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LUMINESCENCE AND PHOTOCONDUCTIVITY OF CERIUM COMPOUNDS

W.M. YEN^a, S. BASUN^b, U. HAPPEK^a AND M. RAUKAS^a^a Department of Physics and Astronomy, The University of Georgia
Athens, Georgia, USA^b A.F. Ioffe Physico-Technical Institute, St. Petersburg, Russia

The study of the luminescence properties of rare earth doped systems historically focuses on systems which exhibit strong luminescence. More recently, extensive studies on materials with high quantum efficiency are in part motivated by the search for new phosphor and scintillator materials. However, a thorough study of certain systems which show very low quantum yield will certainly lead to a better understanding of phosphor materials and rare earth systems in general. As an example of recent studies which address both the fundamental question of relaxation processes in rare earth doped systems and phosphor applications we present studies on cerium-doped lutetium oxide crystals which are characterized by a complete quenching of the $5d-4f$ luminescence and compare its optical properties to that of very efficient cerium doped phosphor material, lutetium oxyorthosilicate. To find the mechanisms which lead to the different quantum efficiency in these systems, extensive absorption, photoexcitation and photoconductivity studies were performed on single crystals. We demonstrate that the radically different emission properties of the investigated systems originate in small but crucial differences in the location of the emitting $5d$ level of the cerium ion with respect to the conduction band of the host — a general result which can be applied to a broad range of materials.

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1. Introduction

Materials doped with Ce^{3+} have attracted the interest of solid state researchers since the early sixties, and most papers focus on the application of these materials as phosphors or scintillators [1]. Despite of more than 30 years of research, one crucial question has not been fully answered: i.e., why do seemingly similar Ce-doped systems show drastically different luminescence properties, ranging from quantum efficiencies of nearly 100% to systems where the luminescence is completely quenched.

High quantum efficiencies can be understood easily in terms of the electronic structure of trivalent cerium: the simple electron configuration $4f^1$ leads

to a 20 000–30 000 cm^{-1} large gap between the lowest level of the 5*d* orbital and the spin-orbit split ground state. Thus, nonradiative multi-phonon relaxation processes are extremely unlikely and luminescence can be observed in the blue and UV spectral region with a characteristic decay time on the order of 10^{-8} s.

The origin of the strong or even complete quenching of the emission in a number of Ce^{3+} doped systems is subject of an ongoing discussion. Several reasons for this behavior, including large Stokes shift, electron transfer and photoionization, have been proposed as possible quenching mechanisms by Blasse et al. [2]. The Stokes shift in cerium compounds is assumed to be too small to result in a complete quenching of the emission [2]. Thus, the most probable quenching mechanism is electron transfer or photoionization, both of which lead to a delocalization of the 4*f* electron followed by a separate nonradiative relaxation process; but, as pointed out already, direct experimental proof has been lacking.

The experimental technique of choice used to study delocalized transitions in solids is photoconductivity, a method which allows to determine the position of impurity energy levels with respect to the conduction and valence band. It has been conventionally used in semiconductor physics but a similar, although refined, approach can be applied to insulators as well. Photoconductivity, if complemented by standard absorption and photoexcitation technique, is a powerful method which provides extremely useful information especially for non-luminescent systems where information about the system via the study of emission cannot be obtained. McClure and coworkers have used this technique to determine the positions of impurity energy levels in the host lattice band gap in a variety of systems [3, 4].

Here we report results on the optical properties and photoconductivity of Ce-doped Lu_2O_3 single crystal fibers, a system which exhibits complete quenching of the emission. We compare these results to those obtained on cerium-doped lutetium oxyorthosilicate, a very efficient and promising scintillator material [5, 6]. These two lutetium-based materials were chosen because they represent extreme cases of the quantum efficiency in Ce^{3+} doped systems. The corresponding results of similar materials (such as Y_2O_3 , La_2O_3) doped with trivalent cerium are discussed briefly.

2. Sample preparation

Lutetium sesquioxide exists in the stable form of bixbyite belonging to the space group T_h^7 (*Ia3*). The structure can be visualized as an incomplete cubic close-packing of the oxygen ions with two vacant sites at the corners of the cube. 25% of the vacancy pairs lie along the body diagonal and 75% along the face diagonal, giving rise to a trigonal C_{3i} and monoclinic C_2 site-symmetry, respectively, for the cations. This material is a host of high density and therefore especially attractive for scintillator application. Most of the studies conducted on doped lutetium oxide so far have been performed on polycrystalline form of Lu_2O_3 (powders, sintered pellets) [7–10]. Undoped single crystals of Lu_2O_3 have been obtained by the Verneuil method or by melt crystallization [11, 12]. Successful laser heated pedestal growth of both Ce-doped and undoped yttrium and lutetium oxide single crystals has been reported recently by our group [13] and Claeys et al. [14]. Another oxide of the same structure, Y_2O_3 , has been studied quite extensively by many authors

and was used in our earlier work as a host material expected to have similar properties [15]. Rare earth, yttrium and scandium oxides have very high melting points, with lutetium oxide having the highest with the value of 2467°C [9] which explains the absence of previous studies on single crystals of that material.

Lutetium oxyorthosilicate, $\text{Lu}_2(\text{SiO}_4)\text{O}$, contains isolated (SiO_4) tetrahedra and separate (not silicon-bonded) oxygen anions, surrounded by four rare earths. The stable type of structure for the rare earths of smaller ionic radii (as well as Y) has monoclinic C_{2h}^6 symmetry ($C2/c$) with two different cationic sites of coordination numbers 6 and 7 [16]. Two independent luminescence centers in these sites have been observed and described by Melcher et al. [5].

$\text{Lu}_2\text{O}_3:\text{Ce}$ and $\text{Lu}_2(\text{SiO}_4)\text{O}:\text{Ce}$ single crystal fibers were prepared from 0.25 mol% Ce-doped Lu_2O_3 and $\text{Lu}_2(\text{SiO}_4)\text{O}$ powder, respectively, provided by Schlumberger-Doll Research Company. The materials for other doped oxides, e.g. $\text{Y}_2\text{O}_3:\text{Ce}$ and $\text{La}_2\text{O}_3:\text{Ce}$, were obtained from Aldrich and RE Acton and prepared in our laboratory.

The starting material was pressed into pellets and annealed in a reducing atmosphere (5% H_2 in N_2) at 1300°C for 2 hours. After cutting the pellets into smaller rods of about 1 mm² cross-section, single crystal fibers were grown using the laser heated pedestal growth method [17]. In this technique, a CO_2 laser melts the end of the source rod (the pedestal) and a seed crystal is dipped into the melt. Crystallization occurs at the seed/melt interface as the seed is pulled upward out of the melt while the source rod is simultaneously fed into the heated zone. The obtained 1–2 cm long fibers have a diameter of about 0.5 mm and are colorless for lutetium oxide, yttrium oxide and lutetium oxyorthosilicate samples, whereas lanthanum oxide fibers exhibit a yellowish color. X-ray diffraction analysis ($\text{Cu } K_{\alpha 1}$, $K_{\alpha 2}$) of the samples showed only one crystalline phase with an uncertainty of 1% due to background noise.

For spectroscopic measurements, the fibers were cut into pieces of proper length (4–9 mm). Samples for transmission and excitation measurements were polished on both ends to optical quality, samples used for photoconductivity experiments were polished flat at the sides as well.

3. Optical spectroscopy

It has been proposed that Ce-doped Y_2O_3 samples do not luminescence efficiently because a large fraction of the Ce ions are in the tetravalent state with empty f shell [18]. Thus, the spectroscopic characterization of the single crystal samples of doped lutetium oxide was started with the IR absorption studies in order to confirm the presence of Ce^{3+} ions in the host lattice. A room temperature detection of Ce^{3+} spin-orbit split ground state transitions in the IR spectral region was performed with a FTIR spectrometer (Bruker IFS66v). Spherical sapphire lenses were used for input and output coupling of the IR radiation to the fibers.

We observed characteristic $4f-4f$ transitions in IR absorption between split ${}^2F_{7/2}$ and ${}^2F_{5/2}$ multiplets of Ce^{3+} for the crystals annealed in a reducing atmosphere. The spectral positions (within experimental error) and the number of observed lines were in agreement with published values [7] for sintered polycrystalline $\text{Y}_2\text{O}_3:\text{Ce}$ and pressed powder samples of $\text{Lu}_2\text{O}_3:\text{Ce}$. A few lines were consider-

ably narrower than those reported for sintered samples, indicating a good quality of the fibers. For the samples annealed in air no Ce^{3+} absorption was observed, confirming the conversion of more than 99% of Ce^{3+} to Ce^{4+} ions.

Visible and ultraviolet absorption spectra were taken on a modified Cary-14R spectrophotometer. A lock-in amplifier was used to increase the signal to noise ratio due to the restricted submillimeter aperture of the fibers. The visible and UV absorption spectra of Ce-doped Lu_2O_3 at both room (RT) and liquid nitrogen (LNT) temperatures are presented in Fig. 1. For the reduced sample, the absorption starts

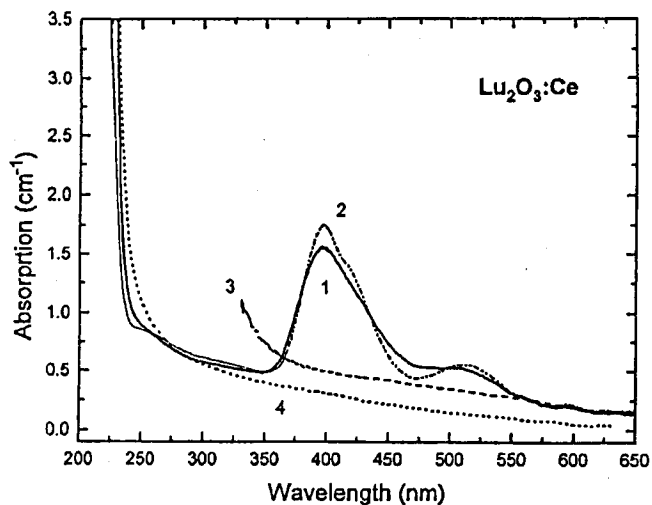


Fig. 1. Absorption spectra of cerium-doped and undoped Lu_2O_3 . Curve 1 (solid line): reduced $\text{Lu}_2\text{O}_3:\text{Ce}$ at RT. Curve 2 (dash-dotted line): reduced $\text{Lu}_2\text{O}_3:\text{Ce}$ at LNT. Curve 3 (dashed line): oxidized $\text{Lu}_2\text{O}_3:\text{Ce}$. Curve 4 (dotted line): undoped Lu_2O_3 .

around 575 nm and the first, relatively weak band has a maximum around 510 nm. The band at 400 nm has a weak shoulder at the low energy side which is more pronounced at low temperature. The 400 nm band is by far the strongest and most noticeable feature in the spectrum (apart from the host absorption below 250 nm). The origin of the strong and weak bands has been assigned previously to the localized $5d$ transitions of cerium ions at C_2 and C_{3i} sites, respectively [7]. The bands disappear with the Ce^{3+} - Ce^{4+} conversion and are therefore clearly associated with transitions of the trivalent cerium ion. Samples annealed in air, i.e. containing mainly Ce^{4+} (no characteristic Ce^{3+} IR absorption lines were observed) exhibit the onset of a strong absorption edge below 370 nm. A similar behavior of trivalent cerium in Y_2O_3 has been previously assigned to an acceptor-like electron transfer from the host valence band to the Ce^{4+} ion ("ligand-to-metal" transfer). We like to mention that the oxidation-reduction process is reversible, i.e. the same absorption results are reproducible after converting Ce^{4+} to Ce^{3+} and vice versa.

Room temperature photoexcitation was performed using a modified Cary-14R spectrophotometer for both UV and visible regions. Relatively long (9 mm) fibers

were vertically placed into the beam in the sample compartment and luminescence was observed from the end of the polished fibers. Different emission wavelengths were distinguished using a set of 10 nm band-pass filters or Schott cut-off filters.

Room temperature photoexcitation and emission studies of $\text{Lu}_2\text{O}_3:\text{Ce}$ did not show any detectable luminescence which could have been ascribed to trivalent cerium. Excitations in the UV and visible spectrum including the main absorption band due to Ce^{3+} yield no luminescence. Pulsed laser light of wavelengths between 280 and 532 nm failed to excite observable luminescence at both room and low temperatures as well. Similarly negative results were obtained on the samples of Y_2O_3 and La_2O_3 doped with Ce. A surprisingly strong excitation band which appears below 275 nm and peaks at 220–230 nm (Fig. 2) for both doped and undoped samples of Lu_2O_3 and Y_2O_3 is most likely due to exciton creation at photon energies close to the band gap. It leads to structureless broad-band emission

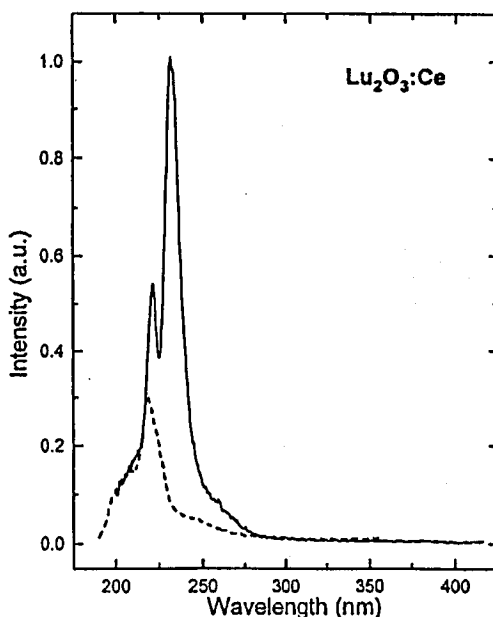


Fig. 2. Room temperature excitation spectrum of cerium-doped (dashed line) and undoped (solid line) Lu_2O_3 .

from the near UV to the red spectral region due to annihilation processes and is described by Kuznetsov et al. [19]. This host-intrinsic emission is quenched for the Ce-doped samples by an order of magnitude or more. Ce is known to reduce the emission intensity when codoped with other rare earths (e.g. Eu^{3+} in Y_2O_3 , [20]). In conclusion, the optical measurements demonstrate that the cerium emission in Lu_2O_3 as well as in Y_2O_3 is totally quenched.

In marked contrast to Lu_2O_3 , $\text{Lu}_2(\text{SiO}_4)\text{O}:\text{Ce}$ exhibits a very high quantum efficiency. The emission intensity of cerium-doped lutetium oxyorthosilicate has

been reported to reach up to 75% of that of the standard scintillator material NaI(Tl), and emits efficiently under a variety of excitation energies (UV, X- and γ -rays) [5]. Our absorption and excitation spectra agree with published results and display several distinct bands which have been assigned to $4f-5d$ transitions of Ce^{3+} (solid line in Fig. 4). Exciting into these bands results in efficient luminescence peaking at 420 nm at room temperature. The lowest $4f-5d$ absorption band peaks at about 360 nm. Thus, this system displays all the characteristic features expected for a Ce^{3+} doped system.

4. Photoconductivity measurements

The absence of any detectable characteristic cerium emission in Lu_2O_3 and Y_2O_3 leads to the conclusion that the strong absorption around 400 nm, although clearly connected to the Ce^{3+} ion, cannot be a simple $4f-5d$ transition. Instead, donor- and acceptor-like electron exchange processes (often labelled as "ionization" and "charge transfer" between the host and impurity ion), which have a large oscillator strength [21], can be assumed [22, 23]. The presented experimental results do point towards liberation of the electron from the impurity ion for the non-luminescent systems under investigation here, and photoconductivity experiments were performed on both high and low efficiency systems.

For the photoconductivity measurements the samples were mounted on the cold finger of a liquid nitrogen cryostat. The fibers were pressed by springs between two nickel meshes serving as transparent electrodes, electrically insulated from the sample mount by two sapphire plates. Photocurrents were excited by a 150 W Xe arc lamp spectrally filtered by a 0.125 m grating monochromator (Thermo Jarrell Ash). Color filters were used to suppress higher order wavelengths. The current flowing through the sample was measured with a Cary 401 vibrating reed electrometer. The excitation source was scanned from long towards short wavelengths.

Photoconductivity spectrum of $Lu_2O_3:Ce^{3+}$ is presented in Fig. 3. There is a striking similarity between the room temperature photoinduced current signal and the absorption: both are characterized by a strong band around 400 nm. The onset of the room temperature photoconductivity signal coincides with the lowest absorption band at 575 nm. The 400 nm photoconductivity band is not observed for undoped samples, whereas for doped samples annealed in air it is nearly 2 orders of magnitude smaller, thus the photoconductivity signal is strongly correlated with the optical absorption. Similar results were obtained for $Y_2O_3:Ce$. For cerium-doped lanthanum oxide again the photoconductivity follows the strong onset of absorption, in this case below 500 nm. In all cases the photocurrent was stationary, i.e. steadily flowing without a build-up of a polarization in the sample.

These data demonstrate that the absorption bands in the visible part of the spectrum cannot be due to pure intra-ion $4f-5d$ transitions of Ce^{3+} since these have localized character which are not expected to lead to photoconductivity. Instead, the cerium ion donates its $4f$ electron to the host through the $5d$ level resonant with the conduction band. In addition, the conductivity explains absence of Ce^{3+} luminescence for excitation into these bands or at higher energy: the lowest $5d$ level of the cerium ion lies already within the conduction band (CB). Delocalized electrons do not return to the $5d$ levels but first relax to the bottom of the CB and

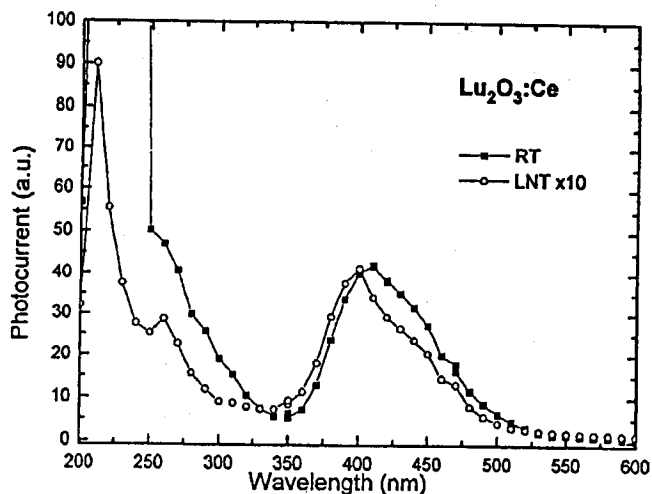


Fig. 3. Photoconductivity spectra of cerium-doped Lu_2O_3 at RT and at LNT. The signal values have been normalized to the incident flux.

subsequently through a sequence of nonradiative processes to the ground state of the cerium ion. At low (liquid nitrogen) temperature, the photoconductivity signal onset is shifted to higher energies (approximately 500 nm), but the overall features of the photocurrent are preserved and essentially temperature independent. We attributed the less than an order of magnitude drop in the photocurrent at low temperatures to capturing of the carriers in shallow traps. The dynamics of carrier recombination depends crucially on the ratio between shallow traps and Ce^{4+} recombination center: partially oxidized samples (high Ce^{4+} concentration) showed almost no temperature dependence of the strength of conductivity signal. We note that the conductivity spectra confirm the assignment of the 220–230 nm band to excitons: the conductivity at this wavelength drops by almost two orders of magnitude at low temperatures because thermal breaking of the excitons is less likely.

Taking into account both the absorption coefficient on the order of 10 cm^{-1} and absolute magnitude of photocurrent at 400 nm peak (10^{-11} A to 10^{-12} A), the distance that an electron in external electric field drifts to reach a recombination site can be estimated to be on the order of 100 Å or longer. This strongly supports the picture of free electrons instead of recharging within a close pair of Ce^{3+} – Ce^{4+} .

To compare this photoconductivity behavior to that of an efficiently luminescent material, we performed photoconductivity experiments on Ce-doped $\text{Lu}_2(\text{SiO}_4)\text{O}$. The room temperature photoconductivity curve (Fig. 4) resembles closely the absorption spectrum. The lowest absorption peak around 360 nm replicates in a strong photoconductivity signal. However, cooling the sample to liquid nitrogen temperature introduces dramatic changes. The onset of the photocurrent shifts from 420 nm to below 340 nm. Thus, the strong photoconductivity peak around 370 nm disappears entirely, in marked contrast to the small signal reduc-

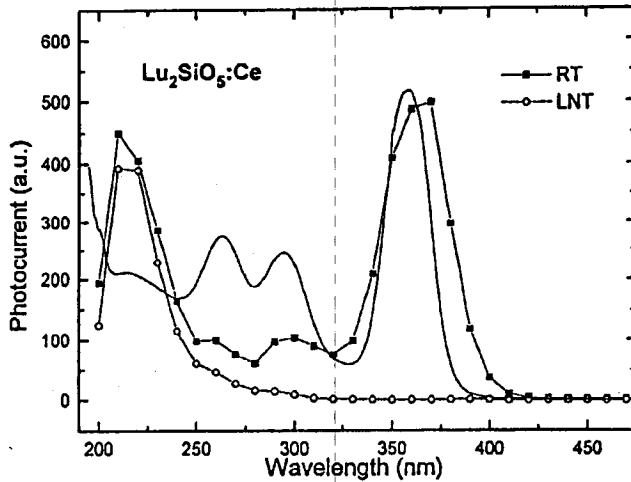


Fig. 4. Absorption spectra of cerium doped $\text{Lu}_2(\text{SiO}_4)\text{O}$ (solid line) and photoconductivity spectra at RT and at LNT. The signal values have been normalized to the incident flux.

tion in the case of Lu_2O_3 . This behavior is consistent with the lowest $5d$ level in oxyorthosilicate being located *below* the bottom of the host CB. The difference between the bottom of CB and localized $5d$ level can be estimated to be some tenths of eV which still enables to observe significant photoconductivity signal at room temperature.

The main result of the conductivity measurements can be summarized as follows: for systems with quenched emission the cerium $5d$ level lies within the conduction band, whereas in efficiently luminescent materials this level lies below the conduction band.

5. Conclusions

We have investigated Ce-doped rare earth (lutetium, lanthanum) and yttrium oxides, systems which are characterized by a total quenching of the $5d$ excited state emission of Ce^{3+} . The dominant absorption bands observed around 400 nm are not due to localized $4f$ - $5d$ transitions but correspond to a true donor-like process which promotes electrons from Ce^{3+} to the CB (i.e. photoionization). We demonstrate that the photoionization process is the main source for the quenching of the luminescence. A comparison of the optical and photoconductivity spectra between luminescent and non-luminescent materials unravel the crucial differences in the mechanisms of low and high quantum efficiency cases. Rather small energetic differences in the location of lowest (emitting) $5d$ level of Ce^{3+} in different hosts lead to totally different excited state decay paths. In lutetium oxyorthosilicate the electron relaxes to the low-lying $5d$ level located below the conduction band and subsequently emits the characteristic Ce^{3+} luminescence, thus the $5d$ level of the Ce-ion acts as a sink for the excitations. In the cerium

doped oxides, the excited electron relaxes to the bottom of the conduction band, which is located below the lowest excited cerium 5d level. Thus, the electron does not return to the cerium 5d level, but relaxes in a nonradiative decay process to the ground state of Ce³⁺, causing the quenching of the luminescence.

Experiments are in progress to investigate the position of the energy levels of cerium and other rare earth ions with respect to the conduction band in a variety of host materials with different luminescence efficiencies.

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