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Temperature dependent spectroscopic studies of the electron delocalization dynamics of excited Ce ions in the wide band gap insulator, Lu_2SiO_5

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Electron delocalization processes of optically excited states of Ce^{3+} impurities in Lu_2SiO_5 were investigated by means of a temperature and spectrally resolved photoconductivity study. By monitoring separately the strength of the photocurrent resulting from excitation into each of the Ce^{3+} $5d$ absorption bands, over a broad temperature region, three different delocalization processes, namely direct photoionization, thermal ionization, and tunneling, have been identified. The relative probabilities and temperature dependencies of each of these processes are discussed. The observed exponential temperature increase in the photocurrent, which spans six orders of magnitude, allows for the exact placement of the lowest energy $5d$ levels of the Ce^{3+} ions within the band gap. For Lu_2SiO_5:Ce^{3+}, the lowest $5d$ state is determined to be 0.45 eV below the conduction band edge. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1603337]

Electron delocalization processes involving optically excited transition metal ($3d$) or lanthanide ($4f$) impurity ions in wide band gap insulators play a central role in determining the utility of insulating materials in various technical applications, such as in scintillators, phosphors, and tunable solid state lasers. For the $5d$ excited states of lanthanides, delocalization can result in the total quenching of the luminescence and appears to be directly related to the precise location of the exited $5d$ states relative to the intrinsic bands of the crystalline host.[1,2] One way of locating the impurity ion ground state relative to the conduction band (CB) edge is to deduce the photoionization threshold energy from the onset of photoconductivity.[3–5] These onsets, however, are inherently difficult to define and can be easily misinterpreted. In this letter, we show that, instead of using the photoionization threshold energy, the energy level structure of the impurity ion can be determined with more precision using the temperature dependence of thermal ionization from the lowest $5d$ state to the CB edge.

A $10\times10\times0.5$ mm Ce-doped Lu_2SiO_5 crystal was mounted between two 90% transparent nickel mesh electrodes and two sapphire plates. Photocurrents were measured with a femtoampere stability using a Keitley 6517A electrometer. 1000 V was applied across the electrodes using the stabilized voltage supply of the same electrometer. Temperature control was achieved by using a cold finger, liquid nitrogen, a cartridge heater, a thermocouple, and a proportional integral differential controller. Tunable monochromatic light was provided by a 300 W cw xenon lamp and a 0.15 m monochromator. Photoconductivity (PC) and photostimulated luminescence (PSL) excitation spectra were corrected for the spectral intensity distribution of the excitation source.

Lu_2SiO_5:Ce^{3+} has been studied extensively since its successful use as a scintillating material in positron emission tomography scanners.[6–8] It is useful to compare PC spectra with the absorption, excitation, and luminescence spectra. Both absorption and luminescence properties are dominated by the vibronically broadened $[Xe]4f^1 \leftrightarrow 5d^1$ transitions localized on the Ce^{3+} ion. As an impurity in Lu_2SiO_5, Ce^{3+} ions reside in both of the two crystallographically-distinct Lu sites.[7] The Ce^{3+} ions residing on the smaller Lu sites (Ce_1) show efficient $5d \rightarrow 4f$ emission around 370 nm upon excitation into any of the crystalline field components of the $5d$ excited manifold [see Fig. 1(a)]. Luminescence from the ions occupying the larger Lu sites (Ce_2) is significantly quenched at room temperature and appears as a weak shoulder on the long wavelength side of the stronger Ce_1 emission [see Fig. 1(b)]. The corresponding excitation spectrum of this shoulder displays, besides the intrinsic Ce_1 $5d$ states, additional Ce_2-related $4f \rightarrow 5d$ transitions; the most intense of these is denoted by the vertical dashed line in Fig. 1(b), and the transitions to the lowest $5d$ level of the Ce_1 and Ce_2 ions appear as a distinct doublet. The photoconductivity (PC) spectrum [Fig. 1(c)] also shows this doublet structure; the lowest energy PC band is located at the same energy as the Ce_2 excitation band. It can therefore be concluded that, in contrast to the luminescence and the excitation properties that are dominated by the Ce_1 ions, the PC properties show contributions from both types of Ce^{3+} ions. At room temperature, all localized $4f \rightarrow 5d$ transitions on Ce^{3+} undergo delocalization processes which lead to photoconductivity;

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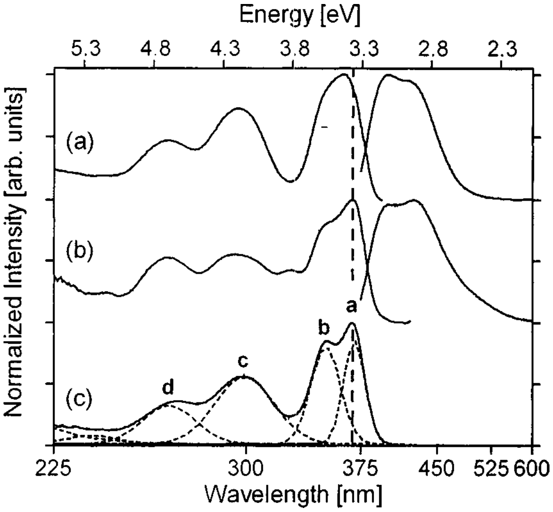

FIG. 1. PSL excitation and emission spectra of Ce_1 ions (a) and Ce_1 plus Ce_2 ions (b) in Lu_2SiO_5. The photocurrent excitation spectrum (c) is fitted with 6 Gaussians (a,b,c,d,...) to estimate the strengths of the PC bands associated with absorption into the different $5d$ states. All spectra were recorded at 293 K.

the origin and temperature dependence of these processes will be considered next.

Figures 2(a) and 2(b) display PC spectra as a function of temperature between 133 and 433 K, in incremental steps of 20 K. At low temperatures and as expected, a significant photocurrent can only be observed upon excitation into the higher energy $5d$ states (bands c and d). When the temperature is raised, excitation into the lowest energy $5d$ states (bands a and b) also begins to induce a photocurrent. The temperature dependence shown in Fig. 2 was reported previously and has been attributed to the ionization of $5d$ states located within the conduction band and to a thermally stimulated process involving $5d$ states located just below the conduction band.[1] In previous studies on this and on other doped insulators,[3–5] the onset of the photocurrent at low temperature has been interpreted as representing the energy from the Ce^{3+} ground state to the CB edge. By this method, a value of 3.5 eV was estimated for the Ce_1 ion in Lu_2SiO_5.[1] Besides the fact that onsets are difficult to determine accurately and consistently, our data demonstrate that the direct transition from the ground state to the CB is not observed, instead, photoionization is always preceded by a transition to a localized state of the impurity ion.

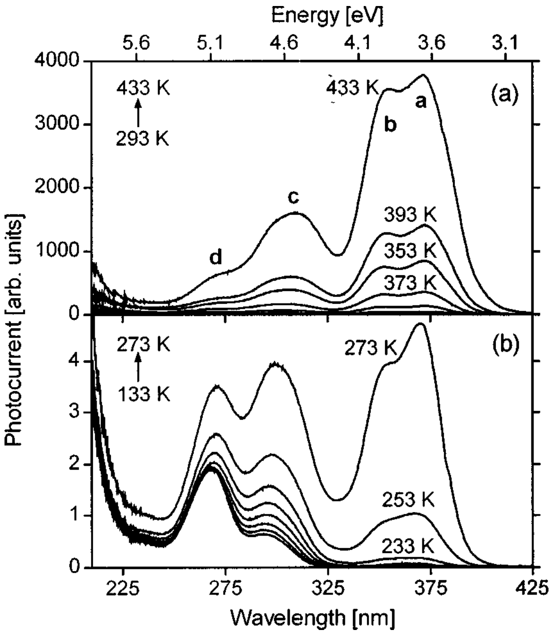

FIG. 2. Photocurrent excitation spectra of $Lu_2SiO_5:Ce^{3+}$ between 133 and 433 K. Note that the y-axis scale units of Figs. 2(a) and 2(b) are the same.

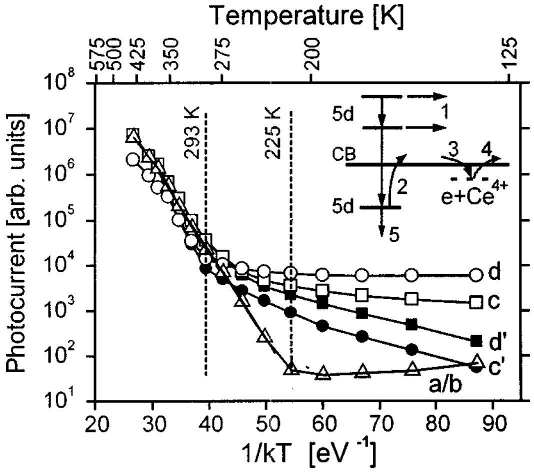

FIG. 3. Temperature dependence of the strengths of the individual PC bands in Ce-doped Lu_2SiO_5. The inset shows the relevant energy levels and the associated delocalisation processes: (1) direct ionization; (2) thermal ionization from the lowest $5d$ level; (3) formation of the Ce-bound exciton; (4) thermal dissociation of the Ce-bound exciton; and (5) $5d\rightarrow 4f$ radiative or nonradiative relaxation.

The rich nature of the spectroscopic features of our data allows for a far more detailed analysis of the temperature dependence. For a given temperature, the strength of the photocurrent resulting from the excitation into each of the $5d$ bands (the PC bands) was estimated by a Gaussian fitting procedure, as exemplified in Fig. 1(c). The variation with temperature of the strengths of these PC bands is plotted on an Arrhenius diagram in Fig. 3.

The temperature dependencies of the strengths of the lowest energy PC bands of both Ce ions (bands a and b) are practically identical and are represented by a single curve (a/b) in Fig. 3. The functional form of this dependence may be approximated by $C_1+C_2\cdot\exp(-\Delta E_1/kT)$. Below 225 K, the exponential term $C_2\cdot\exp(-\Delta E_1/kT)$ is insignificant compared to the temperature independent contribution (C_1), which we assign to an electron tunneling process to adjacent Ce^{4+} ions. Above 225 K, the photocurrent shows an exponential increase over six orders of magnitude which is due to thermally stimulated ionization processes from the lowest Ce^{3+} $5d$ state to the CB (process 2, Fig. 3). From a fit of the a and b data, an activation energy of $\Delta E_1=0.45\pm0.02$ eV is found, which we interpret as the energy separation between the CB bottom and the lowest Ce^{3+} $5d$ state. We note that the activation energies for the Ce_1 and Ce_2 ions have the same value, indicating that the lowest $5d$ states for these ions are located at the same energy below the CB bottom.

The temperature dependence of the strengths of the higher lying PC bands, c and d, arising from excitation into the higher lying $5d$ states resonant with the CB, is more complicated, and can be well fitted to $C_3+C_2\cdot\exp(-\Delta E_1/kT)+C_4\cdot\exp(-\Delta E_2/kT)$. Above room temperature, curves *c* and *d* have essentially the same slope as curves *a* and *b*, indicating that the same energy barrier ΔE_1 controls their temperature dependence. This is attributed to the fact that pumping into the higher $5d$ levels predominantly results in the population of the lowest $5d$ level, from which the same ionization processes described by $C_1 + C_2 \cdot \exp(-\Delta E_1/kT)$ occurs. In addition, a direct ionization process (process 1, Fig. 3) occurs from the higher $5d$ levels (C_1'). Together, these two processes give a temperature independent term $C_3 = C_1 + C_1'$. If this temperature independent contribution is subtracted, curves c′ and d′ (Fig. 3) are obtained that clearly reveal an additional exponential term $[C_4 \cdot \exp(-\Delta E_2/kT)]$ reflecting a second thermally stimulated process with a smaller energy barrier, $\Delta E_2 = 0.08$ eV. Since this temperature dependence is absent in the case of excitation to the lowest $5d$ level, this process can be explained as the formation (process 3, Fig. 3) and subsequent thermal dissociation (process 4, Fig. 3) of a Ce-bound exciton, 0.08 eV below the CB bottom. This exciton, Ce^{4+}+electron in the CB, appears in the course of the relaxation of an electron from the levels in the CB: before the electron becomes strongly bound to Ce^{3+} in the lowest $5d$ state, a short-lived weakly bound state with a higher energy is formed involving Ce^{4+} and CB states. This can explain the observed smaller thermal activation barrier of 0.08 eV. Such an excited state is referred to as an impurity trapped exciton.[4,9] From this study, it is clear that the temperature dependence of the photoconductivity provides valuable information about these exciton states.

The temperature signature of the different PC bands (see Fig. 3) directly provides us with the relative probabilities of the different delocalization processes involved. Absolute values, however, are hard to derive but may be estimated by relating PC data with luminescence data. The Ce^{3+} ion in the lowest $5d$ state can decay by thermal ionization [rate $s \cdot \exp(-\Delta E_1/kT)$] as described earlier (process 2 in Fig. 3), by radiative or by nonradiative $5d \rightarrow 4f$ relaxation (process 5 in Fig. 3). Below 300 K, the thermal ionization efficiency increases exponentially by more than three orders of magnitude (see Fig. 3) while the integrated luminescence intensity remains unchanged.[10] Above 300 K, luminescence starts to quench rapidly and approaches values close to zero around 425 K[10] while the exponential rise in PC intensity remains unaffected in this temperature range (see Fig. 3). Clearly no signature of any luminescence temperature quenching process is present in the PC data. The thermal ionization process seems to have a negligible effect on the population of the $5d$ states so that the thermal ionization rate, even at the highest measured temperature (433 K), must still be smaller than the $5d \rightarrow 4f$ relaxation rate. Since the Ce^{3+} radiative rate is known, $\sim 10^8\ s^{-1}$, this allows us to put an upper limit to the value of s of $10^{13}\ s^{-1}$. This rate is comparable with the values found for s from thermoluminescence studies.[11]

Finally from curves c and d in Fig. 3 we note that the direct ionization process (which gives rise to the temperature-independent component) is in turn 3–4 orders of magnitude weaker than the thermal ionization process at 433 K. The weakness of the direct photoionization process may be related to the fact that the process results in the generation of a single hot electron into the CB with a kinetic energy of the order of 1 eV and with a concomitant amount of momentum. Since single photons have little or no momentum, the small probability of direct photoionization may reflect the absence of momentum conservation in the process.

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[1] M. Raukas, S. A. Basun, W. van Schaik, W. M. Yen, and U. Happek, Appl. Phys. Lett. **69**, 3300 (1996).
[2] W. M. Yen, J. Lumin. **83–84**, 399 (1999).
[3] C. Pedrini, D. S. McClure, and C. H. Anderson, J. Chem. Phys. **70**, 4959 (1979).
[4] D. S. McClure and C. Pedrini, Phys. Rev. B **32**, 8465 (1985).
[5] C. Pedrini and F. Rogemond, J. Appl. Phys. **59**, 1196 (1986).
[6] C. L. Melcher and J. S. Schweitzer, Nucl. Instrum. Methods Phys. Res. A **314**, 212 (1992).
[7] H. Suzuki, T. A. Tombrello, C. L. Melcher, and J. S. Schweitzer, Nucl. Instrum. Methods Phys. Res. A **320**, 263 (1992).
[8] P. Dorenbos, C. W. E. van Eijk, A. J. J. Bos, and C. L. Melcher, J. Phys.: Condens. Matter **6**, 4167 (1994).
[9] W. C. Wong, D. S. McClure, S. A. Basun, and M. R. Kokta, Phys. Rev. B **51**, 5682 (1995).
[10] H. Suzuki, T. A. Tombrello, C. L. Melcher, and J. S. Schweitzer, IEEE Trans. Nucl. Sci. **40**, 380 (1993).
[11] S. W. S. McKeever, *Thermoluminescence of Solids* (Cambridge University Press, Cambridge, 1985).