ABSTRACT
of the thesis for the degree of Doctor of Philosophy (PhD)
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Maratova Aida Gafurkyzy

The features of spectroscopic properties of CsI, RbI, KI and KCl single crystals with lowering lattice symmetry

The general concept of the work: The fundamental laws of the evolution of electronic excitations (EE) in the anionic sublattice have been established on the basis of alkali-halide crystals: during their creation, migration, self-trapping and further radiative (σ- and π-luminescence of self-trapped excitons (STE)) and nonradiative relaxation (decay into primary radiation defects – *F*, *H* and *α*, *I*). A decrease in the lattice symmetry is possible due to local disturbances of the crystal lattice, achieved by introducing impurities of various sizes and charges, dislocations, vacancy defects, as well as plastic and elastic deformation.

The predisposed state of STE, the nucleus of which is a molecular formation (X_2^-), is very sensitive to changes in the symmetry of the surrounding crystal-forming particles, leading to reduction of AHC's lattice symmetry.

According to well-established ideas, depending on the displacement of the centers of mass of the electron and hole subsystems X_2^--ion, the intrinsic luminescence of the AHC can be classified by three different configurations of STE: I – type (on), II – type (weak off) and III – type (strong off).

When the symmetry of the lattice is lowered by deformation, it is possible to modify the AHC's properties, so that the amplification of the quantum output allows the creation of scintillation detectors based on them. At the same time, the increased efficiency of radiation defect formation allowed use AHCs as diametric materials.

In this regard, it is necessary to create such conditions under which scintillators based on AHCs will have the highest possible quantum yield of luminescence. One of these conditions is the effect of uniaxial deformation, which significantly reduces the mean free path of excitons. At the same time, their probability of self-trapping in regular lattice nodes with radiative annihilation sharply increases and the intensity of the glow of the impurity center decreases. The exclusivity of the method of applying uniaxial deformation lies in the fact that the transfer of the energy of EE to the impurity is not carried out.

The effect of directed low-temperature deformation contributes to the enhancement of the AHC's intrinsic luminescence, which in turn contributes to the development of technologies for obtaining modern materials with specified scintillation characteristics.

Plastic deformation causes, as is known, the flow of various processes (reversible and irreversible) in AHCs, as a result of which various deformation defects are created. In the case of AHC's plastic deformation during the interaction of dislocations, to preserve the electroneutrality of the crystal, divacansions are born. Impurity and vacancy defects of plastic deformation play the role of traps for stabilization of halogen radiation defects, as a result of which the efficiency of the creation of X_3^--centers increases in the process of association of interstitial atoms near divacances.

Low-temperature elastic uniaxial deformation does not create vacancy defects, but only changes the lattice parameters. At the same time the deformation significantly affects the process of radiative annihilation of excitons in the GC, which depends on the symmetry of the arrangement of the elements of the exciton hole component (X_2^-).

CsI, RbI, KI and KCl crystals were purposefully chosen as objects of research. On the one hand, these are previously well-studied crystals, for which the basic laws of relaxation of excitations have been studied in great detail. On the other hand, they differ significantly in many properties, including the efficiency of migration of EEs, the efficiency of creating deforming defects, sensitivity to radiation, etc. At a temperature of 80 K, corresponding to our experimental capabilities, the mean free path of anionic excitons to self-trapping in a series of CsI (350 *a*) crystals differs significantly →KI (235 *a*) →RbI (150 *a*) →KCl (2*a*), which is extremely important for the study of luminescent properties, simultaneously with the efficiency of the formation of radiation defects in AHC (*a* is the lattice constant).

In a number of RbI→KI→CsI crystals, the mean free path of excitons increases, thereby increasing the probability of their participation in luminescent processes, which is especially important for the isolation of their own luminescence of crystals. In KCl (2*a*) crystal, excitons created by ionizing radiation are barrier-free self-trapped in the lattice, and the STE luminescence with a maximum at 2.3 eV becomes completely extinguished by 80 K. In such crystals, it is difficult to expect an increase in the intensity of intrinsic luminescence under the influence of low-temperature uniaxial deformation.

The intensity of the intrinsic luminescence of the exciton nature should increase with an increase in the degree of elastic deformation, and the intensity of the luminescence of the impurity nature, on the contrary, will decrease until it disappears, since the transfer of exciton energy to the impurity will worsen due to the inclusion of the mechanism of their self-trapping in regular lattice nodes.

The effect of excitons' self-trapping under the action of elastic deformation allows not only to establish the intrinsic nature of the luminescence of AHCs, but also to influence the configuration of STE.

Thus, with such a contrasting choice of research objects (CsI, RbI, KI and KCl), it will be possible to identify the features of radiative relaxation and the formation of radiation defects stimulated by low-temperature uniaxial deformation.

In this regard, the key scientific question of the relevance of the chosen topic is to find ways to directly influence the STE's predisposing state for purposeful management of the effectiveness of the luminescent channel and the STE's decay channel with the birth of radiation defects.

The aim of the research work is identify the features of the luminescence nature and the mechanisms of radiation defect formation in CsI, RbI, KI and KCl crystals with lowering lattice symmetry by low-temperature uniaxial deformation using experimental methods of luminescence, thermal activation and absorption spectroscopy.

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

1. Synchronization of two independent photon registration channels for the study of integral and spectral parameters of TSL and TL based on highly sensitive digital technology.

2. Investigation of the luminescence nature in CsI, RbI, KI and KCl crystals with lowering lattice symmetry of low-temperature uniaxial deformation by experimental methods of luminescence and thermal activation spectroscopy.

3. Investigation of the mechanisms of radiation defect formation in RbI, KI and KCl crystals with lowering lattice symmetry of low-temperature uniaxial deformation by the experimental method of absorption spectroscopy.

4. Development of a stoichiometric model for evaluating the effectiveness of radiation defect formation based on the dimension of *H*-centers for RbI, KI, KCl and CsI crystals under uniaxial deformation.

5. Analysis of the existing regularities in the relaxation of EEs in AHCs, and on their basis interpretation of the features of the spectroscopic properties of CsI, RbI, KI and KCl crystals with lowering lattice symmetry.

The object of the research work is the features of relaxation of EEs in CsI, RbI, KI and KCl crystals along the channels of radiative annihilation (luminescence) and nonradiative decay with the formation of radiation defects with lowering lattice symmetry by uniaxial low-temperature (85 K) deformation.

The subject of the research work is the nature of luminescence and the mechanisms of radiation defect formation in CsI, RbI, KI and KCl crystals with lowering lattice symmetry of uniaxial low-temperature (85 K) deformation.

The research methods – experimental methods of thermal activation, luminescence and absorption spectroscopy using low-temperature uniaxial deformation, as well as forecasting the effectiveness of stabilization of *H*-centers by comparing the sizes of halogen atoms (R_a^0) with the sizes of the internode ($R_{\max}$) for *fcc* and *vcc* to assess radiation defect formation in CsI, RbI, KI and KCl crystals.

The scientific novelty lies in the fact that experimental methods of luminescence and absorption spectroscopy for the first time:

1. An increase in luminescence intensity was found at 3.67 eV STE with an asymmetric configuration (weak off-center) in CsI crystals with lowering lattice symmetry by low-temperature (85 K) uniaxial elastic deformation with simultaneous suppression of luminescence at 4.27 eV STE with a symmetrical configuration (on-center).

2. The intrinsic nature of E_x-luminescence in RbI (3.1 eV) and KI (3.05 eV) crystals has been established on the basis of a correlated increase in its intensity

with its own σ- and π-luminescences of STE under increasing exposure to the degree of low-temperature (85 K) uniaxial elastic deformation.

3. In RbI and KI crystals, under the influence of low-temperature (85 K) uniaxial elastic deformation, the effect of lowering the concentration of stable radiation defects was found, which was interpreted based on a comparison of the sizes of the interstitial void and the *H*-center for face-centered (NaCl type) and volume-centered (CsCl type) crystals.

The practical significance. A unique method has been developed for synchronous registration of the temporal and spectral dependence of the intensity of tunneling luminescence of alkali-halide crystals (patent for utility model No. 6563 RK dated 22.10.2022).

A certificate was obtained on entering information into the state register of rights to copyrighted objects for the digital technology of registration of photoluminescence, X-ray luminescence, tunnel luminescence and thermally stimulated luminescence of alkali halide crystals (No. 12826 of 26.10.2020).

Intelligent products of the study of EE relaxation in the AHCs with decreasing lattice symmetry form the scientific basis for the development of scintillation detectors based on the AHC. The main mechanism of transfer of ionizing radiation energy absorbed in AHC-scintillators to luminescence centers is associated with the formation of exciton-like excitations, the migration of which to activators leads to the effective excitation of scintillations.

The main provisions submitted for defense:

1. Experimental effect of increasing luminescence intensity at 3.67 eV STE with asymmetric configuration (weak off-center) in CsI crystals with lowering lattice symmetry by low-temperature (85 K) uniaxial elastic deformation with simultaneous suppression of luminescence at 4.27 eV STE with symmetric configuration (on-center).

2. An experimental fact of the intrinsic nature of E_x-luminescence in RbI (3.1 eV) and KI (3.05 eV) crystals, discovered under the influence of uniaxial elastic deformation, which is interpreted by the STE’s radiative relaxation in regular lattice nodes with lowering symmetry.

3. In RbI and KI crystals, under the influence of low-temperature (85 K) uniaxial elastic deformation, the effect of lowering the concentration of stable radiation defects was found, which was interpreted based on a comparison of the sizes of the interstitial void and the *H*-center for face-centered (NaCl type) and volume-centered (CsCl type) crystals.

The reliability of the scientific provisions, results and conclusions formulated in the dissertation work is confirmed by the absolute consistency of the experimental results with the fundamental provisions of condensed matter physics, as well as the use of a method for synchronous registration of the temporal and spectral dependence of the intensity of tunneling luminescence of alkali-halide crystals (Patent for utility model No. 6563 RK dated 22.10.2021, certificate of entry of information in the state register of rights to objects protected by copyright No. 12826, 26/10/2020; No. 12980, 03.11.2020) in combination with a special cryostat that allows to deform crystals at low temperatures (Patents RK No. 14831 of 30.06.2004, No. 26141 of 03.08.2012, No. 28731 of 19.06.2014).

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

The experiments related to the optical creation of excitons (5.85 eV) and electron-hole pairs (6.45 eV,) in CsI crystals in the VUF region of the spectrum were performed in the laboratory of "Physics of Ion Crystals" of the Institute of Physics at the University of Tartu, Estonia. Discussions and processing of the obtained experimental results with subsequent interpretation were carried out on the basis of this laboratory under the guidance of Professor Lushchik A.Ch.

The connection of the topic with the plans of scientific works. The dissertation work has been performed within the framework of a grant project funded by the Ministry of Education and Science of the Republic of Kazakhstan "Direct impact on the radiative relaxation of electronic excitations in order to improve the luminescent characteristics of functional materials based on alkali halide crystals" IRN AP08855672 for 2020-2022 years, as well as a grant from young scientists "Experimental studies of the mechanisms of luminescence of KI, RbI and CsI crystals at the activation by cations-homologues and low temperature deformation" IRN AP09057911 for 2021-2023 years.

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

– 7^{th} International Congress on Energy Fluxes and Radiation Effects, EFRE 2020 (Tomsk, Russian Federation, 14-26 September 2020);

– 13^{th} International conference Functional Materials & Nanotechnologies, FMNT 2020 (Vilnius, Lithuania, 23-26 November 2020);

– European Materials Research Society, E-MRS 2021 (France, Lion, 31 May – 3 June 2021);

– 11th International Conference on Luminescent Detectors and Transformers of Ionizing Radiation (12-17 September 2021, Bydgoszcz, Poland).

Publications. According to the results of the research presented in the dissertation, 11 scientific papers have been published, including: 4 articles indexed in the Science Citation Index Expanded in the Web of Science database, and (or) in peer-reviewed scientific publications with a CiteScore percentile in the Scopus database of at least 25; 1 patent for utility model; 1 certificate of entry of information into the state register of rights to objects protected by copyright; 3 articles in other journals of the Republic of Kazakhstan.

The structure and scope of the dissertation. In accordance with the research objective, objectives and scope of the work is performed, the dissertation work contains an introduction, five sections, a conclusion, a list of cited literature and an annex. The work consists of 38 figures, 8 tables and a bibliography of 111 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 current state of the nature of luminescence and the mechanisms of the formation of radiation defects in AHCs allows us to identify the following basic patterns:

1. The intrinsic luminescence and primary radiation defects in the AHCs are born in one act during the relaxation of free electronic excitation through the self-trapped state of an anionic exciton, the predisposed state of which corresponds to the formation of – $X_2^- e^-$.

2. The locally symmetric dependence of the STE ($X_2^- e^-$) structure in the grating of the AHC, from which radiative relaxation occurs, is a unique platform for studying intrinsic luminescence under the influence of low-temperature uniaxial deformation.

3. The locally symmetric dependence of the structure of STE ($X_2^- e^-$) in the lattice of AHCs from which primary radiation defects (*F*, *H*, *α* and *I*-centers) are born is a unique platform for studying the mechanisms of formation of radiation defects under the influence of low-temperature uniaxial deformation.

4. For KI, RbI, CsI and KCl crystals, the temperature dependence of the degree of relative deformation is systematized, on the basis of which the elastic mechanical stress region is established, as well as the temperature dependence of the linear compression (expansion) coefficient in the absence of external influence.

Conclusions on the second section:

1. A multifunctional spectral complex operating in the photon counting mode, in combination with a special cryostat that performs low-temperature deformation, allows recording the spectra of X-ray luminescence (XRL), tunnel luminescence (TL), thermally stimulated luminescence (TSL), as well as time scanning of tunnel luminescence and integral thermally stimulated luminescence.

2. The spectral region of the equipment (2.0-6.0 eV) fully corresponds to the luminescence range of self-trapped excitons in the AHCs, both in regular lattice nodes and the field of local and low-temperature deformations.

3. On the basis of the “Evolution-300” spectrophotometer, an experimental setup for recording the absorption characteristics of crystals under the influence of uniaxial (elastic/plastic) deformation and radiation in a wide temperature range (85-400 K) has been developed.

4. An original system for obtaining a high technical vacuum ($2.66 \cdot 10^{-3}$ Pa) in a cryostat has been developed, which allows for the deformation of crystals at low temperatures (85 K), by sequential pumping with pre-vacuum and adsorption pumps equipped with special nitrogen traps for capturing technical oil vapors.

Conclusions on the third section:

1. The features of radiative relaxation of STEs in CsI crystals with lowering lattice symmetry of low-temperature (83 K) uniaxial elastic deformation (ε=0.5-0.7%) were investigated by the experimental method of luminescence spectroscopy and the effect of sensitivity of intrinsic luminescence (4.27 eV and 3.67 eV) to elastic deformation and ionizing radiation sources was found.

2. It has been established that the luminescence intensity of elastically deformed CsI crystals increases due to the luminescence flare at 3.67 eV STE with an asymmetric configuration (weak off), while the luminescence is suppressed at 4.27 eV STE with a symmetrical configuration (on).

3. The study of the temperature dependence of CsI luminescence under elastic deformation made it possible to determine the activation energy (Δ=8 MeV) between on (4.27 eV) and weak off (3.67 eV) configurations of STE.

Conclusions on the fourth section:

1. X-ray luminescence spectra were recorded experimentally, on the basis of which the reinforcing effect of elastic deformation on the intensity of all luminescence bands in RbI (3.9 eV (σ), 3.1 eV (E_x) and 2.3 eV (π) and KI (4.16 eV (σ), 3.05 eV (E_x) and 3.3 eV (π) crystals was demonstrated when the lattice symmetry decreases at 85 K, unlike CsI crystals.

2. The intrinsic nature of E_x-luminescence in RbI (3.1 eV) and KI (3.05 eV) crystals has been established on the basis of a correlated increase in its intensity with the intrinsic σ- and π-luminescence's of STE under increasing exposure to the degree of low-temperature (85 K) uniaxial elastic deformation.

3. The uniaxial elastic deformation method, which increases the probability of self-trapping of anionic excitons in regular lattice nodes, allowed to solve the historical controversial issue about the nature of E_x-luminescence in RbI (3.1 eV) and KI (3.05 eV) crystals in favor of intrinsic luminescence.

4. In RbI and KI crystals, an increased concentration of point radiation defects (108 K) and $F^{/}$-centers (105 K), instead of three-halide I_3^--centers (370-390 K) formed during the association of interstitial halogen atoms, was experimentally determined by registering TSL and TSL spectra.

Conclusions on the fifth section:

By experimental methods of luminescence and absorption spectroscopy, as well as by evaluating the effectiveness of stabilization of *H*-centers by comparing the size of halogen atoms (R_a^0) with the size of the internode ($R_{\max}$), the following basic patterns have been established:

1. Uniaxial elastic deformation applied at 85 K reduces the efficiency of formation of radiation defects (V_2 and *F*-centers) in KI and RbI crystals, and in KCl crystals the concentration of radiation defects (V_2, V_4 and *F*-centers) does not depend on the degree of low-temperature uniaxial deformation. The lowering effect of the formation of stable radiation defects in KI and RbI crystals is interpreted by the impossibility of placing *H*-centers in interstitial lattice voids ($R_a^0 > R_{\max}$).

2. The local deformation created by the doping of a light lithium (Li) cation in the KCl matrix increases the efficiency of the formation of radiation defects (V_2 and *F*-centers) in KCl-Li crystals.

3. Plastic deformation, which creates point vacancy defects ($\upsilon_a^+\upsilon_c^-$), promotes radiation stimulation of halogen radiation defects of type V_2, V_4-centers in pure KCl crystals.

4. A semi-quantitative analysis of the evaluation of the effectiveness of radiation defect formation based on the dimension of *H*-centers under uniaxial elastic deformation for face-centered (type NaCl) and volume-centered (type CsCl) AHCs has been developed.

5. On the basis of the mechanism of interaction of two interstitial halogen atoms (*H*-centers), the efficiencies of radiation defect formation in KI, RbI and KCl crystals with lowering symmetry of low-temperature (85 K) uniaxial elastic, local (Li) and uniaxial plastic deformation are interpreted.

In conclusion, the main results are presented:

1. By the experimental method of luminescent spectroscopy, it was found that the luminescence intensity of elastically deformed CsI crystals increases due to the luminescence ignition at 3.67 eV STE with an asymmetric configuration (weak off) while the luminescence is extinguished at 4.27 eV STE with a symmetrical configuration (on).

2. The study of the temperature dependence of CsI luminescence under elastic deformation made it possible to determine the activation energy (Δ=8 MeV) between on (4.27 eV) and weak off (3.67 eV) configurations of STE.

3. X-ray luminescence spectra were recorded experimentally, on the basis of which the reinforcing effect of elastic deformation on the intensity of all luminescence bands in RbI crystals (3.9 eV (σ), 3.1 eV (E_x) and 2.3 eV (π) and KI (4.16 eV (σ), 3.05 eV (E_x) and 3.3 eV (π) with lowering lattice symmetry at 85 K, unlike CsI crystals.

4. The intrinsic nature of Ex-luminescence in RbI (3.1 eV) and KI (3.05 eV) crystals has been established on the basis of a correlated increase in its intensity with its own σ- and π-luminescences of STE under increasing exposure to the degree of low-temperature (85 K) uniaxial elastic deformation.

5. In RbI and KI crystals, an increased concentration of point radiation defects (108K) and $F^{/}$-centers (105K), instead of three-halide I_3^--centers (370-390K) formed during the association of interstitial halogen atoms, was experimentally established by registering TSL and TSL spectra.

6. Uniaxial elastic deformation applied at 85 K reduces the efficiency of formation of radiation defects (V_2 and *F*-centers) in KI and RbI crystals, and in KCl crystals the concentration of radiation defects (V_2, V_4 and *F*-centers) does not depend on the degree of low-temperature uniaxial deformation.

7. A semi-quantitative analysis has been developed to evaluate the effectiveness of radiation defect formation based on the dimension of *H*-centers under uniaxial elastic deformation for face-centered (NaCl type) and volume-centered (CsCl type) AHCs. The lowering effect of the formation of stable radiation defects in KI and RbI crystals is interpreted by the impossibility of placing H-centers in interstitial lattice voids ($R_a^0 > R_{\max}$).

8. Local (Li) and plastic ($\upsilon_a^+\upsilon_c^-$) deformations contribute to an increase in the efficiency of the formation of radiation defects (V_2 and F - centers) in the KCl matrix.