

Time-resolved A_x -luminescence of NaI:Tl under electron pulse irradiation

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This paper studies spectral-kinetic properties of NaI:Tl cathodoluminescence registered in the region of A_x -band with maximum 425 nm within the time interval of 10^{-8} – 10^{-2} s. A_x -luminescence of NaI:Tl crystal has been excited with an electron pulse ($E_e = 0.25$ MeV, $t_{1/2} = 10$ ns, $W = 0.003\dots 0.16$ J/cm²) at temperatures in the range of 65–300 K. It has been found that the cathodoluminescence kinetics of NaI:Tl crystal at 425 nm has beside the exponential decay ($\tau = 235$ ns at $T = 295$ K) also three more components: the fastest exponential decay ($\tau = 12$ ns at $T = 78$ K), post-irradiation rise on a submicrosecond time scale at $T \geq 128$ K and slow exponential decay at $T \geq 160$ K. A model has been suggested according to which A_x -luminescence at 425 nm is caused by $^1P_1 \rightarrow ^1S_0$ electron transition of Tl⁺ ion. It has been explained that the fast decay and post-irradiated rise components are caused by $^3P_1 \rightarrow ^1P_1$ and $^3P_0 \rightarrow ^3P_1$ electron transitions of Tl⁺ ion, respectively. The scintillation process in NaI:Tl has been discussed.

Keywords: Thallium-doped sodium iodide; time-resolved cathodoluminescence; energy transfer; intra-center transitions.

Исследованы спектрально-кинетические свойства A_x -полосы люминесценции NaI:Tl с максимумом 425 нм во временном интервале 10^{-8} – 10^{-2} с. A_x -люминесценция кристалла NaI:Tl возбуждалась импульсом электронов ($E_e = 0,25$ MeV, $t_{1/2} = 10$ нс, $W = 0,003\dots 0,16$ J/cm²) в температурном интервале 65–300 К. Установлено, что в кинетике импульса катодолуминесценции, что регистрируется в области 425 нм, кроме экспоненциального компонента затухания ($\tau = 235$ нс при $T = 295$ К), наблюдается еще три компонента: самый быстрый экспоненциальный компонент затухания с $\tau = 12$ нс (при $T = 78$ К), пострадиационный компонент нарастания (при $T \geq 128$ К) в субмикросекундном диапазоне и медленный экспоненциальный компонент затухания (при $T \geq 160$ К). Предложена модель, согласно которой полоса A_x -люминесценции с максимумом в области 425 нм вызвана $^1P_1 \rightarrow ^1S_0$ электронным переходом Tl⁺-центра. Быстрый компонент затухания и пострадиационный компонент нарастания интерпретируются как обусловленные $^3P_1 \rightarrow ^1P_1$ и $^3P_0 \rightarrow ^3P_1$ электронными переходами Tl⁺-центра, соответственно. Обсуждается сцинтилляционный процесс в NaI:Tl.

Дослідження з часовим розділенням A_x -люмінесценції NaI:Tl при імпульсному електронному опроміненні. В.Яковлев, Л.Трефілова, В.Алексєєв, В.Краснов.

Досліджено спектрально-кінетичні властивості A_x -смуги люмінесценції NaI:Tl з мак-

симумом 425 нм у часовому інтервалі 10^{-8} – 10^{-2} с. A_x -люмінесценція кристала NaI:Tl збуджувалася імпульсом електронів ($E_e = 0,25$ MeV, $t_{1/2} = 10$ нс, $W = 0,003\dots 0,16$ J/cm²) у температурному інтервалі 65–300 К. Встановлено, що у кінетиці імпульса катодолумінесценції, що реєструється в області 425 нм, крім експоненціального компонента загасання ($\tau = 235$ нс при $T = 295$ К) спостерігається ще три компонента: найбільш швидкий експоненціальний компонент загасання з $\tau = 12$ нс (при $T = 78$ К), пострадіаційний компонент наростання (при $T \geq 128$ К) у субмікрорекондному діапазоні і повільний експоненціальний компонент загасання (при $T \geq 160$ К). Запропоновано модель, відповідно до якої смуга A_x -люмінесценції з максимумом в області 425 нм спричинена $^1P_1 \rightarrow ^1S_0$ електронним переходом Tl⁺-центра. Швидкий компонент загасання і пострадіаційний компонент наростання інтерпретуються як обумовлені $^3P_1 \rightarrow ^1P_1$ і $^3P_0 \rightarrow ^3P_1$ електронними переходами Tl⁺-центра, відповідно. Обговорюється сцинтиляційний процес у NaI:Tl.

1. Introduction

NaI:Tl crystals have been widely applied in the scintillation engineering for more than half a century and therefore intensely investigated to understand the mechanisms behind the formation of Tl⁺ center scintillations under irradiation [1–9]. In spite of voluminous literature, there are still debatable questions left in the physics of the luminescence phenomena in NaI:Tl crystals. It is still not clear what processes cause the rise and decay components of the scintillation pulse at room temperature and what is the nature of the state responsible for the Tl-related emission. This paper aims to give answers to the debatable questions by offering the obtained experimental results.

2. Experimental

A NaI:Tl boule was grown by the Stockbarger technique in an evacuated quartz ampoule. A sample with dimensions of $10 \times 8 \times 2$ mm³ was cleaved from the boule in a dry air box. Tl concentration in the sample was chemically determined and amounted to $2 \cdot 10^{-2}$ mol %. The luminescence was excited with an electron pulse (0.250 MeV, 10 ns, $0.003\dots 0.16$ J/cm²) generated by a GIN-600 accelerator at temperatures within 65–300 K. The sample was cooled down to 65 K by evacuating nitrogen vapor from the internal container of the cryostat. The cathodoluminescence pulse was registered by a pulse optical spectrometer equipped with an MDR-3 monochromator, FEU-106 photomultiplier and INSTEK GDS-2204 oscilloscope in a spectral range of 350–1100 nm with a time resolution of 7 ns.

3. Results

3.1. Spectra and decay kinetics of the cathodoluminescence at 78 K

Pulse cathodoluminescence spectra of NaI:Tl sample right after the electron pulse depletion (1) and in 100 ns (2) at 78 K are shown in Fig. 1. One can see that the intensity of the cathodoluminescence after 100 ns decreases about tenfold without affecting the spectrum which fits a Gaussian with parameters $E_m = 2.92 \pm 0.005$ eV and $\text{FWHM} = 0.39 \pm 0.005$ eV. The luminescence of Tl⁺ centers has a complex decay owing to its varying kinetics throughout nano-, micro- and millisecond time scale. This complex decay is illustrated in Fig. 2 and Fig. 3, where the kinetic curves of Tl⁺ center emission are presented in log and log-log scales, respectively. An oscillogram inserted in Fig. 1 demonstrates the fastest decay component with $\tau = 12 \pm 1$ ns.

As for the emission decay kinetics on a microsecond time scale at 78 K, it fits the sum of an exponent and hyperbola (Fig. 2a):

$$I(t) = I_1 \cdot e^{-(t/\tau)} + \frac{I_2}{(1 + \alpha \cdot t)^2}, \quad (1)$$

where I_1 , I_2 — the exponential and hyperbolic component intensities at $t = 0$; τ and α — time constants.

As we can see in Fig. 2a, the exponential component intensity peak I_1 is much greater than the hyperbolic component intensity peak I_2 .

3.2. Temperature dependences

We found that with an increasing temperature from 65 to 300 K the time constant of exponential decay of NaI:Tl emission decreases, whereas its intensity I_1 increases (Fig. 3). Moreover, in the kinetics of the cathodoluminescence pulse at temperatures over 128 K there appears also a post-

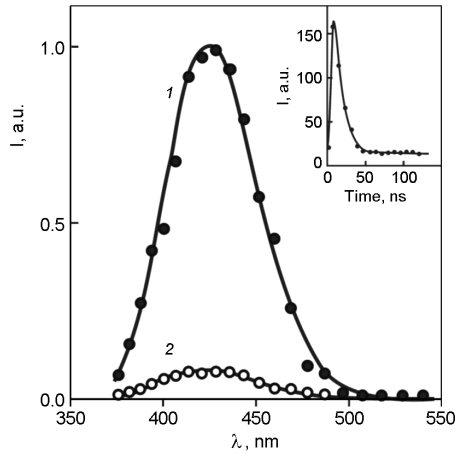


Fig. 1. Cathodoluminescence spectra of NaI:Tl measured at 78 K after the depletion of electron pulse at $t = 0$ ns (1) and $t = 100$ ns (2).

irradiation rise component which peaks faster with the increasing temperature, and at temperatures over 180 K there appears one more exponential decay component with the time constant τ_{slow} considerably longer than that of the exponential one τ which we can see in the expression (1). Further τ will be referred as τ_{fast} .

According to [10] the post-irradiation emission rise of CsI:Tl crystal fits a function $I_0(1 - e^{-t/\tau_{rise}})$. Similarly the same function can be used for NaI:Tl sample but with the sum of components: k_1 — fast rise and k_2 — post-irradiation rise, where $k_1 + k_2 = 1$. Thus, the rise of NaI:Tl cathodoluminescence pulse fits the following function $I_0(k_1 + k_2(1 - e^{-t/\tau_{rise}}))$.

As for the emission decay kinetics at temperature over 180 K, it fits the sum of two exponents:

$$I(t) = I_1 \cdot e^{-t/\tau_{fast}} + I_2 \cdot e^{-t/\tau_{slow}} \quad (2)$$

We also found that the time constants τ_{fast} , τ_{slow} and τ_{rise} remain unchanged in spite of the increase of electron beam power density from 0.003 to 0.16 J/cm². It means that the rise and decay of the cathodoluminescence pulse are caused by monomolecular processes whose thermal activation energy is determined by the angle of temperature dependences for τ_{fast} , τ_{slow} and τ_{rise} time constants which straighten in the Arrhenius coordinates as shown in Fig. 4 and amounted to $E_a(\tau_{rise}) = 0.07 \pm 0.005$ eV, $E_a(\tau_{fast}) = 0.026 \pm 0.002$ eV and $E_a(\tau_{slow}) = 0.29 \pm 0.01$ eV, respectively.

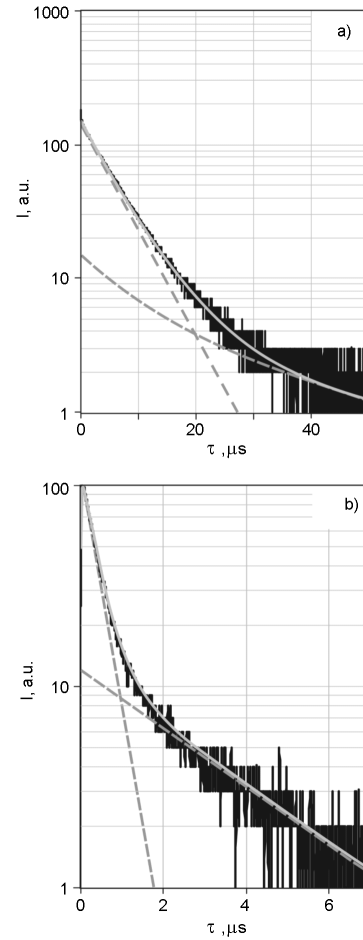


Fig. 2. Cathodoluminescence decay curves of NaI:Tl at 430 nm under 78 K (a) and 236 K (b). Broken lines — experimental curves; dash lines — fitting curves; solid lines — the sum of fitting curves.

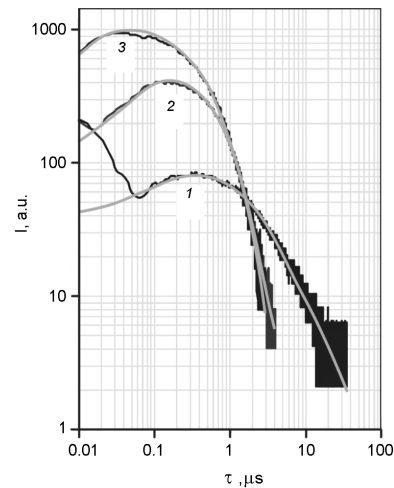


Fig. 3. Cathodoluminescence pulse at $\lambda = 425$ nm under temperatures 128 K (1), 167 K (2) and 252 K (3). Broken lines — experimental curves; solid lines — fitting curves.

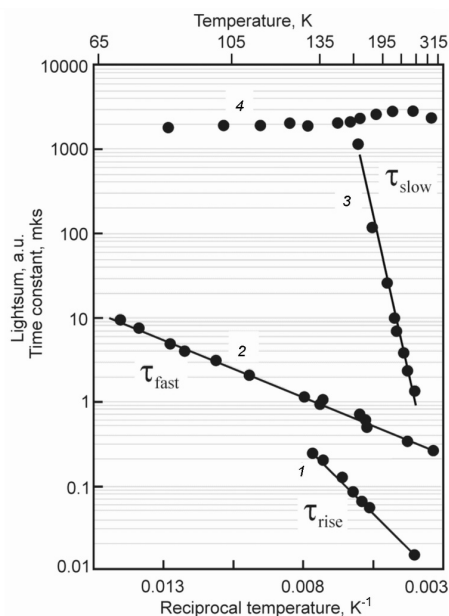


Fig. 4. Kinetics parameters of an emission pulse at $\lambda = 425$ nm vs. reciprocal temperature: 1 — rise time constant, 2 — decay time constant of fast component, 3 — decay time constant of slow component. 4 — 425 nm emission yield vs. reciprocal temperature.

4. Discussion

4.1. The origin of the 425 nm emission in NaI:Tl

Almost all researchers [1–9] claim that this 425 nm emission of NaI:Tl is caused by a single Tl^+ ion transiting from sp to s^2 electron configuration. According to [1], the electron transition of Tl^+ ion from 3P_1 to 1S_0 level is responsible for the 425 nm emission, and the electron population of 3P_1 from 3P_0 level occurs with 0.026 eV activation energy.

Although this inter-combination transition $^3P_1-^1S_0$ is forbidden by the selection rules, it is partially allowed in heavy s^2 -ions, and therefore the luminescence must have a long decay. In fact, the experimentally found as well as theoretically calculated life time of 3P_1 state of isolated Tl^+ ion are 39 ns [11] and 36÷81 ns [12–17], respectively. However, according to our results, about 90 % the initial emission intensity decays with a 12 ns time constant at 78 K. The time independent emission pulse spectrum as well as the fast decay component with time constant about 12 ns under non-selective excitation argue that the 425 nm emission is caused by an allowed radiative electron transition of Tl^+ ion.

The presence of the fast and slow decay components in the emission band of Tl^+ ions

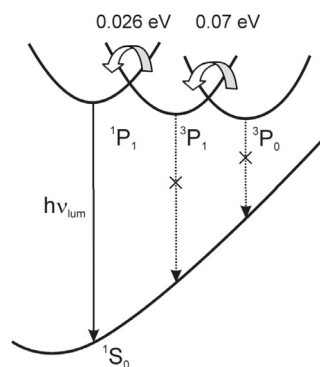


Fig. 5. Scheme of levels for Tl^+ emission center in NaI:Tl crystal.

excited in the activator absorption region is usually explained within the framework of the three-level electron transition model [18, 19], where 1S_0 , 3P_0 and 3P_1 are ground, metastable and radiative levels, respectively, with $^3P_1 \rightarrow ^1S_0$ transition being assumed completely allowed. However, such an explanation also contradicts the results of authors [6, 20] who studying the photoluminescence of NaI:Tl found that at $T \leq 5$ K the 425 nm emission would not arise in the region of $^1S_0 \rightarrow ^3P_1$ transition (A-band absorption). These contradictions can be overcome within the framework of another model of interlevel transitions of Tl^+ emission center whose graphic expression in configuration coordinates is shown in Fig. 5. According to the suggested model, the 425 nm emission is caused by an allowed transition $^1P_1-^1S_0$, whereas the transitions $^3P_1-^1S_0$ and $^3P_0-^1S_0$ are forbidden. The population of the three P levels of Tl^+ center in NaI:Tl is initiated by ionizing radiation. The nanosecond decay component is caused by $^1P_1-^1S_0$ transition, the microsecond decay component is caused by a phonon assistant $^3P_1-^1P_1$ transition which populates 1P_1 level with 0.026 eV activation energy. As for the sub-microsecond rise component at about 130 K, it is caused by phonon assistant $^3P_0-^3P_1$ transition which populates 3P_1 level with 0.07 eV activation energy. These transitions are shown in Fig. 5 by arched arrows.

Thus, the presence of the three components in the cathodoluminescence pulse kinetics with the same spectra is due to the excited Tl^+ ion intracenter transitions which eventually populate 1P_1 level.

4.2. NaI:Tl recombination emission

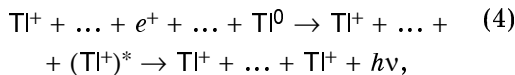
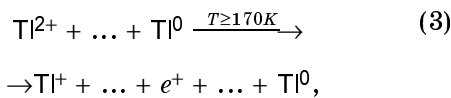
The appearance of another slow exponential decay component with τ_{slow} at $T >$

160 K argues for a presence of another thermally activated process responsible for the formation of Tl⁺ centers in ¹P₁ state. In spite of the fact that the initial intensity of the slow decay component is considerably lower than that of the fast decay component, the emission yield of the slow decay component becomes higher than the emission yield of the fast decay component at temperatures within 180–250 K (Fig. 2b). The total emission yield at various temperatures is shown in Fig. 4 (curve 4). One can see that with an increasing temperature from 170 K, the total emission yield increases by a factor 1.5.

It was earlier established that the slow decay component arises in CsI:Tl and CsI:Na due to a thermal dissociation of [Tl⁺, V_k] complex [10] and [Na⁺, V_k] complex [21], respectively which are also denoted as V_{kA} centers. Unlike V_k centers in CsI lattice, V_k centers in NaI lattice are very unstable. V_k centers are set in motion in NaI lattice at 58 K [22, 23], and therefore Tl⁺ ions capture holes to form Tl²⁺ but not V_{kA} centers. Using the time resolved absorption spectroscopy Deich [24] found that a hole escapes from Tl²⁺ center at temperatures over 150 K in NaI:Tl.

We calculated that the activation energy for the slow component is 0.29 eV which is higher than the diffusion activation energy of V_k centers (0.18 eV [22, 23] or 0.09 eV [24]) in NaI:Tl. Such a big difference in the activation energy allows us to conclude that the slow decay component arises due to a thermal liberation of holes from Tl²⁺ centers.

The following expressions describe the recombination process caused by a thermal dissociation of Tl²⁺ centers:



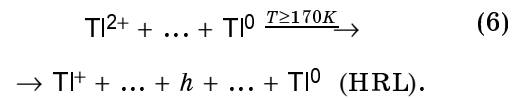
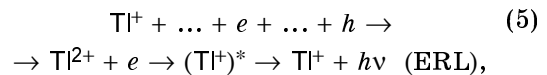
where Tl²⁺ is a hole center; Tl⁰ is an electron center; e⁺ is a hole in the valance band.

In accordance with the formal kinetics law, the slow decay hyperbolic component with an approximation index 2 (see equation 1) is expected to correspond to the formation of excited Tl⁺ centers due to the recombination of Tl⁰ centers with mobile V_k centers similar to CsI:Na [9, 23]. However, the high conversion efficiency of NaI:Tl and its emission decay kinetics with dominating ex-

ponential components indicate that there is an energy transfer mechanism which considerably differs from that in CsI:Na.

4.3. Energy transfer mechanism from NaI lattice to Tl⁺ ions

The authors of [6] excited NaI:Tl in the absorption bands of free and self-trapped excitons as well as in the region band-to-band transitions at T = 2.4 K and arrived at the conclusion that the free excitons give their energy to Tl⁺ ions only at low temperatures. In our case the 425 nm emission yield does not decrease with increasing temperature from 78 to 300 K as shown in Fig. 4 (curve 4). Therefore we believe that the energy transfer in NaI:Tl is mainly caused by band charge carriers, i.e. conduction electrons and valence band holes, whereas in CsI:Tl mainly by localized charge carriers, i.e. V_k and Tl⁰ centers [21, 25, 26]. According to expressions (5) and (6), the excitation mechanism of Tl⁺ center emission in NaI lattice can be either electron- or hole-recombination:



5. Conclusion

The 425 nm emission of NaI:Tl crystals at room temperatures is caused by a radiative transition of Tl⁺ ion from ¹P₁ to ¹S₀ state. The post-irradiation rise of the 425 nm emission is caused by a transition of Tl⁺ ion from ³P₀ to ³P₁ state; the duration of scintillations is determined by the transition time from a metastable ³P₁ to a radiative ¹P₁ state. In order to design fast scintillators, NaI should be doped with an impurity which has no intercombination transitions.

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