Energy relaxation from STE to In\textsuperscript{+} centers in NaI:In\textsuperscript{+} crystals

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Abstract. The energy relaxation from host crystals to impurity centers has been investigated by measuring the absorption and excitation spectra and the temperature dependence of the luminescence spectrum of NaI:In\textsuperscript{+}. In the absorption spectrum, the A, B, and C bands due to the In\textsuperscript{+} centers are confirmed at 3.8, 4.0, and 4.5 eV, respectively. The excitation spectrum for the A\textsubscript{T} luminescence due to the In\textsuperscript{+} centers responds to the energy position of the A, B, and C bands and also the energy region above the exciton transition of NaI. The fact suggests the existence of the energy relaxation from host crystals to the In\textsuperscript{+} centers. The total intensity of the A\textsubscript{T} and A\textsubscript{X} luminescence due to the In\textsuperscript{+} centers exhibits different temperature dependence between the excitations at the C band and host crystals. Under excitation at the C band, the total intensity of the A\textsubscript{T} and A\textsubscript{X} luminescence monotonously declines with increasing temperature from 10 to 300 K. On the other hand, under excitation at host crystals, the total intensity of the A\textsubscript{T} and A\textsubscript{X} luminescence exhibits an increase with increasing temperature from 10 to 50 K, and a decrease with increasing temperature from 50 to 100 K. We discuss the temperature dependence of the total intensity of the luminescence under excitation at host crystals in relation to free excitons and self-trapped excitons.

1. Introduction

For impurity-activated scintillator materials, energy transfers through the energy relaxation from host crystals to impurity centers play a crucial role in the scintillation process. The energy transfer mechanisms have been extensively investigated for Tl\textsuperscript{+}-activated CsI and NaI crystals, which are widely used as scintillator materials. In CsI:Tl\textsuperscript{+} and NaI:Tl\textsuperscript{+}, free excitons (FE), self-trapped excitons (STE) self-trapped holes (STH), etc have an important part to play in the energy transfer processes [1-5].

Though the Tl\textsuperscript{+} ion is well-known activated ions, In\textsuperscript{+} ions are also potential candidates for activated ions, because the In\textsuperscript{+} ions have the outermost 5s\textsuperscript{2} electron configuration in the ground state and belong to a family of Tl\textsuperscript{+}-type ions [6,7]. Thus, when the In\textsuperscript{+} ions are doped into NaI crystals, it is expected that the In\textsuperscript{+} centers in the NaI crystals exhibit high scintillation efficiency like NaI:Tl\textsuperscript{+}. However, the optical studies of NaI:In\textsuperscript{+} have not been reported to our knowledge. In this study, we have investigated the luminescence properties of NaI:In\textsuperscript{+} crystals under excitation in the energy region below and above the fundamental absorption edge of NaI host crystals, in order to obtain an information about the energy transfer processes from host crystals to impurity centers through the FE and STE states.

2. Experimental methods

NaI:In\textsuperscript{+} crystals were grown by the Bridgman method using NaI beads (ALDRICH, 99.999\% ) and InI beads (ALDRICH, 99.999 \%). The optical measurements up to the near vacuum ultraviolet region were
performed at the BL-3B line of UVSOR (Institute for Molecular Science, Okazaki, Japan). Details of this beam line have been reported in Ref. [8]. For optical measurements, the crystals were cleaved into the size about $5 \times 5 \times 1$ mm$^3$ from the ingots in a glove box under N$_2$ atmosphere. The samples were mounted on a cold stage of a liquid helium-flow type cryostat and were set in a vacuum chamber.

3. Experimental results and discussion

Figure 1 shows the absorption and luminescence spectra at low temperatures. The absorption bands due to the In$^+$ centers are observed at 3.8, 4.0, and 4.5 eV, and are called A, B, and C, respectively. The A, B, and C absorption bands are attributed to intra-ionic transitions from the $^1A_{1g}$ ground state to the $^1T_{1u}$, $^3T_{2u}$, $^3E_u$, and $^3T_{1u}$ excited states in the In$^+$ center, respectively [6,7]. The concentration of the In$^+$ center in our NaI:In$^+$ crystal was estimated to be about $2.0 \times 10^{17}$ cm$^{-3}$ from the absorption intensity. When the NaI:In$^+$ crystal is excited by the light corresponding to the C absorption band, the luminescence bands called $A_T$ and $A_X$ appear at 2.8 and 2.1 eV, respectively, which are attributed to the radiative transition from two kinds of minima on the adiabatic potential energy surfaces (APESs) of the $^3T_{1u}$ and $^3A_{1u}$ excited-states [9,10].

![Figure 1. Absorption (solid) and luminescence (broken) spectra of NaI:In$^+$ crystals at 7 and 45 K, respectively. The peak intensity of the C absorption band at 4.5 eV is off the scale.](image)

Figure 2 shows the excitation spectrum for the $A_T$ luminescence at 2.8 eV and reflection spectrum at 7 K. The excitation spectrum for the $A_T$ luminescence band exhibits the remarkable responses at the energy positions corresponding to the A, B, and C absorption bands. It should be noted that the $A_T$ luminescence band is effectively excited at the energy region above the exciton transition of NaI host crystals, whose energy can be estimated to be about 5.6 eV from the reflection spectrum. As shown in the insert of Figure 2, the $A_T$ and $A_X$ luminescence bands due to the In$^+$ center can be seen in addition to the intrinsic luminescence due to STE at 4.15 eV under excitation at 6.2 eV, which corresponds to the energy above the exciton transition of NaI host crystals. The fact indicates the existence of the energy transfer from host lattice to the In$^+$ centers through the FE and STE states at low temperature.

Figure 3 shows the temperature evolution of the luminescence spectra of the NaI:In$^+$ crystals under excitation at 6.2 eV. At the temperature region below 30 K, the $A_T$ luminescence band due to the In$^+$ center and the STE luminescence band are observed at 2.8 and 4.2 eV, respectively. As the temperature increases from 30 to 110 K, the $A_T$ luminescence band decreases and the $A_X$ luminescence band increases with compensation for the decrease of the $A_X$ luminescence intensity. The $A_X$ luminescence band and the STE luminescence band decrease with increasing temperature from 60 K. The STE luminescence band disappears at around 110 K, while the $A_X$ luminescence band exhibits a broadening of the band-shape and a slight decline of the intensity. In order to discuss the energy transfer to the In$^+$ centers, we focus the total integrated luminescence intensity of the $A_T$ and $A_X$ bands due to the In$^+$ center.
Figure 2. Excitation spectrum (solid) for the $A_T$ luminescence at 7 K. For reference, the reflection spectrum of NaI:In$^+$ is shown by a dashed-dotted line. The insert is the luminescence spectra at 45 K under excitation at host crystals, whose energy is shown by downward arrow in Figure 2.

Figure 3. Luminescence spectra of NaI:In$^+$ crystals observed at various temperatures under excitation at 6.2 eV.

Figure 4. Temperature dependence of the total intensity of the $A_T$ and $A_X$ luminescence under the excitation at the C band (crosses) and the host crystals (filled circles). Temperature dependence of the total intensity is normalized at 150 K. Temperature dependence of the luminescence intensity of STE is shown by open circles. The insert is the schematic diagram of the STE luminescence and reabsorption by the In$^+$ centers.

The total intensity of the $A_T$ and $A_X$ luminescence under excitations at 4.5 and 6.2 eV and the STE luminescence intensity are plotted as a function of the temperature in Figure 4. The total intensity of the $A_T$ and $A_X$ luminescence under excitation at 4.5 eV exhibits a monotonous decline with increasing temperature from 10 to 300 K. The monotonous decline will come from the non-radiative transition from the $^3T_{1u}$ APES. In the temperature range above 110 K, the total intensity of the $A_T$ and $A_X$ luminescence under excitation at 6.2 eV also exhibits a monotonous decline with increasing temperature.

We pay attention to the difference of the temperature dependence between the excitations at 4.5 and 6.2 eV in the temperature region 10 to 110 K. According to the previous paper [8], STEs in NaI crystals migrate through lattices by a thermally activated hopping motion above the temperature of about 70 K. Then, the STEs can encounter the impurity ions during the migration and transfer their energies to the
impurity ions. As a result, it is reported that the luminescence related to the impurity centers in NaI crystals is enhanced. In our NaI:In⁺ crystal, however, the total intensity of the A₇ and A₉ luminescence decreases with increasing temperature from 70 K in a similar way to the STE luminescence intensity. The difference between the temperature dependence of the In⁺ center luminescence in our NaI:In⁺ crystal and that reported in the previous paper might come from that of the impurity concentration. Since the concentration of the impurity ions in the previous paper is much larger than that in our NaI:In⁺ crystals, the low concentration of the In⁺ centers might cause the earlier reaching of the STEs to the surface and/or other impurity ions, where STEs recombine nonradiatively, before encountering the In⁺ centers. Then, another energy transfer processes might be dominant.

As discussed in our previous paper [11], the similar temperature dependence of the intrinsic STE and impurity luminescence indicates the potential of an emission reabsorption mechanism for the energy transfer from the host lattice to impurity centers. Therefore, we consider that the temperature dependence of the total intensity of the A₇ and A₉ luminescence in our NaI:In⁺ crystal comes from the energy transfer from the host lattice to impurity centers through reabsorption processes of the FE and STE luminescence. In the temperature region below 60 K, the total intensity of the A₇ and A₉ luminescence increases with increasing temperature. In this temperature range, the STE luminescence intensity is almost constant, while the quantum yield of the FE-related luminescence, which appears at the energy region around 5.6 eV, increases gradually as the temperature rises from 10 to 40 K [1]. Since the A₇ luminescence is also excited at 5.6 eV, as can be seen in the excitation spectrum of Figure 2, the increase of the FE-related luminescence might induce that of the total intensity of the A₇ and A₉ luminescence. In the NaI:In⁺ crystal, the lower energy tail of the broad STE luminescence overlaps with the B absorption band of the In⁺ center. Reflecting the overlap between the STE luminescence and the B band, a slight dent structure can be confirmed at 3.98 eV in the STE luminescence band, which has a Gaussian band-shape intrinsically. Thus, the decrease of the total intensity of the A₇ and A₉ luminescence with increasing temperature from 70 K will come from that of the STE luminescence.

4. Conclusion

The temperature change of the luminescence spectra of NaI crystals doped with In⁺ centers were investigated under the excitation at the C band and host crystals. From the comparison between the temperature changes of the total luminescence intensity due to the In⁺ centers, we concluded the energy relaxation process from host crystals to impurity centers through emission reabsorption.

Acknowledgment

The optical measurements were supported by the Use-of-UVSOR Facility Program of the Institute for Molecular Science, Japan. This work was partially supported by JSPS KAKENHI Grand Number JP16H04003.

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