Luminescence of $K_{1-x}Rb_xCaF_3$ upon the outermost $3p K^+$ and $4p Rb^+$ core ionization

**G. B. Stryganyuk^{1,2}, Ya. M. Chornodolskyy¹, A. S. Voloshinovskii¹,
M. P. Ivanov³, and L. O. Vasylechko⁴**

¹ Ivan Franko National University of Lviv, 8 Kyryla i Mefodiya Str., 79005 Lviv, Ukraine

² HASYLAB at DESY, Notkestr. 85, 22607 Hamburg, Germany

³ Institute for Single Crystal of NASU, 60 Lenin avenue, 61001 Kharkov, Ukraine

⁴ National University "Lviv Polytechnic", 12 S. Bandera Str., 79013 Lviv, Ukraine

Received 26 January 2007, accepted 4 April 2007

Published online 5 June 2007

PACS 78.40.Ha, 78.55.Fv

The luminescence and reflection spectra of $K_{1-x}Rb_xCaF_3$ crystals have been studied using synchrotron radiation. Luminescence of self-trapped exciton and core-valence luminescence are revealed for $KCaF_3$ crystals in UV and VUV spectral range, respectively. The core-valence VUV luminescence of $KCaF_3$ appears after $3p K^+$ core ionization and originates from the radiative recombination of $3p K^{2+}$ core holes with $2p F^-$ valence electrons. The fast UV luminescence of $K_{1-x}Rb_xCaF_3$ crystals has been attributed to the radiative recombination of the holes in $4p Rb^{2+}$ impurity core states with $2p F^-$ valence electrons. The impurity core-valence luminescence of $K_{1-x}Rb_xCaF_3$ reveals the excitation threshold corresponding to the ionization of impurity $4p Rb^+$ core states. Efficient excitation of $4p Rb^+$ related luminescence of $K_{1-x}Rb_xCaF_3$ within the energy range of $3p K^+$ core ionization is considered as an evidence for the hole migration from the host $3p K^+$ core band to the impurity $4p Rb^+$ core states.

phys. stat. sol. (b) **244**, No. 9, 3303–3307 (2007) / DOI 10.1002/pssb.200743035

Luminescence of $K_{1-x}Rb_xCaF_3$ upon the outermost $3p K^+$ and $4p Rb^+$ core ionization

G. B. Stryganyuk^{1,2}, Ya. M. Chornodolsky^{*,1}, A. S. Voloshinovskii¹,
M. P. Ivanov³, and L. O. Vasylechko⁴

¹ Ivan Franko National University of Lviv, 8 Kyrila i Mefodiya Str., 79005 Lviv, Ukraine

² HASYLAB at DESY, Notkestr. 85, 22607 Hamburg, Germany

³ Institute for Single Crystal of NASU, 60 Lenin avenue, 61001 Kharkov, Ukraine

⁴ National University “Lviv Polytechnic”, 12 S. Bandera Str., 79013 Lviv, Ukraine

Received 26 January 2007, accepted 4 April 2007

Published online 5 June 2007

PACS 78.40.Ha, 78.55.Fv

The luminescence and reflection spectra of $K_{1-x}Rb_xCaF_3$ crystals have been studied using synchrotron radiation. Luminescence of self-trapped exciton and core-valence luminescence are revealed for $KCaF_3$ crystals in UV and VUV spectral range, respectively. The core-valence VUV luminescence of $KCaF_3$ appears after $3p K^+$ core ionization and originates from the radiative recombination of $3p K^{2+}$ core holes with $2p F^-$ valence electrons. The fast UV luminescence of $K_{1-x}Rb_xCaF_3$ crystals has been attributed to the radiative recombination of the holes in $4p Rb^{2+}$ impurity core states with $2p F^-$ valence electrons. The impurity core-valence luminescence of $K_{1-x}Rb_xCaF_3$ reveals the excitation threshold corresponding to the ionization of impurity $4p Rb^+$ core states. Efficient excitation of $4p Rb^+$ related luminescence of $K_{1-x}Rb_xCaF_3$ within the energy range of $3p K^+$ core ionization is considered as an evidence for the hole migration from the host $3p K^+$ core band to the impurity $4p Rb^+$ core states.

© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

Most of luminescence processes imply the participation of valence holes at the final radiative stage, whereas the radiative relaxation of core holes is observed in rare instances. In most cases the core hole undergoes the nonradiative Auger-decay within $\tau_A \sim 10^{-12}$ s. The recombination of core holes with valence electrons appears to be radiative only for the wide-gap dielectric crystals, in which the values of ionization energy for the outermost core states (E_{cc}) and forbidden-gap (E_g) satisfy $E_{cc} < 2E_g$ condition [1]. The radiative recombination of outermost core holes with valence electrons causes a new type of intrinsic luminescence which is also known as so-called core-valence luminescence (CVL), Auger-free luminescence or cross luminescence [1, 2]. The investigation of CVL-active materials upon the excitation within the energy range of outermost core ionization gives the possibility to study the processes of hole relaxation within the outermost core states.

The migration of core holes from Rb^+ to Cs^+ ions has been confirmed for $Rb_{1-x}Cs_xF$ solid solutions [3], where the CVL of impurity Cs-clusters was registered at rather small concentration of Cs^+ ions ($x \approx 0.001$) upon the excitation in the energy range of $4p Rb^+$ core ionization. The decrease of decay time

* Corresponding author: e-mail: chornodolsky@ukr.net, Phone: +38 032 296 4366, Fax: +38 032 297 8903

constant for the CVL of Rb-clusters in $Rb_{1-x}Cs_xF$ was considered as an evidence for the energy transfer from Rb^+ to Cs^+ ions due to the hole migration within the overlapping Rb^+ and Cs^+ core bands.

The dynamical behavior of Rb-core excitons through measurement of CVL caused by Cs-core holes in a mixed crystal of $Rb_{0.82}Cs_{0.18}Cl$ under excitation with synchrotron radiation and laser are studied in [4].

The migration of core holes has also been observed for the CVL-active $CsCl-Tl$ crystals [5] where the transfer of core excitation to the Tl^+ impurity was revealed as the reducing of CVL decay time constant from 1.2 ns down to 0.6 ns upon the increasing of Tl^+ concentration up to 1 mol%.

The crystals with CVL are perspective for creation of fast scintillators with time response less than 1 ns [6]. However in many cases the recombination of core hole and valence electron is accompanied by emission in vacuum ultra-violet (VUV) spectral range [7]. What is not useful for scintillator materials. In such cases the migration of core holes to the impurity core level in CVL-active crystals provides the possibility to transform the core-valence luminescence from VUV into ultra-violet (UV) spectral range. With purpose to modify the CVL of $KCaF_3$ and study the core hole mobility the luminescence of $K_{1-x}Rb_xCaF_3$ crystals was investigated in the present work.

2 Experimental details

$K_{1-x}Rb_xCaF_3$ ($x = 0.0, 0.03, 1.0$) single crystals have been grown in graphite ampoules using the Bridgman technique. The concentration of impurity Rb^+ ions was determined from X-ray diffraction (XRD) patterns measured using "DRON-3M" powder diffractometer equipped with $Cu K_\alpha$ radiation source ($\lambda = 1.54178 \text{ \AA}$). Crystalline powders for XRD measurements were obtained by grinding of the single crystals. The volume of perovskite-like cell in $K_{1-x}Rb_xCaF_3$ row follows Vegard's law that allows to determine the concentration of Rb^+ impurity ions. For example, the value of lattice constant $a = 4.378 \text{ \AA}$ determined after Rietveld refinement of XRD pattern corresponds to $x = 0.03$ for $K_{1-x}Rb_xCaF_3$ (Fig. 1).

The luminescence investigation of $K_{1-x}Rb_xCaF_3$ crystals were performed at $T = 10-300 \text{ K}$ upon the excitation with the synchrotron radiation from DORIS storage ring (DESY, Hamburg) using the facility of SUPERLUMI station at HASYLAB [8]. Emission spectra in UV-visible range were measured using ARC "Spectra Pro 308" 30 cm monochromator in Czerny–Turner mounting equipped with HAMAMATSU R6358P detector. VUV–UV emission spectra were measured with the VUV 0.5 meter Pouey monochromator equipped with a solar blind Hamamatsu R6836 photomultiplier. Luminescence excitation spectra were scanned with the resolution of $3.2 \text{ \AA}$ within the wide excitation energy range ($10 \div 35 \text{ eV}$) using primary 2 m monochromator in 15° McPherson mounting. Time resolved spectroscopy technique has been used to separate the fast component of core-valence luminescence. Luminescence excitation and reflection spectra have been corrected on the incident photon flux.

Fig. 1 Dependence of perovskite-like cell volume in $K_{1-x}Rb_xCaF_3$ on the rubidium content (x).

3 Experimental results and discussion

One kind of the intrinsic luminescence of KCaF_3 crystals is caused by the luminescence of self-trapped excitons. The luminescence band of self-trapped exciton (STE) in KCaF_3 is located within 2.5–5 eV range revealing the intensity maximum at 4.1 eV (Fig. 2, curve 1). The excitation efficiency of STE emission reveals the characteristic peak at 10.0 eV (Fig. 2, curve 2) corresponding to the fundamental absorption edge of KCaF_3 . The structure peculiarities of STE luminescence excitation spectrum are well matched with the structure of KCaF_3 reflection spectra (Fig. 2, curve 3). The anticorrelation between the excitation and reflection spectra is clearly observed in the range of band-to-band transitions ($E > E_g$). The positions of exciton peaks in reflection spectrum (curve 3) coincide with the dips in luminescence excitation spectrum (curve 2). In the range of high reflectivity, less light penetrates the crystal and the absorption is also known to be high, i.e., the excitation quanta of this range are absorbed within the near-surface layer where the interaction of excited states with the surface defect is occur. Thus, the peculiarity, observed for the luminescence excitation and reflection spectra in the range of band-to-band transitions, is caused by the reflection losses and by the nonradiative decay of excited states at the surface defects. Such defect-related nonradiative decay processes are especially efficient upon the excitation in the exciton absorption maxima where the penetration depth is minimal for the excitation quanta. When the penetration depth of excitation quanta is small, then the nonradiative decay of excited states predominates because of the high probability of interaction with the surface defect. Such features of luminescence excitation and reflection spectra facilitate the interpretation of peaks origin in the reflection spectra of KCaF_3 crystal (Fig. 2, curve 3). The knowledge about the origin of such spectral features is constitutive in the study of CVL-related processes in KCaF_3 crystal (see Table 1). The results of band structure calculations performed for KMgF_3 crystal [9] were used to identify the main peaks in the reflection spectrum of KCaF_3 . KMgF_3 and KCaF_3 crystals have the same perovskite-like structure and the expected similarity in band structure of these crystals allows us to suggest that the core exciton transitions will be formed in Γ - and X-points of Brillouin zone, and the peaks at 20.4 eV and 21.8 eV correspond to the creation of core excitons in Γ - and X-points, respectively.

Besides the luminescence of self-trapped excitons, pure KCaF_3 crystal possess the intrinsic CVL revealing the characteristic fast decay time constant (1.3 ns) and the double-peaked emission spectrum (7.4 and 8.2 eV) in the VUV spectral range (Fig. 3, curve 1). This luminescence was observed earlier upon the excitation with the electron beam [10]. The CVL of KCaF_3 crystal reveals the excitation threshold at 21 eV (Fig. 3, curve 2) corresponding to the $3p \text{ K}^{2+} \rightarrow 2p \text{ F}^-$ core-to-valence transition. There is no chance to excite the CVL upon the irradiation of KCaF_3 crystal within the energy range of $3p \text{ K}^+$ core exciton creation ($E = 20.4 \text{ eV}$) since at this excitation the free electrons in the conduction band and holes

Fig. 2 Emission spectrum (curve 1, $E_{\text{exc}} = 10 \text{ eV}$), luminescence excitation (curve 2, $E_{\text{em}} = 4.1 \text{ eV}$) and reflection (curve 3) spectra of KCaF_3 at $T = 10 \text{ K}$. The reflection peak positions (see Table 1) are indicated by arrows.

Table 1 Energy position and identification of the main features in the reflection spectra of $KCaF_3$ ($T = 10$ K).

energy position of peaks E , eV	identification of peaks
10.7	2p F^- exciton (Γ -point)
20.4	3p K^+ core exciton (Γ -point)
21.8	3p K^+ core exciton (X-point)
28.4	3p Ca^{2+} core exciton

in the core band don't appear. On the other hand, the CVL is observed for $KCaF_3$ crystal in the range of second excitonic peak (21.8 eV) where the free electrons and core holes may appear after the autoionization of 3p K^+ core exciton in X-point. The sharp dip at 28.4 eV in the CVL excitation spectra of $KCaF_3$ crystal has been attributed to the formation of 3p Ca^{2+} core exciton implying the losses due to the nonradiative decay of excited core states on the surface defects.

The activation of $KCaF_3$ crystal with Rb^+ ions leads to the additional emission band appearance in the UV range (Fig. 3, curve 3) besides the VUV bands of intrinsic CVL. The UV luminescence of $K_{1-x}Rb_xCaF_3$ crystals resembles the CVL observed for $RbCaF_3$ crystals [11]. The UV emission of $K_{1-x}Rb_xCaF_3$ reveals the excitation threshold at $E \approx 17$ eV (Fig. 3, curve 4) that is close to the ionization energy for the 4p Rb^+ core states. Thus, the UV luminescence observed for $K_{1-x}Rb_xCaF_3$ crystals upon the excitation at $E > 17$ eV can be attributed to the radiative 4p $Rb^{2+} \rightarrow 2p F^-$ core-to-valence transitions, the so-called impurity CVL. The excitation spectrum for the impurity CVL of $K_{1-x}Rb_xCaF_3$ (Fig. 3, curve 4) reproduces the structure of one for the CVL of $KCaF_3$ (Fig. 3, curve 2) at $E \geq 21$ eV. This could be considered as an evidence for the energy transfer from K^+ to Rb^+ ions via the core hole migration.

A special attention should be paid to the comparable efficiency for the UV emission of $K_{0.97}Rb_{0.03}CaF_3$ in both the $17 \div 21$ eV and $E > 21$ eV excitation energy ranges (Fig. 3, curve 4). For the energy range $17 \div 21$ eV the absorption coefficient of $K_{1-x}Rb_xCaF_3$ matrix is supposed to be less than one for $E > 21$ eV. This provides the deeper penetration of excitation quanta with $17 \div 21$ eV energy into the crystal and more efficient excitation of impurity Rb^+ ions, since for this case the nonradiative losses on surface defects are essentially reduced [5]. The similar peculiarity has been observed also for the impurity CVL of $Rb_{1-x}Cs_xCl$ crystals [12] and can be successfully applied for the improvement of laser characteristics of CVL-active crystals [13].

The simplified energy structure can be proposed for $K_{0.97}Rb_{0.03}CaF_3$ (Fig. 4) according to some relation between the CVL parameters and crystal band structure. To compile this scheme, the excitation thresholds of impurity and intrinsic CVL were considered to correspond to the ionization of 4p Rb^+ - and 3p K^+ -

Fig. 3 Emission and luminescence excitation spectra of $KCaF_3$ (curves 1, 2) and $K_{0.97}Rb_{0.03}CaF_3$ (curves 3, 4) at $T = 300$ K. The reflection peak positions (see Table 1) are indicated by arrows.

Fig. 4 Simplified energy band scheme of $K_{0.97}Rb_{0.03}CaF_3$ crystal (1, 2 transitions are responsible for impurity core-valence luminescence; ΔE_v – width of valence band).

core states, respectively. The width of CVL spectra ($\Delta E = 3.5$ eV) was suggested to reproduce roughly the width of valence band ΔE_v [1].

4 Conclusion

KCaF₃ crystal reveals the CVL bands in VUV range with maximum at 7.4 and 8.2 eV. Spectral parameters of the CVL, observed for KCaF₃ crystal upon the excitation with synchrotron radiation quanta, are in a good agreement with the literature data on KCaF₃ CVL excited by the electron beam [10]. The excitation threshold of CVL is located at 21 eV corresponding to the ionization of 3p K⁺ core state after transition in X-point of Brillouin zone. The activation of KCaF₃ crystal with Rb⁺ impurity ($K_{0.97}Rb_{0.03}CaF_3$) results in the appearance of impurity CVL which is caused by the radiative 4p Rb²⁺ → 2p F⁻ transitions. The excitation of $K_{1-x}Rb_xCaF_3$ impurity CVL is efficient in the range of relative transparency (17 ÷ 21 eV) of KCaF₃ and also in the energy range of 3p K⁺ core ionization. The latter can be considered as a good evidence for the migration of hole from 3p K⁺ to 4p Rb⁺ core.

Acknowledgement Authors are thankful to Prof. G. Zimmerer for his kind assistance in measurement performance at SUPERLUMI station.

References

- [1] P. A. Rodnyi, Physical processes in inorganic scintillators (CRC Press, Boca Raton, New York, 1997), p. 218.
- [2] M. Itoh, Recent Res. Dev. Phys. **4**, 205 (2003).
- [3] M. Itoh, N. Ohno, and S. Hashimoto, Phys. Rev. Lett. **69**, 1133 (1992).
- [4] T. Tsujibayashi, J. Azuma, Y. Inabe, K. Toyoda, M. Kamada, and M. Itoh, J. Lumin. **122/123**, 899 (2007).
- [5] A. Voloshinovskii, Radiat. Meas. **33**, 565 (2001).
- [6] C. L. Melcher, Nucl. Instrum. Methods Phys. Res. A **537**, 6 (2005).
- [7] M. Kirm, A. Lushchik, C. Lushchik, V. Makhov, E. Negodin, S. Vielhauer, and G. Zimmerer, Nucl. Instrum. Methods Phys. Res. A **486**, 422 (2002).
- [8] G. Zimmerer, Nucl. Instrum. Methods Phys. Res. A **308**, 178 (1991).
- [9] R. A. Heaton and C. C. Lin, Phys. Rev. B **25**(6), 3538 (1982).
- [10] J. Jansons, Z. Rachko, J. Valbis, J. Andriessen, P. Dorenbos, C. W. E. van Eijk, and N. M. Khaidukov, J. Phys.: Condens. Matter **5**, 1589 (1993).
- [11] A. N. Belsky, P. Chevallier, E. N. Mel'chakov, C. Pedrini, P. A. Rodnyi, and A. N. Vasil'ev, Chem. Phys. Lett. **278**, 369 (1997).
- [12] A. S. Voloshinovskii, M. S. Mikhailik, V. B. Mikhailik, P. A. Rodnyi, C. W. E. van Eijk, and G. Zimmerer, J. Lumin. **79**, 107 (1998).
- [13] S. Asaka, M. Itoh, and M. Kamada, Phys. Rev. B **63**, 081104(R) (2001).