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Ground-State Measurement of Pr³⁺ in Y₂O₃ by Photoconductivity[1]

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Abstract—1 at % Pr³⁺-doped Y₂O₃ single-crystal fibers were prepared using a laser-heated pedestal growth method. The emission and excitation spectra of the fibers were measured. The emissions of $4f$–$4f$ transitions from $^1D_2$ to the $^3H_4$ and $^3H_5$ states are found at 620 and 720 nm, respectively. The $^3P_2$, $^3P_1$, $^1I_6$, and $^3P_0$ $4f$–$4f$ absorptions are observed at 456, 472, 482, and 492 nm, respectively. A $4f$–$5d$ absorption band is detected at 288 nm. Photoconductivity measurements show that the $4f$–$5f$ transition of Pr³⁺ around 285 nm produces a direct photocurrent. Taking the onset of photocurrent to be at 320 nm, the ground state of Pr³⁺ is determined at 1.7 eV above the valence band of the host.

1. INTRODUCTION

Trivalent rare-earth (RE^{3+}) ions are important for various applications, such as lamp phosphors and information display materials [1–3]. Recently, some research work on RE^{3+}-doped luminescence materials has been performed to study the delocalization of excited-state electrons [4]. The delocalization of electrons in an excited state is one of the major problems that may cause quenching of luminescence and laser action [5, 6]. In general, such delocalization happens to the d electrons rather than f electrons because the d state of the dopants usually overlap the conduction band of the hosts, which creates a physical path for delocalization [7]. Therefore, the structure of excited states of the RE^{3+} ions relative to the host band gap becomes the key factor that determines the delocalization of electrons.

Theoretical predictions of the band structure relative the host band gap have been carried out for RE^{3+} and RE^{2+} ions in many hosts [8]. However, these predictions also yield some incorrect information [9–11]. Thus, experimental determinations of the band structures are needed. The first set of band structures of RE^{3+} in yttrium aluminum garnet (YAG) was determined and estimated using a photoemission method [12, 13]. The results revealed that the $5d$ states of the ions are close

to the host conduction band and that the $4f$ ground states are close to the host valence band.

In this work, the band structure of the Pr³⁺ ions relative to the Y₂O₃ host is determined using photoconductivity measurements, which are another method for determining the band structures of RE^{3+} in Y₂O₃. Using the photoconductivity method, the ground state levels of Ce³⁺, Tb³⁺, and Er³⁺ ions have been found to be 2.8, 1.3, and –1.0 eV, respectively, with respect to the host valence band [14–16].

Pr³⁺ is the ion next to Ce³⁺ with two valence electrons. Both $4f$–$4f$ and $4f$–$5d$ transitions exist in Pr³⁺-doped materials. The competition of the $5d$ states and the $^1S_0$ state of Pr³⁺ in strontium aluminates is of interest in quantum cutting phosphors [17, 18]. Pr³⁺ has also important applications in long-persistent phosphors and light-emitting diode phosphors (LED). In these cases, photoionization of electrons in excited states is important to the performance of these phosphors; so, the band structure will provide information important for the applications [19, 20].

2. EXPERIMENTAL

Y₂O₃ : Pr³⁺ single-crystal fibers were prepared using a laser-heated pedestal growth (LHPG) method [15, 21]. Y₂O₃ and Pr(NO₃)₃ powder mixtures were made with a proper mole ratio (1% doping concentration) and

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† Deceased.
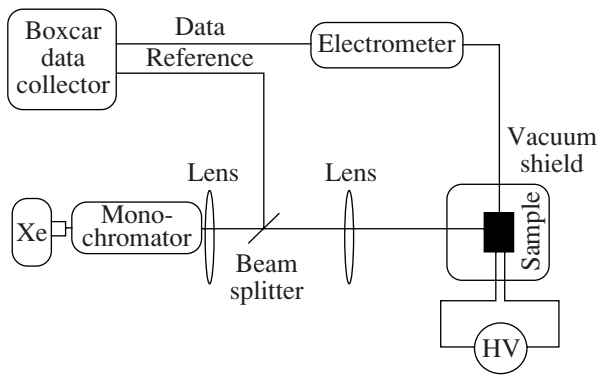[1] The text was submitted by the authors in English.

were heat-treated at 900°C for 2 h. The treated raw materials were remixed, pressed into pellets, and sintered at 1200°C in air in a Linderburg blue tube furnace for 2 h. The sintered pellets were cut and polished into 1×1 mm square rods for laser pulling. The single-crystal fibers were reduced at 1350°C in a 5% H_2 + 95% N_2 gas flow in order to obtain Pr^{3+}. The fiber samples were polished into 300-μm-thick slabs along their fiber axis with two parallel side surfaces.

The photoconductivity spectra of the samples were measured at room temperature. Ni meshes were used to serve as electrodes. The light source for excitation was an Oriel 200-W xenon lamp filtered through an ISA Jobin Yvon Spex monochromator. A light beam was split into two using a beam splitter. One beam was directed to a Boxcar data collector as a reference, and the other was focused onto the sample. The sample was mounted in a thermally and electrically shielded vacuum chamber ($<10^{-5}$ Torr) with a 10000-V/cm voltage, applied across the two ends. A Keithley 6517A electrometer was used both as a high-voltage supply and as a current detector.
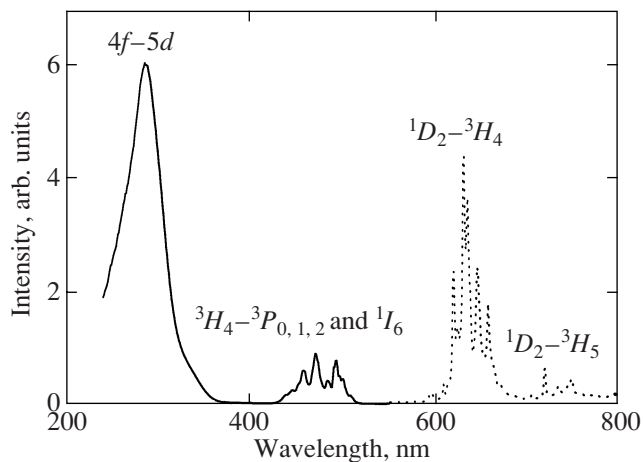
Emission and excitation spectra were collected by a SPEX FluoroMax II spectrometer. A schematic diagram for the experimental setup is presented in Fig. 1.

3. RESULTS AND DISCUSSION

The emission (dotted line) and excitation (solid line) spectra of 1% Pr^{3+} in Y_2O_3 are shown in Fig. 2. The Pr^{3+} emission bands of the $4f$–$4f$ transitions from $^1D_2$ to the $^3H_4$ and $^3H_5$ states are found around 620 and 720 nm, respectively. The Pr^{3+} $^3P_2$, $^1I_6$, $^3P_1$, and $^3P_0$ excitation peaks of the $4f$–$4f$ absorptions are observed at 456, 472, 482, and 492 nm, respectively [22, 23]. The $4f$–$5d$ absorption band of Pr^{3+} is detected at 288 nm. This value is more correct than that from [22] (300 nm).

The photocurrent spectrum measured with a 60-W lamp is depicted in Fig. 3. The photocurrent starts to rise rapidly at about 220 nm, which is consistent with the 5.6-eV band gap of the Y_2O_3 host. Another photocurrent peak is detected at 285 nm, which has a slightly higher energy position than the $4f$–$5d$ excitation peak at 288 nm, indicated as a reference in Fig. 3. This suggests that the bottom of the conduction band relative to the ground state of Pr^{3+} is slightly higher than is the lowest position of the $5d$ states relative to the Pr^{3+} ground state and, therefore, requires a higher energy than the $4f$–$5d$ transition to cause photoionization of the ions and generate a photocurrent. In this system, the major part of the $5d$ states of Pr^{3+} overlaps with the conduction band.

To further investigate the photocurrent at 285 nm, the photocurrent spectra were measured with various excitation light intensities, controlled by adjusting the lamp output power from 40 to 160 W. The photocurrent intensity at 285 nm is observed to vary linearly with the lamp power up to 100 W, as shown in Fig. 4. At higher powers, the photocurrent becomes flat, indicating a sat-
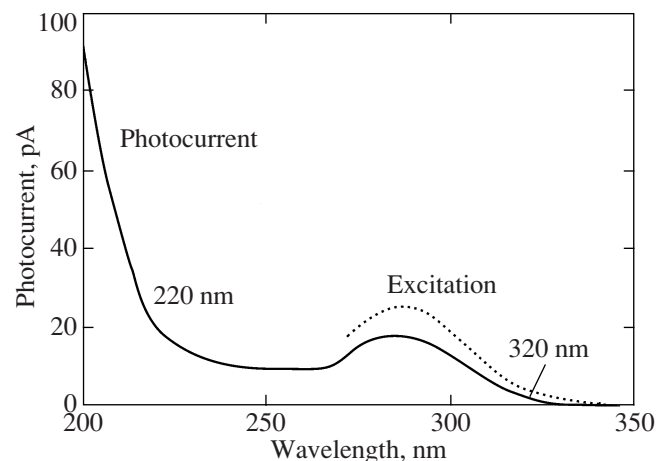

Fig. 2. Emission (dotted) and excitation (solid) spectra of Y_2O_3 : Pr^{3+}.

Fig. 3. Photoconductivity spectrum of Y_2O_3 : Pr^{3+}. For comparison, the excitation peak of the Pr^{3+} $4f$–$5d$ transition is shown (dashed line).
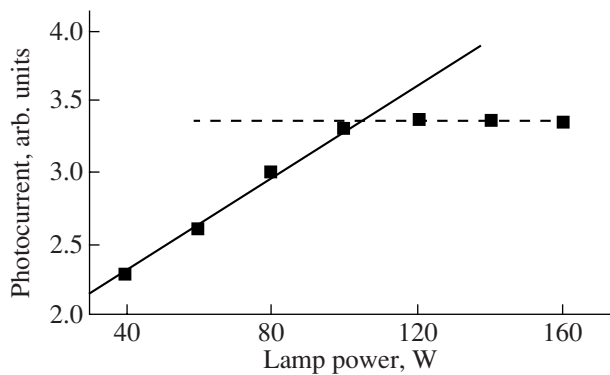
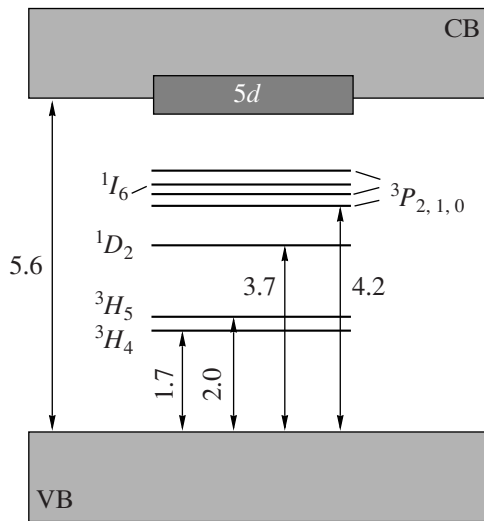**Fig. 4.** Dependence of the photocurrent on the excitation power.

Fig. 5. Diagram of the Pr^{3+} energy levels (in electronvolts) relative to the Y_2O_3 band gap.

urated absorption. The linear variation at lower powers shows that the photocurrent is a single-photon process.

Based on the above information, it is found that the lowest state of the 5d band is just below the conduction band. Taking the onset of photocurrent to be at 320 nm, as indicated in Fig. 3, we find that the ground state is about 3.9 eV below the host conduction band. The band gap width is 5.6 eV; so, the ground state of Pr^{3+} lies 1.7 eV above the valence band. Therefore, the 288-nm 5d peak is about 0.5 eV above the bottom of the conduction band. Considering the temperature dependence, i.e., the thermal ionization of 5d electrons, the actual value may have a ±0.2-eV error. The rest of the Pr^{3+} energy levels can be readily located in the band gap using these two band positions fixed with respect to the band gap, as illustrated in Fig. 5. All energies in Fig. 5 are given in electronvolts.

4. CONCLUSIONS

In summary, single-crystal fibers of Y_2O_3 : Pr^{3+} have been prepared using a laser-heated pedestal growth (LHPG) method. Emission and excitation spectra and photoconductivity have been measured. The ground state position of Pr^{3+} in Y_2O_3 was determined to be 1.7 eV above the host valence band.

ACKNOWLEDGMENTS

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