1. Introduction

Compounds (N(CH₃)₄)₂MeCl₄ (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(CH₃)₄)₂MеΧ₄ (Ме=Mn, Zn, Co; Χ=Cl, Br) [1–4] and (N(CH₃)₄)₂MnCl₄ (5) presents a method for obtaining, structural and optical properties of (N(CH₃)₄)₂MnCl₄ crystals at the temperature of 270 K. However, the issues of the influence of temperature on the behavior of FL spectra remain unresolved. Special attention among the representatives of the A₂BX₄ group is paid to compounds (N(CH₃)₄)₂MeXe (Ме=Mn, Zn, Co) and halogen (Cl, Br, I)). This is because all the declared compounds are based on the electronic configuration of metal (Zn, Mn, Co) or halogen (Cl, Br, I) with their help (by drawing analogies to the allowance for organic cation. Most physical mechanisms can be explained with the help of an optical microscope. Based on the diffraction pattern, it was found that compound N(CH₃)₄Cl и MnCl₂ is crystallized in a monoclinic lattice with spatial group P2₁/c (14) and solid solutions based on them [7, 8]. Currently, the emphasis is placed on (N(CH₃)₄)₂MeCl₂ (Ме=divalent metal) compound due to several PT, manifested below 300 K.

Article [3] presents a method for obtaining, structural features and optical properties of (N(CH₃)₄)₂MnCl₄ 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(CH₃)₄)₂MnCl₄ (Pmca) 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(CH₃)₄)₂MnCl₄ crystal.

All recorded PT temperatures for Ме=Mn are collected in Fig. 1. For this system, phase I at 300 K is always crystallized in a lattice with the Pmca 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(CH₃)₄)₂MnCl₄ crystals. This problem was not explored in papers [3, 4].

The aim of this study is to determine the temperature of phase transitions in the (N(CH₃)₄)₂MnCl₄ 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(CH₃)₄)₂MnCl₄ 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.

2. Literature analysis and problem statement

The main optical, structural, mechanical, and other parameters of crystals of the A₂BX₄ group were studied in papers [1–11]. It was shown that they have seegnetoelastic, segenetoelectric, and superion properties. These papers exclusively deal with the compounds of the A₂BX₄ group with an organic cation. Most physical mechanisms can be explained with their help (by drawing analogies to the allowance for organic cation. Most physical mechanisms can be explained with the help of an optical microscope. Based on the diffraction pattern, it was found that compound N(CH₃)₄Cl и MnCl₂ is crystallized in a monoclinic lattice with spatial group P2₁/c (14) at 270 K. No impurity phases were detected [3].

3. The aim and objectives of the study

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(CH₃)₄)Cl and MnCl₂. 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(CH₃)₄Cl и MnCl₂ is crystallized in a monoclinic lattice with spatial group P2₁/c(14) at 270 K. No impurity phases were detected [3].

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(CH₃)₄)Cl and MnCl₂. 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(CH₃)₄Cl и MnCl₂ is crystallized in a monoclinic lattice with spatial group P2₁/c(14) at 270 K. No impurity phases were detected [3].
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, $E_{\text{max}}$), changes in glow intensity (Fig. 5, $I_{\text{em}}$), integral intensity (Fig. 5, $I_{\text{int}}$), as well as the contribution of each band to the general glow mechanism (Fig. 5, $d$) and FWHM (mean 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$_3$)$_4$)$_2$MnCl$_4$ crystal at different wavelengths of light excitation: $a$ – 271 nm; $b$ – 360 nm](image)

![Fig. 4. Spectra of excitation of (N(CH$_3$)$_4$)$_2$MnCl$_4$ crystal for $\lambda$=539 nm](image)
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
6. Discussion of results of studying photoluminescence

Fig. 3 shows the FL spectra for (N(CH₃)₄)₂MnCl₄ 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 Mn²⁺ ion. This band can be identified as the 4 Т₁ → 6 А₁ 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 ($\Delta T \approx 12\, \text{K}$). 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 I). The peaks in excitation spectra correspond to electron transitions from the main state $^6A_1 \rightarrow \text{Mn}^{2+}$ to various excited states $\text{MnCl}_4^{2-}$ ($T_d$) [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 $\Delta$, are based on the T-S diagrams for $d^5$ electron configuration.

The resulting parameters of Racah and magnitudes of splitting of crystal field satisfactorily correlate with the well-known literary information [4]. The T-S diagram is an -

cleavage of the crystal field satisfactorily correlate with the

The nature of this band was studied in paper [3].

The resulting parameters of Racah and magnitudes of splitting of the crystal field, decomposed into the Gaussian components 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 2.95 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.

### Table 1

| Excitation Band $T_d$ | Position of Peak, eV | Position of Peak, eV | Position of Peak, eV | Position of Peak, eV |
|------------------------|---------------------|---------------------|---------------------|---------------------|
| $^6A_1(S) \rightarrow ^4T_1(G)$ | 2.64 | 2.65 | – | – |
| $^6A_1(S) \rightarrow ^4T_2(G)$ | 2.77 | 2.77 | – | – |
| $^4E(A_1) \rightarrow ^4T_1(G)$ | 2.87 | 2.87 | 2.86 | 2.85 |
| – | 2.90 | – | – | 2.90 |
| $^4T_1(D)$ | 3.27 | 3.26 | 3.30 | 3.24 |
| $^4E(D)$ | 3.35 | 3.38 | – | 3.34 |
| $^4T_1(P)$ | 3.46 | 3.46 | 3.45 | 3.47 |
| $^4A_2(F)$ | 4.34 | – | 4.37 | 4.32 |
| $^4T_1(F)$ | 4.58 | – | 4.63 | 4.56 |
| $C$, eV | 0.365 | 0.381 | – | – |
| $\Delta$, eV | 0.42 | 0.421 | – | – |
| $T$, K | 300 | 290 | 270 | – |

### References

1. Kushnir, O. S., Kityk, A. V., Dzyubanski, V. S., Shopa, R. Y. (2011). Critical behaviour of optical birefringence near the normal–incommensurate phase transition in [N(CH 3)4]2ZnCl4 crystals under the influence of hydrostatic pressure. Journal of Physics: Condensed Matter, 23 (22), 225403. doi: https://doi.org/10.1088/0953-8984/23/22/225403

2. Kunyo, I. M., Kashuba, A. I., Karpa, I. V., Stakhura, V. B., Sveleba, S. A., Katerynchuk, I. M., et al. (2018). The band energy structure and luminescence of the (N(CH 3)4)2MnCl4, the glow bands that are caused by the glow of Mn2+ ion and correspond to $^4T_1 \rightarrow ^4A_1$ transition were determined. The temperature behavior of photoluminescence spectra, excitation spectra, and time of luminescence attenuation for the wavelength of 539 nm were presented.

3. Kushnir, O. S., Kityk, A. V., Dzyubanski, V. S., Shopa, R. Y. (2011). Critical behaviour of optical birefringence near the normal–incommensurate phase transition in [N(CH 3)4]2ZnCl4 crystals under the influence of hydrostatic pressure. Journal of Physics: Condensed Matter, 23 (22), 225403. doi: https://doi.org/10.1088/0953-8984/23/22/225403

4. Rodríguez-Lazcano, Y., Nataf, O., Rodríguez, F. (2009). Electronic structure and luminescence of [(CH 3)4N]2MnX4 (X=Cl,Br) crystals at high pressures by time-resolved spectroscopy: Pressure effects on the Mn-Mn exchange coupling. Physical Review B, 80 (8). doi: https://doi.org/10.1103/physrevb.80.085115

5. Kapustin, V., Semak, S., Panasyuk, M., Rudko, M., Rudik, V. (2019). Temperature evolution of the intra-ion absorption spectra of (NH42H2C2O4)2CoCl4 crystals in the region of their phase transitions. Phase Transitions, 92 (4), 396–405. doi: https://doi.org/10.1080/01411594.2019.1591407

6. Kushnir, O. S., Shelepansky, P. A., Stadnyk, V. Y., Fedorchuk, A. O. (2019). Relationships among optical and structural characteristics of ABSO 4 crystals. Optical Materials, 95, 109221. doi: https://doi.org/10.1016/j.optmat.2019.109221

7. Karpa, I. V., Sveleba, S. A., Kunyo, I. M., Katerynchuk, I. M., Semotyuk, O. V., Blashko, O. I. (2010). Effect of the number of defect density waves on the dynamics of the soliton system in [N(CH 3)4]2CuCl4 and [N(CH 3)4]2Zn0.98Ni0.02Cl4 crystals. Crystallography Reports, 55 (5), 815–820. doi: https://doi.org/10.1134/s1063774510050172

7. Conclusions
8. Sveleba, S. A., Karpa, I. V., Katerynchuk, I. M., Kunyo, I. M., Phitsych, E. I. (2014). Influence of the thickness of \([\text{N(CH}_3)_4]^2\text{Zn}_{0.75}\text{Mn}_{0.25}\text{Cl}_4\) crystal on the phase-transition temperature. Crystallography Reports, 59 (2), 229–237. doi: https://doi.org/10.1134/s1063774514020266

9. Mashiyama, H., Koshiji, N. (1989). A structural study of phase transitions in \([\text{N(CH}_3)_4]^2\text{MnCl}_4\). Acta Crystallographica Section B Structural Science, 45 (5), 467–473. doi: https://doi.org/10.1107/s0108768189006981

10. Marco De Lucas, M. C., Rodriguez, F., Moreno, M. (1990). Optical investigations on \([\text{N(CH}_3)_4]^2\text{MnCl}_4\); A new phase transition at 90 K. Ferroelectrics, 109 (1), 21–26. doi: https://doi.org/10.1080/00150199008211384

11. Ben Bechir, M., Karoui, K., Tabellout, M., Guidara, K., Ben Rhaiem, A. (2014). Alternative current conduction mechanisms of organic-inorganic compound \([\text{N(CH}_3)_4]^3\text{H}\text{ZnCl}_4\). Journal of Applied Physics, 115 (15), 153708. doi: https://doi.org/10.1063/1.4871662

12. Zhou, Q., Dolgov, L., Srivastava, A. M., Zhou, L., Wang, Z., Shi, J. et. al. (2018). Mn\(^{2+}\) and Mn\(^{4+}\) red phosphors: synthesis, luminescence and applications in WLEDs. A review. Journal of Materials Chemistry C, 6(11), 2652–2671. doi: https://doi.org/10.1039/c8tc00251g

13. Kashuba, A., Zhydachevskyy, Y., Semkiv, I., Franiv, A., Kushnir, O. (2018). Photoluminescence in the solid solution \(\text{In}_{0.5}\text{Tl}_{0.5}\text{J}\). Ukrainian Journal of Physical Optics, 19 (1), 1. doi: https://doi.org/10.3116/16091833/19/1/1/2018

14. Artem'ev, A. V., Davydova, M. P., Berezin, A. S., Brel, V. K., Morgalyuk, V. P., Bagryanskaya, I. Y., Samsonenko, D. G. (2019). Luminescence of the Mn\(^{2+}\) ion in non-Oh and Td coordination environments: the missing case of square pyramid. Dalton Transactions, 48 (43), 16448–16456. doi: https://doi.org/10.1039/c9dt03283e

15. Zhang, J., Zou, H., Qing, Q., Yang, Y., Li, Q., Liu, Z. et. al. (2003). Effect of Chemical Oxidation on the Structure of Single-Walled Carbon Nanotubes. The Journal of Physical Chemistry B, 107 (16), 3712–3718. doi: https://doi.org/10.1021/jp027500u

16. Griffith, J. S. (2009). The Theory of Transition-Metal Ions. Cambridge University Press, 468. Available at: https://www.cambridge.org/ua/academic/subjects/chemistry/chemistry-general-interest/theory-transition-metal-ions/format-PB&isbn=9780521113995

17. Sugano, S. (1970). Multiplets of Transition-Metal Ions in Crystals. Academic Press, 348. Available at: https://www.elsevier.com/books/multiplets-of-transition-metal-ions-in-crystals/sugano/978-0-12-676050-7

18. Liem, L. N., Tran, N. (2018). Calculations of the Racah parameter B for Mn\(^{4+}\) and Mn\(^{2+}\) ions doped in CaAl\(_2\)O\(_4\). IOP Conference Series: Materials Science and Engineering, 343, 012026. doi: https://doi.org/10.1088/1757-899x/343/1/012026

19. Bolesta, I., Furgala, Y., Kityk, I. (1996). Effects of phase transitions in luminescence features of \([\text{N(CH}_3)_4]^2\text{MnCl}_4\) single crystals. Phase Transitions, 56 (1), 1–10. doi: https://doi.org/10.1080/01411599608207834