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Optical absorption, luminescence, and electron paramagnetic resonance (EPR) spectroscopy of crystalline to metamict zircon: Evidence for formation of uranyl, manganese, and other optically active centers

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Abstract

A spectroscopic study on seven natural zircon crystals representing varying coloration and degree of short-range order has been conducted using Raman, optical absorption (OA), time-resolved laser-induced luminescence (TRL), and electron paramagnetic resonance (EPR) spectroscopy. There is a systematic increase in the line width of the central Gd^{3+} transition in the EPR spectra with decreasing short-range order as defined by Raman spectroscopy. In the luminescence spectra, the broad-band yellow photoluminescence centered at about 560 nm is restricted to samples with a high degree of short-range order. In contrast, photoluminescence related to trivalent rare earth elements was detected in zircon with both intermediate and high degrees of short-range order, but not in one heterogeneous, intermediate to highly metamict sample. Furthermore, short-lived greenish luminescence, typical of uranyl ions, could be detected in the luminescence spectra of partly and strongly metamict zircon. Reabsorption lines related to the presence of tetravalent U were found in luminescence spectra of both well-ordered and metamict samples. These observations give evidence for the occurrence of hexavalent U, besides the tetra- and pentavalent forms in natural zircon. It appears that pentavalent U initially present in crystalline zircon converted to tetra- and hexavalent U in highly metamict samples. For a well-ordered green zircon crystal from Caldas Minas, Minas Gerais (Brazil), spectra of Mn^{2+} (or Mn^{4+}) were detected by both EPR and luminescence spectroscopy, demonstrating that Mn centers may be present in this mineral. Potential color centers are discussed. Green coloration of natural zircon cannot be assigned exclusively to the presence of U^{4+} as suggested previously. Furthermore, no significant influence of the Nb^{4+} center on zircon coloration, including reddish color, was found. Yellow coloration may be related to the absorption due to charge-transfer bands of Pr^{4+}.

Keywords: Zircon, metamict, uranium, uranyl, luminescence, Raman, EPR, coloration