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Kyoto University
Temperature Dependence of Photoluminescence Spectra of Nondoped and Electron-Doped SrTiO$_3$: Crossover from Auger Recombination to Single-Carrier Trapping

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We report unusual photoluminescence (PL) behaviors in highly photoexcited SrTiO$_3$ crystals at low temperatures. The PL spectrum and dynamics show abrupt changes below 150 K in both nondoped and electron-doped SrTiO$_3$ samples. We clarified that the PL dynamics in both nondoped and electron-doped SrTiO$_3$ is well described by the same simple model involving single-carrier trapping, radiative bimolecular recombination, and nonradiative Auger recombination. The unusual temperature dependence of PL dynamics is caused by the crossover from Auger recombination at high temperatures to single-carrier trapping at low temperatures. We discuss the temperature-dependent PL dynamics in conjunction with the high carrier mobility of SrTiO$_3$ at low temperatures.

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Perovskite oxides have long been a subject of interest because of their unusual magnetic, electric, dielectric, and optical properties [1,2]. SrTiO$_3$ is one of the most important and potentially useful perovskites, both from the viewpoint of fundamental physics and its potential for device applications. SrTiO$_3$ is a wide-gap semiconductor with a band gap energy of 3.2 eV. On the basis of electron doping, the electric properties of SrTiO$_3$ vary significantly from insulating to semiconducting, metallic, and even superconducting [3–5]. Doped or photogenerated carriers in SrTiO$_3$ show high mobility at low temperatures [6], which results in large conductivity and enhancement of the dielectric constant [7,8]. Moreover, the recent discovery of two-dimensional electron gases (2DEGs) of the LaAlO$_3$/SrTiO$_3$ heterointerface prompts further interest in SrTiO$_3$ [9–13]. Despite the insulating properties of SrTiO$_3$ and LaAlO$_3$, a metallic 2DEG system is formed at the interface. Unique electric and magnetic properties of the LaAlO$_3$/SrTiO$_3$ heterointerface, such as magnetoresistance and superconductivity, are observed at low temperatures [12,13]. Despite extensive studies on the electronic structures and electric properties of SrTiO$_3$ bulk crystals and heterostructures [3–23], the carrier dynamics that determines these unique low-temperature multifunctional properties remains unclear.

Photoluminescence (PL) spectroscopy is one of the most powerful methods for studying carrier dynamics of semiconductors. Quantitative evaluation of carrier dynamics provides further understanding of the unique low-temperature properties of SrTiO$_3$ bulk crystals and heterostructures. Much effort has so far been devoted to the understanding of low-temperature PL properties, and it is reported that a broad green PL band appears around 2.5 eV [6,14–16]. Extrinsic defects and impurities affect the green PL spectra and dynamics of SrTiO$_3$ crystals [16–19], and the intrinsic carrier dynamics has not yet been clarified at low temperatures. Under intense photoexcitation, however, defect and impurity PL usually saturate, and a blue PL band appears in nondoped SrTiO$_3$ at room temperature [20]. The intrinsic carrier recombination processes determine the room-temperature blue PL band. A similar blue PL band has been observed in electron-doped SrTiO$_3$ [21] and LaAlO$_3$/SrTiO$_3$ heterointerfaces [22]. Understanding of the blue PL dynamics provides a further insight into carrier recombination processes behind SrTiO$_3$ bulk crystals and SrTiO$_3$-based heterostructures.

In this Letter, we study the PL dynamics of highly excited SrTiO$_3$ over a wide range of temperature from 10 to 450 K and report the first observation of unusual PL behaviors at low temperatures. At around 150 K, the PL dynamics shows abrupt change in both nondoped and electron-doped SrTiO$_3$, and the PL spectrum changes in electron-doped SrTiO$_3$. The PL dynamics at all temperatures measured in both nondoped and electron-doped SrTiO$_3$ samples is well explained by the simple model involving single-carrier trapping, bimolecular radiative recombination, and nonradiative Auger recombination. We clarify that the crossover from Auger recombination at high temperatures to single carrier trapping at low temperatures plays a crucial role in temperature-dependent PL dynamics in SrTiO$_3$.

We used commercially available nondoped SrTiO$_3$ and electron-doped SrTi$_{1-x}$Nb$_3$O$_9$ ($x = 0.01$ and 0.02) single crystals (Furuuchi Chemical Co.). Nondoped samples were annealed under oxygen flow for 24 h at 700 K to reduce oxygen vacancies. All samples were 0.5 mm thick. Time-resolved PL spectra were measured with a time resolution of 40 ps using a streak camera and a monochromator. The excitation light source was an optical parametric amplifier system based on a regenerative amplified mode-locked Ti:sapphire laser with a pulse duration of 150 fs and a repetition rate of 1 kHz. The excitation photon energy was
The laser spot size on the sample surface was measured carefully using the knife-edge method. Measurements were performed over a wide range of temperature from 10 to 450 K.

Figure 1(a) shows the time-gated (0–8 ns) and time-integrated PL spectra of nondoped SrTiO$_3$ at 10 and 300 K under an excitation density of 8.9 mJ/cm$^2$. The broad blue and green PL intensities are normalized by their peak intensities for comparison. At 300 K, a broad blue PL band appears at around 2.9 eV in the time-gated PL spectrum, and this time-gated PL spectrum shows good accordance with the time-integrated PL spectrum. The decay time of the broad blue PL band is 1–30 ns at 300 K, and it increases with a decrease of the laser intensity [20]. In contrast, three components are observed at 10 K: the time-gated PL spectrum shows a sharp peak at 3.2 eV and a broad band at around 2.9 eV, and the time-integrated PL spectrum shows a green broad PL band at 2.5 eV. The green PL shows a long decay time of milliseconds, and its initial state was assigned to impurity centers or self-trapped excitons [14–16].

The temperature dependence of the blue and green PL intensities is shown in Fig. 1(b). Here, we distinguished the broad blue PL spectra from the broad green PL spectra using the time-gated PL spectra, because the 0–8 ns integration interval of the time-gated PL spectra is much shorter than the millisecond decay time of the green PL and is comparable to or longer than the nanosecond decay time of the blue PL. The green PL intensity is obtained by subtracting the blue PL band from the time-integrated spectrum. With decreasing temperature below 150 K, the green PL intensity increases abruptly, while the blue PL intensity decreases. This behavior indicates that the near band-edge carriers for blue PL transform rapidly into the deep state for green PL and this transfer rate is temperature dependent.

Figure 2 shows the decay curves of blue PL in nondoped SrTiO$_3$ at 10, 100, 200, and 400 K under an excitation density of 8.9 mJ/cm$^2$. The decay profiles have two decay components: a nonexponential fast decay with a subnanosecond time constant and a single-exponential slow decay with a time constant of several nanoseconds. These decay dynamics can be well explained by the rate equation of photcarriers. When the densities of photoexcited electrons and holes are equal (photocarrier density, $n$), the rate equation for the photocarriers can be simplified and written as follows [20,23,24]:

$$\frac{dn}{dt} = -An - Bn^2 - Cn^3, \quad I_B \propto Bn^2, \quad (1)$$

where $A$, $B$, and $C$ represent the nonradiative single-carrier-trapping rate, radiative bimolecular recombination coefficient, and nonradiative Auger recombination coefficient, respectively. $I_B$ denotes the blue PL intensity and is proportional to the square of the photocarrier density. The $B$ coefficient is negligibly small because of the low PL efficiencies of the SrTiO$_3$ samples. The PL dynamics shows single-exponential decay in the low carrier density region and nonexponential decay due to Auger recombination in the high carrier density region. The solid curves in Fig. 2 are given by Eq. (1), and the experimental results are well described by the above simple rate equation. The fast and slow components in Fig. 2 are contributed by the Auger recombination ($C$ coefficient) and single-carrier trapping ($A$ coefficient), respectively. The inset shows an enlarged view of the PL decay profiles in the subnanosecond region at 10 and 400 K. At 10 K, the PL intensity decays slower than at 400 K, reflecting the reduction in the $C$ coefficient with decreasing temperature.

The PL decay curves at all temperatures are well reproduced by the same rate equation, as shown in Fig. 2. The $A$ and $C$ coefficients are obtained as the best-fit parameters, and are summarized as a function of temperature in Fig. 3. The $A$ coefficient shows an abrupt increase below 150 K,
The obtained best-fit parameter \( \hbar \omega \) is 40 meV, which is very close to the energy of the zone boundary TO\(_3\) phonon of 41 meV [28]. Intrinsic Auger recombination determines the PL decay dynamics over a wide temperature range.

To gain a deeper understanding of the temperature-dependent PL dynamics of SrTiO\(_3\), we examined the temperature dependence of the PL spectrum and decay in electron-doped SrTiO\(_3\). Figure 4(a) shows the time-gated (0–8 ns) PL spectra of SrT\(_{0.99}\)Nb\(_{0.01}\)O\(_3\) at different temperatures. The excitation density of 0.12 mJ/cm\(^2\) is so weak that the Auger recombination between photocarriers is negligibly small. The blue PL band is observed at 300 K. However, the blue PL band shows a sudden reduction and green PL appears below 150 K. At 10 K, the PL peak is located at 2.5 eV and the spectrum shape is almost identical to the green PL band in nondoped SrTiO\(_3\). The PL dynamics in electron-doped SrTiO\(_3\) at room temperature is dominated by the Auger recombination of doped carriers and photocarriers [20]. In this case, the PL decay curves are given by single-exponential decays and their decay rates are given by

\[
\tau^{-1} = 2A + CN_e^2,
\]

where \( N_e \) is the density of doped electrons. Figure 4(b) shows the PL decay profiles in SrT\(_{0.99}\)Nb\(_{0.01}\)O\(_3\) at 50, 250, and 450 K, where the PL intensity is integrated over the spectrum. All PL dynamics show single-exponential decay curves with a time constant of a few nanoseconds. The temperature dependence of the decay rate \( \tau^{-1} \) is shown in the inset of Fig. 4(b). At high temperatures, the decay rate decreases monotonically with reducing temperature, and changes abruptly at 150 K. This temperature dependence suggests that at high temperatures the decay dynamics is determined by the Auger recombination, while at low temperatures below 150 K the single-carrier trapping dominates the decay dynamics.

While the green PL in nondoped SrTiO\(_3\) shows nonexponential decay with a decay time of a few milliseconds at 10 K (data not shown), the green PL in electron-doped...
SrTiO₃ decays in a few nanoseconds [Fig. 4(b)]. These observations indicate that the fast green PL decay of electron-doped SrTiO₃ at low temperatures is determined by the decay rate described in Eq. (3). Although the PL spectral shape in electron-doped SrTiO₃ is different from that of nondoped SrTiO₃ at low temperatures, we attempt to determine the $C$ coefficient from PL dynamics of electron-doped SrTiO₃ using Eq. (3). The $C$ coefficient obtained by the PL dynamics of electron-doped SrTiO₃ is shown in Fig. 3, where we assumed that the carrier-trapping rate in electron-doped SrTiO₃ follows the same temperature dependence as nondoped SrTiO₃. These observations indicate that our model described by Eq. (1) works well in both electron-doped and nondoped SrTiO₃ over a wide temperature range.

As mentioned above, the green PL decay time of nondoped SrTiO₃ ($\tau \sim \text{ms}$) is much larger than that of electron-doped SrTiO₃ at low temperatures. In nondoped SrTiO₃, the blue PL decreases slightly at low temperatures, while the blue PL in electron-doped SrTiO₃ disappears below 150 K. The blue PL intensity follows $I_B \propto BN_{\text{p}}\rho$, where $\rho$ is the photoexcited hole density [20]. Since the doped electron density $N_e$ is almost independent of temperature [4], the PL dynamics of electron-doped SrTiO₃ is determined by the dynamics of photoexcited holes. We conclude that rapid energy relaxation of holes occurs into the deep states and the hole density abruptly decreases at low temperatures below 150 K in electron-doped samples.

In conclusion, we studied the temperature dependence of carrier dynamics in nondoped and electron-doped SrTiO₃ by means of time-resolved PL measurements. The simple model involving single-carrier trapping, bimolecular recombination, and Auger recombination well describes the PL dynamics at all temperatures in both nondoped and electron-doped SrTiO₃. The phonon-assisted Auger recombination determines the temperature-dependent PL dynamics. At low temperatures, rapid energy transfer occurs from the near band-edge state of blue PL to the deep state. The low-temperature PL dynamics is closely related to high mobility of carriers at low temperatures.

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