

Energy transfer between Tl^+ -type impurities in NaCl crystals

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We have investigated the energy transfer from Tl^+ centers to In^+ centers at RT in co-doped NaCl: Tl^+ , In^+ crystals by measuring absorption, photo-excitation, luminescence and time-resolved spectra. The A' luminescence band of the In^+ centers is observed under excitation at the absorption band of the Tl^+ centers. The A' luminescence band of the Tl^+ centers measured at a forward configuration exhibits a dent structure at 4.2 eV corresponding to the A absorption band of the In^+ centers.

The facts indicate the existence of the energy transfer from the Tl^+ to In^+ centers through the emission-reabsorption mechanism. On the other hand, the A' luminescence of the Tl^+ centers shows a non-exponential decay profile. As the concentration of the In^+ centers increases, the non-exponential decay profile becomes faster. The resonance energy transfer giving the non-exponential decay profile is discussed on the basis of the dipole-dipole interaction.

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1 Introduction Energy transfer mechanism in solid crystals is one of the interesting research topics in solid state physics. The energy transfer mechanism depends strongly on the distance between donor and acceptor. The resonance energy transfer mechanism efficiently works at a short distance between donor and acceptor and the emission-reabsorption process is known as the long-distance energy transfer mechanism. Although the energy transfer process between various impurity ions in solid crystals has been extensively investigated [1–5], there have been a few reports on the energy transfer between Tl^+ -type impurities in alkali halide crystals [6].

The Tl^+ -type impurities have a strong oscillator strength due to the $s^2 \rightarrow sp$ transitions and exhibit the intense luminescence at room temperature (RT), especially in alkali halide crystals [7, 8]. Since alkali halide crystals are transparent up to the ultraviolet energy region of a wide band gap, the crystals are a suitable host for impurities exhibiting the luminescence. Therefore, Tl^+ -type impurities in alkali halide crystals are an ideal system for observing the energy transfer between impurities.

In this paper, the energy transfer from the Tl^+ to In^+ centers has been studied in co-doped NaCl: Tl^+ , In^+ crystals. The well-known optical properties and intense lumines-

cence of the Tl^+ and In^+ centers in NaCl crystals would help us to discuss the mechanisms of the energy transfer from the Tl^+ to In^+ centers.

2 Experimental procedure In this study, we prepared the NaCl single crystals doped with the Tl^+ and/or In^+ centers by using the Bridgman method.

The optical measurements were performed at the BL-3B line of UVSOR (Institute for Molecular Science, Okazaki, Japan). The light beam from 750 MeV electron storage ring of synchrotron radiation was monochromatized using a 2.5-m off-plane Eagle type monochromator. The luminescence and excitation spectra were measured by using a monochromator connected with a charge coupled device (CCD) detector and a photomultiplier, respectively. Intensities of incident and transmitted light were evaluated by using a silicon diode sensor. Here, the spectral resolution was about 5 meV. The measurements of the time-resolved luminescence spectra were carried out in our laboratory by using an ArF excimer laser with the photon energy at 6.42 eV and pulse duration of about 15 ns, and using a detection system consisting of a monochromator and an intensified CCD detector. All the optical measurements were performed at RT.

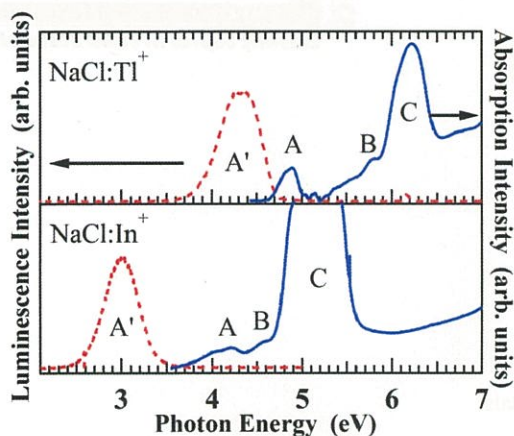


Figure 1 Luminescence (broken lines) and absorption (solid lines) spectra of NaCl:Ti⁺, NaCl:In⁺ crystals at RT.

3 Experimental results Figure 1 shows the luminescence and absorption spectra of NaCl:Ti⁺ and NaCl:In⁺ single crystals. The absorption bands labeled with A, B, and C in order of increasing photon energy are observed at 4.9 eV, 5.8 eV, and 6.3 eV for NaCl:Ti⁺ crystals and at 4.2 eV, 4.6 eV, and 5.2 eV for NaCl:In⁺ crystals, respectively. The A, B, and C absorption bands are attributed to the interionic transitions from the ground ¹S₀ state to the excited ³P₁, ³P₂, and ¹P₁ states in the *ns*²-like centers, respectively [7, 8]. When the alkali halide crystals doped with the *ns*²-like centers are irradiated by the photons with energies corresponding to the respective absorption bands, the luminescence bands called A' appear at 4.3 eV for NaCl:Ti⁺ crystals and at 3.0 eV for NaCl:In⁺ crystals, respectively. The A' luminescence bands are caused by the radiative transitions from the relaxed excited states of ³P₁. It should be noted that the A' luminescence band in NaCl:Ti⁺ crystals has a large overlap with the A absorption band in NaCl:In⁺ crystals. The fact indicates the potential of the energy transfer from the Ti⁺ centers to the In⁺ centers in NaCl:Ti⁺, In⁺ crystals.

The concentrations of the impurity centers in the crystals used in this study were estimated from the optical absorption spectra using Smakula's equation [9, 10]. The concentration of the Ti⁺ centers is an almost constant one of about 1–3 × 10¹⁷, and that of the In⁺ centers varied from 2 × 10¹⁷ to 3 × 10¹⁸ cm⁻³. The average distances *R* between the impurity centers are calculated to be 7–14 nm from the concentrations of the Ti⁺ and In⁺ centers under assumption of a random distribution of the Ti⁺ and In⁺ centers.

Figure 2 shows the excitation spectra of (a) NaCl:In⁺, (b) NaCl:Ti⁺, and (c) NaCl:Ti⁺, In⁺ crystals. As shown in Fig. 2(b), the A' luminescence band in NaCl:Ti⁺ crystals is efficiently excited in the energy regions around 4.8 eV and 6.1 eV, where the A, B, and C absorption bands of the Ti⁺ centers are located. In NaCl:In⁺ crystals, the A' luminescence band of the In⁺ centers is efficiently excited at the A,

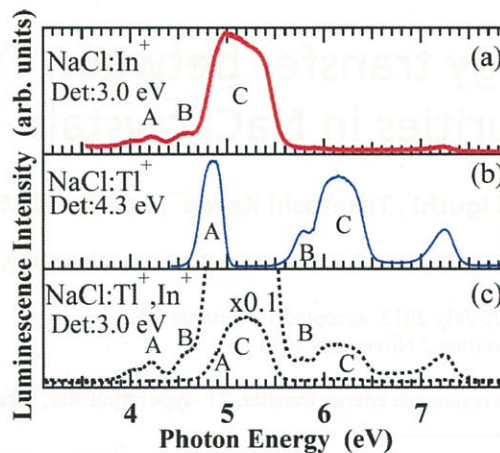


Figure 2 Excitation spectra of (a) NaCl:In⁺ (thick line), (b) NaCl:Ti⁺ (thin line), and (c) co-doped NaCl:Ti⁺, In⁺ crystals (dotted line) at RT.

B, and C absorption bands of the In⁺ centers. In NaCl:Ti⁺, In⁺ crystals, the excitation spectrum for the A' luminescence band of the In⁺ centers has the broad band around 6.1 eV in addition to the A, B, and C bands of the In⁺ centers. Since the 6.1 eV band corresponds to the excitation band for the A' luminescence band in NaCl:Ti⁺ crystals, the energy transfer from the Ti⁺ centers to the In⁺ centers would occur in NaCl:Ti⁺, In⁺ crystals.

Figure 3 shows the luminescence spectra measured by a forward configuration for NaCl:Ti⁺, In⁺ crystals. The thick, thin, and dotted lines are the spectra in the samples with the different thickness. For all samples, the A' luminescence bands of the In⁺ and Ti⁺ centers are observed at 3.0 eV and 4.3 eV, respectively. The A' luminescence band of the Ti⁺ centers has a dent structure around 4.2 eV. Since the A absorption band of the In⁺ centers, which is drawn by the broken line, is located at 4.2 eV, the dent structure around 4.2 eV is attributed to the reabsorption by the A absorption band of the In⁺ centers. As the sample thickness increases, the dent structure becomes remarkable and the A' luminescence of the In⁺ centers increases in the relative intensity to that of the Ti⁺ centers. These facts indicate the existence of the energy transfer through the reabsorption-emission mechanism.

Figure 4 shows the decay profiles of the A' luminescence of the Ti⁺ centers. In NaCl:Ti⁺ crystals, the A' luminescence exhibits a single exponential decay profile with the decay time of about 500 ns. In NaCl:Ti⁺, In⁺ crystals, on the other hands, the A' luminescence exhibits a non-exponential decay profile. With increasing concentration of the In⁺ centers, the non-exponential decay profile becomes faster in the early stage. The non-exponential decay profile will come from a resonance energy transfer through the dipole-dipole interaction.

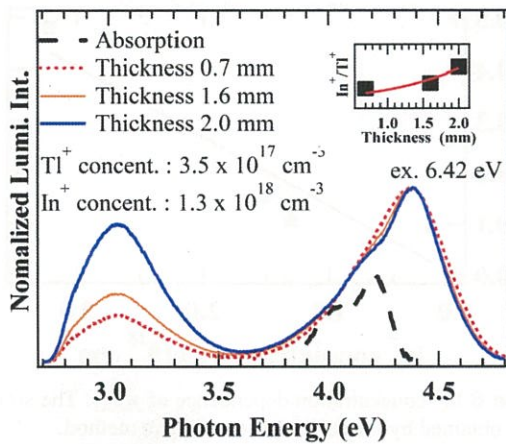


Figure 3 Luminescence spectra for NaCl:TI⁺, In⁺ crystals. The broken line indicates the absorption spectrum of NaCl:In⁺ crystals. The inset shows the intensity ratio of the A' luminescence of the In⁺ centers to that of the TI⁺ centers plotted as a function of sample thickness.

4 Discussion According to the Förster model of the energy transfer [11, 12], the energy transfer rate P_{sa} from donor to acceptor for an electric dipole-dipole interaction mechanism is given by

$$P_{sa} = \frac{3c^4 \hbar}{4\pi n^4 R^6} \frac{\Sigma}{\tau_D} \int f_a(E) f_b(E) \frac{dE}{E^4}, \quad (1)$$

where $\int f_a(E) f_b(E) \frac{dE}{E^4}$ is the spectral overlap integral between the shape function $f_a(E)$ of the emission band and that $f_b(E)$ of the absorption band, τ_D is the radiative decay time of the donor in the absence of acceptor, and Σ is the absorption coefficient cross-section of acceptor. The critical distance R_0 is defined as the distance R between donor and acceptor under the condition of $P_{sa} \cdot \tau_D = 1$.

In our sample, the shape function of the A absorption band of the In⁺ centers and the shape function of the A' luminescence band of the TI⁺ centers are shown in Fig. 5. Both shape functions are normalized to be unity in the area. The spectral overlap integral between the shape functions was estimated to be about $4.2 \times 10^{-3} \text{ eV}^{-5}$. τ_D was estimated to be about 500 ns from the slop of the single exponential decay profile of the A' luminescence in NaCl:TI⁺ crystals. The absorption coefficient cross-section Σ of the In⁺ centers is estimated to be $1.3 \times 10^{-18} \text{ eVcm}^2$. In applying these values to Eq. (1), the critical distance R_0 was calculated to be about 2 nm.

The critical distance of 2 nm is smaller than the average distance between the impurity centers estimated from the impurity concentrations, mentioned above. This result might imply that the energy transfer through the emission-reabsorption is dominant in our samples. In fact, as shown

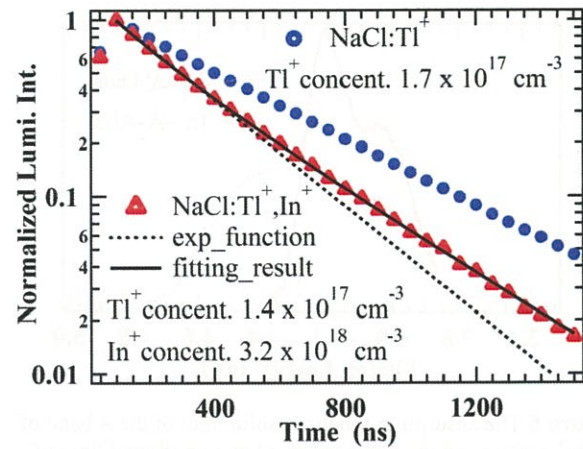


Figure 4 Decay profiles of the A' luminescence of the TI⁺ centers of NaCl:TI⁺ crystals (filled circles) and NaCl:TI⁺, In⁺ crystals (filled triangles). The dotted and solid lines show the fitted results by using an exponential function and a non-exponential function, respectively.

in Fig. 3, the energy transfer through emission-reabsorption exists in our samples.

The ArF excimer laser light does not penetrate into the sample because of the large absorption coefficient for the excited laser light. Thus, the A' luminescence of the TI⁺ centers is considered to occur near the crystal surface. In the forward configuration, the A' luminescence passed through the sample with the thickness of d decreases in the intensity by $\exp(-\alpha d)$, where α is the re-absorption coefficient for the luminescence. The A' luminescence of the In⁺ centers, which is caused by the re-absorption of the A' luminescence of the TI⁺ centers, will be proportion to the amount of the light absorbed in the sample. Since the amount of the light absorbed in the sample is given by $1 - \exp(-\alpha d)$, the intensity ratio of the A' luminescence of the In⁺ centers to that of the TI⁺ centers has the thickness dependence such as $\exp(\alpha d) - 1$. The intensity ratio of the A' luminescence of the In⁺ centers to that of the TI⁺ centers is plotted as a function of the sample thickness in the insert of Fig. 3. The solid curve is the fitted result. The luminescence spectral change with changing sample thickness is explained by the emission-reabsorption mechanism.

In the case of the energy transfer through the emission-reabsorption mechanism, the luminescence from the donor never exhibits the non-exponential decay profile. As shown in Fig. 4, the A' luminescence of the TI⁺ centers in NaCl:TI⁺, In⁺ crystals exhibits the non-exponential decay profile. This fact indicates that the resonance energy transfer from the TI⁺ to In⁺ centers occurs in our samples, in addition to the emission-reabsorption. The resonance energy transfer process might occur between impurity centers with the smaller distance than the critical distance. We estimate the critical distances R_0 from the non-exponential decay profiles of the A' luminescence of the TI⁺ centers.

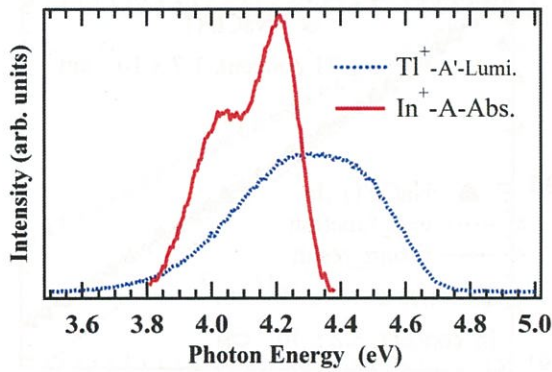


Figure 5 The absorption function (solid line) of the A band of the In^+ centers and the luminescence function (dotted line) of the A' band of the Tl^+ centers.

According to previous papers [13], the non-exponential decay profile due to the dipole-dipole interaction is given by the following equation:

$$I(t) \propto \exp\left(-\frac{t}{\tau_D} - \gamma_{LRRT} \left(\pi \frac{t}{\tau_D}\right)^{\frac{1}{2}}\right), \quad (2)$$

where γ_{LRRT} is the fitting parameter related with the probability of the energy transfer process and is given as follows:

$$\gamma_{LRRT} = N_A \frac{4}{3} \pi R_0^3. \quad (3)$$

Since N_A is the concentration of acceptor, γ_{LRRT} is proportional to the concentration of acceptor. From the slope of the concentration dependence of γ_{LRRT} , the critical distance R_0 can be estimated. In applying Eq. (2) to the non-exponential decay profile shown in Fig. 4, we get $\gamma_{LRRT} = 0.43$. From the non-exponential profiles in the co-doped samples with the various In^+ concentrations, the concentration dependence of γ_{LRRT} is obtained. γ_{LRRT} is plotted as a function of the In^+ concentration in Fig. 6. The straight line is obtained by applying the least square method to the experimental data. From the slope of the straight line, the critical distance R_0 is estimated to be about 3 nm. This value is close to the one estimated from the overlap between the absorption and luminescence bands.

5 Conclusion We have measured the absorption, luminescence, excitation, and time-resolved luminescence spectra of the NaCl crystals co-doped with Tl^+, In^+ centers. The A' luminescence band of the Tl^+ centers in the spectrum observed at the forward configuration exhibits the dent structure around 4.2 eV, which is attributed to the re-absorption by the A absorption band of the In^+ centers. As the sample thickness increases, the dent structure around 4.2 eV becomes remarkable and the A' luminescence of the

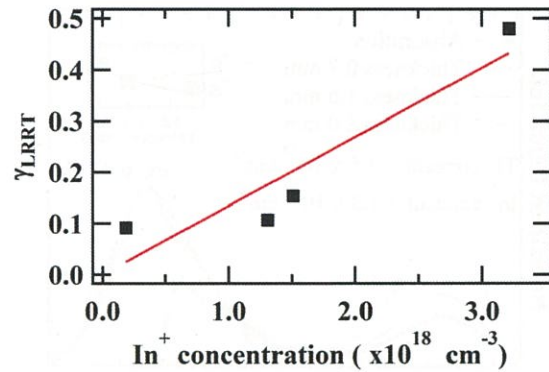


Figure 6 In^+ -concentration dependence of γ_{LRRT} . The straight line is obtained by means of the least square method.

In^+ centers increases. These facts indicate the existence of the energy transfer through the emission-reabsorption mechanism. On the other hand, in the co-doped NaCl: Tl^+, In^+ crystals, the A' luminescence of Tl^+ centers shows a non-exponential decay profiles, reflecting the resonance energy transfer through the dipole-dipole interaction. We estimate the critical distance characterizing the resonance energy transfer from the non-exponential decay profile on the basis of the energy transfer model. This value is closed to the critical distance calculated from the overlap between the luminescence and absorption bands.

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