The Influence Of Low Temperature Uniaxial Stress On Structure Of Self-Trapped Excitons In Alkali Halide Crystals

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Abstract – The influence of low temperature uniaxial deformation on a structure of self-trapped excitons (STE) in irradiative relaxation in alkali halides crystals is experimentally established. In face-centered crystals there is a redistribution of luminescence intensities for the advantage of symmetric configuration of STE (strong → weak → on or III → II→ I-types), and in volume-centered crystals – for the advantage of asymmetric configuration of STE (on → weak or I → II-types). The external deformation on direction <100> leads to anions' effective sliding in direction <110> which coincides with STE stress direction that in turn brings to mainly STE's symmetric configuration creation, and deformation in direction <110> acting on perpendicular STE' length leads to their stretching that in turn brings to STE's symmetric configuration creation with more polarization degree.

1. Introduction

Nowadays the intrinsic luminescence of alkali halide crystals (AHC) is interpreted as irradiative relaxation of self-trapped excitons (STE) that consist of three configurations [1]. The base for three classifications of STE is value of Stocks Shift luminescence loses. It is considered that if Stocks Shift values are S_R =0.25÷0.34 then it describes self-trapped exciton of I-type with central-symmetric (on) configuration; if Stocks Shift values are S_R =0.35÷0.46, then it describes self-trapped exciton of II-type with weak asymmetric (weak off) configuration; if Stocks Shift values are S_R=0.46÷0.65, then it describes self-trapped exciton of II-type with strong asymmetric (strong off) configuration.

It is reasonable to expect to influence on the processes of creation, migration and self-trapping of excitons that are sensitive to symmetric arrangement of crystal creative particles changing nearest environment around STE. One of such methods that bring to crystal structure symmetry lowering is uniaxial stress.

The present work represents analysis on influence of elastic stress influence on intrinsic luminescence of alkali halide crystals with a consideration of self-trapped exciton configurations. From the experimental point of view, at elastic stress a unique situation for investigation of AHC's intrinsic luminescence: all existing impurity luminescence that are characteristic for irradiative annihilation of self-trapped excitons

disappear because of exciton free path decrease before self-trapping; as a result dominative luminescence becomes self-trapped exciton luminescence in regular lattice sites [2].

2. Experimental device

The main point of the device is cryostat that we worked out and patented. The cryostat was used for crystal luminescence characteristics measuring at direct influence of low temperature (100 K) elastic stress. The deformation degree of the crystal is given by the step of compression screw (Δl=1 mm at full turn of crystal holder) and is determined with the following formula:

$$\varepsilon = \frac{l_0 - l}{l_0} \cdot 100\% = \frac{\Delta l}{l_0} \cdot 100\%,$$

where l_0 is the initial crystal length before deformation, which is measured with a micrometer or microscope, l is the length of the crystal after deformation.

The cryostat construction allows to determine experimentally Δl and to set the necessary crystal deformation degree, and mechanical stress can be taken off at any time and renewed at different temperatures. The necessary value of crystal relative deformation (ε, %) at 80 K inside of cryostat is calculated by Δl, then the value is set with the turn of cryostat head on nonius scale (S) according to calibration curve.

3. The experimental results

3.1 Crystal deformation on crystallographic direction <100>

Figure 1 shows the X-ray (XR) luminescence spectra for KI (a), RbI (b) and NaBr (c) at 100 K before (1) and at different levels (2 – ε =0,8%, 3 – ε =1,2%) of low temperature stress on crystallographic direction <100>. The dashed line shows approximate spectral area for three types of STE according to the values of relative Stocks shift – S_R (Fig. 1). As it is seen from the Fig. 1a the luminescence spectra for KI crystal has three bands: σ (4,17 eV), π (3,3 eV) and E_x (3,02 eV), their intensity ratio changes according to the level of low temperature stress. It follows from the given experimental results (Fig. 1a) in KI crystal with the growth of relativity level in three bands σ (3,89 eV), E_x (3,1 eV) and π (2,3 eV),the ratio of uniaxial stress intensities (curves 2 and 3 with respect to 1) E_x – luminescence converts to π – luminescence as in the

case of excitation with phonons with energy corresponding to exciton excitation.

The same effect of luminescence band redistribution between off (π) and weak off (E_x) – centers is also found in the XR spectra of RbI crystal at low temperature uniaxial stress (Fig. 1b). RbI crystal XR spectra also consists of three bands: σ (3,89 eV), E_x(3,1 eV) and π (2,3 eV), their intensity ratio also changes according to the level of low temperature stress. In RbI crystal with the relative uniaxial stress degree growth (curve 1 and 3 with respect to 1) π – luminescence intensity decreases gradually and E_x (3,1 eV) – luminescence intensity increases, i.e. there is a redistribution between them. Note, there is a growth of σ-luminescence intensity (curve 3, Fig. 1b) which is of the structure of self-trapped exciton with on-configuration. At the first sight there is contradiction in the luminescence band redistribution between π- и E_x-luminescence in KI and RbI crystals at low temperature stress. E_x-luminescence intensity decreases and π-luminescence – increases in KI crystal, and in RbI crystal – vice versa.
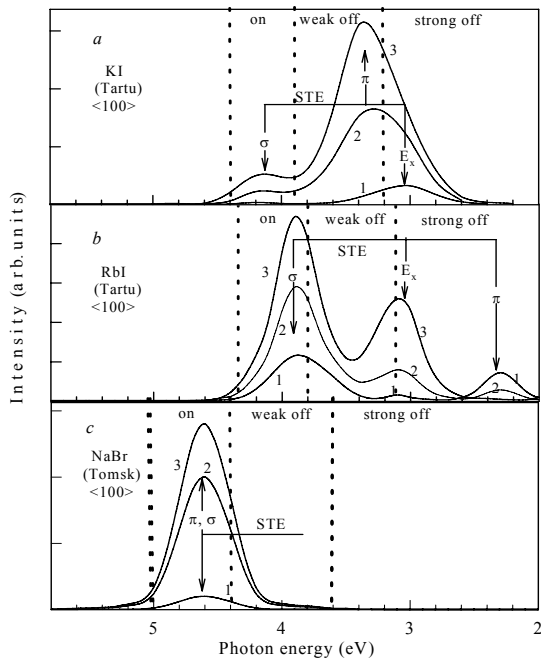

Fig. 1. The X-ray luminescence of KI (a), RbI (b) and NaBr (c) crystals at 100 K before (1) and at different levels (2 – ε =0,8%, 3 – ε =1,2%) of low temperature stress on crystallographic direction <100>

This contradiction becomes obvious if to take onto consideration the structure of self-trapped exciton, which irradiative relaxation finishes with E_x – и π-luminescence. In KI crystal E_x – luminescence refers to the structure of strong off-center and on spectral content is at low energy part of irradiation spectra with

respect to π-luminescence, which refers to the structure of weak off-center. In RbI crystal π-luminescence refers to the structure of strong off – center and on spectral content is at low energy part of irradiation spectra with respect to E_x – luminescence, which refers to the structure of weak off-center. From here it follows that uniaxial elastic low temperature stress promotes the creation of self-trapped exciton of more symmetric configuration in the direction – strong →weak or III→ II types.

If π – luminescence in RbI crystal has the structure of strong off – configuration, in KI crystal – weak off-configuration, and in NaBr crystal – on-configuration. In NaBr crystal where ther is only luminescence band of self-trapped exciton with symmetric on-configuration, the uniaxial stress strengths its intensity without band luminescence redistribution effect (compare curves 2 and 3, Fig. 1). These results unambiguously prove that uniaxial stress acts effectively in the diretion that brings asymmetric STE to symmetric configuration (strong →weak →on or III→ II→ I-types).

3.2 The crystal deformation on crystallographic direction <110>

In CsI and CsBr crystals where self-trapped excitons are orientated in direction <100>, the directed deformation in <110> can contribute in the STE luminescence with "assymetric" configuration in opposite direction – on→weak off →strong off.
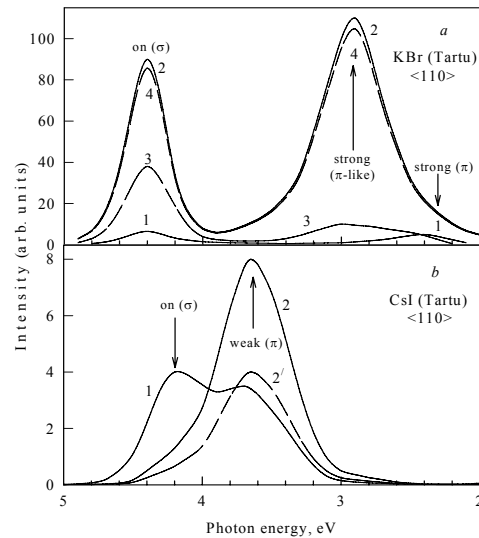

Fig. 2. The X-ray spectra luminescence of KBr (a) and CsI (b) crystals at 100 K before and at low temperature deformation (ε=1.5%) on crystallographic direction <110>

The experimental results on low temperature uniaxial (<110>) stress in KBr (a) and CsI (b) are presented in Fig. 2. It is seen that in this case there is neatly expressed effect of STE intrinsic luminescence strengthening too. But at deformation in direction

<100> the dominion luminescence was σ-luminescence (See Fig. 2), and at deformation in direction <110> the dominion luminescence was the one with a maximum of 2.95 eV with a big relative Stocks shift 1 – before deformation; 2 – at uniaxial stress (100K); 2'- normalized spectra of curve 2with respect to curve 1; 3- after uniaxial stress removal; 4 – at additional deformation till initial stress level. (S_R=0,56) which is typical for STE with strong asymmetric configuration (Fig. 2, curve 2). Note, there were not any additional registered luminescence bands except intrinsic σ -, π -luminescence at the absence of deformation in XR spectra of KBr crystal (Fig. 2, curve 1). As for luminescence band at 2.95 eV nature – we can suppose it is connected with exciton luminescence self-trapped near divacancies $-e_d^0$ (3.4eV), quartets of vacancies $- e_q^0$ (2.88 eV) or non controlled impurities.

From all above mentioned competing luminescence for spectral content the most suitable is luminescence of excitons self-trapped near quartets of vacancies $- e_q^0$ (2.88 eV). However in KBr crystal large vacancy formations as quartets of vacancies, which are completely immovable at low temperatures are created at high temperatures (300 K) by plastic deformation (ε = 4–6 %) [5]. If luminescence at 2.95 eV at RX spectra of KBr crystal is considered to be connected with quartets of vacancies then after stress removal this luminescence intensity must remain unchanged as the concentration of earlier created vacancy defects in crystal with temperature lowering remains constant. After stress removal at the same temperature (100 K) acting in direction <110> the luminescence intensity at 2.95 eV sharply decreases and only 10% intensity remains (Fig. 2a, curve 3). If we set the same deformation levels at 100K then practically the same values for σ – intensity and luminescence at 2.95 eV appear (Fig. 2a, curve 4); this effect is conditioned by elastic deformation but not lattice vacancy defects that are created by plastic deformation. Also there is no argument to bind the luminescence with maximum at 2.95 eV with luminescence of excitons self-trapped near impurity as impurity luminescence completely disappear under stress because of exciton free path reduction before self-trapping near impurity [6]. Since this such luminescence is typical for crystal's intrinsic lattice then it reasonable to assume its appearance as a result of elastic deformation on different STE configurations.

If uniaxial stress in face centered (F) AHC is applied in crystallographic direction <110> then there is a possibility of stretching perpendicular to the stress of bihaloid STE nuclei that makes possible the creation of STE with strong-asymmetric configuration – strong off (π – like) (Fig. 2a).

In lattices of CsI type the uniaxial stress within crystal is realized in crystallographic direction <110>. That is why during the CsI crystal stress there must be observed the exciton component stretching along STE direction which brings to asymmetric configuration. Here we think prevailing will be lattice stretching then compression. This agrees with experimental results on measurements of uniaxial stressed CsI crystal XR luminescence (Fig. 2 b).

In CsI crystal at uniaxial stress the luminescence band at 4.25 eV disappears; it has STE central-symmetric configuration (Fig. 2 b) on which Stocks shift is S_R =0.26. however the unixial stress of CsI crystl brings to the strengthening of luminescence band with maximum at 3.67 eV that corresponds to asymmetric (weak off) STE configuration (S_R=0.37).

Thus, at low temperature uniaxial stress in face centered AHC there is a redistribution of luminescence intensity in favor of STE's symmetric configuration, and in body centered AHC – vice versa – in favor of STE's asymmetric configuration.

The influence of low temperature elastic uniaxial stress (100 K) on a configuration of self-trapped excitons (STE) in irradiative relaxation in alkali halides crystals (AHC) is experimentally established with luminescence spectroscopy. In face-centered crystals there is a redistribution of luminescence intensities for the advantage of symmetric configuration of STE (strong →weak →on or III→ II→ I – types), and in volume-centered crystals, vice versa – for the advantage of asymmetric configuration of STE (on →weak or I→ II – types). The external deformation on direction <100> leads to anions' effective sliding in direction <110> which coincides with STE stress direction that in turn brings to mainly STE's symmetric configuration creation, and deformation in direction <110> acting on perpendicular STE' length leads to their stretching that in turn brings to STE's symmetric configuration creation with more polarization degree.

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