Observation of new band in stimulated luminescence of solid nitrogen

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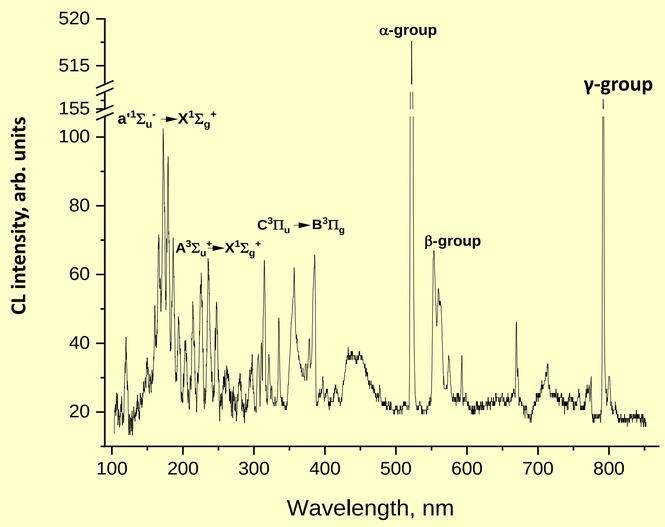
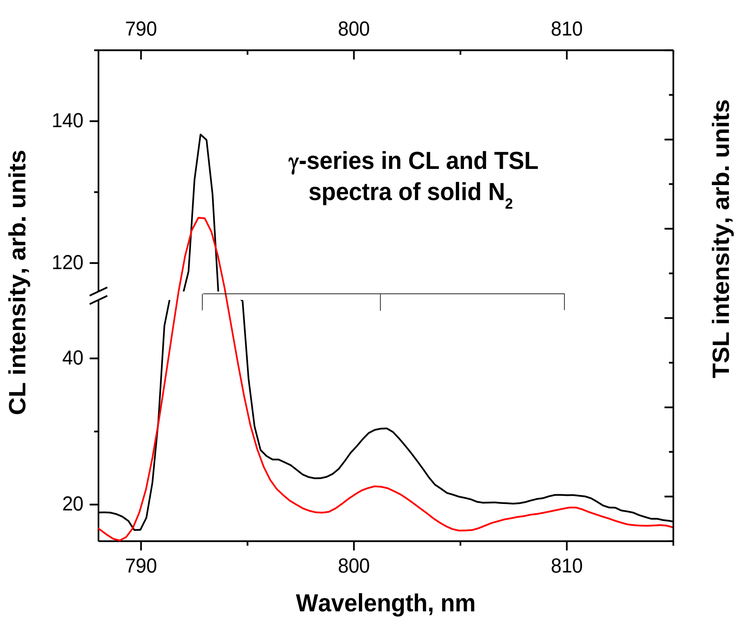
Cathodoluminescence spectrum of solid nitrogen



The CL of nitrogen films of different thicknesses when excited by electrons with energies of 0.5, 1, and 1.5 keV was studied. A comparison of the CL spectra obtained under different conditions showed that there is no correlation in the behavior of emission from the ^2D state of the N atom and the γ-line, which could be expected in the case of the formation of the γ-line emitting centers via electron attachment to the N(^2D) atom.

γ- series in spontaneous and stimulated luminescence



λ, nm Experim.	*E*, eV Experim.	*E*, eV Theory[5]	Harmonic frequency, cm^{-1} Theory[5]	Harmonic frequency, cm^{-1} Experim.
794	1.563	1.55	469 (lowest)	125
802	1.545			
810	1.531			

As it was found in [5], the lowest optically accesible excited state 1^1B_{3u} of isomer **N_4 (D_{2h})** lies 1.57 eV above the ground state ^1A_g. A barrier to dissociation of this state is about 6.5 kcal/mol, that prevents dissociation of isomer in this state at low temperatures and creates condition for the **„cage effect“** scenario of the neutralization reaction. The estimated energy of the radiative transition $1^1B_{3u} \rightarrow {}^1A_g$ of isomer **N_4** of **D_{2h}** configuration is about 1.55 eV, that is very close to the experimentally measured position of the γ–line (1.563 eV), however, the harmonic frequency is much less than the lowest calculated one. Because of this the final assignment requires further experimental and theoretical studies.

Introduction

Nitrogen solids gained general recognition as classical model molecular crystals which attract much attention in diverse fields of science – physics and chemistry of interstellar and solar systems, material science, specifically, the problem of polynitrogen compounds considered as environment-friendly high energy-density materials (HEDM). Energy storage, transformation, and its release are the focus of studies and among the methods used spectroscopy is one of the most effective. Optical spectroscopy of solid nitrogen has a long story and its recent trends were reviewed in [1]. Despite an impressive progress there are still questions under discussion and the most long-standing one concerns identification of, the so-called γ-line, situated in the near infrared (NIR) range. Connection of this line with interaction of nitrogen species with electrons was established in [2, 3]. According to [2] the γ–line appears as a result of the electron attachment to the metastable N(^2D) atom forming nitrogen anion in the excited state N^- (^1D). However, this suggestion does not explain the red satellite of the γ–line. Moreover, finding the second satellite of the γ–line in the spectrum of spontaneous luminescence excited with an electron beam [3] calls into question the identification of the γ–line as the emission of nitrogen anion N^-.

Here we present new results on the study of spontaneous and stimulated luminescence in nitrogen solids in NIR range. Irradiation was performed in dc regime with an electron beam of subthreshold energy. Relaxation dynamics was monitored by emission spectroscopy – cathodoluminescence (CL) and nonstationary luminescence (NsL), along with optical and current activation spectroscopy: TSL and TSEE.

Neutralization scenarios

$N_4^+ + e^- \rightarrow N_4^{**} \rightarrow N_2^* + N_2^* + \Delta E_1 \rightarrow N_2 + N_2 + 2h\nu + \Delta E_2$

Scenario „cage exit“ with dissociation of the transient products N_4^{**} into N_2^*.

$N_4^+ + e^- \rightarrow N_4^{**} \rightarrow N_4^* \rightarrow N_4 + h\nu + \Delta E$

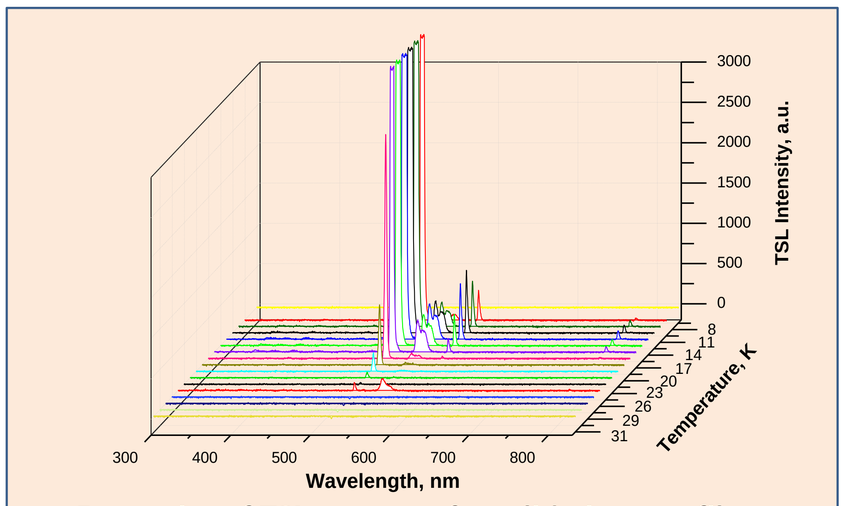
Scenario „cage effect“: the excited N_2^* molecule relaxes with a ground state N_2 to form N_4^*.

The probability of scenarios is determined by the presence of barriers to dissociation.

Summary

The NIR spectra of stimulated and spontaneous luminescence are similar. The correlation of all lines in the stimulated luminescence with the stimulated current TSEE indicates their common origin and connection with the neutralization reaction. The correlation of the NsL γ–line with the NsL of the N_4^+ dissociative recombination product N_2 ($a'^1\Sigma_u^-$) indicates a probable connection of the γ–series with N_4. The measured *E* of the transition is close to the predicted one, but the difference in harmonic frequencies requires further research.

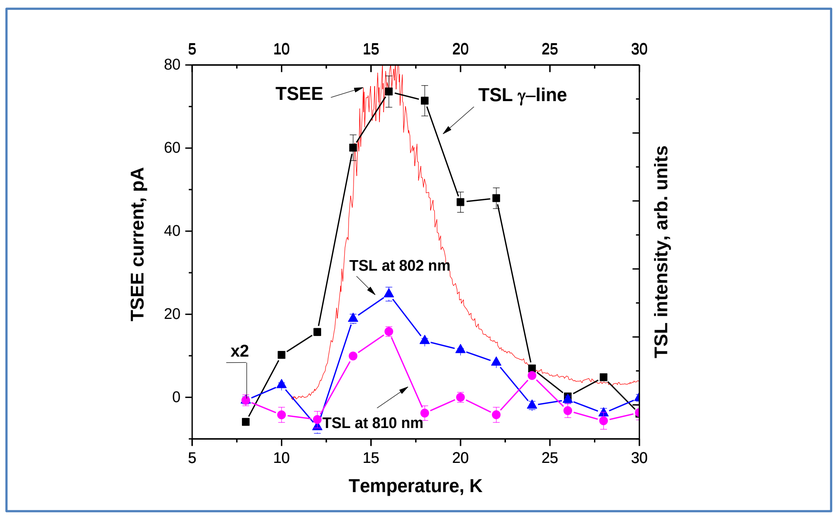
Thermally Stimulated Luminescence of N_2 film



Dynamics of TSL spectra of a solid nitrogen film recorded in the visible and NIR ranges

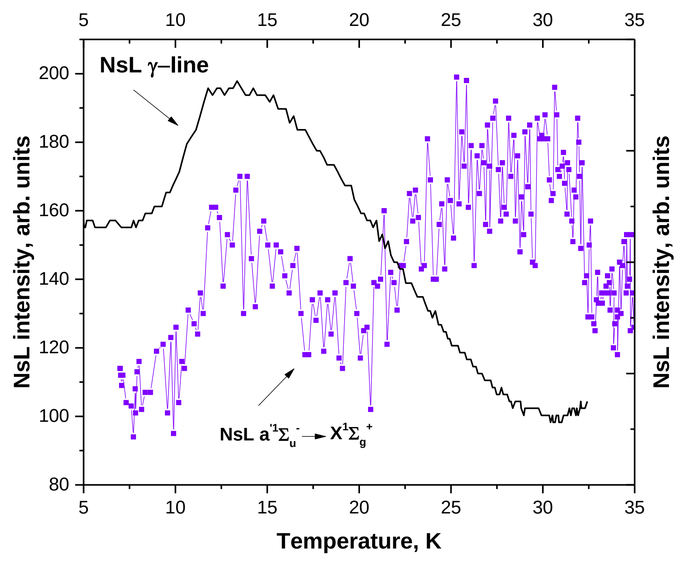
It was found that the TSL detected at the γ-line correlates not only with the TSL recorded at the α-band, connected with the $^2D \rightarrow {}^4S$ transition of N atom. Such a correlation was also found for the TSL recorded at the ($^1S \rightarrow {}^3P$) transition of O atom (β-group near 560 nm). It is noteworthy that even for the O atom, characterized by a very high positive electron affinity χ = 1.46 eV, the neutralization channel of relaxation is predominant.

TSL at γ-series wavelengths



The similar behavior of all these lines in the stimulated luminescence (TSL) and their correlation with the stimulated current (TSEE) indicate common origin of these lines and their connection with the neutralization reaction.

NsL γ-line and $a' \rightarrow X$ transition



The correlation of the γ–line NsL in the range of low temperatures (5-20 K) with the NsL measured at the 0-4 band of the $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ transition, which is the “fingerprint” of the tetranitrogen cation N_4^+ [4], indicates possible connection of the γ–line with the neutralization of N_4^+, which proceeds however *via* the **„cage effect“** scenario.

References:

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