



## Temperature-dependent photoconductivity of $\text{Ce}^{3+}$ -doped $\text{SrAl}_2\text{O}_4$

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### Abstract

Long persistence  $\text{SrAl}_2\text{O}_4:\text{Ce}^{3+}$  single-crystal fibers were prepared using laser-heated pedestal growth method. Four 5d levels split due to crystal field were found in excitation spectrum with peaks at 3.65, 3.87, 4.26, and 4.79 eV, respectively, and the  $\text{Ce}^{3+}$  emission band was observed at 3.22 eV in this host. Temperature-dependent photoconductivity was performed. The results from the photoconductivity measurements indicated that the four 5d manifolds were located at 1.3, 0.5, 0.1, and  $-0.1$  eV ( $\pm 0.05$  eV), respectively, relative to the bottom of the host conduction band. The  $\text{Ce}^{3+}$  ground state was then calculated at 2.7 eV above the host valence band.

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### 1. Introduction

Interactions between the impurity electrons and the host ligand ions play an important role in luminescence, solid-state lighting, and solid-state laser applications. In research of high efficient lighting materials (such as fluorescence lamp

materials and LED materials) or high-power solid-state laser materials (such as materials for tunable solid-state UV lasers) [1–3], people found that the energy dissipation into host material is one of the major power losses in these applications. The energy dissipation into host material is stronger for materials with 5d–4f transitions because the interactions between 5d excited state and the host are much stronger than that of the 4f–4f transitions due to a more extended radial part of the 5d electron wave function. In many practical applications such as photon cutting,

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tunable solid-state laser and LEDs, the dipole allowed 5d–4f transitions are strongly preferred so that the research on the nature of the excited state dynamics of 5d electrons becomes important.

The nature of the energy positions of impurity ions in the host band gap has not been clearly understood yet. The influence of dopant on the host band structure at the doping place has not been revealed. A tentative theory of energy difference among all trivalent and divalent rare-earth ions which was developed based on survey of many literatures related to 4f–5d transitions of rare-earth ions in various hosts [4]. But most of the data collected from other work were from measurements at different temperatures, with different doping concentrations, different material forms, (i.e. powder, ceramics, crystal), and different preparation procedures (with different kinds and amount of flux content). It is possible to use such a tentative relation as a guide line to estimate energy position relative to the host band, but experimental determination may generate much more solid information.

Photoconductivity (PC) is one of the most reliable and trustable methods to determine the relative band positions between 5d states and host band gap. In this work, the properties of the SrAl<sub>2</sub>O<sub>4</sub> single-crystal fiber doped with 1 at% of Ce<sup>3+</sup> ions were investigated. The results from the PC measurements indicated that the four 5d manifolds were located at 1.3, 0.5, 0.1, and –0.1 eV ( $\pm 0.05$  eV), respectively, relative to the bottom of the host conduction band. The Ce<sup>3+</sup> ground state was then calculated at 2.7 eV above the host valence band.

## 2. Experimental

In most of the cases, samples in single-crystal form were better than ceramic or powder form samples in terms of quality. Powder and ceramic sample usually were polycrystalline and had more defects due to non-uniformity in preparation. In this work we chose to prepare single-crystal samples. The Ce<sup>3+</sup>-doped SrAl<sub>2</sub>O<sub>4</sub> single-crystal fibers were prepared using the laser-heated pedestal growth (LHPG) method [5]. SrCO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>

powders (with 99.99% purity) were mixed with Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> at a cation mole ratio of 1:1:0.01. The mixture was sintered in pellet form at 1200 °C for 5 h. The feed and the seed material for LHPG growth were cut from these pellets. The prepared single-crystal fibers were transparent, 1 cm long and 0.8 mm in diameter. The fibers were annealed in a N<sub>2</sub>+5% H<sub>2</sub> reducing gas at 1350 °C for 2 h to reduce the Ce from the 4+ to the 3+ valence state.

SrAl<sub>2</sub>O<sub>4</sub> has a stuffed tridymite structure with a 6.5 eV band gap. Emission and excitation spectra of the 1 at% Ce<sup>3+</sup> doped sample were obtained with a Spex FluoroMax II spectrometer at room temperature.

For the PC measurements, the fibers were polished into 300 m slabs with two parallel faces. The thin slabs were mounted between transparent sapphire plates with the Ni mesh electrodes placed between the sapphire plates and fibers. The sample sandwich was then mounted into an electrically shielded vacuum cryostat. A Keithley 6517A electrometer was used as a high-voltage supply and as a current detector. The applied voltage across the samples was 10,000 V/cm. An Oriel 200 W UV-enhanced xenon lamp, filtered through a Jobin Yvon Spex monochromator, was used as light source. A boxcar was used to collect and analyze the data.

## 3. Results and discussion

Ce<sup>3+</sup> has a single outer electron with two 4f “ground” states, <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub>. Because of this simple energy structure, the 5d states of the Ce<sup>3+</sup> ion have been intensively studied. In SrAl<sub>2</sub>O<sub>4</sub> host, Ce<sup>3+</sup> emission was found as a broadband emission peaking at 3.22 eV and excitation peaks when monitoring this emission (3.22 eV) were found at 4.79, 4.26, 3.87 and 3.65 eV, corresponding to the four of the possible 5d field split components [6]. Quenching of the Ce<sup>3+</sup> emission due to 5d energy position relative to the host band gap was reported in rare-earth oxide hosts [7,8]. To generate emission the position of the 5d energy levels of the emitting center must be lower than the host conduction band. Experimentally, these positions

could be determined by measuring the PC spectra of the material under different temperature. The idea of the PC measurement was that once the electron went up to the conduction band by taking an excitation photon, it became a free electron. By applying a high voltage across the sample, a current signal would be generated by the freed electrons [9,10]. We hence could scan the light source within the excitation region, and recorded the photocurrent intensity to tell the wavelength dependence of the photoionization. Generally, the onset of the photocurrent would tell that at what photon energy (wavelength) the electron could be delocalized to the conduction band, and hence gave the information about band positions of the impurity electronic states relative to the host band gap [11].

In this work, the PC measurements of the sample were carried out at room temperature ( $T_1 = 290$  K) and at low temperature ( $T_2 = 140$  K). The low temperature was achieved by mounting the sample on a liquid nitrogen-cooled cold finger. The 140 K low temperature was stabilized with a cartridge heater and a heating control system. The temperatures were accurately calibrated for instrumentation errors. The sample was applied a 10,000 V/cm high voltage in a  $10^{-3}$  torr vacuum. The current signal was detected by the Keithley electrometer with an accuracy of 0.1 fAmp. The background was found by keeping the system at the temperature for a day.

The PC spectra were measured by scanning the photon energy using a Jobin Yvon monochromator. Data were collected and averaged with a boxcar. The PC spectra at both temperatures were shown in Fig. 1, where the excitation spectrum was also depicted together with the PC spectra for comparison. The room temperature PC spectrum was close to the shape of the excitation spectrum. The lower intensity at lower-energy side of the PC spectrum indicated that the thermal assistance is required at that energy to ionize the electrons. The two PC spectra at different temperatures were almost identical except for a peak shift to higher energy in the lower temperature spectrum which was also a consequence of thermal ionization. Thermal ionization of 5d electrons depended strongly on temperature and the energy position

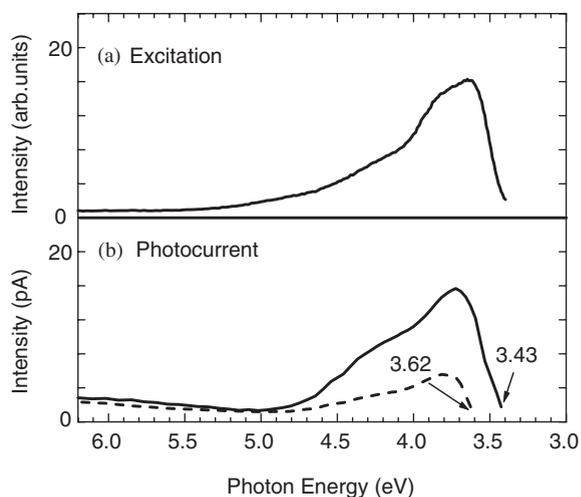


Fig. 1. Photocurrent spectra; (a) excitation spectrum recorded at 3.22 eV emission; (b) photocurrent spectrum measured at room temperature, 290 K (solid curve, onset at 3.43 eV); at 140 K (dashed curve, onset at 343 nm).

of the excited state relative to the host conduction band. The distance between the conduction band and the excitation photon energy ( $\Delta E$ ) determined the rate of thermal ionization ( $W_t$ ) at the given temperature, as it was given by

$$W_t = s e^{-\Delta E/kT}, \quad (1)$$

where  $s$  is an ionization frequency factor,  $k$  the Boltzmann constant, and  $T$  the temperature in Kelvin. From the energy shift of the PC signal onset positions at two different temperatures [12], the position of the lowest component of the 5d manifold relative to the bottom of the host conduction band could be calculated. Because the thermal ionization rates were the same at the onset wavelengths at two temperatures, by taking the excitation intensity into account, we have

$$I_1 s \exp(-\Delta E_1/kT_1) = I_2 s \exp(-\Delta E_2/kT_2), \quad (2)$$

where  $I_1$  and  $I_2$  are the excitation intensities at the two onset positions and  $I_2/I_1$  could be estimated from excitation spectrum;  $\Delta E_1$  and  $\Delta E_2$  the distances in energy from the onset wavelengths to the bottom of the host conduction band. The energy distances to the bottom of the host

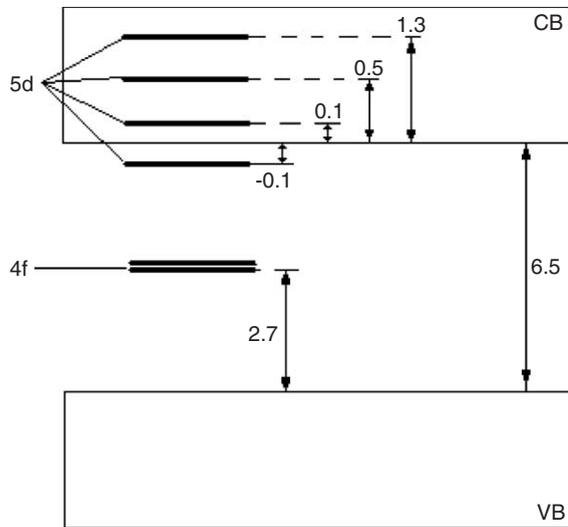


Fig. 2. Energy diagram of Ce<sup>3+</sup> in SrAl<sub>2</sub>O<sub>4</sub>. CB and VB denote the conduction band and valence band of the host, respectively. All the numbers are with the units of eV.

conduction band can then be given by

$$E_2 = [T_2/(T_1 - T_2)][(\Delta E_1 - \Delta E_2) - T_1 T_2 k \ln(I_2/I_1)]. \quad (3)$$

For  $T_1 = 290$  K,  $T_2 = 140$  K,  $I_2/I_1 \approx 3$  and  $\Delta E_1 - \Delta E_2 = 0.19$  eV in Eq. (3), we found that the first onset energy (at 290 K and 3.43 eV) was 0.35 eV below the bottom of the host conduction band, and the second onset energy (at 140 K and 3.65 eV) was 0.16 eV below the bottom of the host conduction band. Thus the 5d component corresponding to the absorption/excitation peak located at 3.65 eV was found to be 0.1 eV below the bottom of the host conduction band. The calculated value was in very good agreement with the estimate obtained from the thermoluminescence glow measurements. If we assigned the first 5d band at 3.65–0.1 eV below the bottom of the host conduction band, with the band gap energy of SrAl<sub>2</sub>O<sub>4</sub> was 6.5 eV (measured from diffused reflection spectrum of the undoped ceramics sample), the ground state of Ce<sup>3+</sup> in SrAl<sub>2</sub>O<sub>4</sub> was found to be 2.7 eV above the top of the host valence band. The other 5d bands of Ce<sup>3+</sup> at 4.79, 4.26 and 3.87 eV were found to be 1.3, 0.5 and 0.1 eV above the bottom of the host conduction

band (Fig. 2). The data from the experimental measurements and calculation method were correct and accurate. We estimated the error would be no more than 0.05 eV that mainly came from the estimate of the band gap energy of the host.

#### 4. Conclusions

The positions of the 5d states relative to the host band gap were the key factor that determined the electron behavior in that level. In SrAl<sub>2</sub>O<sub>4</sub>, the Ce<sup>3+</sup> 5d levels were found at 4.79, 4.26, 3.87 and 3.65 eV, which were 1.3, 0.5, 0.1 and -0.1 eV relative to the bottom of the host conduction band, respectively, by the photoconductivity measurements.

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