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The nature of luminescence of KI and KI-Na crystals at low temperature deformation after natural decrease in the symmetry of the lattice

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The X-ray luminescence spectra at low temperature (90K) uniaxial deformation were researched for KI and KI-Na crystals, that were stored for more than 10 years. The following regularities were observed: firstly, the intensities of the intrinsic emission bands at 3.3 eV (π) and 4.1 eV (σ) become equal in comparison with freshly grown crystals; and secondly, with an increase in the degree of low-temperature uniaxial deformation, a gradual shift of the emission spectra occurs in two directions: the luminescence maximum at 3.3 eV shifts towards short wavelengths, the final position is fixed at 3.9 eV, which practically merges with σ -luminescence; the radiation maximum at 3.0 eV (Ex-radiation) is shifted toward long wavelengths, the final position which is fixed at 2.8 eV. Thus, low temperature uniaxial deformation leads to the separation of the emission spectra at 3,3 eV(π) $\rightarrow$ 3,9 eV and 3.0 eV (E_x) $\rightarrow$ 2,8 eV, which are interpreted by the separation of weak $\rightarrow$ on and weak $\rightarrow$ strong exciton configurations , respectively.

Keywords: E_x -radiation, low temperature uniaxial deformation, KI, KI-Na, X-ray luminescence.

Introduction

The luminescence of alkali halide crystals (AHC) is very sensitive to a decrease in the symmetry of the lattice by impurity homologs of various sizes, the degree

of elastic and plastic deformation [1-7]. Cation and anion homologs, as well as vacancies, promote the effective relaxation of electronic excitations around itself, as a result of which we find the luminescence of an self-trapped exciton in the field of point defects [1, 2].

Experiments on low temperature deformation show that the elastic deformation leads to an increase in the probability of radiative annihilation of self-trapped excitons at regular lattice sites because of the shortening of the mean free path of electronic excitations [1-4]. On the basis of the KI-Tl crystal, the intensity redistribution was favored in favor of intrinsic luminescence with an increase in the degree of elastic deformation [5].

The peak of thermally stimulated luminescence in a high-temperature region with a maximum at 340 K was detected in an undeformed KI crystal. It corresponds to the thermal destruction of $(I_3^-)^0_{aca}$ - centers and is absent in the case of low temperature deformation [8]. This means that in the field of uniaxial deformation there is practically no association of *H*-centers with each other, the product of which are $(I_3^-)^0_{aca}$ - centers. But in this case low temperature intense peaks of thermally stimulated luminescence of V_K, V_F, V_{KA}, and F' - centers were recorded.

The luminescence of self-trapped excitons with maxima at 4.42 eV and 2.3 eV was recorded in KI crystals at low temperature deformation along the <100> and <110> directions [9].

However, until now it has not been possible to investigate the features of the luminescence of AHC under conditions of a natural decrease in the symmetry of the lattice by prolonged storage at room temperature in vacuum, which is very important for predicting the efficiency of operated scintillation detectors.

Alkali halide scintillators as reliable detectors are used in such super-active experiments, such as the energy registration of particles of dark matter [10-11]. The basis of the installation are 25 ultrapure NaI crystals weighting about 250 kilograms. It is assumed that as the Weak Interaction Matter Particles (WIMP) passes through such a crystal, electronic excitations arise in it, their further relaxation ends with a flash of light.

Concerning the nature of E_x-radiation in KI and RbI crystals, the controversy is still going on and the question has not been resolved.

Thus, the relevant issue is to increase the quantum yield of luminescence and to identify the nature of the luminescence of alkali halide crystals, which are scintillation detectors.

Technique of experiment

The physical essence of the X-ray luminescence spectrum of alkali halide crystals is based on recording the spectral composition of the crystal radiation at constant irradiation with X-rays. The energy of the X-ray quantum at absorbing by the crystal is spent on the excitation of the electronic subsystem, as a result of which high-energy electronic excitations are created in alkali halide crystals. In a very short time, they are transformed into low-energy electronic excitations

- excitons, the further relaxation of which finishes either with the creation of radiation defects or with the emission of a crystal.

The X-ray luminescence spectra of the crystals were automatically scanned by the high- speed monochromator MSD-2 and the detector H8259-01 (Hamamatsu) in the photon counting mode, the sensitivity of which has a maximum value in the range 200-800 nm. The spectra were scanned in automatic mode using a program developed by us. Further spectra were processed by the Origin.

When choosing the sources of ionizing radiation, the most suitable was the bremsstrahlung radiation from the X-ray unit RUP-120 (3 mA, 100 kV). This is due to the fact that the hard X- ray radiation, unlike the characteristic, firstly, penetrates the entire thickness of the crystal, and, secondly, does not create structural defects that impair the optical transparency of the crystal in the spectral range 2-6 eV. Reabsorption of radiation spectra by radiation defects is excluded. The design of the cryostat made it possible to determine experimentally and determine the required degree of deformation of the crystal. The uniaxial deformation in the <100> direction of the crystals was carried out at 100 K using a special cryostat [12].

The crystals were grown at the Institute of Physics of the Tartu University, Estonia, with a special technique including processing of the alloy with gaseous halogen, multiple zone melting, and then growing according to the Stockbarger method in a vacuum ampule or by the method of Kyropoulos in a helium atmosphere.

Results and Discussion

The emission spectrum of a self-trapped exciton (STE) in KI crystal at 4.2K consists of two components: σ-luminescence with a maximum of 4.15 eV and a π-luminescence with a maximum of 3.31 eV [13]. σ-luminescence corresponds to the singlet state of an exciton, and π-luminescence - a triplet state. At the optical creation of electron-hole pairs and in X-excitation, the intensity of σ-luminescence upon heating begins to be quenched only after 60 K, and to 80 K it decreases only three times, and π-emission only at temperatures above 90 K [14]. This means that if STE are created, then at 100 K they can be reliably recorded. In the X-ray luminescence spectrum of the non-stressed KI crystal, in addition to weak σ- and π-luminescence, a more intense glow with a maximum of about 3.02 eV is seen.

The application of an uniaxial compression leads to a strong increase in the emission of STE [15]. Moreover, the σ- and π-luminescence of STE increase almost identically. The luminescence 3.02 eV increases with compression, too, although less efficiently. In the phosphorescence spectrum of a deformed KI crystal, luminescence at 3.02 eV is also present: it says that it can arise as a result of tunnel recombinations between radiation defects.

In the X-ray spectra of a deformed KI crystal, the intensity of σ- and π-luminescence of STE increases 12-15 times. In this case, luminescence with a maximum at 3.02 eV disappears. The effect of amplification of STE luminescence

upon lowering the symmetry of the lattice is patented as a method of enhancing the intrinsic luminescence of alkali halide crystals [16].

In principle, uniaxial deformation along the crystallographic direction <100> lowers the symmetry of the crystal structure of alkali halide crystals. The point symmetry group decreases from O_h to D_{4h}. In the uniaxially deformed crystal, along with the compression directions, there are also tensile directions. According to the estimates of [17], the compression in absolute value is an order of magnitude larger than the stretching. Therefore, in a uniaxially compressed crystal, as the symmetry of the lattice is lowered, pairs of closely spaced anions are created, which promote self-trapping of electronic excitations in AHC.

X-ray luminescence spectra were studied for low temperature (100 K) uniaxial deformation of KI and KI-Na crystals after prolonged (more than 10 years) storage at room temperature (Figures 1, 2).

The first shows the X-ray luminescence spectrum of KI crystal that was stored at room temperature for a long time at 100 K, depending on the degree of relative uniaxial deformation. Curve 1 is a non-deformed state of the investigated object KI. Curves 2-6 demonstrate the change in the X-ray luminescence spectrum as a function of the degree of uniaxial deformation, while the degree of deformation was purposefully increased uniformly from 0.04 % to 0.2 %.

X-ray luminescence spectra of KI and KI-Na crystals, which were stored at room temperature for a long time after uniaxial deformation at 100 K, are presented in Figure 2 for a correct explanation of the processes. KI crystal is represented by two curves before deformation (curve 1) and after deformation to 0.2 % (curve 2). Curve 3 shows the X-ray luminescence spectrum of the KI-Na crystal at 0.2 %

Figure 2 shows X-ray luminescence spectrum of KI-Na crystal that was stored for a long time at room temperature after uniaxial deformation up to 0.2 % at 100 K for a correct explanation of the proceeding processes.

The analysis of figures 1 and 2 allows us to identify the following patterns:

1) A natural decrease in the symmetry of KI crystals (zone-purified) and KI-Na (0.3 %) leads to a sharp decrease in the intensity of π (3.3 eV) and E_x (3.0 eV) luminescence bands, which become comparable with intensity of σ (4.17 eV)-luminescence;

2) External mechanical low temperature deformation radically changes the spectral composition of the X-ray luminescence;

3) With increasing degree of deformation, the luminescence spectra are gradually shifted in two directions: the maximum of the bands π (3.3 eV) - the luminescence shifts towards short wavelengths, the final position is fixed at 4.39 eV (section A in Figure 1); the maximum of the bands E_x (3.0 eV) - the luminescence shifts towards long wavelengths, the final position of which is fixed at 2.63 eV (plot B in Figure 1);

4) An analogous displacement of the luminescence bands was also observed for the KI-Na crystal (0.3 %).

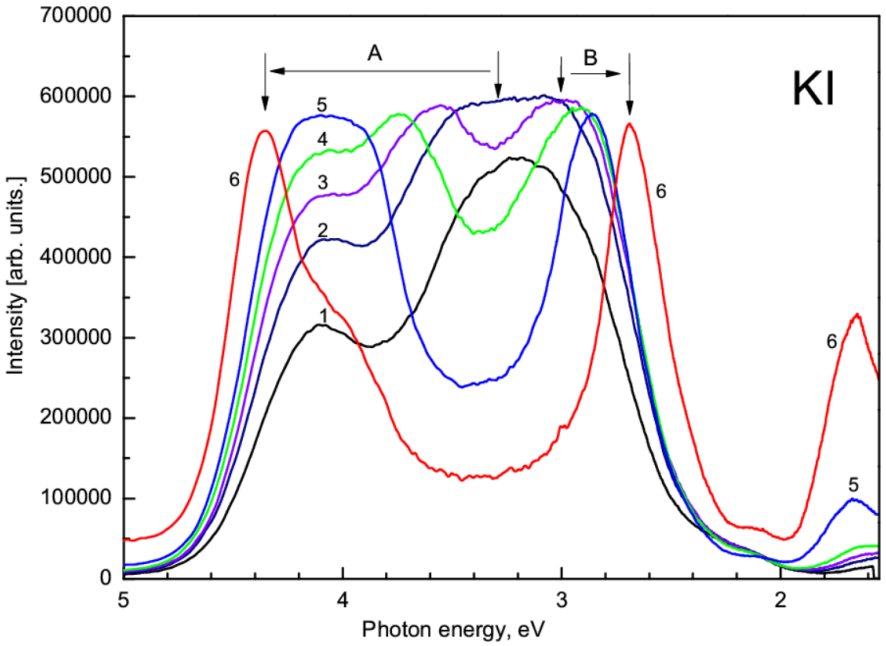

Figure 1. X-ray luminescence spectra of KI crystal stored at room temperature for a long time at 100 K, depending on the degree of relative uniaxial deformation: 1 - before deformation, 2 - at 0.04 %, 3 - at 0.08 %, 4 - at 0.12 % , 5 - at 0.15 %, 6 - at 0.2 %.

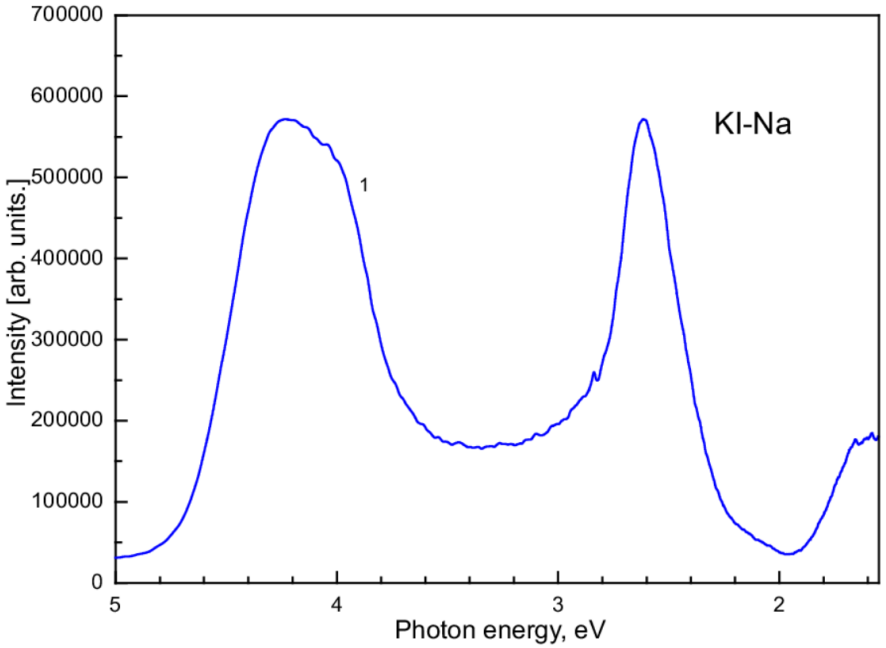

Figure 2. The X-ray luminescence spectrum of a KI-Na crystal that was stored for a long time at room temperature after uniaxial deformation up to 0.2 % at 100 K.

Experiments show that low temperature uniaxial deformation leads to the separation of emission spectra at 3.3 eV (σ) $\rightarrow$ 4.39 eV and 3.0 eV (E_x) $\rightarrow$ 2.63 eV.

According to Kanno's suggestion [7], there are three types of STEs that can differ in structure from the geometric point of view. In crystals of the I group, the core of the STE occupies two halogen sites (on-type STE on-type with D_{2h} symmetry), in crystals of group III there is one halogen site (STE of the strong off type with C_{2v}), group II has some intermediate weakly asymmetric position with

a weak off configuration). The displacement of the nucleus from the centrally symmetric position to the strongly asymmetric leads to a decrease in the degree of spatial overlapping of the wave functions of the nucleus and the electron and, correspondingly, to an increase in the lifetime of the STE.

At the moment of self-trapping of the exciton, there is a violation of both the translational symmetry in the region of the creation of STE and the inversion symmetry in the process of the intercombination S-T transition into STE. This leads to the appearance of adiabatic instability, spontaneously leading to the formation of off-configuration STE in a number of alkali halide crystals.

In KI and KI-Na crystals, depending on the degree of deformation, the mechanism of separation of closely spaced π (3.3 eV) and E_x (3.0 eV) luminescence bands was demonstrated experimentally. As a result, π (3.3 eV)- luminescence of self-trapped exciton, which has an asymmetric configuration, acquires a symmetric (weak $\rightarrow$ on), and E_x (3.0 eV)-luminescence, on the contrary, assumes a more asymmetric configuration, according to the Kanno classification [7].

Concerning the nature of E_x (3.0 eV)-luminescence in KI and KI-Na crystals an important experimental result is obtained - that it becomes dominant and its maximum correlates with an increase in the degree of low-temperature deformation (3.0 eV $\rightarrow$ 2.63 eV), and not with the concentration of sodium ions in crystals. As a rule, low temperature elastic deformation leads to an increase in intrinsic luminescence due to impurities, which is interpreted by the growth of self-trapping of halogen excitons at regular lattice sites [1-5]. This effect was specially investigated for the KI-Tl crystal and a redistribution of the intensity was observed in favor of intrinsic luminescence with an increase in the degree of elastic deformation [5]. On the basis of the experimental data, we can assume that we are dealing with halogen exciton-like formations of various configurations, which are very sensitive to the degrees of low temperature deformation.

Conclusion

In X-ray luminescence spectra, at low temperature (100 K) uniaxial deformation of KI and KI-Na crystals, stored for a long time at a room temperature, the following regularities were observed:

- in the absence of deformation, the intensities of the intrinsic emission 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;
- with an increase in the degree of low-temperature uniaxial deformation, the radiation spectra are gradually shifted in two directions: the radiation maximum at 3.3 eV shifts toward short wavelengths up to 3.9 eV, which practically coincides with σ-luminescence; the radiation maximum at 3.0 eV (E_x-radiation) shifts toward long wavelengths up to at 2.85 eV.

Consequently, an uniaxial deformation at 100 K leads to the separation of the emission spectra at 3.3 eV (π) $\rightarrow$ 4.39 eV and 3.0 eV (E_x) $\rightarrow$ 2.63 eV, which

are interpreted by the splitting of weak → on and weak → strong configurations excitons, respectively.

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

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