The thermostimulated luminescence of radiation defects in KCl, KBr and KI crystals at elastic and plastic deformation

K Shunkeyev, L Myasnikova, A Barmina, N Zhunturina, Sh Sagimbaeva, Z Aimaganbetova and D Sergeyev

Zhubanov Aktobe Regional State University, Aktobe, Kazakhstan

E-mail: shunkeev@rambler.ru

Abstract. The efficiency of radiation defects formation in alkali halide crystals (AHC) was studied by the method of absorption spectroscopy. However, it is not possible to study the deformation-stimulated processes in detail by the absorption spectrum of radiation defects due to the limited sensitivity compared with luminescent spectroscopy. In this regard, thermally stimulated luminescence (TSL) of radiation defects at elastic and plastic deformation was applied in AHC. In the absence of deformation, the dominant peaks in TSL are $\left(X_{\text{i}}\right)^{\text{acac}}_{\text{X}}$ -centers. After elastic deformation, low temperature peaks of TSL corresponding to $F^-$, $V_K$- and $V_F$-centers became dominant. After plastic deformation, the peaks of TSL corresponding to $\left(X_{\text{i}}\right)^{\text{acac}}_{\text{X}}$ -centers became dominant. The elastic deformation contributes to the increase in concentration of low-temperature $F^-$, $V_K$- and $V_F$-centers, and the plastic one contributes to that of high temperature $\left(X_{\text{i}}\right)^{\text{acac}}_{\text{X}}$ -centers (peaks of TSL in KCl at 360K, in KBr at 365K, in KI at 340K), composed by divacancies created by plastic deformation. At elastic deformation, unrelaxed interstitial halogen atoms are converted into $V_K$- and $V_F$-centers, and due to this fact the long-range interaction is absent, the result of which are the $X_{\text{i}}$ -centers.

1. Introduction

At AHC lattice symmetry lowering by low temperature elastic, high-temperature plastic deformation and by light cations, the increase in the luminescence intensity of self-trapped excitons (STE) occurs [1-3]. This effect is very important for the search of scintillation materials based on AHC. However, in many cases the decay of electronic excitations into radiation defects is not taken into account, what is important in the integration of all kinds of luminescence to increase the quantum yield of the scintillator luminescence. It is known that low temperature uniaxial deformation can reduce the effectiveness of radiation defect formation in AHC [4-7]. However, these experimental results have been obtained on the basis of absorption spectroscopy for recording the optical density of radiation defects, which is not able to take into account the small amount of radiation defects, which are clearly manifested in the TSL.
2. Experimental results and discussion

2.1. KCl

The TSL measurement of radiation defects at AHC lattice symmetry lowering is carried out taking into account various disturbing factors. From the change in intensity of TSL, which characterizes the concentration of thermally destroying radiation defects, we can assume the effectiveness of their formation after exposure to external factors (elastic and plastic deformation, cationic impurities of different size, etc.).

Figure 1 shows the TSL of KCl crystals in the absence of deformation, at low temperature elastic deformation and after plastic deformation. From figure 1 (curve 1), it follows that at the absence of deformation the low temperature peaks of TSL of Na$^{+}$-, $H_{A}$($Na$)-, $V_{k-}$ и $V_{f}$ were recorded, the maximum destroying temperature of which corresponds to the destruction of the TSL peaks at 125K, 140 K, 205 K and 235 K, respectively, and high temperature peaks of TSL were recorded at temperatures 360 K and 420 K, which are caused by thermal destruction of $V_{4a} = \{ Cl_{1}^{+} \}_{\text{aux}}$, $F'$ and $V_{2} = \{ (Cl_{1}^{+}) \}_{\text{aux}}$ centers. At the same time, the dominant peaks are high-temperature ones characteristic of pure crystals, in which the impurity concentration is maximally reduced; the impurity serves as shallow traps for stabilizing mobile interstitial atoms of halogen and unrelaxed holes.

The low temperature elastic deformation of KCl crystal leads to the increase of intensity peaks of TSL of Na$^{+}$-, $H_{A}$-, $F'$-, $V_{k}$ and $V_{f}$-centers more than 3–4 times (curve 2) in comparison with that of the undeformed crystal (curve 1). At the same time, TSL peaks near 360 K and 420 K disappear, which correspond to high-temperature aggregate formations of halogen $V_{k}$ and $V_{f}$ centers. In the absence of deformation, the TSL high-temperature peaks are dominant, and after low temperature elastic deformation, low temperature peaks are dominant. The low temperature elastic deformation contributes to the self-trapping of mobile interstitial halogen atoms and unrelaxed holes in regular lattice sites.

Thus, after low temperature elastic deformation by TSL, in KBr crystals we have recorded an increased concentration of $F'(185 K)$-, $V_{k}(205 K)$- and $V_{f}(235 K)$ centers compared to the original crystal, apparently due to self-trapping and transformation of unrelaxed hole and movable halogen atoms.

Figure 1 (curve 3) represents the TSL of KCl crystal after impact of plastic deformation. Firstly, the intensities of low temperature peaks of TSL (curve 3) reduced compared with the elastically deformed crystal (curve 2), but remain dominant relative to undeformed crystal (curve 1); secondly, the most intense peaks became $\{ Cl_{1}^{+} \}_{\text{aux}}$ and $\{ (Cl_{1}^{+}) \}_{\text{aux}}$-centers, which are destroyed at 360 K and 420 K (curve 3). It is known that $\{ Cl_{1}^{+} \}_{\text{aux}}$-centers are formed by reacting of two interstitial halogen atoms ($H$-centers) in regular lattice sites, and their efficiency increases significantly if the association of $H$-centers occurs in divacancies field ($\nu^{+}_{s} \nu^{+}_{i}$), created by plastic deformation.
2.2. KBr
From figure 2 (curve 1) we can assume that at the absence of deformation the low temperature peaks of TSL of $F^\prime$-, $V_{K^-}$ and $V_f$-centers were recorded, the maximum destruction temperature of which corresponds to the TSL peaks at 120 K, 180 K and 235 K, respectively. From high temperature TSL peaks two peaks at temperatures 365 K and 440 K were recorded, which are caused by thermal destruction of $V_i = (Br_f)^{\infty}_w K^+ Br_f$ and $V_i = (Br_f)^{\infty}_w$-centers.

The low temperature elastic deformation of KBr crystal leads to increase in intensity of TSL peaks of $V_{K}(180 K)$- and $V_f(240 K)$-centers. Thus, the peaks in the region of 365 K and 440 K disappear; they correspond to high-temperature aggregate formations of halogen $V_i$ and $V_i$-centers. Also amplify TSL peaks intensities, located in the area of $F^\prime$-centers destruction temperatures (about 120-130 K for KBr).

Thus, after low temperature elastic deformation by TSL in KBr crystals we have registered high concentrations of $V_{K}$-, $V_f$- and $F^\prime$-centers compared to those of the original crystal.

The basic pattern of plastic deformation impact is as follows: firstly, the intensities of low temperature $V_{K}$-, $V_f$- and $F^\prime$-peaks decreased in comparison with those of the elastically deformed crystal but remain dominant relative to the undeformed crystal; secondly, the most intense peaks became the peaks of $(Br_f)^{\infty}_w$ and $[(Br_f)^{\infty}_w]$-centers.

2.3. KI
In undeformed KI crystal (figure 3, curve 1), the TSL peak in high temperature region at 340 K was recorded; the peak corresponds to thermal destruction of $(I_f)^{\infty}_w$-centers, which is absent at low temperature deformation. This means that at uniaxial deformation field as expected, there is no association between $H$-centers (which produces $(I_f)^{\infty}_w$-centers). Thus the low temperature intense TSL peaks of $V_K$, $V_f$, $V_{KA}$ and $F^\prime$-centers were recorded by analogy with KBr and KCl crystals (curve 2).

The effects of plastic deformation on TSL of KI crystal are shown in figure 3 (curve 3). Thus the basic pattern is similar for KBr and KCl crystals, and it is as follows: firstly, the intensities of low-temperature $V_{K}$-, $V_f$- and $F^\prime$-peaks (curve 3) decreased in comparison with those of the elastically deformed crystal (curve 2), but remain dominant relative to those of undeformed crystal (curve 1); secondly, the most intense peaks became $(I_f)^{\infty}_w$ and $[(I_f)^{\infty}_w]$-centers, which are destroyed at 365K and 420K (curve 3).

Assuming that at uniaxial compression in KI crystal the concentration of $H$-centers generated by the decay of STE will decrease, apart from inefficiency of their association we can expect the change of their stability channels or conversion into other hole centers, which in interaction with the $F$-centers allow recombination luminescence.
3. Conclusion

The experimental results on registration of thermally stimulated luminescence of radiation defects in KCl, KBr and KI crystals under the influence of low temperature elastic and plastic deformation allow us to establish the following patterns:

- at low temperature elastic deformation of AHC, the high temperature TSL peaks disappear (in KCl at 360 K, in KBr at 365 K, in KI at 340 K), corresponding to the halogen formations $X_1^-$ and $(X_1)_2^-$, which are created by interacting of mobile halogen atoms ($H$-centers);

- at low temperature elastic deformation of AHC, the intensity of low temperature TSL peaks of $F'(120 K)$-, $V_{K}'(180 K)$- and $V_F(235 K)$-centers increase significantly (10 times more) due to their high concentration;

- at low temperature elastic deformation, redistribution of high temperature TSL peaks intensities ($X_j^-$ and $(X_j)_2^-$-centers) in favor of low temperature occurs due to the high concentration of stabilized $F^-$-, $V_K^-$- and $V_F^-$-centers;

- at low temperature elastic deformation, the redistribution of high intensity TSL peaks ($X_j^-$ and $(X_j)_2^-$-centers) takes place in favor of low temperature ones due to high concentration of stabilized $F^-$-, $V_K^-$- and $V_F^-$-centers;

- after plastic deformation, the effectiveness of $X_j^-$ and $(X_j)_2^-$-center formation increases (TSL peaks in KCl at 360 K, in KBr at 365 K, in KI at 340 K), which are created by the interaction of two $H$-centers in the field of vacancy formations;

- vacancy formations (divacancies $u_i^-u_i^-$ and quartets of vacancies $-2(u_i^-u_i^-)$) play the role of traps for the stabilization of unrelaxed holes and interstitial halogen atoms with the formation of $F^-$-, $V_K^-$- and $V_F^-$-centers;

- increase in TSL peak intensity of self-trapped holes ($V_K^-$-centers) is due to the decrease in the mean free path of unrelaxed holes in regular lattice sites.

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