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Trapping processes of 5d electrons in Ce^{3+} doped $SrAl_2O_4$

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Abstract

Ce^{3+}-doped $SrAl_2O_4$ single-crystal fibers have been prepared by laser-heated pedestal growth method. A broad emission band peaking at 385 nm and originating from the Ce^{3+} 5d–4f transition is observed with excitations at 340, 320, 291, and 259 nm, which correspond to the crystal field splitting components of the Ce^{3+} 5d states in $SrAl_2O_4$. The emission shows strong persistence for longer than 10 h after UV radiation at 254 nm from mercury lamp. Trapping dynamics of 5d electrons of Ce^{3+} in $SrAl_2O_4$ host is studied. The electron traps at 0.75 eV are found to be responsible for the long persistent phosphorescence. Excitation-dependent thermoluminescence spectra are also recorded and analyzed. The lowest 5d state of Ce^{3+} in $SrAl_2O_4$ is found to be about 0.1 eV below the host conduction band.

Keywords: Long persistence; Delocalization; Trapping; Thermoluminescence

1. Introduction

Excited state dynamics of impurity electrons is of great interest from the fundamental physics point of view and is very important to some current applied problems such as the quenching of luminescence and the decrease of luminescence efficiency [1,2]. The energy level positions of the 5d excited states relative to the host band gap are very important information in studying the interaction between the 5d electrons and the ligand ions [3]. In general, when 5d electron's energy level is above the host conduction band it will have the possibility to delocalize. The delocalization of the 5d electrons through photo-excitation is called photoionization. Thermally assisted photoionization, in which phonons assist the promotion of electrons from emitting 5d components to the conduction band, has also been observed [4,5].

Ce^{3+} ion is one of the most attractive trivalent rare-earth ions for 5d state dynamic research. Ce^{3+} contains only one outer electron, and is commonly regarded as having two ground states $^2F_{5/2,7/2}$ thus it has only 5d excited states. If all Ce^{3+} 5d bands are higher than the conduction, it may not be able to emit [6,7]. In many hosts, where luminescence from the Ce^{3+} 5d state is observed, at least one of the Ce^{3+} components of the 5d states lies below the bottom of the conduction band from which emission occurs [8].

$SrAl_2O_4$ is one of the important alkali earth aluminates hosts. It has been intensively studied as a host for long persistent phosphors. Trapping mechanism of trivalent rare-earth ions as trapping centers had been studied [9,10]. We chose this host to study the Ce^{3+} excited state dynamics because that: (1) Ce^{3+} has never been studied in this host. Aluminates were important hosts for long persistent phosphors and plasma display panels (PDP). Therefore, excited state dynamics study of the 5d electrons in an aluminate host would present more information for these application [11]; (2) The Ce^{3+}-doped $SrAl_2O_4$ had almost all types of actions that we had listed above, i.e. trapping, delocalization and relocalization. It was important for practical applications to better understand the processes in this complicated system.

In this work, the properties of the $SrAl_2O_4$ single crystal fiber doped with 1 at% of Ce^{3+} ions have been investigated.

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A long persistent afterglow emission is observed in this material. Thermoluminescence (TL) results indicate that the long afterglow arises from a deep electron trap and the trapping process is related to delocalization of the excited electron through the host conduction band. Trapping mechanism is studied and energy positions of 5d states are estimated.

2. Experimental

The Ce^{3+}-doped $SrAl_2O_4$ single-crystal fibers have prepared using the laser-heated pedestal growth (LHPG) method [12]. $SrCO_3$ and Al_2O_3 powders (with 99.99% purity) are mixed with $Ce_2(CO_3)_3$ at a cation mole ratio of 1:1:0.01. The mixture is sintered in pellet form at 1200 °C for 5 h. The feed and the seed materials for LHPG growth are cut from these pellets. The prepared single-crystal fibers are transparent, 1 cm long and 0.8 mm in diameter. The fibers are annealed in a 95% $N_2 + 5\%$ H_2 reducing gas at 1350 °C for 2 h to reduce the Ce from the 4^+ to the 3^+ valence state.

$SrAl_2O_4$ has a stuffed tridymite structure with a 6.5 eV band-gap. The band gap was obtained by measuring the diffused refection spectrum of the ceramic samples. The β phase, a pseudo-hexagonal structure predominated at higher temperatures. At lower temperatures, the structure became the α phase, a monoclinic structure [13]. The unit cell parameters of the monoclinic α phase are $a = 10.20$ Å, $b = 20.26$ Å and $c = 8.42$ Å, and $\gamma = 60.53°$. The phase transition temperature is at 650 °C. All our experiments were performed using the α phase samples. There are two Sr^{2+} sites in α phase $SrAl_2O_4$ crystal that are surrounded by nine O^{2-} ions with low point symmetry. Generally, the Al^{3+} sites (0.51 Å) are too small for Ce^{3+} (1.034 Å) to sit in thus Ce^{3+} would prefer to stay in the Sr^{2+} sites (1.12 Å), which requires charge compensation. In fact, 90% Ce^{3+} ions occupy one of the Sr^{2+} sites and there is only 10% Ce^{3+} occupies the other Sr^{2+} site because it is difficult to compensate the extra charge of Ce^{3+} in this site comparing with the other. There are two possible charge compensations: (1) Two Ce^{3+} ions substitute three Sr^{2+} ions. This will leave a Sr^{2+} ion vacancy; (2) Two Ce^{3+} ions substitute two Sr^{2+} ions with an extra interstice O^{2-} ion. Since each of the Sr^{2+} sites has been surrounded by nine O^{2-} ions, it must be very hard to get an extra O^{2-} ion close to the Sr^{2+} site as an interstice ion. Therefore it is believed that the Sr^{2+} vacancy should be the major type of charge compensation. For this fact, one of the Sr^{2+} site is lager and easier for Ce^{3+} to get in and the other may be more suitable for serving as a vacancy [14]. In this work we consider that the Ce^{3+} has only one dominant emission center.

Emission and excitation spectra of the 1 at% Ce^{3+}-doped sample were obtained with a Spex FluoroMax II spectrometer at room temperature. Afterglow spectrum of the sample was recorded using a Jobin Yvon CCD camera. The decay curve of the afterglow was measured using a Spex 500 M spectrometer equipped with a cooled GaAs PMT. A 50 W 254 nm enhanced mercury lamp was used to irradiate the sample before each measurement. The mercury lamp used in this work had 95% percent of its light out put at 254 nm emission.

The TL glow measurements were carried out with a cartridge heater, an Omega temperature control system and a vacuum cryostat that was capable of reaching liquid nitrogen temperature. The light sources for irradiation were the mercury lamp and xenon lamp as described above. The irradiation wavelength of the light source was selected by the Jobin Yvon Spex monochromator. The line width of the irradiation light was about 10 nm in Gaussian shape determined by the slit width of the monochromator. After a 30 min irradiation, the sample was heated with the cartridge heater at a rate of 0.1 °C/s. The TL glow signal was collected by a GaAs PMT in combination with a boxcar. Data collection was started from 0 °C. A 380 nm interference filter was mounted in front of the PMT to select only the Ce^{3+} glow signal at 385 nm (3.22 eV).

3. Results and discussions

In $SrAl_2O_4$ host, Ce^{3+} emission was found as a broadband emission peaking at 3.22 eV as shown in Fig. 1 (dashed lines). The right shoulder of the emission made it visible and gave it a deep blue appearance. Excitation peaks (Fig. 1, solid line) of the emission at 3.22 eV were found at 4.79, 4.26, 3.87 and 3.65 eV, shown as the dotted lines, corresponding to the four of the possible 5d field split components.

The emission at 3.22 eV of Ce^{3+} exhibited a long persistent afterglow. The afterglow spectra were recorded with a Jobin Yvon CCD camera, after the sample had been irradiated with a 50 W 254 nm enhanced mercury lamp for 30 min. The afterglow spectra were taken at 1, 10 s and

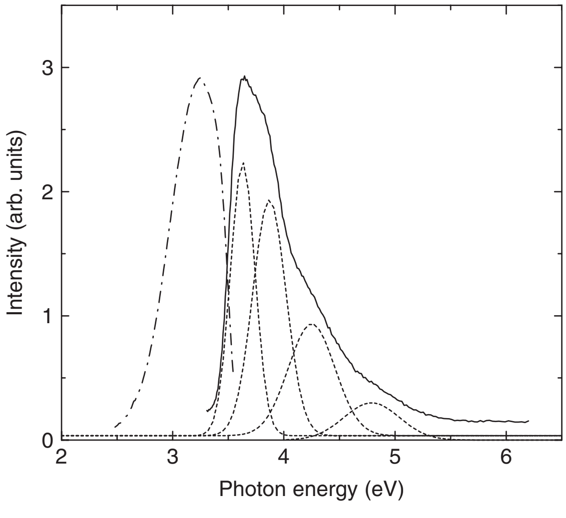

Fig. 1. Emission (dashed line, excited at 3.65 eV) and excitation (solid line, detected at 3.22 eV) spectra of $SrAl_2O_4$:Ce^{3+} single-crystal fiber (dotted lines: Gaussian deconvolution of the excitation spectra).

1 min delays, respectively, from the time that the lamp was switched-off and the spectra peaking at 3.22 eV were shown in Fig. 2. The afterglow decay curve detected at 3.22 eV was depicted in Fig. 3, where the persistence time of the Ce^{3+} afterglow was found to be longer than 10 h. The dashed line in the figure denoted the limit of the sensitivity of normal eyes in a completely dark environment.

TL studies were carried out in this material in order to determine the source of the persistence and the trapping mechanism. The sample was cooled down to a temperature below −100 °C in a vacuum (less than 10^{-2} torr) cryostat with liquid nitrogen. The TL glow spectra were presented in Fig. 4, where was no TL glow signal detected from −100 to 0 °C. There was no TL signal after exposure to 3.35 and 3.65 eV radiations, corresponding to no 5d absorption and the maximum 5d absorption (Fig. 1), respectively. This result indicated that the 5d band absorption maximum arose from a component of the 5d state which lay below the host conduction band. The electrons that were promoted into this 5d state were localized and hence were unable to be trapped into the defects, which would produce the persistent afterglow.

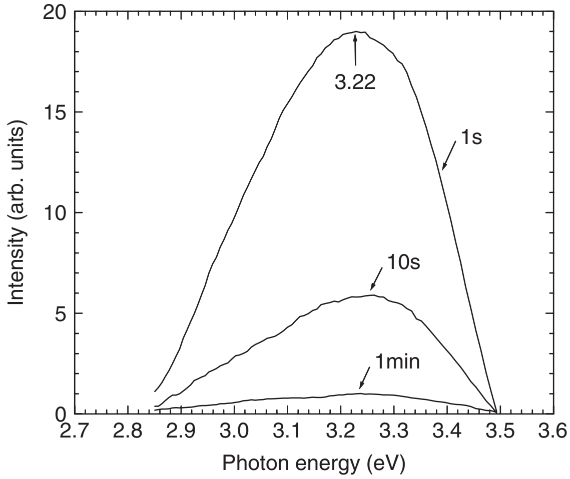

Fig. 2. Afterglow spectra of the sample at $t = 1$, 10 s and 1 min after the 30 min mercury lamp irradiation was switched off.

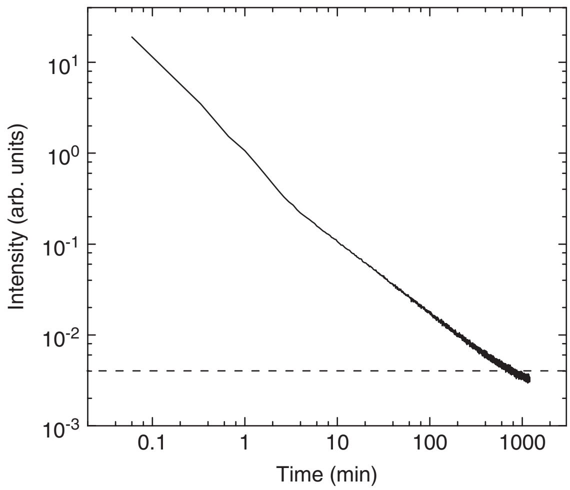

Fig. 3. Afterglow decay curve detected at 3.22 eV, after the sample had been irradiated by a mercury lamp for 30 min. (the dashed line was the limit of the eye detection in dark.)

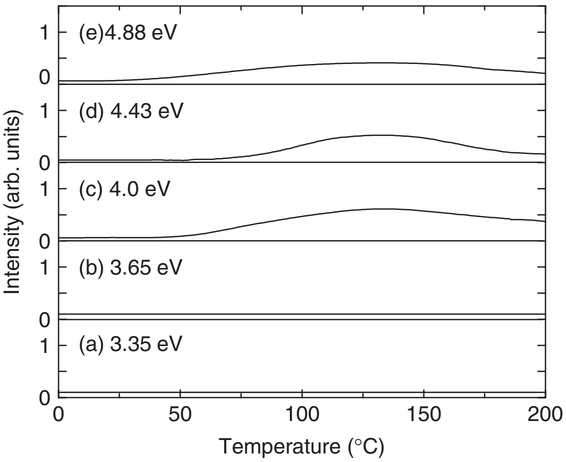

Fig. 4. Thermoluminescence spectra after the sample had been irradiated for 30 min at −100 °C by the Xe or mercury lamp light at (a) 3.35 eV, (b) 3.65 eV, (c) 4.0 eV, (d) 4.43 eV and (e) 254 nm (4.88 eV), respectively. (There was no TL signal observed from –100 to 0 °C).

If shorter wavelength irradiation (above 4.0 eV) used, Ce^{3+} electrons were excited into higher lying components of the 5d states and a TL glow peak was generated, appearing at around 130 °C (Fig. 4), where only one type of trap was assumed for simplicity. The determination of an electron trap was based on the facts that, in most of the cases, the Ce^{3+} ground state was about 2 eV above the host valence band, so that the thermal promotion for electrons to the Ce^{3+} ground state to generate a hole to be trapped was almost impossible. Since the ground state of the Ce^{2+} ions was higher than the host conduction band, Ce^{2+} ions could also exist. Therefore, the traps must be for electrons for that a state of an ionized Ce^{4+} plus a trapped electron could exist and a state of a reduced Ce^{2+} plus a trapped hole could not.

The trap depth and the *s*-factor were evaluated using the peak shape methods as described in McKeever's book [15]. The trap depth was evaluated by

$$E = c_\omega (kT_m^2/\omega) - b_\omega (2kT_m), \tag{1}$$

where c_ω, b_ω and ω were the parameters that were defined in Ref. [15] and T_m the peak temperature of the TL glow curve. As it was found that the peak shape was more symmetric than non-symmetric, the trapping kinetics should be close to the second order kinetics. Therefore, following the second-order mechanism, taking the parameters $c_\omega = 3.54$, $b_\omega = 1.0$, the depth of the trap was evaluated to be 0.75 eV. The detrapping *s*-factor was calculated using

$$\beta E/kT_m^2 = s[1 + (b-1)2kT_m/E]e^{-E/kT_m}, \tag{2}$$

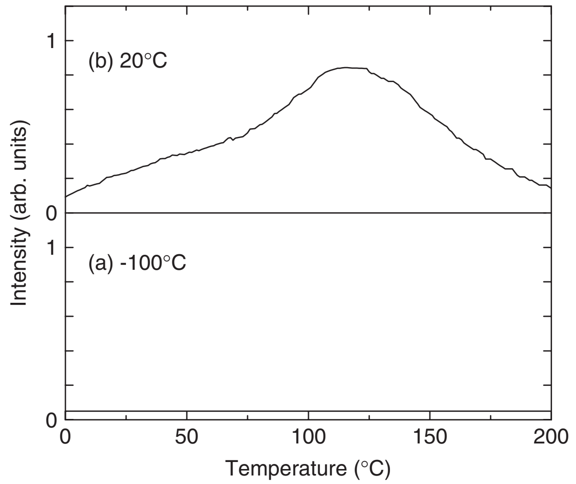

Fig. 5. Thermoluminescence spectra after the sample had been through a 30 min irradiation by a 3.65 eV Xe lamp light at (a) $-100\,^{\circ}$C and (b) 20 °C, respectively.

where $\beta = 0.1\,^{\circ}\mathrm{C/s}$ was the heating rate, $b = 2$ the order of trapping kinetics and E the trap depth. The *s*-factor was evaluated to be 1.0×10^7.

As there was no TL glow signal by 3.65 eV irradiation, we found the only reason could be that the 3.65 eV absorption band was below the conduction band. Whereas 4.0 eV absorption peak must be above the host conduction band, the 4.0 eV excitation photoionized the electrons directly into the conduction band and produced TL glow signal. To illustrate this point, the TL glow spectra were also measured under room temperature (20 °C) irradiation at 3.65 eV instead of irradiation at $-100\,^{\circ}$C. Room temperature was chosen because it was below the 130 °C activation temperature of the trap, and it was high enough to thermally ionize some of the electrons from the lowest 5d state to the conduction band. As shown in Fig. 5, a TL glow peak similar to those obtained at low temperature with higher energy irradiation became evident in the room temperature measurements. The TL glow signal was about 100–1000 times weaker than the ones irradiated at –100 °C. Therefore, the background signal and the influence of heating ramp must be strong. The bump at 50 °C and the shift of the TL glow peak (115 °C) in Fig. 5 was regarded as the results from the background noises. If we defined that the null signal under $-100\,^{\circ}$C irradiation (background limit) was 100 times weaker than the TL glow signal with irradiation at 20°C then, we have, $W_{20} = 100\, W_{-100}$, where W_{20} was thermal ionization rate at 20 °C, and W_{-100} the one at –100 °C. Using the thermal ionization $W_{\mathrm{T}} = W_0\,\mathrm{e}^{-\Delta E/kT}$ and plugging the temperatures in the equation, we had the 5d band at 3.65 eV was about 0.2 eV below the conduction band ($\Delta E = 0.17$ eV). If we took the null signal intensity as 10 times weaker than the TL signal in Fig. 5, then we would have the 5d state was about 0.1 eV below the conduction band ($\Delta E = 0.08$ eV).

4. Conclusion

Trapping processes of the Ce^{3+} excited state electrons were observed and analyzed. It was proved that trapping excited state electrons required the energy of the electrons to be higher than the conduction band energy of the host. Thermal assistance could be needed if the electron levels were lower than the bottom of the conduction band of the host. From excitation dependent thermoluminescence the lowest 5d level of Ce^{3+} 5d electron was estimated to be 0.1–0.2 eV below the host conduction band.

Acknowledgements

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