The deformation stimulated luminescence in KCl, KBr and KI crystals

K Shunkeyev¹, D Sergeyev¹, W Drozdowski², K Brylev³, L Myasnikova¹, A Barmina¹, N Zhanturina¹, Sh Sagimbaeva¹ and Z Aimagambetova¹

¹Zhubanov Aktobe Regional State University, Aktobe, Kazakhstan
²Nicaus Copernicus University in Torun, Torun, Poland

E-mail: shunkeev@rambler.ru

Abstract. Currently, strengthening of the intensity of luminescence in alkali halide crystals (AHC) at lattice symmetry lowering is discussed as a promising direction for the development of scintillation detectors [1-3]. In this regard, for the study of anion excitons and radiation defects in the AHC anion sublattice at deformation, the crystals with the same sizes of cations and different sizes of anions were chosen. In the X-ray spectra of KCl at 10 K, the luminescence at 3.88 eV, 3.05 eV and 2.3 eV is clearly visible. The luminescence at 3.05 eV corresponds to the tunneling recharge \([F^*, H]\). Luminescence at 3.88 eV is quenched in the region of thermal destruction of \(F^\prime\)-centers and characterizes tunneling recharge of \(F^\prime\), \(V_K\)-centers. In KCl at 90 K, the luminescence of self-trapped excitons (STE) is completely absent. In KBr at deformation not only STE luminescence, but also deformation stimulated luminescence at 3.58 eV were recorded, the last one corresponds to tunneling recharge of \(F^\prime\), \(V_K\)-centers. In KI crystal at 10 K and 90 K at deformation, only STE luminescence is enhanced. There are no deformation luminescence bands in KI compares with KBr and KCl crystals.

1. Introduction
The luminescence of self-trapped excitons in alkali halide crystals is considered as the intrinsic matrix luminescence, and it currently has been studied in detail [4-7]. The present study is aimed at investigation of the luminescence of electronic excitations in the anion sublattice of AHC matrix.

2. Experimental results and discussion

2.1. KCl
The intrinsic luminescence of KCl crystal due to self-trapped exciton luminescence at 10 K consists of one band with maximum at 2.3 eV with \(\pi\)-polarization (curve 1, figure 1a) [8]. The curve 2 of figure 1a shows the X-ray spectra of KCl crystal at deformation recorded at 10 K. From these spectra the luminescence bands with maxima at 5.15 eV, 3.88 eV, 3.05 eV and 2.3 eV are clearly visible. It should be noted that in KCl crystal the luminescence with a peak at 5.15 eV has been recorded for the first time and its nature remains unclear, apparently linked to the free exciton radiative relaxation.

Simultaneous exposure of low temperature (10 K) and the uniaxial deformation (\(\varepsilon=1.3\%\)) seem to have created favorable conditions for recording luminescence of free excitons in KCl crystal. The last
luminescence band at 2.3 eV refers to the self-trapped exciton radiative relaxation, which due to the temperature quenching has not been recorded at 90 K (curve 2, figure 1b).

The luminescence bands at 3.88 eV and 3.05 eV characterize the tunnel recharge between the radiation defects F' and V_K, F* and H, respectively. This is evidenced by their temperature dependence. The temperature dependence of the luminescence band at 3.88 eV in KCl crystal shows that it undergoes the maximum quenching at temperature region (120 K) when F'-centers are thermally annealed (inset, figure 1b). The slow decline of the luminescence intensity at 3.88 eV in the temperature range of 10 to 80K, apparently, is associated with a thermal delocalization of hole radiation defects, which interact with the F'-centers. Ranging from 80K to 140K the thermal annealing of F'-centers takes place.

Figure 1. X-ray and tunneling luminescence of KCl, KBr and KI crystals before deformation (1), at deformation (ε=1.3%) (2), tunneling luminescence (3)

From these experimental results we assume that the low temperature elastic deformation of KCl crystal facilitates efficient formation of F', V_K and F, H-pairs.

Therefore, it is assumed that the effect of luminescence amplification is most likely associated with the tunneling recharge of different charged radiation defects created under the influence of X-ray radiation. Figure 1a (curve 3) shows the spectrum of the tunneling luminescence of KCl crystal at low temperature deformation in <100> directions after X-ray irradiation at 10 K.

Algorithm of experiment was carried in the following sequence. After the vacuum obtaining in cryostat, the crystal was cooled to 10 and 90 K, and at this temperature it was deformed uniaxially to the degree $\varepsilon=2\%$, and then the crystal was irradiated for one hour by X-ray in mode 3 mA, 120 kV. After the termination of X-ray radiation, the tunneling luminescence of KCl crystal was recorded, i.e., in the absence of the exciting photons.

From figure 1b we see the luminescence with the maximum at 3.88 eV is also dominant in the spectrum of tunneling luminescence of KCl crystal deformed at 90 K, indicating the process of recharging between the ground states of stable radiation defects.

From comparison of X-ray spectra (curve 1, figure 1b; curve 2, figure 1a) and the tunneling luminescence (curve 2, figure 1b) of KCl crystal deformed (ε=2%) at low temperature, it is clear that the appearing luminescence band is observed in the tunneling luminescence spectra of these crystals. The contribution increase of the tunneling luminescence in the X-ray spectra of deformed KCl crystal is related to a large number of F'-centers and hole V_K-centers and with the increase in the tunneling probability of radiation defects due to oriented action of uniaxial compression.
Therefore, luminescence at 3.88 eV in KCl crystal at low temperature deformation was interpreted as tunneling recharge of radiation defects, most likely, $F'$ and $V_k$-centers.

Such tunnel processes usually occur at temperatures much lower than the liquid nitrogen temperature (4.2 K), as in the case of our experimental conditions. Apparently, the low temperature deformation creates favorable conditions for the formation of interacting pairs of radiation defects, tunneling charge of which is carried out easily.

2.2. KBr

Similar low temperature deformation was carried out for KBr crystals. In KBr crystal compared with KCl crystal, the ionic radii of halogens increase 1.1 times. The figures 1c and 1d show the luminescent characteristics of KBr crystal.

The intrinsic luminescence of KBr crystal caused by the luminescence of self-trapped exciton at 10 K consists of two bands with maxima at 4.42 eV ($\sigma$) and 2.28 eV ($\pi$) (curve 1, figure 1c) [8]. The curve 2 in figure 1d shows that the significant effect is a considerable increase of $\sigma$- and $\pi$-luminescence of self-trapped exciton and new bands with maxima at 3.58 eV and 2.75 eV (curve 2, figure 1d) [9].

From a comparison of X-ray spectra (curve 1, figure 1d) and tunneling luminescence (curve 2, figure 1d) of KBr crystal deformed ($\varepsilon$=2%) at low temperature, it is clear that a new luminescence band at 3.58 eV is observed also in the spectrum of tunneling luminescence. The temperature dependence of the X-ray spectrum of KBr crystal, predeformed at 90 K shows that the observed luminescence band with a maximum at 3.58 eV is most thermally annealed at 110 K, i.e., in the temperature region, when $F'$-centers are thermally destroyed (inset, figure 1d). This suggests that one of the partners responsible for tunneling luminescence at 3.58 eV is indeed $F'$-center having the structure ($v_s^+e^-e^-$).

2.3. KI

Similar experiments were continued for KI crystal (figure 1e, 1f). In this case, in KI crystal the ionic radii of halogens compared with KCl crystal increase by 1.2 times. Thus, among KCl, KBr and KI crystals the halogen radius gradually increases according to the following sequence $R(\text{Cl})$=1.81 Å, $R(\text{Br})$=1.96 Å and $R(\text{I})$=2.2 Å.

The intrinsic luminescence of KI crystal caused by the exciton self-trapping luminescence at 10 K consists of two bands with maxima at 4.15 eV ($\sigma$) and 3.3 eV ($\pi$) (curve 1, figure 1e) [8, 10]. In optical creation of electron-hole pairs and at X-ray excitation, the intensity of $\sigma$-luminescence at heating begins to be quenched only after 60 K, and at 80 K it decreases only 3 times [2, 11]. While $\pi$-luminescence is quenched only at temperatures above 90 K [2]. This means if self-trapped excitons are created, they can be trustworthy recorded at 90 K.

The results of measurements of X-ray spectra at low temperature uniaxial deformation on example of KI crystal are shown in figure 1f. We obtain the similar results as in the case with KCl and KBr crystals. It should be emphasized that in comparison with KCl crystal (curve 1, figure 1d) in KI crystal the intensity of intrinsic luminescence increases about 100 times at low temperature deformation (curve 2, figure 1d).

Luminescence at 3.02 eV increases at compression also, although less efficiently. This band is observed in the phosphorescence spectrum of the deformed KI crystal, and we can assume that it can occur as a result of tunneling recombination between the radiation defects (curve 3, figure 1f). By analogy with KCl and KBr, one would assume that it can be associated with the tunneling luminescence between the ground states of $F'$ and $V_k$-centers. In the same energy region in KI, the exciton self-trapped near impurity of Na$^+$ (3.0 eV) radiates as well.

3. Conclusion

The experimental results allow us to establish the following patterns of luminescence of KCl, KBr and KI crystals at low temperature uniaxial deformation:
1. The buildup of intensity of self-trapped excitons luminescence and luminescence of tunneling radiation defects.

2. In crystals KCl at low temperature deformation, new luminescence bands with maxima at 3.88 eV and 3.05 eV were recorded, the nature of which is associated with the tunneling recharge of radiation defects – $F'$- and $V_K$-centers.

3. In KBr crystals at low temperature deformation in $<100>$ directions, new luminescence bands with maxima at 3.58 and 2.75 eV were recorded. It is assumed that the luminescence at 3.58 eV is associated with the tunnel recharging between the ground states of $F'$- and $V_K$-centers.

4. In KI crystals at low temperature deformation, the luminescence of self-trapped excitons with maxima at 4.42 eV and 2.3 eV was recorded.

This work was supported by grants of the Ministry of Education and Science of the Republic of Kazakhstan 4903/ GF4 and 4904/GF4.

References

[1] Lisitsyna L, Kassymkanova R, Esil'baev D and Dauletbekova A 2013 *Phys. Solid State* 55 1034 S1063783413050211
[2] Shunkeev K, Sarmukhanov E, Barmina A, Myasnikova L, Sagimbaeva Sh and Shunkeyev S 2008 *Phys. Solid State* 50 1799 S1063783408100016
[3] Nishimura H, Tsujimoto T, Nakayama M, Horiguchi T and Kobayashi M 1994 *J. Phys. Soc. Japan* 63 2818 JPSJ.63.2818
[4] Shunkeyev K, Zhanturina N, Aimaganbetova Z, Barmina A, Myasnikova L, Sagymbaeva Sh and Sergeyev D 2016 *Low Temp. Phys.* 42 580 1.4960008
[5] Lushchik A, Lushchik Ch, Vasil’chenko E, Kirm M and Martinson I 2002 *Surf. Rev. Lett.* 9 299
[6] Shunkeyev K, Sergeyev D, Myasnikova L, Barmina A, Zhanturina N, Shunkeyev S and Aimaganbetova Z 2014 *Russ. Phys. J.* 57 451 s11182-014-0261-3
[7] Popov A and Balanzat E 2000 *Nucl. Instrum. Methods B* 166 545
[8] Song K and Williams R 1994 *Self-trapped excitons* (Berlin: Springer Verlag) 10.1007-978- 3-642 -85236-7
[9] Shunkeyev K, Sarmukhanov E, Barmina A, Myasnikova L and Shunkeyev S 2007 *J. Applied Spectroscopy* 74 71 s0812-007-0011-1
[10] Babin V, Elango A, Kalder K, Maaroos A, Shunkeyev K, Vasilchenko E and Zazubovich S 1999 *J. Lumin.* 81 71 S0022-2313(98)00051-9
[11] Shunkeyev K, Myasnikova L, Barmina A and Sagimbaeva Sh 2012 *J. of Phys.: Conf. Series* 400 042002 1742-6596/400/4/042002