher the concentration, the shorter the luminescence decay time. The interpretation of luminescence decay time in natural apatites is promising but more complex because of energy transfers between the various luminescence activators present in the crystal lattice. Luminescence is a powerful technique for detecting the presence of REE in apatites down to parts per million levels, though quantifying the concentration is still a challenge.

Keywords: Apatite, time-resolved spectroscopy, Raman, luminescence, REE

Introduction

Apatite [Ca₅(PO₄)₃(F,Cl,OH)] is one of the most common accessory minerals in both terrestrial rocks and meteorites. They have recently been identified in situ on Mars by the ChemCam LIBS instrument onboard the Curiosity rover (Forni et al. 2020). They are also a very important component of bones or teeth as well as a primary source of phosphorous for biological processes. Apatites are sensitive tracers of volatiles and fluid-rock interactions in metamorphic rocks (Harlov 2015) and magmatic rocks (Webster and Piccoli 2015), as well as in meteorites (McCubbin and Jones 2015). They are important minerals for thermochronological and geochronological investigations of processes occurring at various depths and temperatures (Chew and Spikings 2015). Last, but not least, apatite offers an unusual range of applications in ecology, agronomy, biology, medicine, archeology, environmental remediation, and materials science (Rakovan and Pasteris 2015; Gómez-Morales et al. 2013). Therefore, it is important to constantly improve the tools used for the characterization of the structure and chemistry of apatite. To this aim, vibrational spectroscopies such as infrared and Raman, as well as luminescence spectroscopy, can provide rich amounts of information. This fact, along with several practical advantages, makes them useful tools when exploring the physical and/or chemical properties of apatite.

Raman spectroscopy is useful for a quick, non-destructive, and non-ambiguous identification of apatites down to the microscale (Antonakos et al. 2007). In addition, Raman spectroscopy provides valuable information on the type of apatite: hydroxylapatite vs. fluorapatite vs. chlorapatite (Antonakos et al. 2007). It can also be used to assess the crystallinity of apatite and to track possible carbonate incorporation in apatite through CO₃²⁻ substitution for PO₄³⁻ tetrahedra (Awonusi et al. 2007; and see Pasteris and Beyssac 2020 and references therein).

Laser excitation during Raman analysis may also induce emission of luminescence in apatite. Luminescence is used here as a generic term describing all kinds of photoluminescence, e.g., fluorescence, luminescence, or phosphorescence (see Gaft et al. 2015 and Waychunas 2014 for further details). Because the luminescence signal can be extremely strong, such that it can