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Excited State Host-Guest Interaction in Sm³⁺-Doped Zirconia*

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Abstract

The photoluminescence and vibrational Raman properties of monoclinic(m) and cubic(c) zirconia doped with Sm³⁺ are reported. The m-ZrO₂ doped with Sm³⁺ provides stronger luminescence than the c-form when excited with UV radiation. The spectral results indicate that exclusive excitation of the donor, zirconia, leads to sensitized luminescence for the acceptor, the samarium(III) ion. The emission spectrum consists of a broad and several sharp bands characteristic of f-f transitions within Sm³⁺. The broad band emission centers at 507 nm at liquid N₂ temperature, and blue-shifts to 491 nm at room temperature. The excitation profile consists of a broad band at 328 nm, when monitored both at the donor and acceptor emission lines. A spectral overlap region is evident between the zirconia emission and the Sm³⁺ absorption, leading to an efficient energy transfer in the system. The intensity ratio of the acceptor/donor emission increases by two-fold upon changing the temperature from 77 to 298 K. Hence an efficient energy-transfer persists even at room temperature: albeit a competing thermal non-radiative process decreases the overall emission intensity. Enhancement of the energy-transfer process has also been noted with increased dopant levels, where Raman studies indicate a dominance of the monoclinic phase up to at least 10 % Sm substitution. Details of these studies will be presented and discussed. [*Sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, BES, US Dept. of Energy, under contract DE-AC05-00OR22725 with ORNL, managed & operated by UT-Battelle, LLC, and by Commissariat à l'Énergie Atomique and Electricite de France.]