Excitation energy dependence for electron traps in CaTiO$_3$:Pr, Al single crystals

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Abstract. We investigated the red afterglow process of CaTiO$_3$:Pr, Al through photoluminescence and thermoluminescence measurements by using fabricated single crystals. The crystals with several cubic millimeter in size were obtained through a flux method. We found that the afterglow properties varied with the excitation energy. At room temperature, the red afterglow was observed for the charge transfer from Pr$^{3+}$ to Ti$^{4+}$ excitation and the direct excitation of Pr$^{3+}$, while not observed for the interband excitation of CaTiO$_3$ due to the relaxation process going through $4d^15d^1$ state of Pr$^{3+}$. For the direct excitation of Pr$^{3+}$ at 80 K, the excited electrons did not reach to trap states for afterglow due to a potential barrier, which can overcome with thermal assistance at room temperature. For the charge transfer excitation at 80 K, the excited electrons could reach the traps with excess energy.

1. Introduction

Persistent luminescence phosphors have attracted attention for applications in warning sign, soft illumination and medical imaging. In particular, such red phosphors having long emission time are demanded to realize white afterglow. CaTiO$_3$(CTO) doped with Pr$^{3+}$ ions is a promising candidate. Several reports of the red afterglow on CaTiO$_3$:Pr (CTO:Pr) and CaTiO$_3$:Pr, Al (CTO:Pr, Al) have been made so far [1–7]. Their red emission originates from $^1D_2 \rightarrow ^3H_4$ transition of Pr$^{3+}$ ions. There are three major excitation bands for this emission. That is, interband transition in CTO (Interband), metal to metal charge transfer from Pr$^{3+}$ to Ti$^{4+}$ (MMCT) and direct excitation in Pr$^{3+}$ ions ($^3H_4 \rightarrow ^3P_J$). The afterglow characteristics are largely dependent on the correlation of the energy levels of these excitation bands. However, this has not been discussed much yet. In the past reports, furthermore, the afterglow process has been discussed for powder samples. In order to discuss the excited states in more detail, it is necessary to perform spectroscopic measurements on single crystal samples.

In this work, we fabricated single crystals of CTO:Pr and CTO:Pr, Al by a flux method and investigated the relaxation processes of the excited states through photoluminescence (PL) decay and thermoluminescence (TL) glow curves with their excitation energy dependence. The temperature dependence of the relaxation processes at each excitation energy were discussed in detail based on configuration coordination diagrams.
2. Experimental Procedures

The single crystals of CTO:Pr and CTO:Pr, Al were grown by a flux method. A mixture of CaCO_3, TiO_2, Pr_2(OCO_3)_{3}·8H_2O, Al_2O_3 powders were prepared in the molar ratio of CaCO_3 : TiO_2 : Pr_2(OCO_3)_{3}·8H_2O : Al_2O_3 = 0.999 : 1 − 2x : 0.0005 : x (x = 0 and 0.0005). The mixture and KF flux were heated at 1100°C for 12 h in a platinum crucible. Then, they were cooled slowly back to 800°C for 40 h. Finally, we obtained several crystals from the crucible through washing the flux by hot water at room temperature. The crystal structures were identified as CTO by powder X-ray diffraction measurements. The existence of Al ions in the CTO:Pr, Al samples was confirmed through energy dispersive X-ray spectrometry measurements.

A solid-state UV laser (266 nm) and a charge-coupled device camera were used for normal PL measurements. A monochromatic output from a xenon arc lamp and a photomultiplier with a band-pass filter were used for photoluminescence excitation (PLE), PL decay curve and TL glow curve measurements, where the red emission of Pr^{3+} was only detected. In the PL decay curve measurements, the samples were exposed to an excitation light for 10 min. And then, the PL intensities were monitored for 20 min after the excitation light was blocked by a mechanical shutter. In the TL glow curve measurement, the samples were cooled to 80 K and then exposed to excitation light for 60 min. After the exposure, the TL intensity was monitored while the sample was gradually heated with a rate of 5 K/min.

3. Results and Discussions

Figure 1 shows the photographs of typical single crystal samples of (a) CTO:Pr and (b) CTO:Pr, Al. The former was light brown and 2 × 2 × 2 mm in size, and the latter was light greenish yellow and 2 × 2 × 1 mm in size. It was found that their body colors correlated with the density of impurities and/or vacancies were changed by Al-doping. These crystals show red emission under 365 nm excitation. Figure 2 shows the PL and PLE spectra of CTO:Pr and CTO:Pr, Al crystals. The $^1D_2 \rightarrow ^3H_4$ emission of Pr^{3+} was commonly observed in the PL spectra. In the PLE spectra, we confirmed the three excitation bands of “Interband”, MMCT and “$^3H_4 \rightarrow ^3P_J$”, as mentioned above. The band shape for MMCT was clearly affected by Al-doping. This indicates that the Al-doping changes the ligand field around Pr^{3+} ions through structural relaxation or charge compensation in CTO.

Figure 3 shows the PL decay curves of CTO:Pr and CTO:Pr, Al crystals, where they were...
excited at the excitation bands of “Interband”, MMCT and \(^3H_4 \rightarrow ^3P_J\). The corresponding excitation wavelengths were 300, 370 and 455 nm, respectively. A promising long afterglow was confirmed in CTO:Pr, Al rather than in CTO:Pr. This indicates that Al-doping contributes the formation of deep electron traps. The excited electrons can smoothly transfer to some electron traps induced by Al doping through the MMCT state. However, the holes generated complementally to the Pr ground level are thought to stay without moving because the ground level is far from the valence band maximum as 0.4 eV [4]. Therefore, the observed afterglow phenomena are considered to be mainly based on electron traps. The afterglow time \(\tau\) was defined as the time which the initial PL intensity became 1/1000. CTO:Pr, Al had quite long afterglow time as \(\tau = 375\) s and 221 s for the excitation bands of the MMCT and \(^3H_4 \rightarrow ^3P_J\), respectively. On the other hand, the “Interband” excitation resulted in quite short \(\tau\) of 24 s. The tendency that the relaxation time for the “Interband” excitation is much faster than the
other was similarly observed also when the “Interband” and MMCT were excited by a 266 nm and 355 nm laser, respectively. This suggests that the relaxation process for the “Interband” excitation is quite different from that for other excitations regardless of excitation intensity.

The excitation energy dependence of the relaxation processes can be interpreted by using a configuration coordinate diagram of energy levels for Pr$^{3+}$ in CTO:Pr, Al. The relaxation processes after the three excitation bands were summarized in figure 4. For the $^3H_4 \rightarrow ^3P_J$ and MMCT excitations, excited electrons lead to some electron traps contributing to afterglow, as indicated by the processes (a) and (b) in the diagram, respectively. According to the report of Zhang et al., 4f$^5$5d$^1$ excitation band of Pr$^{3+}$ locates around 300 nm in the PLE spectrum of CTO:Pr [8]. Therefore, the “Interband” excitation leads Pr$^{3+}$ ion to the 4f$^5$5d$^1$ state and then to the $^1D_2$ state without reaching to the traps, as indicated by the process (c).

Figure 5 shows TL glow curves of CTO:Pr, Al for the three excitation bands. Each glow curve includes several intrinsic peaks. They correspond to electron traps, and the peak near 290 K contributes to the afterglow in particular. The TL intensity for the MMCT excitation was much greater than that of the other. It should be noted that the TL intensity for the $^3H_4 \rightarrow ^3P_J$ excitation was smaller than that for the MMCT excitation, while the afterglow time was about the same at room temperature. Regarding the peak around 290 K, we also measured the intensity by changing the starting temperature of the glow measurement. Then, the peak intensity gradually increased as the starting temperature was changed from 80 K to 180 K. This suggests that an activation energy is necessary for the state transition from the MMCT to the electron trap state. The excitation energy dependence of the relaxation processes at 80 K can be also interpreted by using the energy diagram for Pr$^{3+}$ in CTO:Pr, Al. The relaxation processes from the two excitation bands were summarized in figure 6. For the $^3H_4 \rightarrow ^3P_J$ excitation, excited electrons transfer to traps through the MMCT state hardly occurs due to the potential barrier ($\Delta E$), as indicated by the process (a). The barrier can be overcome by thermal assistance at room temperature. For the MMCT excitation, on the other hand, electrons can reach to traps even at 80 K with the excess energy, as indicated by the process (b).

4. Conclusion
The single crystals of the red afterglow phosphor CTO:Pr and CTO:Pr, Al were grown by a flux method. They showed commonly the PL for $^1D_2 \rightarrow ^3H_4$ transition of Pr$^{3+}$ ions. The PLE spectra had three excitation bands: “Interband”, MMCT and $^3H_4 \rightarrow ^3P_J$. The red afterglow processes was investigated for the each excitation band, mainly focusing on CTO:Pr, Al with long afterglow time. For the “Interband” excitation, the afterglow time was much shorter than that for the MMCT excitation and $^3H_4 \rightarrow ^3P_J$. The time reduction was caused by the direct relaxation from 4f$^5$5d$^1$ to $^1D_2$ state of Pr$^{3+}$. In the TL glow curve measurement, it was found that excited electrons for the $^3H_4 \rightarrow ^3P_J$ excitation hardly move to traps at 80 K due to a potential barrier. For the MMCT excitation, the electrons overcome the barrier using excess energy even at low temperature.

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