

Intrinsic luminescence of CaF₂ crystals under simultaneous excitation of pulsed accelerated electrons and stimulated emission of semiconductor CdSse

V. Shtan'ko, E. Chinkov, A. Shrayber, S. Stepanov*

National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050, Tomsk, Russia

ARTICLE INFO

Keywords:

CaF₂ crystals
Self-trapped excitons
Cathodoluminescence
Stimulated emission of semiconductors
Cross-luminescence

ABSTRACT

Nominally pure CaF₂ crystals were grown by Stockbarger method. Pulse cathodoluminescence (PCL) spectra were studied. PCL spectra of CaF₂ crystals at room temperature were excited by pulse of accelerated electrons and simultaneous stimulated emission of CdSse crystal. It was shown that the simultaneous excitation of the crystals CaF₂ leads to a reduction efficiency of creation of self-trapped excitons (STEs) and the appearance of short-lived emission in the UV region of the spectrum.

1. Introduction

Pure fluorite crystals intensely luminescence when excited near the fundamental absorption edge. The large Stokes shift, about 7 eV, suggests that there is a significant lattice relaxation in the excited state. When an electron makes a transition to the conduction band the lattice distortion occurs near the hole with the formation of a molecular ion X₂⁻, occupying two anion lattice sites in the direction of a dense packing < 100 >, or V_k center. The localization of the conduction electron on cations surrounding the V_k center leads to the formation of a precursor state or an unrelaxed exciton (Lindner et al., 2001a). Unrelaxed excitons in CaF₂ and SrF₂ crystals show a broad structureless absorption in the visible region (Tanimura, 2001; Thoma et al., 1997).

The decay of the precursor is accompanied by the transformation of the unrelaxed exciton into the off-center configuration of the exciton. X₂⁻ molecular ion spontaneously undergoes a combined translational and rotational motion. The localization of the electron on anion vacancy leads to the formation of F center, in the immediate proximity of which the H center is located, oriented along the < 111 > direction. In the present paper we name this F–H pair as relaxed STE.

On the basis of measurements of optically detected EPR (Call et al., 1975) and time-resolved optical spectroscopy (Williams et al., 1976), it was found that intrinsic luminescence and unstable absorption at T = 10 K in a CaF₂ crystal comes from the triplet states of one configuration of relaxed STE, whose thermal equilibrium occurs at a temperature of about 50 K.

Depending on the distance between the components of the F–H pair

in the CaF₂ lattice, four configurations of relaxed STEs can be formed. The energy costs of each formation of STE configurations are about the same (Adair et al., 1985). In order to describe the structure of STE in (Leung H et al., 1992) was introduced a geometric factor, which characterizes electron-hole separation. Calculations (Leung H et al., 1992) also show that at zero temperature the closest configuration of STE forms, with an increase of temperature there is a relaxation of the on-center exciton in more separated pairs of defects (Song, 2003).

The radiative annihilation of relaxed STEs in a CaF₂ crystal is accompanied by the appearance of triplet luminescence ($h\nu_{\max} \approx 4.4$ eV). Many researchers report the additional bands in the lower energy side of the luminescence of relaxed STEs. This nanosecond luminescence ($h\nu_{\max} \approx 3.44$ eV, $\tau = 10$ ns) was observed at temperature from 4 to 77 K, rapidly decreased with increasing temperature (Williams et al., 1976) and was attributed to the singlet exciton emission (Becker et al., 1998). There is no consensus on the nature of this luminescence. In alkali halide crystals singlet luminescence is observed at the higher energies than the luminescence of relaxed STEs (Song and Williams, 1993).

New bands in the high-energy side of the luminescence spectrum of relaxed STEs in crystals with a fluorite structure were investigated in (Rodnyi, 2004; Mysovsky and Radzhabov, 2010). In BaF₂ crystals the core-valence transitions were at 220 nm (5.63 eV). This luminescence is characterized by a short decay time ~1 ns (Rodnyi, 2004) and is also called as crossluminescence or Auger-free luminescence. In pure crystals CaF₂ and SrF₂ the new bands have much lower intensities, than the luminescence of relaxed STEs, they rapidly decrease with temperature

* Corresponding author. National Research Tomsk Polytechnic University, Tomsk, Russia.

E-mail address: stepanova@tpu.ru (S. Stepanov).

increase, and they are almost independent of impurities (Mysovsky and Radzhabov, 2010; Stellmer et al., 2015).

To study the photo-induced transformation of relaxed STEs in crystals with a fluorite structure the cascade excitation technique is used. The first (radiation) pulse is used to create the defects and the second (laser) pulse, delayed for some time, is used to excite them. It was shown (Eshita et al., 1984a; Tanimura et al., 1989) that the optical excitation of relaxed STEs in the region of the electronic absorption component is accompanied by an efficient transformation of some configurations of relaxed STEs into others.

The results are interpreted within the local excitation mechanism. The excitation of the electron localized at the anion vacancy causes the migration of the X_2^- molecular ion along adiabatic potential surfaces, which connects the various configurations of relaxed STEs. The motion is regarded (Eshita et al., 1984b) as a hop of an interstitial atom. Optical excitation in the region of the hole absorption component is accompanied by the transformation of relaxed STEs into spatially separated $F-H$ pairs (Eshita et al., 1984a), which confirms theoretical calculations (Song, 2003).

To study the photo-induced transformation of unrelaxed STEs it is necessary to reduce the delay time between radiation and laser pulses. Combined spectroscopy of synchrotron and laser radiation action was used (Watanabe et al., 2013) to study the mechanisms of formation of the defects in a BaF_2 crystal. However, this method is very sensitive to the pre-history of the crystal. Synchrotron radiation constantly generates short-lived and long-lived defects and the laser light excites them.

The method of simultaneous excitation of crystals with the fluorite structure by pulse of accelerated electrons (PAE) and pulsed cathodoluminescence of semiconductors from the II–VI group (and their solid solutions) was proposed in (Shtan'ko and Chinkov, 1997). It was found that the simultaneous excitation of a CaF_2 crystal by PAE and stimulated emission of a ZnSe crystal in the region of the electronic absorption component of relaxed STE leads to the appearance of short-lived emission (SLE) in the UV spectral region.

The nature of the luminescence in the UV region is unknown. On the one hand, luminescence in UV appears in a pure CaF_2 crystal, both under excitation of ionizing radiation (Mysovsky and Radzhabov, 2010) and the simultaneous action of PAE and SE (Shtan'ko and Chinkov, 1997). On the other hand, a weak structureless band with a maximum at 220 nm was detected (Terekhin et al., 2015) under excitation by high-energy photons of CaF_2 crystals with a high content of barium impurity and was attributed to the so-called extrinsic (impurity) cross-luminescence.

The aim of this work was to study the spectral-kinetic characteristics of the intrinsic luminescence of a CaF_2 crystal under the simultaneous excitation of a pulse of accelerated electrons and pulsed cathodoluminescence of semiconductors II–VI group. In contrast to the technique used in (Shtan'ko and Chinkov, 1997), in these experiments the ZnSe crystal was replaced with a CdSSe crystal, the stimulated emission of which did not overlap with the spectral region of the electronic absorption component of relaxed STEs in a CaF_2 crystal.

2. Experimental details

2.1. CaF_2 crystals preparation

Nominally pure CaF_2 crystals were grown by Stockbarger method in the Vavilov State Optical Institute (St. Petersburg, Russia) by V.M. Reyterov. The samples were transparent to ~ 115 nm and had no selective absorption bands caused by the presence of oxygen or lead impurities (Arkhangelskaya et al., 1980; Radzhabov et al., 2007). The samples were cleaved from one crystal in air along (111) plane into 2-mm-thick, 10-mm-diameter disks. Further the samples were cleaved into rectangular plates and polished with diamond paste.

The size of rectangular plates was $2 \times 5 \times 10$ mm³. The impurity

Table 1
Concentrations of metal impurities.

Metal	Mg	Mn	Fe	Cu	Cr	Ti	Al
Concentration, ppm	50	10	7	2	10	15	20

contents analyzed by the inductively coupled plasma atomic emission spectroscopy method in Table 1 are shown. According to the results of the analysis the content of barium impurities in CaF_2 crystals was less than the detection limit (20 ppm).

2.2. Experimental techniques

The pulse cathodoluminescence was studied by time-resolved spectrometry (Aluker et al., 1987). For excitation of pulse cathodoluminescence the electron source as a compact high current accelerator of GIN-400 type with a vacuum diode was used. The electron pulse duration at FWHM was 12 ns, the average energy of the accelerated electrons was 280 keV. The sample was placed in vacuum chamber, the excitation energy density varied from 0.027 to 0.086 J/cm².

The luminescence decay kinetics was recorded with the photomultiplier PMT-97 using the monochromator MDR-23 (200–2000 nm spectral range, 1.3 nm/mm-inverse linear dispersion) and a digital oscilloscope TetrionxDPO 3034 (300 MHz). Time-resolved measurement of the spectra was performed by scanning along the wavelengths and by recording the luminescence decay kinetics; the emission spectrum was reconstructed by the emission intensity at a given time I_t relative to the moment of the excitation pulse action (the time required to achieve the maximum amplitude of the electron beam current is assumed as $t_i = 10$ ns).

In the photoelectric detection mode, the measurement of the luminescence spectra of samples requires repeated exposure. The cumulative effect of the previous pulses (sample temperature increasing, interaction of mobile charge carriers with long-lived defects, etc) leads to distortion of the shape of the measured spectra. The value of the optical signal measured at a fixed wavelength, in a series of successive pulses of radiation tended to decreasing and was the nature of damped oscillations. Measurement accuracy reaches 20–25%. Therefore, the irradiation pulse repetition frequency is chosen $\sim 10^{-3}$ Hz. Samples before each subsequent measurement of exposure and additional unfiltered light were discolored by high-pressure mercury lamp. The set of measures made it possible to reduce the measurement error in a series of radiation pulses up to 5%. Control was provided by measurements on parallel cleaves of fresh samples.

The source for the synchronous optical excitation of the CaF_2 crystal was single crystals of the semiconductors of the II–VI group. Crystals were selected, the emission of which should have a high intensity and a sufficiently limited spectral range in order to be able to selectively and effectively excite the radiation defects created in the CaF_2 crystal. At a low excitation density the luminescence of the II–VI semiconductors is spontaneous, and when the density rises above a certain threshold, it is forced, which appears in a superlinear increase of the radiation intensity in a limited spectral range. For experiments in this work the II–VI group crystals were selected, which had the minimum threshold excitation density of stimulated emission (SE).

Position adjustment of the spectrum maximum of the SE single crystals semiconductors was carried out by choosing their chemical composition (Permogorov and Reznitsky, 1992), geometry and excitation density (Shtan'ko et al., 1991). The CdS_xSe_{1-x} ($x = 0.4$) crystals were grown by the static Davydov-Markov method from the vapor phase in the «Platan» Research Institute (Fryazino, Russia). The value of the pulse energy SE of a CdSSe crystal was ~ 4 mJ.

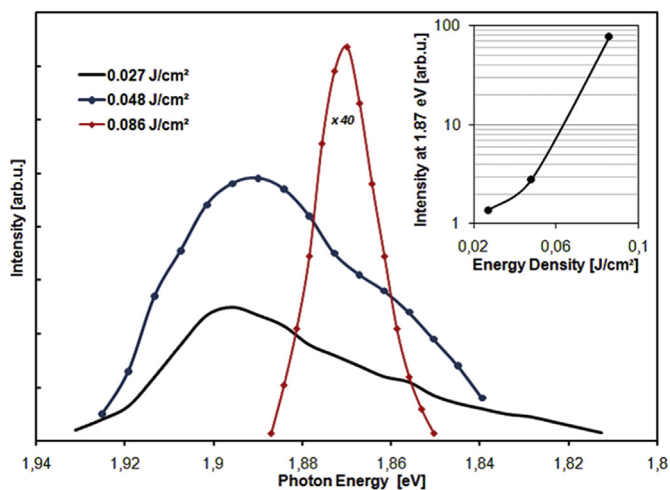


Fig. 1. PCL spectra of $\text{CdS}_x\text{Se}_{1-x}$ ($x = 0.4$) crystal measured at 295 K after 10 ns relative to the end of PAE at different energy densities.

3. Results

3.1. Luminescence CdSse crystal

At low-energy density excitation of a PAE, the edge-emission spectrum of a CdSse crystal is a wide structureless band (Fig. 1). With the increase in the excitation density the emission maximum of a CdSse crystal there is the shift to 1.87 eV and the decrease FWHM to 0.012 eV. Angle distribution of the emission becomes not a homogeneous: about 85–90% of the light energy is emitted in the plane of the irradiated face with an angular divergence of ~ 0.12 rad.

Therefore, the SE at 1.87 eV of a CdSse crystal does not overlap with the absorption of short-lived (relaxed STE) (Williams et al., 1976) and long-lived radiation defects (Chinkov and Shtan'ko, 1997), but overlaps only with the absorption of unrelaxed STE (Tanimura, 2001) in a CaF_2 crystal.

3.2. Cathodoluminescence in CaF_2 crystal

Fig. 2a shows the luminescence spectrum of a CaF_2 crystal, measured at 295 K under electron excitation. The spectrum has a complex structure, which is in good agreement with the results obtained under excitation of the CaF_2 crystal by X-ray (Mysovsky and Radzhabov, 2010), electrons (Williams et al., 1976; Chinkov and Shtan'ko, 1997) and high-energy photons (Stellmer et al., 2015; Lindner et al., 2001b; Fedorov et al., 2009; Mikhailik et al., 2006). The wide band at 4.43 eV can be assigned to the luminescence of relaxed STEs. The luminescence spectrum at high-energy side has a very low intensity, which is in good agreement with the results under X-ray and VUV irradiation of CaF_2 (Mysovsky and Radzhabov, 2010; Stellmer et al., 2015).

The emission band at 4.43 eV is asymmetric with an extended part at the low-energy side. We believe that the band broadening is due to the perturbed STEs (Tsujiyayashi et al., 2000) created during mechanical treatment and after long-term polishing of the samples (Cramer et al., 2005). A high concentration of point defects can be created, for example, under the motion of edge dislocation in different slip planes.

Fig. 2d shows decay kinetic curves of STE luminescence. The decay curves were normalized to unity for a better comparison. The characteristic luminescence decay time of STE in CaF_2 is $\tau = (1.0 \pm 0.05)$ μs . This value agrees well with the finding by Lindner et al. (2001b) under band-gap excitation of CaF_2 , i.e. when creating excitons or states above the bottom of the conduction band.

When the excitation photon energy increases, the number of

secondary electron-hole pairs increases strongly. Decay curves of the relaxed STE luminescence depends on the excitation photon energy and demonstrates the deviations from exponential decay law (Fedorov et al., 2009). In the case of CaF_2 we could not see spectral differences in the luminescence decay curves. The most red shift luminescence peak of relaxed STEs in time after stopping excitation is found for BaF_2 , while in CaF_2 he is very small.

Fig. 2b shows the luminescence spectrum measured under simultaneous irradiation of a CaF_2 crystal by PAE and SE of a CdSse crystal. The wide band at 4.4 eV can be related to STE luminescence. We also could not find a differences in the luminescence decay time under simultaneous excitation of CaF_2 crystal by PAE and SE (Fig. 2e) from what was observed when the a CaF_2 crystal was irradiated with electrons (Fig. 2d).

The first important conclusion is the change of the spectral shape of the luminescence spectrum of relaxed STEs. Under simultaneous excitation of a CaF_2 crystal by PAE and SE of a CdSse crystal the center of gravity of the luminescence spectrum of relaxed STEs has shifted aside high photon energies.

To describe this effect quantitatively we decomposed spectra (Fig. 2a,b) into three Gaussian functions (Table 2). We attribute this spectral characteristic to a superposition of contributions from relaxed configurations STE proposed by Williams et al. (1976). Due to the overlap of spectral ranges of luminescence we could not precisely determine the time decay constants of STE configurations.

The second important observation is that simultaneous excitation of a CaF_2 crystal leads to a decrease in the luminescence intensity of relaxed STEs. In our experiments, the stimulated emission of a semiconductor overlapped with the absorption of only unrelaxed STE (Tanimura, 2001). As stated in Table 1 the synchronous excitation of the a CaF_2 crystal by PAE and SE of a CdSse crystal is accompanied by a decrease in the efficiency of creating only two of the four configurations of relaxed STEs proposed by Williams (Williams et al., 1976). In experiments using the cascade excitation technique (Eshita et al., 1984a), when laser radiation overlapped the region of the electronic absorption component of relaxed STEs in SrF_2 crystal, mutual photoinduced transformation of only two configurations of relaxed STEs was also observed.

Finally, the synchronous excitation of a CaF_2 crystal by PAE and SE of a CdSse crystal is accompanied by the appearance of intense SLE in the UV spectral region. Fig. 2c shows the SLE spectrum of a CaF_2 crystal. After measuring the SLE spectrum, the CaF_2 crystal was covered with an aluminum plate, the thickness of which was higher than the extrapolated depth of the accelerated electrons penetration. Thus, the CaF_2 crystal was excited only by the SE of a CdSse crystal. However, luminescence was not detected.

The intensity of SLE increases during the first few nanoseconds after the cessation of excitation and decreases very rapidly with time. Such a fast decay cannot be ascribed to the spontaneous decay of the STE. We could not accurately determine the times of growth and decay of this luminescence due to insufficient time resolution of the measuring system (~ 7 ns).

It was noted above that optical stimulation of relaxed STEs in crystals with a fluorite structure is accompanied by the transformation of some configurations of relaxed STEs into other or spatially separated $F-H$ pairs. However, the appearance of SLE in the UV region in experiments using the cascade excitation technique was not reported. Thus the optical excitation of unrelaxed STEs leads to a decrease of the efficiency of creating relaxed STEs, as well as to the appearance of SLE in the UV spectral region.

4. Discussion

4.1. Singlet exciton emission

Both in alkali halide (Song and Williams, 1993) and in crystals with

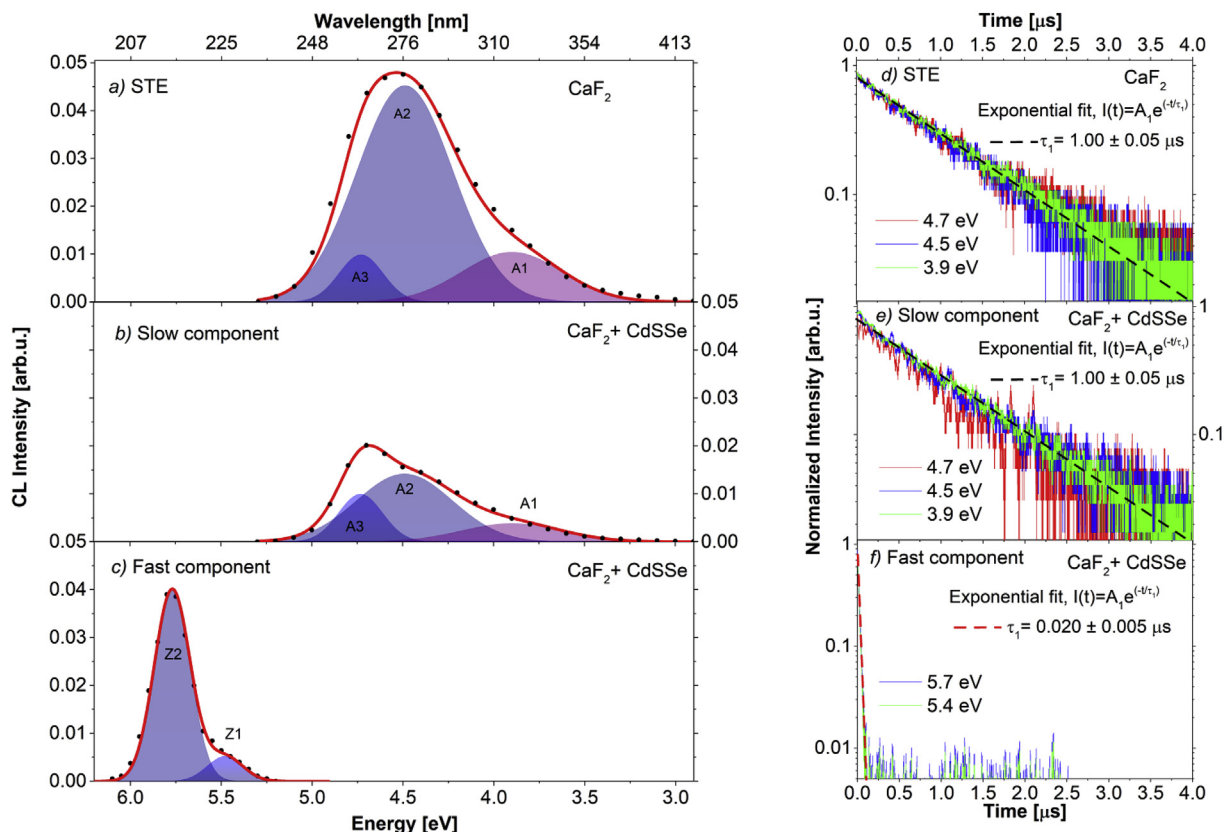


Fig. 2. PCL spectra of CaF_2 crystal measured at 295 K after 10 ns relative to the end of PAE (a), PAE and SE of a CdSSe crystal (b, c). PCL decay kinetic curves of STE luminescence (d), slow (e) and fast (f) component of the luminescence spectrum under simultaneous excitation of CaF_2 crystal by PAE and SE.

a fluorite structure, singlet transitions are located on the energy scale by 1–2 eV higher than triplet transitions. The photon emission should occur from the lowest excited singlet state. It is possible that the complex structure of the SLE spectrum in a CaF_2 crystal (Fig. 2c) is due to the created centers of different nature. Compared to alkali halides (Song and Williams, 1993) the relaxed STE luminescence in the high-energy side of the STE band in the CaF_2 and SrF_2 fluorite crystals has a very low intensity (Williams et al., 1976; Mysovsky and Radzhabov, 2010; Stellmer et al., 2015; Eshita et al., 1984a).

4.2. Unrelaxed exciton emission

We assume that SLE in a CaF_2 crystal can be attributed to transitions from the precursor that shows the wide structureless absorption (Tanimura, 2001). The state of an exciton with a hole that did not pass the stage of self-trapping in the lattice can be the precursor of STE. Two relaxation channels of an electron-hole pair are found in alkali halide (Shibata et al., 1994). The recombination of an electron with a self-trapped hole in both alkali halide crystals and in crystals with a fluorite structure lead to the formation of relaxed STEs. Recombination of an electron with an unrelaxed hole does not lead to the formation of STE in

alkali halide crystals and is accompanied by the formation of spatially separated $F-H$ pairs (Shibata et al., 1994).

When a CaF_2 by PAE and SE of a CdSSe crystal is simultaneously excited, recombination of an electron with an unrelaxed hole is also accompanied by a decrease in the efficiency of creating relaxed STEs. However, unlike alkali halide crystals in crystals with a fluorite structure, synchronous optical excitation of both relaxed (Shtan'ko and Chinkov, 1997) and unrelaxed STEs (Fig. 2,b, see also Table 1) does not produce an increase in the efficiency of creating spatially separated $F-H$ pairs, but is accompanied by the appearance of SLE in UV spectral region.

In unrelaxed STE in CaF_2 the hole component of the F_2^- is oriented along the $\langle 100 \rangle$ direction with a trapped electron in the diffuse orbitals. When an electron recombines with an unrelaxed hole, there should be no change in the energy of radiative transitions in a wide spectral range, because the energy costs of creating different configurations of STEs in fluorite crystals are about the same (Adair et al., 1985).

Table 2

Position, FWHM, and relative area weight of the Gaussian band set.

Emission Band	Position (eV)	FWHM (eV)	Relative Area Weight		Area Ratio
			$\text{CaF}_2 + \text{PAE}$	$\text{CaF}_2 + \text{PAE} + \text{SE}$	
A1	3.90	0.65	0.007	0.002	3.5
A2	4.49	0.62	0.030	0.009	3.3
A3	4.73	0.29	0.003	0.003	1
Z1	5.48	0.23	–	0.001	–
Z2	5.77	0.23	–	0.010	–

4.3. Intrinsic cross-luminescence

SLE band cannot be due to extrinsic core-valence luminescence (Terekhin et al., 2015) as barium impurities in CaF₂ crystals was not found.

At the same time, the spectral-kinetic characteristics of cross-luminescence in a BaF₂ crystal are well studied. The condition for the appearance of cross-luminescence is given by

$$E_{VC} < E_g$$

where E_g is the band gap and E_{VC} is the energy difference between the top of the valence band and that of the core band.

The SLE spectra in the CaF₂ crystal have much in common with the spectra of intrinsic cross-luminescence in the BaF₂ crystal: an intense band with a complex structure on the high-energy side and broadening on the low-energy side (Fig. 2c).

Core electrons are excited by ionizing radiation into the conduction band, core holes quickly recombine with valence electrons with the appearance of their own cross-luminescence. Valence holes relax to the ceiling of the valence band and self-trapped to V_k centers form. The recombination of conduction electrons with V_k centers is accompanied by the appearance of emission of relaxed STEs.

It is usually considered that the intrinsic cross-luminescence in CaF₂ cannot be because the width of the core zone is higher than the width of the main forbidden band (Aguado et al., 1999). However, these calculations of the band structure were performed for the unperturbed lattice and were not experimentally verified. For example, calculations (Letz and Parthier, 2006) indicate that the formation of the F center is accompanied by a slight distortion of the lattice, whereas the formation of the H center is accompanied by a very large deformation of the CaF₂ lattice.

The process of STEs formation with the capture of an electron on an unrelaxed hole is accompanied by a significant distortion of the lattice and the associated local change in the band structure. In contrast to the optical creation of excitons or states just above the bottom of the conduction band, under irradiation by with high-energy electrons of high density, the number of secondary electron-hole pairs increases. F - H pairs can exist no longer isolatedly but overlap with each other.

We assume that under excitation by high-energy electrons, there is a localization of electronic excitations in correlated pairs. For example, in SrF₂ crystal under optical excitation of relaxed STEs, the mutual conversion of only two of the four possible configurations of STEs is predominantly observed (Eshita et al., 1984a). In the CaF₂ crystal under selective optical excitation of unrelaxed STEs, there is a decrease in the efficiency of creating also two of the possible configurations of relaxed STEs (Table 1).

5. Conclusion

In summary we showed that the synchronous excitation of a pure CaF₂ crystal by a pulse of accelerated electrons and stimulated emission

of a CdSe crystal is accompanied by a decrease in the efficiency of creating only two of the four possible configurations of relaxed STEs and the appearance of an intense short-lived emission in the UV region.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by Tomsk Polytechnic University CE Program.

References

- Adair, M., Leung, C., Song, K., 1985. *J. Phys. C Solid State Phys.* 18, L909–L913.
- Aguado, A., Ayuela, A., Lopez, J., Alonso, J., 1999. *J. Phys. Soc. Jap.* 68, 2829–2835.
- Aluker, E., Gavrilov, V., Deich, R., Chernov, S., 1987. *Fast Radiation Stimulated Processes in Alkali Halide Crystals*. Riga: Zinatne, pp. 186.
- Arkhangelskaya, V., Reiterov, V., Trofimova, L., 1980. *J. Appl. Spectrosc.* 32, 67–72.
- Becker, J., Kirm, M., Kolobanov, V.N., Makhov, V.N., Mikhailin, V.V., Vasil'ev, A.N., Zimmerer, G., 1998. Coexistence of triplet and singlet exciton emission in alkaline earth fluoride crystals. *Electrochem. Soc. Proc* 415–419 98-25.
- Call, P., Hayes, W., Kabler, M., 1975. *J. Phys. C Solid State Phys.* 8, L60–L62.
- Chinkov, E., Shtan'ko, V., 1997. *J. Phys. Solid Stat.* 39, 1060–1064.
- Cramer, L., Cumby, T., Leraas, J., Langford, S., Dickinson, J., 2005. *J. Appl. Phys.* 97, 103533.
- Eshita, T., Tanimura, K., Itoh, N., 1984a. *J. Phys. State Sol.* 122, 489–500.
- Eshita, T., Tanimura, K., Itoh, N., 1984b. *Nucl. Instrum. Methods Phys. Res. B1*, 452–455.
- Fedorov, N., Belsky, A., Constant, E., Descamps, D., Martin, P., Vasil'ev, A., 2009. *J. Lumin.* 129, 1813–1816.
- Letz, M., Parthier, L., 2006. *J. Phys. Rev.* B74, 064116.
- Leung, C.H., Zhang, C., Song, K., 1992. *J. Phys. Condens. Matter* 4, 1489–1495.
- Lindner, R., Reichling, M., Williams, R., Matthias, E., 2001a. *J. Phys. Condens. Matter* 13, 2339–2346.
- Lindner, R., Williams, R., Reichling, M., 2001b. *J. Phys. Rev.* B63, 075110.
- Mikhailik, V., Kraus, H., Imber, J., Wahl, D., 2006. *Nucl. Instrum. Methods Phys. Res.* A566, 522–525.
- Mysovsky, A., Radzhabov, E., 2010. *IEEE Trans. Nucl. Sci.* 57, 1200–1203.
- Permogorov, S., Reznitsky, A., 1992. *J. Lumin.* 52, 201–223.
- Radzhabov, E., Nepomnyashchikh, A., Kirm, M., 2007. *J. Phys. Stat. Sol.* A204, 670–676.
- Rodnyi, P., 2004. *J. Radiat. Meas.* 38, 343–352.
- Shibata, T., Iwai, S., Tokizaki, T., Tanimura, K., Nakamura, A., Itoh, N., 1994. *J. Phys. Rev.* 49, 13255–13258.
- Shtan'ko, V., Chinkov, E., 1997. *Tech. Phys. Lett.* 23, 837–838.
- Shtan'ko, V., Oleshko, V., Namm, A., Tolmachev, V., Tereshchenko, E., 1991. *J. Appl. Spectrosc.* 55, 1110–1114.
- Song, K., 2003. *J. Low Temp. Phys.* 29, 754–758.
- Song, K., Williams, R., 1993. *Self-Trapped Excitons*. Springer Verlag, Berlin.
- Stellmer, S., Schreit, M., Schumm, T., 2015. *Sci. Rep.* 5, 15580.
- Tanimura, K., 2001. *J. Phys. Rev. B.* 63, 184303.
- Tanimura, K., Katoh, T., Itoh, N., 1989. *J. Phys. Rev. B.* 40, 1282–1287.
- Terekhin, M., Makhov, V., Lebedev, A., Sluchinskaya, I., 2015. *J. Lumin.* 166, 137–142.
- Thoma, E., Yochum, H., Williams, R., 1997. *J. Phys. Rev. B.* 56, 8001–8011.
- Tsujibayashi, T., Watanabe, M., Arimoto, O., Itoh, M., Nakanishi, S., Itoh, H., Asaka, S., Kamada, M., 2000. *J. Lumin.* 87–89, 254–256.
- Watanabe, M., Azuma, J., Asaka, S., Tsujibayashi, T., Arimoto, O., Nakanishi, S., Itoh, H., Kamada, M., 2013. *J. Phys. Status Solidi.* B250, 396–401.
- Williams, R., Kabler, M., Hayes, W., Stott, J., 1976. *J. Phys. Rev. B.* 14, 725–740.