International Journal of Luminescence and Applications (ISSN: 2277-6362)
Vol. 5, No. 1, February 2015. Article ID: 076. pp.140-144.

# The Specifics of Irradiative Annihilation of Self-Trapped Excitons at Low Temperature Uniaxial Stress in KI Crystal

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***Abstract***— *The strengthening of intrinsic luminescence of KI crystal at low temperature uniaxial stress is interpreted on the basis of exciton self-trapping process. The modeling results show potential barrier decrease for excitons self-trapping with the temperature and stress degree raise. The free path contraction of electronic excitation up to five times is experimentally proven by the introduction of Thallium of different concentration. Thus, the experimental fact of intrinsic luminescence strengthening of KI crystal is due to the probability increase of exciton self-trapping with irradiative annihilation in lattice regular sites at lattice symmetry lowering by uniaxial stress.*

***Keywords***— *exciton, uniaxial stress, thallium,scintillator*

## 1. INTRODUCTION

High quantum luminescence output is one of the required physical parameters for the development of optic materials, and solid state scintillators in particular.

In KI-Tl, NaI-Tl scintillators the main creation channels of initial radiation defects and luminescence nature are proven on the basis of alkali halide crystals (AHC) [1]. The reason of this phenomenon is the decay of electronic excitations at the moment of self-trapping with the creation of radiation defects and luminescence emission [2]. The self-trapping probability of electronic excitations (excitons) with irradiative annihilation depends, first of all, on the exciton's free path before self-trapping [3]. Traditionally exciton's free path is estimated by a probe impurity method: an impurity introduction of different concentration (for example, KI-Tl and NaI-Tl) provides location impurity's particles on given distances, which serve as a scale for the estimation of exciton's free path before self-trapping. In KI-Tl crystal the intensity of Thallium luminescence plays an indicator role of the energy transfer of a free exciton to Thallium impurities at their interaction. As a result free exciton's energy emits the crystal as impurity luminescence. Thus, the probe impurity in the crystal is an activator on transforming free exciton's energy into impurity luminescence. As a result, quantum output of scintillators luminescence increases [4]. At lattice symmetry lowering by low temperature elastic stress the energy transfer from excitation to an impurity does not occur; this is a unique method for strengthening AHC intrinsic luminescence.

## 2. MODEL REPRESENTATIONS

The evidence for the strengthening effect of the intrinsic luminescence at lattice symmetry lowering by uniaxial stress takes place at temperatures (4.2-100K), at which there is a potential barrier for free excitons self-trapping, as with the temperature raise the number of excitons transforming into self-trapped state increases. The detailed explanation of this phenomenon's nature and potential barrier's estimation depending on temperature can be given with the introduction of fluctuating potential, induced with phonons.

Taking into account an exciton moves in the phonon field of a lattice the exciton's kintetic energy can be written as [5]:

$$A = A_h - V, \tag{1}$$

where $A_h = \frac{\hbar}{2m}\kappa$ – input of hole's kinetic energy, $\hbar$ - Plank's constant, $k = \frac{3\pi}{a}$ – exciton's wave vector, $a$ – lattice constant, $m$ – exciton's effective mass, $V$ – periodic potential conditioned by exciton-phonon interaction.

The influence of periodic potential can be taken into account with the help of exciton's effective mass. The periodic potential is called disturbance potential in work [6]. Such disturbance for self-trapping exciton can be lattice fluctuations which cause fluctuating potential for the field of moving exciton:

$$\varphi_f = \sqrt{2Bk_BT}, \tag{2}$$

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where $B=\frac{E_d^{\,2}}{2\beta a^3}$ – lattice relaxation energy (energy gain at lattice relaxation around exciton), $E_d$ – deformatio $\delta=\frac{\Delta a}{a_0}$n potential, $k_{\mathrm{B}}$ – Boltzmann constant, $T$ – temperature, $\beta=1.17\cdot10^{10}$ – module of volumetric elasticity of KI crystal.

Using (1) and (2) the expression for potential barrier of excitons' self-trapping (STPB) in AHC can be written as follows [7]:

$$E=4(A-\varphi_f)^3\left(1-3\frac{BC}{\left(A-\varphi_f\right)^2}\right)^{3/2}\frac{1}{27B^2} \qquad (3)$$

where $C=\frac{e^2}{\varepsilon' a}$ – input of optic phonons in lattice relaxation energy, $e$ - electron charge, $\varepsilon'$ - crystal's static dielectric penetrability. Each of the values included in expression (3) depends on lattice constant, its temperature dependence derived from analysis of exciton's wave vector [7] is:

$$a(T)=\frac{a_0\hbar}{\hbar\sqrt{mk_{\mathrm{B}}T}} \qquad (4)$$

where $a_0$ - lattice constant at absolute zero, $j$ - parameter depending on thermal influence on interatom and interion distances (for AHC it varies from 0.01 to 0.1) [8].

Using expressions (3), (4) and dependence of $A$, $B$, $C$ on lattice constant, $\varepsilon(T)=\frac{a(T)}{a_0}$ [8] we derive:

$$E_a=4\left(A\left[\varepsilon(T)\right]^2-\varphi_f\right)^3\left(1-3\frac{BC}{\left(A\left[\varepsilon(T)\right]^2-\varphi_f\right)^2}\right)^{3/2}\frac{1}{27B^2\left[\varepsilon(T)\right]^6} \qquad (5)$$

$A$, $B$, $C$ values at uniaxial stress change and can be expressed through [9]:

$$A'=\frac{\left(2+1/(1-\delta)^2\right)}{3}A,\ B'=\frac{1}{(1-\delta)^{7/3}}B,$$

$$C'=\frac{(3-\delta))}{3}C \qquad (6)$$

where – degree of uniaxial stress showing ratio of absolute change of lattice constant to initial one.

The Figure 1 shows the application of uniaxial stress at temperature increase in the range 4.2-100K; where from we can see decrease of exciton self-trapping potential barrier.

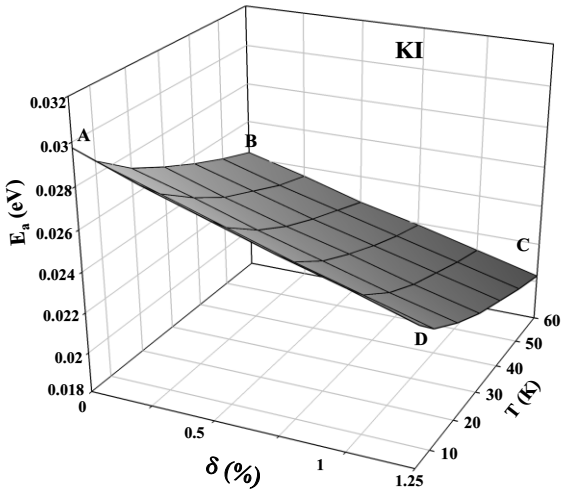


**Fig. 1: The dependence of the height of STB in KI crystal on temperature and deformation**

Curve AB on Figure 1 corresponds to the STPB dependence on temperature at stress degree 0.5%. At A STPB is 0.0297 eV, at B – 0.0243 eV, i.e. decreases for 18%. The influence of uniaxial stress at fixed temperature can be analyzed by curves AD (4.2K), BC (60K). The energy difference between A and D is 93.24%, B and C – 93.33%. At stress degree $\delta=3\,\%$ the temperature influence is low, this can be seen from the Figure 1 (DC). The prevailing influence of uniaxial stress on STPB in comparison with temperature can be seen from the built dependence.

STPB change can be more obviously analyzed on the surface of exciton adiabatic potential (AP), the functional is given as:

$$E=A\mu^2-B\mu^3-C\mu, \qquad (7)$$

where $E$ – energy of exciton state, $\mu$ – ratio of lattice constant to the radius of localization field. The energy difference between minimum and maximum of the functional (7) allows to estimate STPB.

The dependence of functional (7) on temperature and stress can be presented as:

$$E(\mu,\varepsilon(T))=A\left[\varepsilon(T)\right]^2\mu^2-B\left[\varepsilon(T)\right]^3\mu^3-C\varepsilon(T)\mu,$$

$$E = \frac{A\left(2+1/(1-\delta)^2\right)}{3}\mu^2 - \frac{B}{(1-\delta)^{7/3}}\mu^3 - \frac{C(3-\delta)}{3}\mu .$$

The surface of AP in KI crystal is shown on Figure 2.

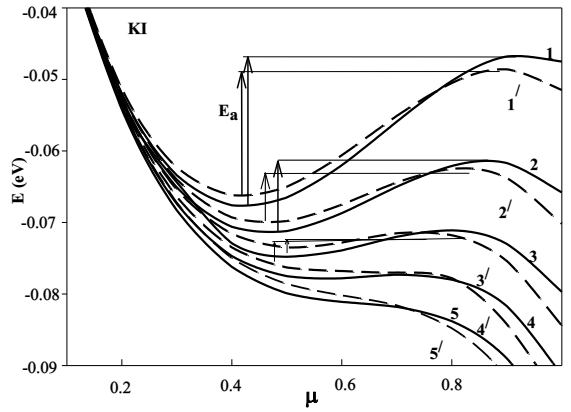


**Fig. 2: The surface of the adiabatic potential of excitons in KI crystal (1, 2, 3, 4, 5 respectively – at 4.2K, 20K, 40K, 60K, 80K, dashed – at stress 1%)**

As defined from the AP surface (Figure 2) the functional peaks before stress are observed at $\mu$ values less one (0.9). This means the exciton is self-trapped in the field of linear size a little more than lattice constant. The smooth STPB decrease is obviously shown up to the temperatures 60K. The surface of adiabatic potential begins to smooth in the temperature range 60-80K; this means STPB decrease to low values. After plastic stress the maximums in AP shift as the radius of exciton's localization increases due to the decrease of lattice constant. At uniaxial stress the surface of adiabatic potential has not any extremums at 80K, i.e. considerable part of excitons transfers into self-trapped state.

## 3. EXPERIMENTAL METHODS AND RESULTS

KI crystals with different $Tl^+$ concentration fit for the reaserch of the exciton self-trapping process at AHC symmetry lowering by uniaxial stress. The core of the experiment is the choice of the Thallium concentration so that the distances between them in the lattice were sizeable to the exciton's fre $a$ [10], while in KCl crystal, for example – $2a$; (where $a$ - lattice constant);

Third, $Tl^+$- ion concentration in KI crystal can be experimentally defined by the maximum absorption band of $Tl^+$center (4.3eV). Thallium concentration ($N_{Tl}$) in KI crystal was determined by spectrophotometric method registering absorption spectra of Thallium Tl-center similar to the determining the concentration of F-centers in alkali halide crystals by Smakula formula:

$$N_{Tl} = 0.87 \cdot 10^{17} \frac{n}{\left(n^2+2\right)^2} \frac{1}{f} K_{\max}\left(sm^{-1}\right)\Delta H\left(eV\right),$$

where $f$ – oscillator power of Tl-center absorption band $\left(f_{Tl} = 0.17\right)$, $n$ – light refraction coefficient in KI crystal in the spectrum range corresponding to the maximum of Tl-center absorption band ($\lambda = 287$ nm or $E = 4.3$ eV), $K_{\max}$ – absorption coefficient of Tl-center defined experimentally registering optic density D of this center $K_{\max} d = D_{\max}$ ($d$ – crystal width).

The Figure 3 shows luminescence spectra of KI crystal with different $Tl^+$ concentrations X-rayed in the absence (curve 1) and at low temperature stress (curves 2 and 3).

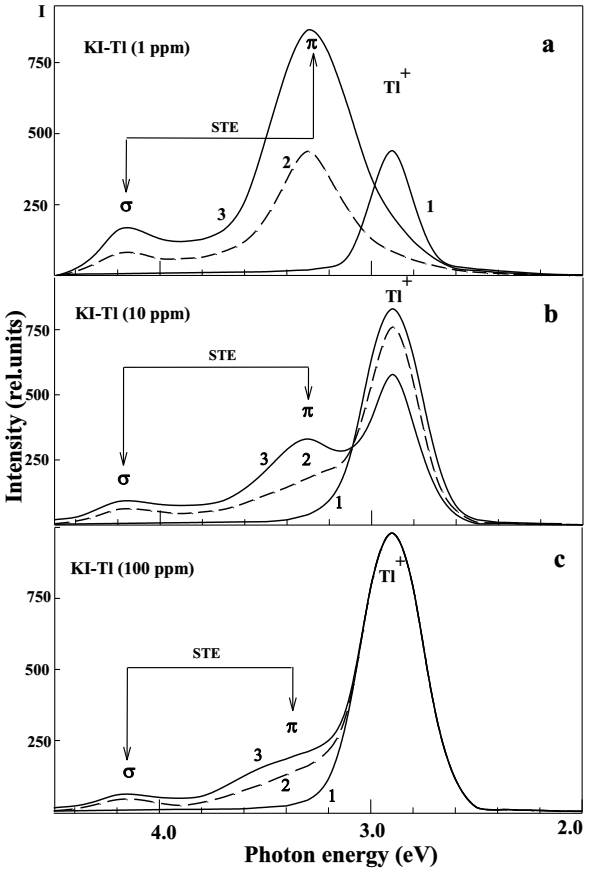


**Fig. 3: The spectra of the luminescence of crystal KI-Tl at (1) and after low temperature uniaxial stress at 100K (2 – 0,5÷0,8%, 3 –1,5÷2,0%): a – 1 ppm; b – 10 ppm; c – 100 ppm.**

The only luminescence band of Tl-center with maximum at 2.85 eV was registered in KI-Tl crystal at all experiments in the stress absence (Fig. 3, a, b, c, curves 1). It should be noted STE intrinsic luminescence

with $\sigma$ - (4.15 eV) and $\pi$ - (3.3 eV) polarization was not registered.

The intrinsic luminescence with $\sigma$- and $\pi$-polarization appears in KI-Tl crystal at lattice symmetry lowering with low temperature stress as a result of irradiative annihilation of self-trapped action in regular lattice sites (Fig. 3, a, b, c, curves 2, 3).

We have analyzed on Fig. 3 that the intensity growth effect of intrinsic luminescence is maximum at Thallium concentration at the level of 1ppm, which corresponds to the distance between Thallium $r = 228a$ (Fig. 1a). In this case inter-Thallium distances are almost equal to the exciton's free path before self-trapping in regular lattice sites ($r = \lambda$). This is a unique condition for the experiment on effectiveness estimation of exciton's self-trapping at lattice symmetry lowering by low temperature stress. With the growth of relative deformation degree the luminescence intensity of $Tl$-center sharply decreases and intensity of STE intrinsic $\sigma$- and $\pi$-luminescence increases in change (Figure 3, a, curves 2 and 3).

This experimental result obviously shows the self-trapping probability of free excitons in regular lattice sites with irradiative annihilation sharply increases due to the free path reduction.

The Thallium concentration was purposefully increased to 10ppm, which corresponds to inter-Thallium distance $r = 55 \div 75a$ for the estimation of the reduction degree of exciton's free path before self-trapping.

When inter-Thallium distance in KI-Tl crystal becomes shorter than exciton's free path before self-trapping ($r = \lambda$) it is obviously seen intensity growth of STE $\sigma$- and $\pi$-luminescence (Figure 3, b, curves 2 and 3) is accompanied with the $Tl$-center intensity decrease. This experiment at least allows to estimate the bottom limit of exciton's free path reduction before self-trapping $- r = 55 \div 75a$.

Using these experimental data (Figure 3, a, b) we assume the exciton's free path before self-trapping at lattice symmetry lowering reduces for 5 times.

With the increase of Thallium concentration up to 100ppm, which corresponds to inter-Thallium distance $r = 20 \div 25a$, the effect becomes non prevailing. This means in this Thallium concentration range the difference between stressed and non stressed crystal disappears and excitation efficiency of $Tl^+$-luminescence becomes identical.

The similar experiments on intensity redistribution of intrinsic and impurity luminescences were observed also in KI crystal with $Na^+$ impurity.

## 4. DISCUSSION

The excitons' free path in AHC strongly depends on their self-trapping process. The migration of electronic excitations in the impurity can terminate either with the excitation energy transfer to impurity luminescence centers or self-trapping process. The transfer to self-trapped state is accompanied with the barrier overcoming, which height depends on the lattice's local deformation. The modeling results show the STPB height decreases with the temperature and stress degree growth. The excitons are self-trapped not reaching impurity particles, the excitons' free path shortens.

It is known in KI the exciton's free path is several thousands of lattice constant at 4.2K and reaches 230 lattice constants at 80K. This fact confirms the STPB decrease with the temperature raise.

The STPB decrease with the stress degree growth allows to confirm experimentally discovered main effect: the intensity of STE's intrinsic $\sigma$- and $\pi$- luminescence bands increase at stress application. The value of this growth is maximal in KI with minor $Tl^+$ concentration and decreases with its growth. Although in KI-Tl with 10 ppm concentration we obviously can see the intensity increase of $\sigma$- and $\pi$-luminescence is accompanied with $Tl^+$-luminescence decrease. With the applied stress degree (see curves 2, 3, 4 Fig. 3) the values of the ratios $\sigma/Tl^+$ and $\pi/Tl^+$ increase. In KI-Tl with considerable concentration of $Tl^+$ the intensity of $\sigma$- and $\pi$-bands also increase but $Tl^+$-luminescence is saturated. However in this case the ratios $\sigma/Tl^+$ and $\pi/Tl^+$ increase in comparison with non stressed crystal.

## 5. CONCLUSION

Thus, it is established with the increase of relative deformation degree in KI-Tl (10 ppm) $Tl^+$-luminescence intensity decreases and simultaneously STE intrinsic luminescence ($\sigma$- and $\pi$-) intensity (in regular lattice sites) increases for the same value. We interpreted this experimental result as follows: with the relative deformation degree growth the quasiexciton's free path before self-trapping shortens for the account of probability growth of excitons' self-trapping with irradiative annihilation in regular lattice sites. With the Thallium concentration increase the intensities of impurity luminescence before and after stress become sizeable due to the fact the exciton reaches the impurity center in any case; that is why the intensity growth of intrinsic luminescence is notable only at minor Thallium concentrations.

Thus, the model approximation on STPB height depending on temperature and degree of uniaxial stress allow to confirm experimentally discovered effect of the intrinsic luminescence strengthening with the deformation degree growth.

**ACKNOWLEDGMENTS**

This work was supported by the grant funding of Ministry of Education and Science of the Republic of Kazakhstan No 1955/GF3, 1332/GF-OT.

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