

Luminescence kinetics of alkali halide crystals doped with nitrite anions

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The investigation results of the ${}^1B_1 \rightarrow {}^1A_1$ -luminescence decay kinetics of impurity nitrite anions in alkali halide single crystals are considered. The measurements were carried out at 4.2 K. The connection between the decay time and the structure parameters of the luminescence spectrum is discussed.

Рассмотрены результаты спектрального исследования кинетики затухания фотолюминесценции ${}^1B_1 \rightarrow {}^1A_1$ примесных анионов нитрита в щелочно-галогидных кристаллах. Измерения проведены при 4,2 К. Обсуждается связь между временем затухания и параметрами структуры спектра люминесценции.

Analysis of spectral characteristics of molecular anions (MA) (O_2^- , S_2^- , Se_2^- , NO_2^- , PO_2^- , and others) in ionic crystals and also in electrolyte aqueous solutions allowed to determine a series of general regularities concerning intramolecular and intermolecular interaction in condensed media [1–6]. In particular, fine effects of electron-phonon and phonon-phonon interaction, the features of libration-rotational motion of MA in a crystal matrix, mechanisms of optical line broadening have been studied. It is provided by the presence of highly informative well-defined vibronic structure in low-temperature spectra as narrow zero-phonon lines (ZPL) that are accompanied by structural phonon wings (PW). In many crystals, however, besides of fine structure, there are lines (diffuse or structureless at all) in activator electron-vibrational absorption and emission spectra that are characterized by a considerable broadening [3, 6]. In most cases properties and origin of these lines are out of attention. The goal of this work is to study spectral and kinetic characteristics as well as the nature of all components of ${}^1B_1 \rightarrow {}^1A_1$ luminescence spectrum in a series of alkali halide crystals containing the NO_2^- (nitrite) impurity anion.

The LiCl, NaCl, KCl, KBr and CsCl (undoped and NO_2^- impurity activated) single

crystals were grown from melted alkali halide salts by Stockbarger technique in evacuated quartz ampoules. The concentration C_0 of impurities introduced as corresponding MNO_2 salts in the melt was 0.2 to 0.5 mol %. Taking into consideration high hygroscopicity of LiCl salt, these crystals were studied in ampoules they were grown in. The luminescence spectra were investigated at 4.2 K. The luminescence was excited by a N_2 laser ($\lambda_{ex} = 337$ nm, pulse halfwidth $\tau_{0.5} = 10$ ns, average power $W \sim 3$ mW) and registered using a DFS-12 spectrometer. Time measurements of luminescence spectra were made using stroboscopic method [7]. The average luminescence decay time (τ) was computed by numerical integration as

$$\tau = \int_0^{\infty} I(t) t dt \cdot \left[\int_0^{\infty} I(t) dt \right]^{-1}, \quad (1)$$

where $I(t)$ is the luminescence intensity at time t ; t , time past after the exciting pulse termination. In each case, we took into consideration the contribution of matrix luminescence (inactivated crystal) into the activator luminescence spectrum. In the temperature range from 4.2 to 77 K, this luminescence is a continuous background

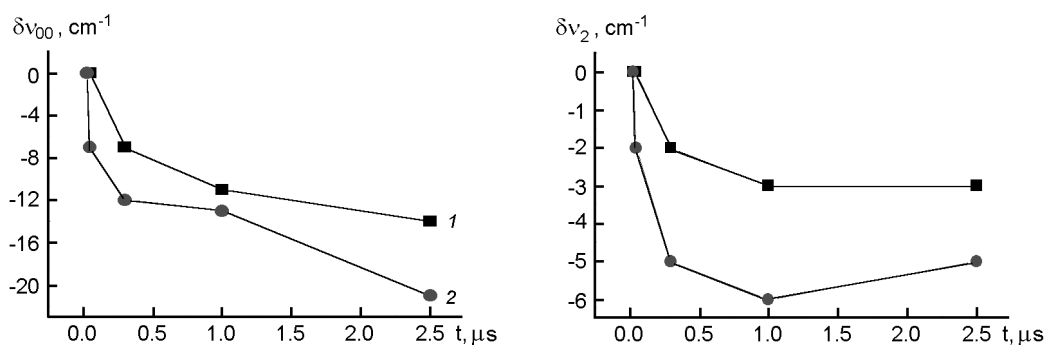


Fig. 1. The ν_{00} (a) and ν_2 (b) time dependence of type I LC (1) and II (2) in LiCl-NO_2^- crystal at 4.2 K.

with the effective extinction time $\tau \leq 5-7$ ns, that is shorter than the activator afterglow.

At 4.2 K, the vibronic structure in the activator luminescence spectrum becomes apparent as several series of intense narrow ZPL, a series of diffuse lines and a continuous line [3, 6]). The ZPL are accompanied by structural PW (fine structure) at long-wave side. The vibronic series differ in band maximum positions (ν_{max}), band spacings, intensity, and afterglow time (τ). This evidences the formation of different types of impurity luminescence centers (LC) in the crystals. The distance between vibronic maximums in these series is about 790 to 830 cm^{-1} and corresponds to the frequency of intramolecular totally symmetric bending vibration ν_2 of NO_2^- MA in the ground electron state. The spectral parameters and afterglow times of some LC are given in the Table.

One or two (in CsCl) series of ZPL+PW (type I LC) become apparent in the luminescence spectra. The ZPL are of about 2 to 14 cm^{-1} half-width [1-3, 6]. At 4.2 K, such a fine structure corresponds to strong interaction between the local vibration ν_2 and appropriate electron transition and a weaker interaction with the matrix phonons. The structure is characterized by a relatively small inhomogeneous broadening (IB) of the line. Thus, the local environment of impurity MA, to which correspond the ZPL+PW series in electron-vibration spectra, is characterized by a rather high order. The ZPL maximum positions in those series are described well by approximated formula for anharmonic oscillator,

$$\nu_{ZPL}(n_2) = \nu_{00} - (n_2\nu_2^0 + n_2^2\chi_{22}), \quad (2)$$

where ν_{ZPL} and ν_{00} are wave numbers that define the positions of vibronic ZPL copy

maxim and 00-lineum; ν_2^0 , the harmonic frequency of bending vibration (in cm^{-1}); n_2 , the quantum number of this vibration; χ_{22} , the corresponding anharmonicity coefficient.

The integral ZPL (I_{0n}) intensity dependence on the vibration quantum number n in the series is described satisfactorily by the Poisson distribution. The vibronic copy of the 00-line is caused by generation of n quanta of ν_2 vibration. Its intensity is determined as:

$$I_{0n} \sim e^{-(P_\lambda)} \frac{P_\lambda^n}{n!}, \quad (3)$$

where P_λ is so-called relative Stokes losses for the local vibrations (in quanta of this vibration). In analyzed systems, it is just the third and fourth vibration repetitions of 00-line that have the maximal intensity, and $P_\lambda \sim 4$ in this connection. The law of ZPL intensity decay is close to exponential one, that also corresponds to the case of localized excitation and a rather high ordering degree of local MA environment. The comparison of τ_1 parameter (type I LC) in considered matrices shows that it has maximal value in case of LiCl crystals. In this case, the 00 transition frequency also reaches its maximum (see Table). Analysis of measurement results for time evolution of activator afterglow spectra has shown what follows. The increase of time passed after the light excitation pulse end is accompanied by a low-frequency ZPL shift. The value of this shift depends on quantum number n_2 and corresponds to time-dependent decrease of 00 line and bending vibration ν_2 frequencies (Fig. 1). These peculiarities are demonstration of the fine struc-

Table. The parameters of the NO_2^- luminescence centers in alkali halide crystals at 4.2 K

Crystal	Dopant C_0 , % mol.	LC type	τ , ns	ν_{00} , cm^{-1}	ν_2^0 , cm^{-1}	P_λ , vibration quanta ν_2
LiCl	NaNO_2 0.2	I	900 ± 80	26892 ± 3	821 ± 2	3.9 ± 0.2
		II	~ 950	26990 ± 5	830 ± 6	~ 5
		III	1200 ± 100	26300 ± 100	825^*	~ 5
NaCl	NaNO_2 0.4	I	10 ± 3	25975 ± 4	830 ± 4	~ 4
		II	~ 30	26180 ± 10	810 ± 10	~ 4
			~ 30	26010 ± 10	800 ± 10	~ 4
			~ 30	25950 ± 10	805 ± 10	~ 4
			~ 30	25950 ± 10	790 ± 10	~ 4
		III	400 ± 50	25600 ± 10	807^*	~ 5
KCl	KNO_2 0.4	I	24 ± 5	25037 ± 3	802 ± 3	4 ± 0.2
		III	~ 40	25400 ± 100	802^*	~ 5
KBr	KNO_2 0.5	I	25 ± 5	24932 ± 4	795 ± 4	3.9 ± 0.2
		III	~ 30	25500 ± 100	795^*	~ 5
CsCl	CsNO_2 0.4	Ia	17 ± 5	24700 ± 2 [3]	799.9 [3]	3.8 [3]
		Ib	~ 15	24458 ± 2 [3]	800 [3]	~ 4
		III	~ 30	24600 ± 100	800^*	~ 5

ture IB. Note that proportion between integral intensities of ZPL and PW are essentially independent of t in the instantaneous luminescence spectra. The mentioned LC can be ascribed to NO_2^- MA that replace regular halide anions in the lattice. The local symmetry of the impurity MA is C_{4v} [1].

The diffuse structure (type II LC) appears as a series of vibronic bands with $\gamma = 40$ to 60 cm^{-1} in LiCl and NaCl matrices; contribution of this structure to the total spectrum is insignificant [6]. The relative integral intensity distribution for this vibration lines agrees with formula (2). At the same time, parameter P_λ exceeds that for ZPL + PW series by one quantum ν_2 vibration in the LiCl matrix. Due to low intensity of such lines, determination of their decay time (τ_2) is of estimating character. The time behavior of maximum position of corresponding vibronic lines and ν_{00} and ν_2 frequencies in LiCl crystals is similar to that for the type I LC considered above (see Fig. 1).

The weakly defined structure (in NaCl matrix), or practically diffuse electron vibration line (in other matrices) with the decay time τ_3 also is due to activator (type III LC), since it is located within the same spectral region as thin or diffuse structure [3, 6] and does not become apparent in in-

nactivated crystals. Assuming that the vibronic series of 00 line copies per local ν_2 vibration contributes predominantly to the total structureless contour, the last was separated into a series of vibronic components as Gaussian shape lines. The intervals between maxima of these lines were taken as average frequencies of ν_2 vibration that corresponds to I and II LC while the relative distribution of their intensities was determined using formula (2). We have minimized the difference between theoretical and experimental contour by varying the width and position of chosen components as well as the P_λ values. It has been found that the half-widths of chosen components amount 1200 to 1300 cm^{-1} that, at helium temperatures, is to be related with significant IB (as compared to type I and II LC). The last statement agrees with results of time measurements: the afterglow extinction curve for such LC deviates noticeably from exponential dependence. Increase of t is accompanied by a red shift of the band maximum (ν_{max} , Fig. 2). These peculiarities can be associated with different variants of impurity anions NO_2^- inclusion at intrinsic lattice defects or interstitial sites. It is expedient to assume a similar nature for type II LC. Attention should be given to the formation possibility of dimers, trimers, and

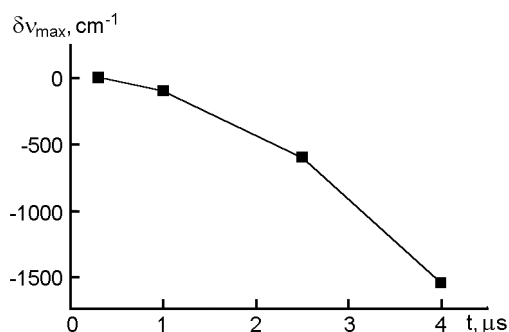


Fig. 2. The v_{max} time dependence of type III LC in LiCl-NO₂⁻ crystal at 4.2 K.

other nitrite anion associations and MnO₂ microcrystals. Note that fine structure in the luminescence spectra of NaCl-NO₂⁻ crystals is due to formation of such microcrystals [6].

Consideration of the Table data shows that, in general, the spectroscopic parameters of LC are different for the same matrix. The Stokes loss P_λ for the local vibration v_2 in the luminescence centers of III type exceeds P_λ for I and II type LC approximately by one quantum of this vibration. Reduction of cation M⁺ or anion Hal⁻ radii is accompanied by increase of relative energy gap between combining ¹A₁ and ¹B₁

electron states (ΔE) as well as by increasing v_2 local vibration frequency. The last tend is to be associated with decrease of the impurity MA effective size [8]. For all the set of chosen LC, there is no correlation between relative energy gap ΔE and luminescence lifetime. In this connection, a regular increasing in τ is observed at rising IB for the corresponding spectrum ($\tau_1 < \tau_2 < \tau_3$). The latter, in particular, can be associated with symmetry decreasing of the impurity nitrite anion surrounding.

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Кінетика люмінесценції лужно-галогідних кристалів з домішкою аніонів нітриту

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Розглянуто результати спектрального дослідження кінетики загасання фотолюмінесценції ¹B₁ → ¹A₁ домішкових аніонів нітриту в лужно-галогідних кристалах. Вимірювання проведено при 4,2 К. Обговорюється зв'язок між часом загасання і параметрами структури спектра люмінесценції.