High Resolution Measurement of the Photoionization Threshold of Ce^{3+} in CaS and SrS

J. Fleniken, Judith Grimm[+], U. Happek,

Department of Physics and Astronomy, The University of Georgia, Athens, GA 30602, USA

The optical properties of rare earth or lanthanide impurities have been studied experimentally in a great number of host materials. Much attention has been placed on optical transitions involving the $4f^{n}$ and $4f^{n-1}\ 5d^{1}$ configurations. These transitions are used in a number of luminescent devices such as lasers, cathode ray tubes and fluorescent lamps. Less understood but also of great importance in characterizing the optical properties of doped insulators are transitions involving both the localized states of the impurity ion and delocalized states of the host lattice, i.e. electron transfer. Paramount to this description is the determination of the impurity ground state energy relative to the host conduction and valence bands, since this determines the thresholds at which electron transfer occurs. Beyond these thresholds, relaxation, and thus emission, of the excited impurity ion occurs via mechanisms that may include both impurity and host lattice states.

In this contribution we present the results of measurements of the photoionization threshold of CaS: 0.1% Ce^{3+} and SrS: 0.1% Ce^{3+} using a technique based on thermally stimulated luminescence (TSL). This method determines the radiative energy threshold of TSL, i.e. the threshold for electron trapping via the conduction band, thus establishing the photoionization threshold. Previous measurements of photoionization thresholds have included methodologies based on photoemission and photoconductivity. Photoemission requires high impurity concentrations (in the order of 10%) and determines ionization thresholds with a resolution of about 0.5eV. Determining ionization thresholds using photoconductivity, one generally assesses whether or not the zero phonon line of an impurity absorption band lies within or below the conduction band, thus in the case of Ce^{3+} the resolution is determined by the splitting of the 5d levels. For materials that exhibit efficient electron trapping at low temperatures, TSL offers a method for sensitivity and resolution. TSL also offers the ability to distinguish between charge transfer and direct determination of ionization thresholds with high photoionization as well as discrimination of different impurity occupation sites, thus avoiding the problem of signals comprised of multiple components.

For both CaS: Ce^{3+} and SrS: Ce^{3+} the photoionization threshold was found near the center of the first excited $5d^{1}$ band (T_{2g}). This placement of the conduction band edge relative to the impurity states is consistent with efficiency and thermal quenching properties of these materials. Figure 1 below gives the TSL signal as function of the radiative excitation energy superimposed on the excitation spectrum of CaS: 0.1%Ce^{3+}, showing the photoionization threshold within the first excited $5d^{1}$ band (T_{2g}). The threshold is determined with a resolution (0.05eV) much smaller than the band with. These results are novel in that they represent, to our knowledge, the most precise measurements of a Ce^{3+} ionization threshold.

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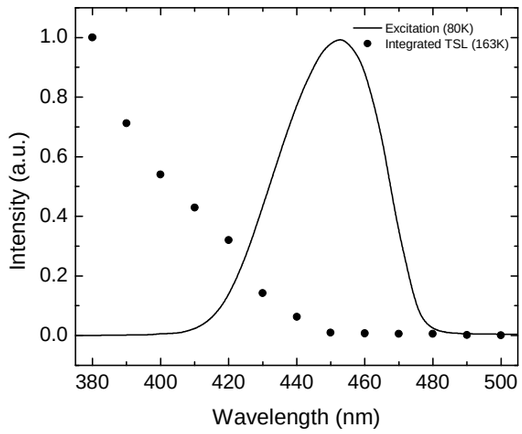

Figure 1. The integrated TSL plotted as a function of the excitation wavelength (dots) and the excitation spectrum (solid line) in the 375nm-500nm region.

[+] Present address:
Department of Chemistry and Biochemistry, University of Bern, CH-3012, Bern Switzerland