Effect of intrinsic luminescence of alkali halide amplification by low temperature deformation

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Abstract. By using luminescence spectroscopy, we have established the influence of low-temperature uniaxial deformation on the configuration of a self-trapped exciton (STE) in alkali halide crystals (AHC) at the instant of radiative relaxation. In face-centered crystals, there occurs the redistribution of the luminescence intensity from the asymmetric configuration of STE to the symmetric one (III → II → I-types), whereas in volume-centered crystals, on the contrary, the evidence counts in favour of the asymmetric configuration of STE (I → II – types). The external deformation in the <100> direction leads to an effective sliding of anions in the <110> direction that coincides with the direction of the STE squeeze which classically makes for the creation of the symmetric STE configuration in the <110> direction, acting perpendicularly to the STE’ length results in their stretching, which in turn brings into the creation of the asymmetric STE configuration with a higher degree of the polarization.

1. Introduction
It is well known that structure of self-trapped exciton (STE) in alkali halide crystals (AHC) corresponds to the \( X_2^- e^- \), hole component of which has \( (X_2^-)_n^0 \) - molecule that is located in to anion lattice sites and orientated on crystallographic axis <110> for face-centered AHC and <100> for body-centered AHC [1, 2]. According to contemporary conceptions [1] the intrinsic AHC luminescence can be classified with three AHC configurations. The base for all three exciton classification is values of Stock luminescence shift - \( S_R = (E_{ex}^\sigma - E_{(\sigma,\pi)}^I)/E_{ex}^\pi \), where \( E_{ex} \) - the locations of free exciton absorption maximums with n=1; \( E_\sigma \) and \( E_\pi \) – the locations of singlet (\( \sigma \)) and triplet (\( \pi \)) AHC maximums accordingly. It is thought [1] that if values \( S_R =0.25\div0.34 \) then it self-trapped exciton of I-type with central-symmetric (on) configuration; if \( S_R =0.35\div0.46 \), then it is self-trapped exciton of II-type with weak-asymmetric (weak off) configuration; if \( S_R =0.46\div0.65 \), then it is self-trapped exciton of III-type with strong-asymmetric (strong off) configuration. The present work represents the analysis of the influence of elastic stress on intrinsic luminescence of alkali halide crystals taking into account the self-trapped exciton configuration.

2. Experimental device
The luminescence device allows registering AHC luminescence spectra in a wide range in an automatic mode from a remote control MSD-2; the crystals are previously stressed in vacuum at low
temperatures in a special cryostat. The cryostat construction allows to determine experimentally and to set the necessary crystal deformation degree.

3. The experimental results and discussion

The structure of the STE in AHC is sensible to the location of crystals-formation particles. Here we come across the question: how directed (<100>) uniaxial stress, which lowers the lattice symmetry can influence on different STE configurations 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: $\sigma$ (4,17 eV), $\pi$ (3,3 eV) and Ex (3,02 eV), their intensity ratio changes according to the level of low temperature deformation. It follows from the given experimental results (Fig.1a) in KI crystal with the growth of relativity level in three bands $\sigma$ (3,89 eV), Ex (3,1 eV) and $\pi$ (2,3 eV),the ratio of uniaxial stress intensities (curves 2 and 3 with respect to 1) Ex-luminescence converts to $\pi$- luminescence as in the case of excitation with phonons with energy corresponding to exciton excitation.

The same effect of luminescence band redistribution between off ($\pi$) and weak off (Ex)-centers is also found in the XR spectra of RbI crystal at low temperature uniaxial deformation (Fig.1b). RbI crystal XR spectra also consists of three bands: $\sigma$ (3,89 eV), Ex (3,1 eV) and $\pi$ (2,3 eV), their intensity ratio also changes according to the level of low temperature deformation. In RbI crystal with the relative uniaxial stress degree growth (curve 1 and 3 with respect to 1) $\pi$-luminescence intensity decreases gradually and Ex (3,1 eV)-luminescence intensity increases, i.e. there is a redistribution between them. Note, there is a growth of $\sigma$-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 $\pi$- and Ex-luminescence in KI and RbI crystals at low temperature deformation. Ex-luminescence intensity decreases and $\pi$-luminescence – increases in KI crystal, and in RbI crystal – vice versa.

This contradiction becomes obvious if to take into consideration the structure of self-trapped exciton, which irradiative relaxation finishes with Ex- and $\pi$-luminescence. In KI crystal Ex- luminescence refers to the structure of strong off-center and on spectral content is at low energy part of irradiation spectra with respect to $\pi$-luminescence, which refers to the structure of weak off-center. In RbI crystal $\pi$- luminescence refers to the structure of strong off-center and on spectral content is at low energy part of irradiation spectra with respect to Ex-luminescence, which refers to the structure of weak off-center. From here it follows that uniaxial elastic low temperature deformation promotes the creation of self-trapped exciton of more symmetric configuration in the direction - strong $\rightarrow$weak or III $\rightarrow$ II types.

If $\pi$-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 there is only luminescence band of the self-trapped exciton with symmetric on-configuration, the uniaxial stress strengths its intensity without band luminescence redistribution effect. These results unambiguously prove that uniaxial stress acts effectively in the direction that brings asymmetric STE to symmetric configuration (strong $\rightarrow$weak $\rightarrow$on or III $\rightarrow$ II $\rightarrow$ I-types).

The crystal deformation on crystallographic direction <110>. Note, among AHC in CsI and CsBr crystals that have body-centered crystal lattices self-trapped excitons are orientated on crystallographic direction <100>.

The experimental results on low temperature uniaxial (<110>) stress in CsI (c) are presented in Fig.1. If uniaxial stress in face centered 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 ($\pi$-like).
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. 1c).

In CsI crystal at uniaxial stress the luminescence band at 4.25 eV disappears; it has STE central-symmetric configuration (on) (Fig. 1c) which Stocks shift is $S_R = 0.26$. However the uniaxial stress of CsI crystal 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 deformation 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.

![Figure 3](image-url)

**Figure 3.** The X-ray luminescence of KI (a), RbI (b) and CsI (c) crystals at 100 K before (1) and at different levels ($2 - \varepsilon = 0.8\%$, $3 - \varepsilon = 1.2\%$) of low temperature stress. 2'- normalized spectra of curve 2 with respect to curve 1.
4. Conclusion

Thus, STE structure is sensitive to low temperature deformation: in face centered AHC there is a redistribution of luminescence intensity in favor of STE symmetric configuration, and in body centered AHC – vice versa – in favor of STE asymmetric configuration. The effect of luminescence’s amplification of self-trapped excitons with symmetric configuration is explained by the compression of self-trapped exciton along its length, and the luminescence’s amplification with asymmetric configuration - by self-trapped exciton stretching at the influence of low temperature uniaxial deformation.

The experimental method for the determination of the activation energy between channels of radiative and non-radiative annihilation of self-trapped excitons in alkali halide crystals was worked out. The principle of the method lies in the registration of the temperature dependence of self-trapped excitons’ luminescence with and without the influence of low temperature uniaxial elastic stress.

The activation energy of temperature luminescence quenching of self-trapped excitons was determined in crystals: KBr (for $\sigma$: $\Delta \varepsilon=7$ meV) $\rightarrow$ NaBr (for $\pi$, $\sigma$: $\Delta \varepsilon=38$ meV) $\rightarrow$ RbI (for $\sigma$: $\Delta \varepsilon=68.9$ meV) $\rightarrow$ KI (for $\pi$: $\Delta \varepsilon=37$ meV; for $\sigma$: $\Delta \varepsilon=33.7$ meV). The energy values reflect the potential barrier separating radiative and non-radiative decay channels of self-trapped excitons.

The output increase of the crystals’ intrinsic luminescence is explained by the potential barrier’s growth. The potential barrier decreases the probability of radiative defect creation at the STE decay.

The decrease of emission halfwidth ($\Delta H$) for self-trapped excitons at fixed temperature (100K) for elastic stressed crystals was experimentally determined: KI (for $\pi$: $\Delta H=0.03$ eV; for $\sigma$: $\Delta H=0.02$ eV), RbI (for $\sigma$: $\Delta H=0.03$ eV), NaBr (for $\pi$, $\sigma$: $\Delta H=0.03$ eV), KBr (for $\sigma$: $\Delta H=0.006$ eV).

The frequency increase of active fluctuations of self-trapped excitons in elastic stressed crystals was experimentally determined: KI (for $\pi$: $\Delta \omega=0.44 \times 10^{12}$ s$^{-1}$; for $\sigma$: $\Delta \omega=0.41 \times 10^{13}$ s$^{-1}$), RbI (for $\sigma$: $\Delta \omega=0.25 \times 10^{13}$ s$^{-1}$), NaBr (for $\pi$, $\sigma$: $\Delta \omega=0.56 \times 10^{13}$ s$^{-1}$), KBr (for $\sigma$: $\Delta \omega=0.04 \times 10^{13}$ s$^{-1}$).

The decrease of Huang-Rhys parameter in elastic stressed crystals was experimentally determined: KI (for $\pi$: $\Delta S=31$; for $\sigma$: $\Delta S=26$), RbI (for $\sigma$: $\Delta S=40$), NaBr (for $\pi$, $\sigma$: $\Delta S=29$), KBr (for $\sigma$: $\Delta S=4$).

On the basis of the increase of activation energy of temperature luminescence quenching, emission band contraction of self-trapped excitons, frequency increase of active fluctuations of self-trapped excitons, decrease of Huang-Rhys parameter the attenuation of exciton-phonon interaction in elastic stressed KI, RbI and NaBr crystals is established.

References

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