

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