ANNOTATION

dissertations for the degree of Doctor of Philosophy (PhD) in the specialty 6D060400 – «Physics»

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Exciton-like luminescence of crystals NaCl, KCl, KI, and RbI in the field of light homologue cation and elastic deformation

Relevance of the topic.

Alkali-halide crystals (AHC) are "model objects" for the study of physical processes in a variety of materials, and their attractiveness is justified by important technical applications as multifunctional materials. LiF and NaF crystals have high optical transparency in a wide range of the spectrum from vacuum ultraviolet to infrared (95-1500 nm). AHC are traditionally used as ionizing radiation dosimeters and scintillation detectors, and are also of great interest in the development of optical quantum generators and optical storage devices.

Currently, the NaI crystal, which has a high quantum luminescence yield and is used as a reference scintillator, is also used as the main detection node in ultra-virtual experiments for detecting the energy registration of dark matter particles.

Despite of the long history of AHC using and research of AHC, the mechanisms of the formation of the scintillation pulse in these systems have not been fully elucidated. The study of the external influence on the mechanisms of energy transfer in scintillators will allow us to determine the real ways to improve the quality of scintillation detectors.

To determine the maximum yield of luminescence associated with exciton energy transfer, the free path of excitons before their self-trapping plays an important role. In this regard, it is necessary to establish a physical parameter that allows you to influence the free path of the exciton before their self-trapping.

A direct factor affecting the efficiency of the radiative relaxation of the electronic excitations of the AHC is uniaxial deformation, which, as experiments show, significantly reduces the free path of excitons before self-trapping and subsequent radiative annihilation. As a result, a sharp increase in the probability of exciton self-trapping in regular lattice sites is expected, and, as a result, an increase in the intrinsic (exciton) luminescence of the AHC. The mechanism of energy transfer to the luminescence centers due to the formation of correlated electron-hole pairs is also not excluded.

A huge number of experimental and theoretical studies of the processes of creation and evolution of electronic excitations (EEV) in the AHC have been carried out. Along with the emissive decay channel of EEV (the appearance of various types of luminescence), special attention was paid to the theoretically not predicted non – emissive decay channel with the formation of point defects of the crystal lattice of pairs of Frenkel defects - F, H and α, I .

The targeted deformation effect on the predisposing states of various EEVs (anionic excitons, valence holes, electron-hole pairs) in the AHC will allow us to obtain original experimental results on a comprehensive study of the relationship between the two above - mentioned channels of EEV annihilation-radiative relaxation (luminescence) and a non-trivial non-radiative channel (additional to heat release) of radiation defect formation.

According to modern concepts, the self-trapped exciton (STE) in the AHC corresponds to a formation whose hole component has the structure of a X_2^- quasihalide molecule located in two adjacent anionic lattice sites and oriented along the crystallographic axes <110> in face-centered AHCs.

Depending on the location of the hole component relative to the two anionic lattice nodes involved in its formation, there are three types of STE configuration: centrally symmetric (on-center), weakly asymmetric (weak off-center), and, in the case of a strong shift of X_2^- towards one of the anionic nodes, strongly asymmetric (strong off-center).

It was the sensitivity of the STE characteristics (for example, the Stokes shift value) to the local symmetry of the crystal-forming particles involved that gave rise to the original idea of studying the evolution / efficiency of various EEV decay channels under conditions of local and elastic deformation affecting the symmetry of their nearest crystal environment.

In our study, the local deformation of the lattice is carried out by targeted doping of the AHC with light homologous cations, the ionic radii being significantly smaller than the main lattice cation (for example, NaCl-Li, KCl-Na).

The study of the relaxation processes of STE AHC in the field of perturbing factors is a very promising and relevant direction for the creation of materials with specified physical characteristics (radiation-sensitive or radiation-resistant), as well as the search for optical materials with a wide range of transparency, even when exposed to ionizing radiation.

The aim of the dissertation is to establish the direct effect of the light homologue cation and elastic deformation, which reduce the symmetry of the crystal lattice, on the predisposing radiative states of exciton-like electronic excitations in NaCl, KCl, KI, and RbI crystals.

To achieve the goal, the following **main tasks** were set:

1. Modernization of the spectral complex with photoelectronic multipliers of the H 8259 type of the company "Namamatsu", operating in the photon counting mode, controlled by special programs based on the digital technology SpectraScan and ThermoScan in the spectrum range of 200-850 nm with a preset set of scanning speeds (1÷50 nm/s), allowing the registration of 5 luminescent characteristics of the AHCs in conditions of low-temperature (85-95K) deformation: X-ray luminescence, tunnel luminescence (TL), thermally stimulated luminescence (TSL), as well as a time scan of tunnel luminescence and integral thermally stimulated luminescence.

2. A comprehensive study of the effect of a light cation and uniaxial low-temperature (82÷85 K) deformation on the luminescent and thermal activation characteristics of NaCl, KCl, KI, and RbI crystals.

3. Investigation of the effect of elastic deformation on the exciton-like luminescence configurations of NaCl, KI, and RbI crystals.

4. Application of elastic deformation to study the nature of the intrinsic luminescence of excitons of an RbI crystal.

5. Optical creation and recombination formation of near-sodium exciton-like luminescence in KCl matrices.

The object of the study is exciton - like electronic excitations in NaCl, KCl, KI, and RbI crystals when the lattice symmetry is lowered by light homologous cations (Li, Na) and low-temperature (82÷85 K) uniaxial elastic deformation.

The subject of the study is the peculiarities of luminescence of exciton-like electronic excitations in NaCl, KCl, KI, and RbI crystals under lowering of the lattice symmetry by light cations and low-temperature (82÷85 K) uniaxial deformation.

Research methods-experimental methods of luminescence and thermal activation spectroscopy, based on the registration of spectra in the photon counting mode using local and low-temperature elastic deformations that reduce the lattice symmetry of NaCl, KCl, KI, and RbI crystals.

The scientific novelty lies in the fact that the work for the first time:

1. Experimentally determined the direct effect of uniaxial elastic deformation, applied in the crystallographic direction <100> on the structure of the asymmetric configuration of self-trapped excitons in crystals of NaCl, which was increased intensity (7-10 times) π – luminescence with a maximum at 3.5 eV with a full width at half maximum of 0.75 eV at 85K.

2. In the crystals of NaCl-Li in the low-temperature elastic deformation in the spectra of thermally stimulated luminescence discovered a new emission band with a maximum at 2.7 eV, which is interpreted by the formation of exciton-like luminescence in the field of lightweight lithium.

3. Using low-temperature elastic deformation, the intrinsic nature of E_x -luminescence in RbI crystals is established on the basis of a linear increase in the intensity of E_x -luminescence (3.1 eV) synchronously with the intrinsic σ-luminescence (3.89 eV) of STE with an increase in the degree of elastic deformation (ε=0.5÷1.0%).

4. The optical generation of near-sodium exciton-like luminescence with a maximum of 2.8 eV in KCl-Na crystals under photoexcitation in the VUV region of the spectrum and recombination formation of near-sodium exciton-like luminescence were experimentally established.

Practical significance. A highly sensitive method for registration the thermally stimulated luminescence spectra of alkali-halide crystals has been developed (patent for invention No. 34978 of the Republic of Kazakhstan dated 02.04.2021). An original method of influencing the free path of excitons in alkali-halide crystals has been developed (utility model patent No. 5978 of the Republic of Kazakhstan dated 09.04.2021). The author's certificate for the digital scanning technology of integrated tunnel luminescence and thermally stimulated luminescence of alkali-halide crystals (No. 12980, dated 03.11.2020) was obtained.

The main provisions submitted for defense:

1. A direct effect of uniaxial elastic deformation of the asymmetric configuration exciton-like structures in the crystals of NaCl, which was increased intensity in the range of π –luminescence with a maximum at 3.5 eV with a full width at half maximum of 0.75 eV at 85K.

2. The use of low-temperature elastic deformation to determine the nature of the E_x – luminescence with a maximum at 3.1 eV and RbI crystals on the spectra of X-ray luminescence depending on the degree of compressive strain (ε=0,5÷1,0%).

3. Experimental demonstration of the mechanism of separation of π (3.3 eV) and E_x (3.0 eV) – STE luminescence in long-stored KI crystals by X-ray luminescence spectra depending on the degree of deformation.

4. Optical creation under photoexcitation in the VUV region of the spectrum and recombination formation of near-sodium exciton-like luminescence with a maximum at 2.8 eV in KCl-Na crystals.

The reliability of the results obtained in the dissertation and the validity of the scientific provisions are confirmed by the consistency of the experimental results with the fundamental provisions of condensed matter physics, as well as the use of modern experimental methods for registering the luminescent characteristics of the studied crystals based on digital technology, controlled by special programs SpectraScan and ThermoScan (Patent for invention 34978 RK dated 02.04.2021, Author's certificate №12980, 03.11.2020) in combination with a cryostat that allows deforming crystals at low temperatures (Patents RK №14831 dated 30.06.2004, №26141 of 03.08.2012, №28731 of 18.06.2013).

The work was performed at the scientific center "Radiation Physics of Materials" of the K. Zhubanov Aktobe Regional University.

Experiments at low temperatures (10 K) related to the optical creation of near-sodium excitons in KCl-Na crystals in the VUV region of the spectrum with a photon energy of 7.62 eV and their radiative relaxation were performed in the laboratory of "Physics of Ionic Crystals" of the Institute of Physics of the University of Tartu, Estonia.

The connection of the topic with the plans of scientific works. The dissertation was carried out in accordance with the plan of research work under the project of grant funding of the Ministry of Education and Science of the Republic of Kazakhstan "Directed effect on the radiative relaxation of electronic excitations in order to improve the luminescent characteristics of functional materials based on alkali-halide crystals" AP08855672 for 2020-2022.

Approbation of the study. The main results of the thesis were presented and discussed at the following meetings:

– 12-th International conference "Nuclear and radiation physics" (Almaty, 24-27 June 2019);

– 20th anniversary conference on radiation effects in insulators (Nur-Astana, August 19-23, 2019);

– 13th International conference Functional Materials & Nanotechnologies (Vilnius, November 23-26, 2020).

Publication of research results. Based on the materials of the dissertation work, 10 scientific papers were published, including: 3 articles in peer-reviewed scientific journals included in the Web of Science and Scopus databases, 2 articles in journals included in the list recommended by Committee for Quality Assurance in the Field of Education and Science and Ministry of Education and Science of the Republic of Kazakhstan, patents for inventions and utility models, 1 author's certificate, 2 articles in other journals of the Republic of Kazakhstan.

Scope and structure of the work. The dissertation work consists of an introduction, four main sections, a conclusion and a list of references. The work consists of 5 tables, 42 figures and a bibliography containing 139 titles.

The main content of the dissertation.

The introduction presents the relevance of the dissertation work and its main provisions.

Conclusions on the first section:

The analysis of the literature review on the materials of radiative and non-radiative annihilation of electronic excitations in alkali-halide crystals reveals the following main regularities:

1. The luminescence spectra of self-trapped excitons in NaCl, KCl, KI, and RbI crystals are in the spectral range from 6.0 to 2.0 eV. The short-wave part of the STE luminescence in the AHC is σ - polarized (S-singlet glow), and the long-wave part has partial π - polarization (T - triplet glow). It is established that the STE configuration in the AHC can be classified by the values of relative Stokes losses. In the objects selected for the study, namely, in the crystals of NaCl, KCl, KI, and RbI, all three types of STE are registered: centrally symmetric (on), weakly asymmetric (weak off), and strongly asymmetric (strong off). A scheme of adiabatic potentials was investigated to explain the transitions between singlet and triplet states of STE. With an increase in temperature, a decrease in the luminescence intensity of excitons in the AHC is recorded, which was associated with a reduction in the free path of excitons before self-trapping. Note that, in general, the maximum value of the exciton luminescence intensity is recorded at extremely low temperatures (4.2 K).

2. The decay of self-trapped excitons in AHC occurs through two channels: radiative and non-radiative with the formation of primary radiation defects (*F*-and *H*-centers, α and *I*-centers). The transition of STE from a single-haloid to a two-haloid state is studied. Knowing the temperature of defect formation allows you to determine and estimate the lifetime: short-lived and stable defects. It is found that in the temperature range from 100 to 200 K, the efficiency of creating stable F-centers increases several times.

3. The effect of elastic deformation on the AHC leads to a rather sharp increase in the intensity of the STE luminescence. Elastic deformation in one particular crystallographic direction reduces the lattice symmetry, and therefore leads to a decrease in the height of the potential barrier separating the quasi-free and self-trapped exciton states. The increase in the intensity of STE luminescence

occurs due to the weakening of the channel responsible for the radiation creation of defects. The dependence of the X-ray luminescence radiation intensity on the degree of mechanical compression at 80 K is shown on the example of the KBr crystal. A linear section is clearly observed that characterizes the elastic part of the strain, as well as the saturation region associated with the plastic part of the strain.

4. Based on the analysis of the literature review on AHC, the problem statement of the dissertation work is determined.

Conclusions on the second section:

1. The physical basis of luminescence and thermal activation spectroscopy is analyzed by recording the spectra of X-ray luminescence, tunnel luminescence, thermostimulated luminescence, and integral thermostimulated luminescence of AHC.

2. The spectral complex is automated, which allows to register the X-ray, TL, TSL spectra, as well as the time scan of TL and the integral TSL of the AHC under the influence of uniaxial deformation in a wide temperature range (85÷300K) with special controlled programs SpectraScan and ThermoScan.

3. The technical characteristics of the SpectraScan program are tested by scanning the radiation spectra of the AHC using a high-power monochromator MSD-2 and a photoelectron multiplier of the type H 8259 of the company "Namamatsu", operating in the photon counting mode in the spectrum range of 200-850 nm with set speeds (1÷50 nm/s).

4. The technical characteristics of the ThermoScan program are tested by scanning the intensity of light signals with a photoelectronic multiplier and the temperature of linear heating of a copper-constantane thermocouple sample through the corresponding controllers with a graphical representation of the scanning protocols.

Conclusions on the third section

On the basis of absorption, thermal activation, and luminescence spectroscopy with the use of local and elastic deformation, the processes of radiative relaxation of electronic excitations of radiation defect formation in the NaCl matrix are studied and the following main regularities are established:

1. Experimental recording of the X-ray luminescence spectra of NaCl (Harshaw), NaCl-Li, and NaCl (Halite) crystals at 85K, it was found that the ratio (I_π/I_σ), the intensity of the bands of π (3.5 eV) - and σ-luminescence (5.2 eV) is up to 2 times deformation, and at elastic deformation (ε=1%) 8 times, i.e., the increase in the intensity of luminescence occurs due to π-luminescence.

2. In the elastically deformed (ε=1%) NaCl-Li in the thermally stimulated luminescence spectra at 115 K, radiation with a maximum of 2.7 eV was detected, which was interpreted as the result of recombination of electrons released during thermal ionization of F' centers with localized $H_A(Li)$ centers.

3. It is found that in the NaCl matrix, with a decrease in the symmetry of the elastic strain lattice, exciton auto localization in the regular lattice nodes is activated and the transfer of exciton energy to impurities (Br) significantly worsens.

As a protected position, the following formulation of the study is presented: «The direct effect of uniaxial elastic deformation on the asymmetric configuration of exciton-like formations in NaCl crystals, which is registered by an increase in the intensity in the region of the π –luminescence spectrum with a maximum at 3.5 eV with a half-width of 0.75 eV at 85K».

Conclusions on the fourth section

1. The X-ray luminescence spectra for the first time revealed an increase in both σ-luminescence of self-trapped excitons and E_x-luminescence (band maxima at 3.89 eV and 3.1 eV, respectively) in RbI single crystals subjected to elastic uniaxial deformation at 93 K. The intensity of these glows increases linearly with an increase in the relative degree of uniaxial deformation of the crystal up to a value, and at higher values of $\varepsilon = 1\%$, saturation of the luminescence occurs. The nature of the dependence $I = f(\varepsilon)$ for the intensities of σ- and E_x-luminescence allows us to assert the intrinsic nature of the E_x-luminescence associated with the radiative relaxation of the self-trapped exciton in the field of local deformation of the regular RbI lattice.

2. The X-ray luminescence spectra were studied under low-temperature (100K) uniaxial deformation of KI and KI-Na crystals stored at room temperature for a long time. The following regularities are found: first, in the absence of deformation, the intensities of the natural radiation bands at 3.3 eV (π) and 4.1 eV (σ) become comparable to each other in comparison with freshly grown crystals, where the ratio differs by an order of magnitude (10/1), respectively; secondly, with an increase in the degree of low-temperature uniaxial deformation, the radiation spectra gradually shift in two directions: the maximum of radiation at 3.3 eV is shifted towards short wavelengths, the final position is fixed at 3.9 eV, which is almost the same as σ-luminescence; the maximum of radiation at 3.0 eV (E_x -radiation) is shifted towards long wavelengths, the final position of which is fixed at 2.85 eV.

Thus, the low-temperature uniaxial deformation leads to the separation of the radiation spectra at 3.3 eV (π)→3.9 eV and 3.0 eV (E_x) →2.85 eV, which are interpreted by isolating weak→on and weak→strong exciton configurations, respectively.

The transformation of the 3.0 eV radiation band is clearly expressed by radiation with a maximum at 2.8 eV, showing that the radiation is of the same nature and is not associated with a sodium impurity, since the radiation of impurity origin practically disappears under elastic deformation.

3. In the KCl-Na crystal, radiative relaxations with a maximum at 2.8 eV of the auto localized exciton in the sodium – $e_s^0(Na)$ field are experimentally demonstrated during direct optical creation of a near-sodium exciton with a photon energy of 7.62 eV, and during hole-electron recombination during X-ray excitation in the temperature range from 150 K to 300 K- $e_s^+(Na) + e^- \rightarrow e_s^0(Na)$ as well as electron-hole recombination under optical stimulation in the spectrum of F ' centers (1.5 eV) at 90 K, previously irradiated with X – rays of the crystal - $e^- + V_{KA}(Na) \rightarrow e_s^0(Na)$.

The increase in the radiation intensity at 2.8 eV of the KCl-Na crystal under X-ray excitation in the temperature range from 150 K to 300 K, when all exciton-like radiation is extinguished, is interpreted as an increase in the free path of the unreliaxed hole with an increase in temperature to room temperature (300 K).

For the first time in KCl-Na crystals, the registration of the X-ray luminescence spectra from the sodium concentration allowed us to detect the luminescence spectra of near-sodium exciton-like formations with maxima at 2.8 eV and 3.1 eV, corresponding to single and paired sodium centers.

Thus, in the KCl-Na crystal, the unique possibilities of creating self-trapped electronic excitation in the field of the light sodium ion – $e_s^0(Na)$ by three mechanisms – exciton, hole-electron recombination, and electron-hole recombination-are experimentally realized, the radiative relaxation of which ends in luminescence with a maximum at 2.8 eV.

In conclusion, the main results and conclusions of the dissertation work are presented.