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INFLUENCE OF PHASE TRANSITIONS ON THE TEMPERATURE BEHAVIOR OF PHOTOLUMINESCENCE SPECTRA IN A $(N(CH_3)_4)_2MnCl_4$ CRYSTAL

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Monocrystals $(N(CH_3)_4)_2MnCl_4$ were grown from an aqueous solution of salts by slow evaporation at room temperature. The effect of phase transitions on the behavior of photoluminescence spectra, as well as excitation spectra and time of attenuation of the glow band of 539 nm is studied in the temperature range of 4.5–300 K. Based on the studies of the spectra of photoluminescence of the $(N(CH_3)_4)_2MnCl_4$, the glow bands, which are caused by the glow of the Mn^{2+} ion and correspond to the $^4T_1 \rightarrow {}^6A_1$ transition, were determined. The temperature evolution of photoluminescence spectra (4.5–300 K) of the $(N(CH_3)_4)_2MnCl_4$ crystal demonstrates anomalies of their parameters at the points of phase transitions. Temperature dependences of crystal photoluminescence spectra of the $(N(CH_3)_4)_2MnCl_4$ crystal prove the existence of phase transitions in the temperature intervals from 100 to 300 K. The excitation spectra for the luminescence band of 539 nm and their temperature evolution (4.5–300 K) are shown. The bands of around 2.93 and 2.96 eV are quickly damped with temperature, so at the temperatures above 170 K and 270 K, the bands of 2.96 and 2.93 eV are not observed, respectively. Peaks in the excitation spectrum correspond to electron transitions from the basic state of $^6A_1$ Mn^{2+} to various excited states $MnCl_4^{2-}$ (Td). Their excitation energies are explained by a model of crystals using the Tanabe-Sugano diagrams. The Racah B and C parameters, as well as the splitting of crystal field Δ, were calculated based on the Tanabe-Sugano diagrams for d^5 of electronic configuration. The temperature behavior of the time of attenuation of the photoluminescence band of 539 nm was studied. The resulting time of attenuation of the photoluminescence band increases at an increase in temperature. The kinetics of attenuation of the photoluminescence band of 539 nm of a crystal is well described by an exponential function

Keywords: photoluminescence, glow spectra, excitation spectra, phase transitions

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1. Introduction

Compounds $(N(CH_3)_4)_2MeCl_4$ (Me=Mn, Co, Zn) are of interest both in terms of basic science and in practical terms. The simultaneous existence of organic and inorganic components in the crystal structure determines the complex of properties characteristic of both organic and inorganic substances. Inorganic components determine their electrical, magnetic, and thermal properties, while the organic part provides crystals with plastic and luminescent properties.

A change in their dimensions and conditions of obtaining makes it possible to change the properties of crystals, opening the way of purposeful synthesis of compounds with predetermined properties.

A characteristic feature for crystals of this type is the existence of disproportionate phases in them, caused by the spatial disordered fragments of the structure with a change in temperature. That is why the establishment of the nature and mechanism of sequential phase transitions (PT), depending on temperature, is of interest. This makes a significant contribution to the development of PT theory and the possibility to extrapolate the results of these studies to other similar groups of crystals.

One of the main conditions of modern material science is the problem of obtaining high-quality monocrystalline samples. One of the most sensitive research methods for detecting all sorts of impurities is FL. Studies of the temperature behavior of the spectra of photoluminescence (FL) of $(N(CH_3)_4)_2MnCl_4$ crystal will make it possible to prove the high quality of the resulting compound. This will allow finding the use of $(N(CH_3)_4)_2MnCl_4$ crystal as sensors of external fields (temperature, pressure, etc.), while the manifestation of dimensional effects significantly expands the scope of application. In connection with the prospect of widespread use of $(N(CH_3)_4)_2MnCl_4$ compound in the instrument structures, the study of the interval of temperatures suitable for use is relevant.

2. Literature analysis and problem statement

The main optical, structural, mechanical, and other parameters of crystals of the A_2BX_4 group were studied in papers [1–11]. It was shown that they have segnetoelectric, segnetoelastic, and superion properties. These papers exclusively deal with the compounds of the A_2BX_4 group with an organic cation. Most physical mechanisms can be explained with their help (by drawing analogies to the allowance for electronic configuration of metal (Zn, Mn, Co) or halogen (Cl, Br, I)). This is because all the declared compounds are based on the BX_4 tetrahedron, which determines most optical transitions near the prohibited slit, as reported in papers [1–4]. The existence of isotropic points is also shown. However, the issues related to the influence of temperature on the behavior of the FL spectra remain unresolved. Special attention among the representatives of the A_2BX_4 group is paid to compounds $(N(CH_3)_4)_2MeX_4$ (Me=Mn, Zn, Co; X=Cl, Br) [1–4] and solid solutions based on them [7, 8]. Currently, the emphasis is placed on $(N(CH_3)_4)_2MeCl_4$ (Me=bivalent metal) compound due to several PT, manifested below 300 K.

Article [3] presents a method for obtaining, structural features and optical properties of $(N(CH_3)_4)_2MnCl_4$ crystals at the temperature of 270 K. However, the issues of the influence of temperature on the behavior of FL spectra remain unresolved. This approach is used in paper [4], but the luminescence spectra were studied for the orthorhombic phase of the $(N(CH_3)_4)_2MnCl_4$ (*Pmcn*) crystal. All this suggests that it is appropriate to conduct a study on the influence of phase transitions on the temperature evolution of photoluminescence spectra in the $(N(CH_3)_4)_2MnCl_4$ crystal.

All recorded PT temperatures for Me=Mn are collected in Fig. 1. For this system, phase I at 300 K is always crystallized in a lattice with the *Pmcn* spatial group. In addition to structural transformations shown in Fig. 1, it was also reported about the possibility of the PT at a temperature of 90 (12) K [10]. As a result, the existence of declared phase transitions (9, 10) can have a significant impact on the spectra of the FL of the $(N(CH_3)_4)_2MnCl_4$ crystals This problem was not explored in papers [3, 4].

T, K	168 ⟹	261 ⟹	273 ⟹	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P12_1c1$	$P112_1n$	$P2_1c11$	*Pmcn*

Fig. 1. Temperatures of the PT for $(N(CH_3)_4)_2MnCl_4$ crystals [8]

3. The aim and objectives of the study

The aim of this study is to determine the temperature of phase transitions in the $(N(CH_3)_4)_2MnCl_4$. crystal with the temperature of photoluminescence evolution spectra. This will make it possible to determine the interval of working temperatures suitable for the use of $(N(CH_3)_4)_2MnCl_4$ crystal as sensors of temperature, pressure, etc. In order to achieve this goal, the following tasks need to be addressed:

– to conduct low-temperature studies of the FL spectra, excitation, and attenuation of FL bands;

– to identify the detected bands and to establish the main parameters of the FL excitation bands;

– to establish the temperatures of phase transitions.

4. The procedure of synthesis and study of photoluminescence spectra

Monocrystals were grown from a water solution of salts by slow evaporation at room temperature. The original materials for their synthesis were tetramethylammonium chloride $N(CH_3)_4Cl$ and $MnCl_2$. These components were dissolved in distilled water with an appropriate molar ratio. The grown crystals have a characteristic light green color. Fig. 2 shows microphotographs of the samples obtained at different thicknesses with the help of an optical microscope. Based on the diffraction pattern, it was found that compound $N(CH_3)_4Cl$ и $MnCl_2$ is crystallized in a monoclinic lattice with spatial group $P2_1/c(14)$ at 270 K. No impurity phases were detected [3].

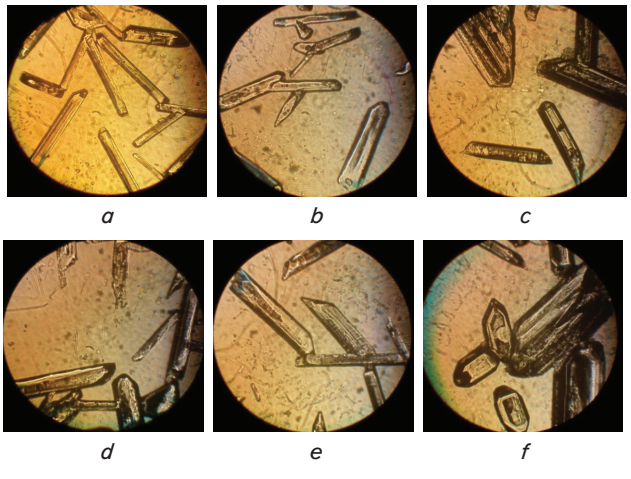

Fig. 2. Photos of polycrystalline samples of $[N(CH_3)_4]_2MnCl_4$ crystal at different values of thickness of monocrystals: *a* – ~1200 μm; *b* – ~800 μm; *c* – ~720 μm; *d* – ~600 μm; *e* – ~550 μm; *f* – ~350 μm

The excitation spectra and glow of FL at liquid helium temperature were measured using the Horiba/Jobin-Yvon Fluorolog-3 spectrofluorometer (France), which is equipped with a continuous xenon lamp (450 W) and a photomultiplier Hamamatsu R928P (Japan). The FL excitation spectra were adjusted by the lamp's radiation spectrum.

The FL spectra were adjusted for the spectral characteristic of the spectrometry system used in our experiment. Finally, low-temperature FL measurements were performed using a closed-loop helium cryostat.

5. Results of studying the photoluminescence spectra

The study of the FL spectra (Fig. 3) was conducted to identify the main optical transitions and identify the bands. The experiment was conducted at wavelengths of light excitation of 271 nm and 360 nm. The analysis was carried out by decomposing the spectra into Gaussian components. Further analysis of the bands obtained as a result of the decomposition of the glow spectra into the Gaussian components was performed. In order to identify the main glow bands, the excitation spectra for the band of 539 nm (Fig. 4) were measured in the spectral range of 550–650 nm.

Fig. 5 shows the temperature dependence of the position of a glow band maximum (Fig. 5, *a*, E_{max}), changes in glow intensity (Fig. 5, *b*), integral intensity (Fig. 5, *c*), as well as the contribution of each band to the general glow mechanism (Fig. 5, *d*) and FWHM (means the full width of the peak at its half maximum, Fig. 5, *e*). The study of the excitation spectra in a narrow energy range is shown in Fig. 6, *a*, and their temperature behavior in Fig. 7. In Fig. 5, 7 vertical bands correspond to the position of structural transformations taken from the data [19]. The time of attenuation of the FL band of 539 nm at different temperatures and excitation energy is shown in Fig. 8–10.

Fig. 8 shows FL attenuation at 8 K in the glow band of 539 nm. As one can see from Fig. 8, 9, exponential function [13] makes it possible to obtain the highest convergence at the approximation of experimental data for description of temporary FL intensity relaxation of in the $(N(CH_3)_4)_2MnCl_4$. In this case, the coefficient of deviation of obtained time of attenuation of the FL band of 539 nm (Fig. 10) is $(N(CH_3)_4)_2MnCl_4$ for different temperatures.

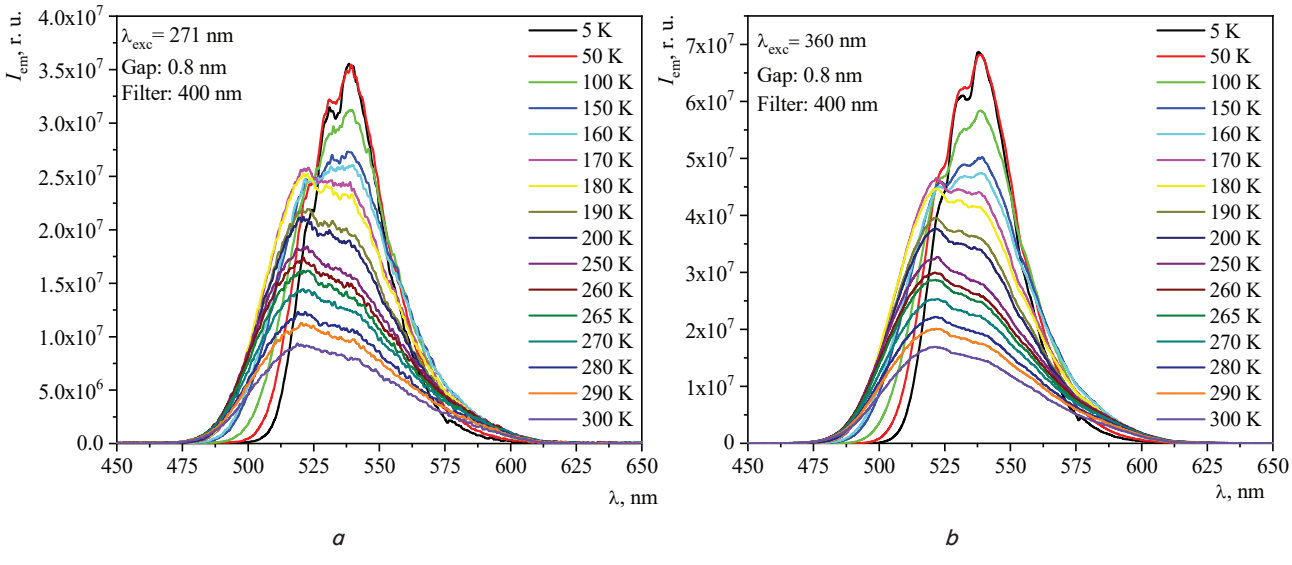

Fig. 3. Spectra of FL of $(N(CH_3)_4)_2MnCl_4$ crystal at different wavelengths of light excitation: *a* – 271 nm; *b* – 360 nm

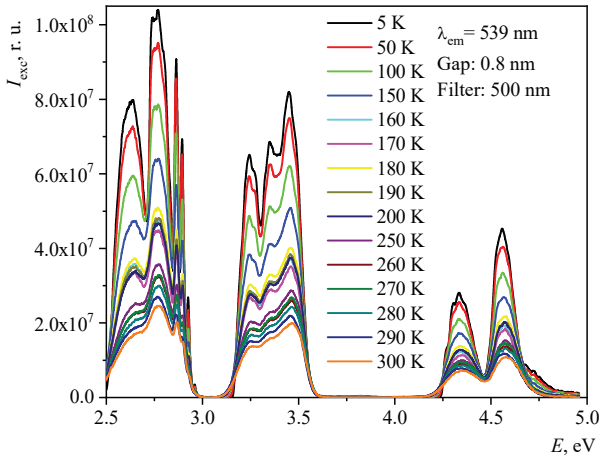

Fig. 4. Spectra of excitation of $(N(CH_3)_4)_2MnCl_4$ crystal for λ=539 nm

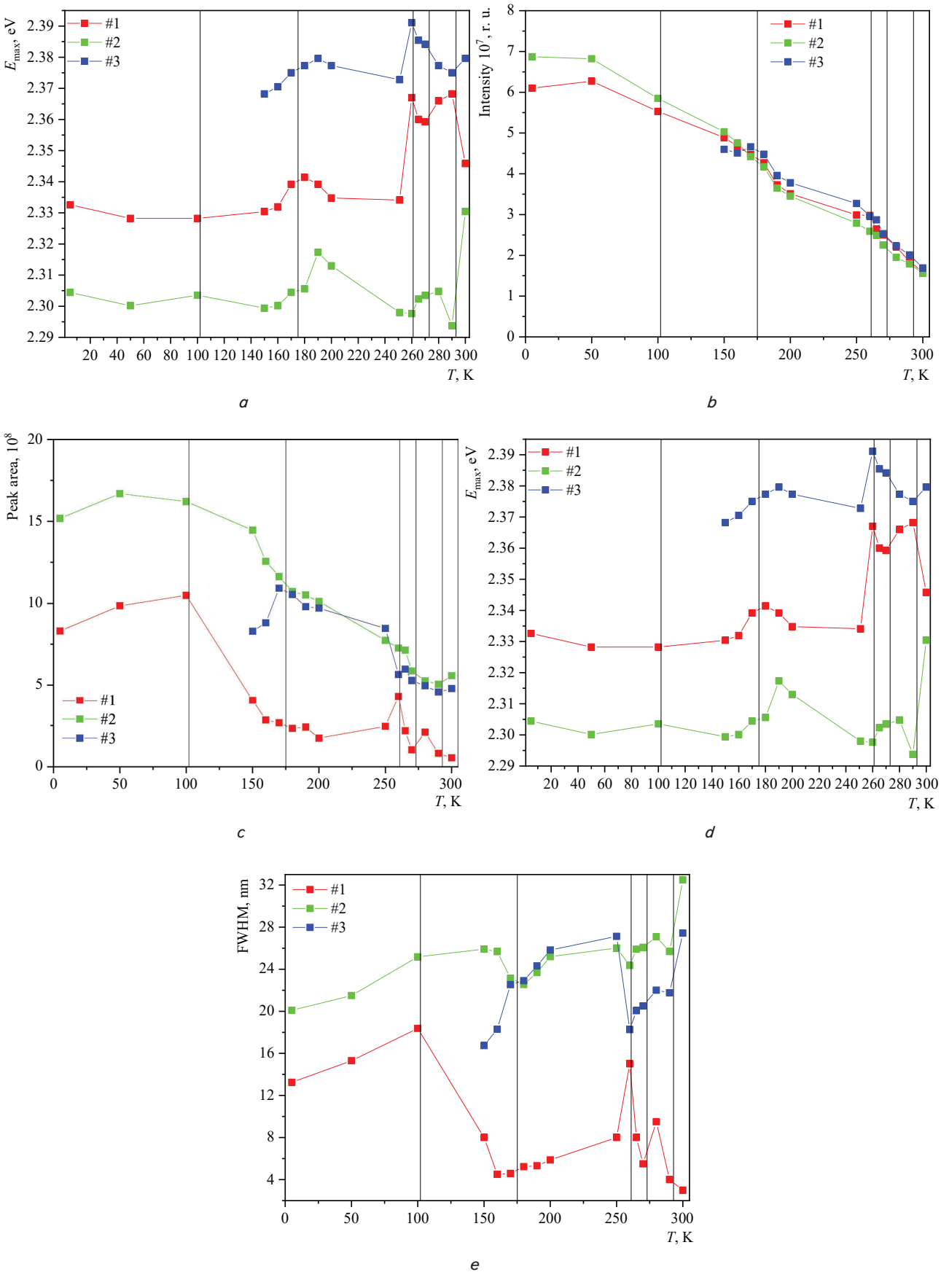

Fig. 5. Temperature dependence: *a* – position of the maximum of a glow band; *b* – change in glow intensity; *c* – integral intensity; *d* – contribution of each band into general glow mechanism; *e* – FWHM

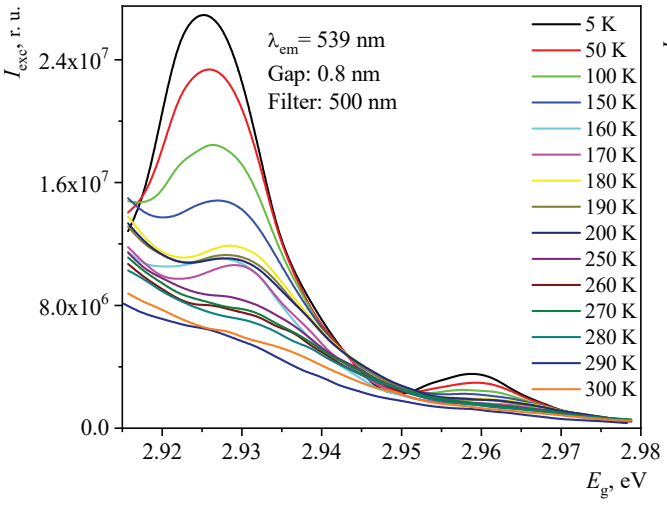

Fig. 6. Spectra of excitation of $(N(CH_3)_4)_2MnCl_4$ crystal for λ=539 nm in the range of 2.91–2.98 eV

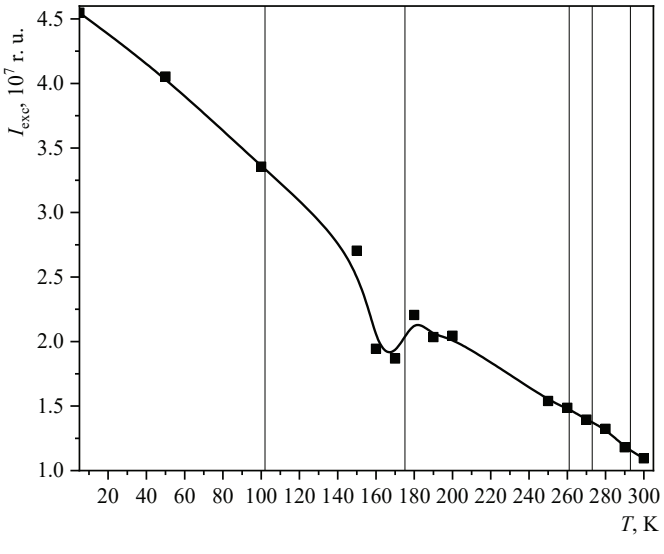

Fig. 7. Temperature dependence of glow intensity of band of excitation 4.56 eV

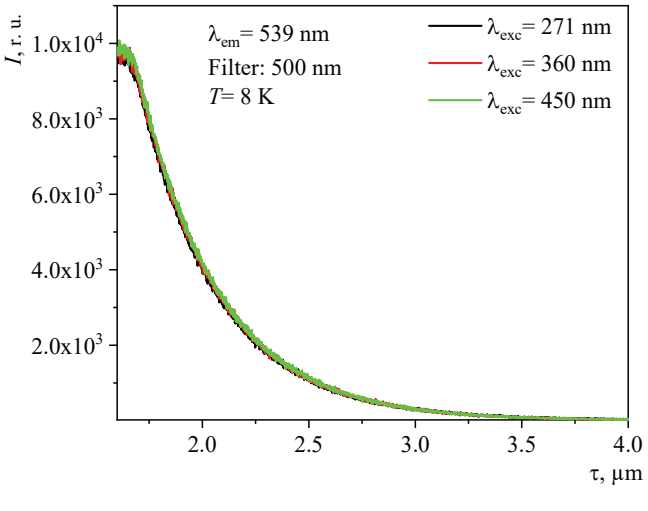

Fig. 8. Luminescence attenuation of $(N(CH_3)_4)_2MnCl_4$ at 8 K in glow band of 539 nm

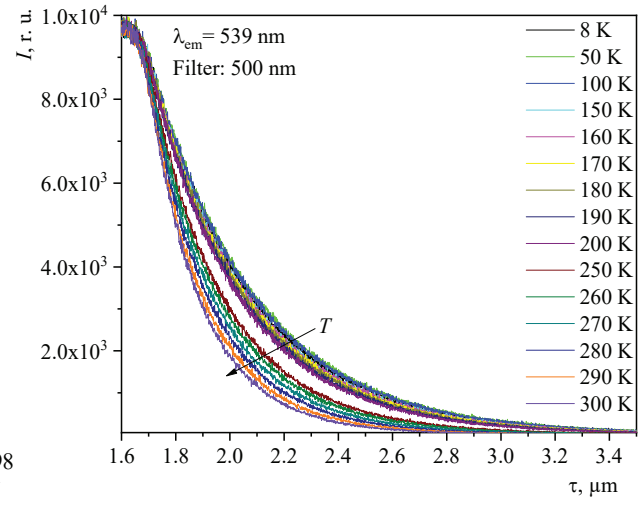

Fig. 9. Temperature behavior of luminescence attenuation of $(N(CH_3)_4)_2MnCl_4$ in glow band of 539 nm

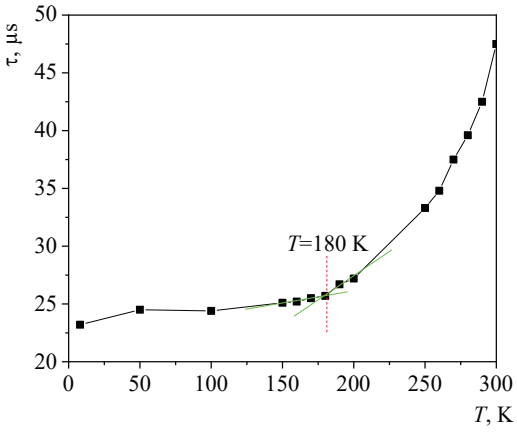

Fig. 10. Temperature dependence of attenuation time of glow band of 539 nm $(N(CH_3)_4)_2MnCl_4$

6. Discussion of results of studying photoluminescence

Fig. 3 shows the FL spectra for $(N(CH_3)_4)_2MnCl_4$ crystal. Two glow bands of λ=531.5 nm (#1) and 539 nm (#2) were identified. It should be noted that at the temperature of 150 K and above, there appears another strip about 523 nm (#3) (Fig. 5). Taking into consideration the information about luminescence spectra given in papers [11, 14] and in this study, it is possible to assume the existence of some common mechanisms for FL formation. After analyzing the glow spectra of other Mn-containing compounds [3, 4, 15], we can assume that the observed glow band corresponds to the glow of the Mn^{2+} ion. This band can be identified as the $^4T_1 \rightarrow {}^6A_1$ transition.

Fig. 3 shows that as the temperature rises, the position of the maximum glow spectrum shifts to the short-wave area. Fig. 5, *a* shows that deviations from quasi-linear dependence about 175, 261, 273, and 293 K can be caused by the transformation of structural phases [8, 9, 19]. Similar behavior was found in the temperature dependence of glow intensity (Fig. 5, *b*). It should be noted that integral intensity, the contribution of each of the bands (*P*) and FWHM indicate a sharp drop in temperatures T>100 K. As reported in [9], at temperatures of 90 K, there may be a structural phase tran-

sition ($\Delta T \approx 12$ K). Based on these arguments, it can be assumed that appearance of band #3 is caused by the structural transformation. The nature of this band was studied in paper [3].

Based on the excitation spectra, the positions of the main excitation bands were detected (Table 1). The peaks in excitation spectra correspond to electron transitions from the main state $^6A_1$ Mn^{2+} to various excited states $MnCl_4^{2-}$ (T_d) [16]. Their excitation energy can be explained by crystal models using the Tanabe-Sugano (T-S) diagrams. The Racah B and C parameters, as well as splitting of crystal field Δ, are based on the T-S diagrams for d^5 electron configuration.

Table 1

Transition energy taken at the maximum of the band of excitation spectra at T=300 K (Fig. 4)

Excitation band T_d	Position of peak, eV	Position of peak, eV [4]	Position of peak, eV [3]	Position of peak, eV [19]
$^6A_1(S) \rightarrow {}^4T_1(G)$	2.64	2.65	–	2.63
$\rightarrow {}^4T_2(G)$	2.77	2.77	–	2.74
$\rightarrow {}^4E, {}^4A_1(G)$	2.87	2.87	2.86	2.85
–	2.90	–	–	2.90
$\rightarrow {}^4T_2(D)$	3.27	3.26	3.30	3.24
$\rightarrow {}^4E(D)$	3.35	3.38	–	3.34
$\rightarrow {}^4T_1(P)$	3.46	3.46	3.45	3.47
$\rightarrow {}^4A_2(F)$	4.34	–	4.37	4.32
$\rightarrow {}^4T_1(F)$	4.58	–	4.63	4.56
B, eV	0.084	0.082	–	–
C, eV	0.365	0.381	–	–
Δ, eV	0.42	0.421	–	–
T, K	300	290	270	–

The resulting parameters of Racah and magnitudes of cleavage of the crystal field satisfactorily correlate with the well-known literary information [4]. The T-S diagram is analyzed in accordance with the procedure [17, 18]. It should be noted that the bands around 2.93 and 2.96 eV quickly attenuate with temperature. One *may see* that the band of 2.96 eV at the temperatures above 170 K and the band of 2.93 eV at 270 K are not observed. It can also be caused by structural transformations. For the other bands in the excitation spectra, the temperature behavior is similar. For example, a change in the peak intensity of the excitation band at 4.56 eV is shown in Fig. 7. Similarly to the glow spectra, we observe a deviation from the linear dependence in the region of 170 K, which is caused by structural changes (Fig. 7).

The resulting time of luminescence attenuation increases at a temperature increase, and temperature behavior (Fig. 10) proves the existence of a phase transition in the crystal at around 170–180 K.

7. Conclusions

1. Based on the research into the spectra of photoluminescence of the $(N(CH_3)_4)_2MnCl_4$, the glow bands that are caused by the glow of Mn^{2+} ion and correspond to $^4T_1 \rightarrow {}^6A_1$ transition were determined. The temperature behavior of photoluminescence spectra, excitation spectra, and time of luminescence attenuation for the wavelength of 539 nm were presented.

2. Analysis of the T-S diagrams allowed finding the Racah parameters and the magnitude of splitting the crystal field. The resulting values are well correlated with well-known data in the literature. It was established that the glow spectrum is characterized by the band of about 530 nm, corresponding to the glow of the Mn^{2+} ion.

3. Decomposition into the Gaussian components suggests that the energy level is split into two components at temperatures of less than 150 K and into three components at temperatures over 150 K. The temperature behavior of the main characteristics of a glow band, decomposed into the Gaussian components, proves the existence of structural transformations that were previously envisaged. The temperature behavior of the excitation spectra of the band of 539 nm indicates a structural phase transition at the temperatures close to 170 and 270 K. The existence of phase transitions is proved by the research into the temperature dependence of the time of luminescence attenuation for the wavelength time of 539 nm.

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