The Peculiarities of Temperature Quenching of Self-Trapped Exciton Luminescence in Alkali Halide Crystals at Elastic Stress

K.Sh. Shunkeyev*, Y.T. Sarmukhanov*, A.A. Barmina*, L.N. Myasnikova*,
Sh.Zh. Sagimbaeva*, S.K. Shunkeyev**

Aktobe State Pedagogical Institute, 34 Moldagulov Str., Aktobe, 030000, Kazakhstan, E-mail: shunkeev@rambler.ru
***Al Farabi Kazakh National University, 96a Tole bi ave., Almaty, 050012, Kazakhstan*

Abstract – The temperature luminescence quenching of self-trapped exciton (STE) in alkali halide crystals (AHC) at lattice symmetry lowering by low temperature uniaxial stress has been investigated with the methods of luminescence spectroscopy. The experimental results at low temperature uniaxial stress reveal that for crystals whose quantum luminescence yield is close to 1 ($\eta \rightarrow 1$, CsI) or close to zero ($\eta = 0{,}0021$ KCl, $\eta = 0{,}0014$ KBr), STE non irradiative transmission activation energy does not change much (in CsI $\varepsilon = 219$-223 meV, in KBr $\varepsilon = 26$-33 meV); for all crystals (KI, RbI, CsBr, NaBr, NaCl) values for activation energies of exciton non irradiative annihilation sharply increase. The effect of AHC intrinsic luminescence intensity increase is interpreted by increase of potential barrier of STE non irradiative decay at lattice symmetry lowering by low temperature stress.

1. Introduction

The effect of self-trapped exciton luminescence intensity increase was earlier found for many alkali halide crystals [1-4]; it is probably conditioned by two mechanisms: either by the decrease of potential barrier that separates quasi free and self-trapped exciton states, or by the decrease of effectiveness of exciton non irradiative decay channel (into initial radiation defects). Proceeding from literature data [1, 2] we can state that there is no potential barrier for exciton self-trapping in the considered temperature range (around 100 K); and all excitons are in self-trapped state only. That is why the probability of the first mechanism is very low; for example, in KI crystal at 80÷100 K but free exciton luminescence is quenched completely, and STE luminescence has maximum intensity [1, 2]. It is known that in the temperature range when STE luminescence quenching starts then the radiation defect creation effectiveness increases. This effect takes place because the prevailing mechanism now is non irradiative exciton decay into radiation pairs (*F*, *H*-pairs). That is why it is very interesting and perspective from experimental point of view to use such a technique that would yield information on exciton annihilation simultaneously in two channels at AHC lattice symmetry lowering by low temperature uniaxial stress. We think this problem can be experimentally realized by alkali halide crystals STE luminescence quenching measuring with and without low temperature uniaxial stress and estimating STE luminescence quenching energy estimating for every case. In such approach the activation energies are equated by potential barrier between irradiative and non irradiative decay channels of self-trapped exciton.

2. Experimental device

Low temperature uniaxial stress in crystallographic direction <100> was realized in special cryostat. The crystals luminescence spectra scanning was done in automatic mode with speed of 10 and 20 nmps with a step of 5 K in the process of crystal self heating from 100 to 300 K and higher to complete quenching of the registering luminescence. The crystal heating speed was 0.02°/s.

All experiments on temperature dependence of X-ray luminescence were carried out on crystals with maximum lowered non controlled impurity concentration. This is done to avoid excitation energy transfer onto impurities and thus, to register STE intrinsic luminescence change only.

The investigation objects were KBr, KI, NaCl, NaBr, RbI, CsI and CsBr monocrystals cultivated by special method worked out at the Institute of Physics of Academy of Sciences of Estonia; it includes the gaseous haloid treat, 60-fold zone melting, and then cultivation on Stockbarger method in vacuumed ampoule or on Kiropulosos method in helium atmosphere.

3. The experimental results

The Figure 1 shows by the example of KI crystal the results of X-ray luminescence spectra dependence on temperature before (curve 1) and at (curve 2) low temperature uniaxial stress at 100 K. The choice of KI crystal was not random; first, maximum STE luminescence strengthening was registered at uniaxial stress [3,4]; the second, STE π-luminescence (3.3 eV) around 100 K is not quenched; the third, the free exciton contribution does not exist as in the considered temperature range (100 K) excitons are in self-trapped state only.

A reference signal was chosen to be a STE π-luminescense intensity change with a maximum at 3.3 eV. From the STE π-luminescence dependence from temperature it follows that in stressed KI crystal the quenching process in low temperature range occurs with lag, and with the temperature increase they are quenched together and at 180÷200 K they are practically quenched (compare curves 1 and 2, Fig. 1a). The survey X-ray luminescence at 100 K (curve 1) and 200 K (curve $2^{/}$) of stressed KI crystal also is given on the inset of Fig. 1c where we can see that main part of STE π-luminescence is quenched at heating to 200 K. π-luminescence intensity dependence on inverse temperature built in Arrenous coordinates allows to estimate activation energy of STE π-luminescence temperature quenching, i.e. STE non irradiative decay with π-polarization. It is known from literature [1, 2] that STE π-luminescence activation energy (ε) is 132 ÷ 136 meV without stress. We obtained the folowing results for zone purified (z.p.) KI crystal for ε: before stress ε=132 meV with correlation of R=0.997 and after stress ε=169 meV with correlation of R=0.998 (Fig. 1b). Thus low temperature iniaxial stress increases barrier of non irradiative STE decay in KI crystal for 37 meV. This might mean the increase of barrier that separates irradiative and non irradiative STE defect creation channels. Note *F*-center creation effectiveness starts growing in the considered temperature range for KI crystal. We got interested in this fundamental effect, to estimate potential barrier that separates irradiative and non irradiative defect creation channels in KI, to establish its experimental feasibility for other AHC where the effect of intrinsic luminescence increase at low temperature uniaxial stress was found.

The same method was used for estimating values for activation energy of STE σ – luminescence intensity quenching for KBr (see table) before and after low temperature stress.

In principle, value of ε for non stressed KBr crystal initially is not great, around 26 meV and after stress – 33 meV. It is assumed that in KBr at low temperature uniaxial stress the effectiveness of radiation defect (*F*-center) creation remains un changed.

We managed to register redistribution between two bands (3.67 eV and 4.27 eV) in STE intrinsic luminescence in zone purified CsI in the absence of stress. The luminescence at 3.67 eV quenches to temperature of 170 K with activation energy 50 meV (see table) and the main part of the luminescence (4.27 eV) intensity quenching falls into the range of temperatures to 300 K with activation energy 219.8 meV (see table). In CsI at low temperature stress the luminescence at 3.67 eV disappears and the prevailing luminescence in X-ray luminescence spectra remains the one at 3.67 eV that quenches with activation energy of 66 meV. In the temperature range (100 ÷ 195 K) a previously disappeared luminescence band at 4.27 eV appears that in the range of 170-175 K reaches a maximum value and then remains an only luminescence band instead of the one at 3.67 eV; the temperature quenching of the band continues to 510 K. The activation energy estimated on intensity growth incline of luminescence band at 4.27 eV is 8 meV that corresponds to the potential barrier for free exciton self-trapping [1]. The intensity of the luminescence band at 4.27 eV has maximum value at 175 K and the following temperature growth brings to gradual quenching with activation energy of 223 meV (see table).

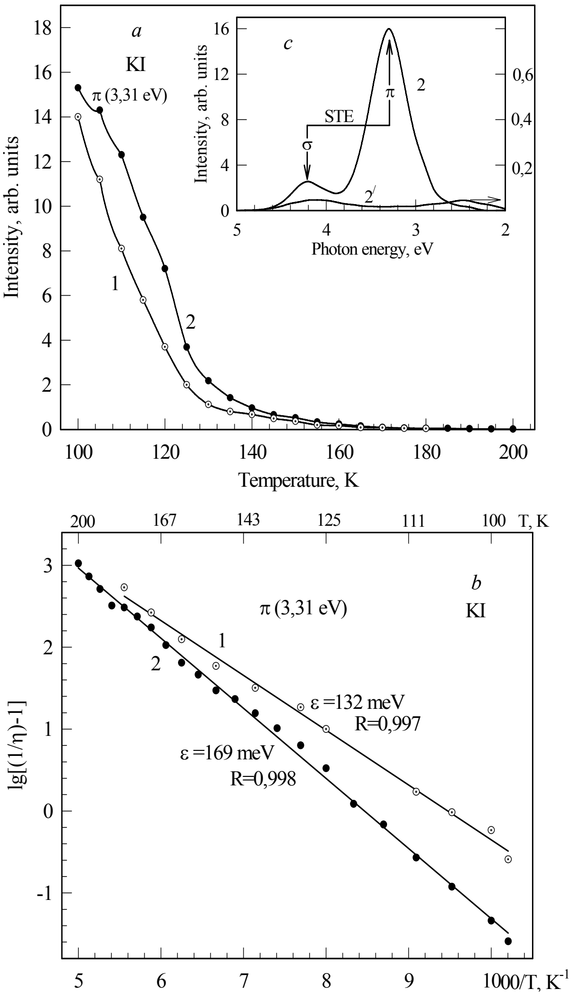

Fig. 1 – Temperature depenedence of π-luminescence (3.3 eV) of self-trapped in KI crystal before (1) and at low temperature (100 K) uniaxial stress (2)

- a – intensity dependence of π – luminescence with an increase of $I \sim f(T)$;
- b – intensity dependence of π – luminescence built in Arrenous coordinates $lg[(1/\eta)-1]$;
- c – X-ray luminescence spectra for KI crystal after stress at 100 K (2) and 200 K ($2^{/}$).

For CsI quenching activation energy for luminescence at 4.27 eV remains constant independently on uniaxial stress degree and has high values at 219.8 ÷ 223 meV. This means in CsI the lattice barrier between exciton irradiative and non irradiative decay channels is so high that all STE annihilate irradiative.

The temperature dependence of X-ray luminescence of deformed KI, KBr, NaCl, CsBr, RbI, NaBr and CsI crystals showed that STE can be divided into 2 groups according to the change of activation energy (ε) of non irradiative transfer of STE: $\varepsilon \approx$ const (KBr и CsI) and $\varepsilon_d > \varepsilon$ (KI, NaCl, CsBr, RbI and NaBr), where ε_d – value of activation energy at low temperature uniaxial stress.

The table shows the values of STE luminescence intensity putting down activation energies for some AHC in the absence and in the presence of low temperature uniaxial stress. The values of ε, obtained by the authors are given in brackets.

Crystal	STE luminescence band maximum (eV)	STE structure	Luminescence quantum yield (η) rel. CsI at 5 K	Activation energy ε (meV) before stress	Activation energy ε_d (meV) at uniaxial stress
KI	3.04	weak off (E_X)	–	18	–
	3.31	weak off (π)	0.13	132 (132)	(169)
	4.16	on (σ)	0.038	–	–
KBr	2.28	strong off (π)	0.014	37	–
	4.42	on (σ)	0.029	23 (26)	(33)
NaCl	3.35	weak off (π)	0.023	99 (103)	(138)
	5.35	on (σ)	0.017	32 (32)	(66.7)
CsBr	3.55	strong off (π)	0.019	100 (95)	(140)
	4.74	on (σ)	0.008	–	–
RbI	2.3	strong off (π)	–	–	–
	3.10	weak off (E_X)	0.012	–	–
	3.89	on (σ)	0.044	43 (43.7)	(113.2)
NaBr	4.62	on (π)	0.1	160 (154.7)	(192.7)
CsI	3.67	weak off (π)	1	50 (50)	(66)
	4.27	on (σ)	1	220 (219.8)	(223)

From the above-mentioned it follows that AHC intrinsic luminescence increase effect at low temperature stress is bound with lattice barrier increase that separates irradiative and non irradiative channels of STE defect creation channels.

References

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