Effect of local environment on crossluminescence kinetics in SrF$_2$:Ba and CaF$_2$:Ba solid solutions

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Spectral and kinetic properties of extrinsic crossluminescence (CL) in SrF$_2$:Ba(1%) and CaF$_2$:Ba(1%) are compared with those of intrinsic CL in BaF$_2$ and are analyzed taking into account EXAFS data obtained at the Ba $L_{III}$ edge and results of first-principles calculations. The CL decay time was revealed to be longer in SrF$_2$:Ba and CaF$_2$:Ba compared to BaF$_2$. This fact contradicts the expected acceleration of luminescence decay which could result from an increased overlap of wave functions in solid solutions due to shortening of the Ba–F distance obtained in both EXAFS measurements and first-principles calculations. This discrepancy is explained by the effect of migration and subsequent non-radiative decay of the Ba (5$p$) core holes in BaF$_2$ and by decreasing of the probability of optical transitions between Ba (5$p$) states and the valence band in SrF$_2$:Ba and CaF$_2$:Ba predicted by first-principles calculations.

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I. INTRODUCTION

It is well known that so-called crossluminescence (CL) also known as core-valence luminescence or Auger-free luminescence is due to radiative recombination of electrons from the valence band with the holes created in the uppermost core band. CL is observed in a number of wide band-gap ionic crystals in which the Auger decay of these holes is energy forbidden. For BaF$_2$ crystal, an example of the well-known CL-active material, CL can be represented as radiative electronic transitions from the F$^−$ (2$p$) valence band to the Ba$^{2+}$ (5$p$) core band; although it is generally accepted that the core hole becomes self-trapped before the radiative CL transition takes place. In BaF$_2$ such transitions give a rather bright broadband luminescence in the ultraviolet region with a maximum at 220 nm.

The important characteristic of CL is its short decay time $τ \sim 1$ ns. This property of CL has resulted in a rather strong interest to CL crystals as possible fast scintillators in previous years although up to now CL-based scintillation detectors have found limited applications (see, e.g., Refs. [3] and [4]). However, nowadays the interest to CL scintillators has reappeared because of increasing demand for ultrafast radiation detectors for high-energy physics experiments at high-luminosity accelerators and for positron emission tomography based on time-of-flight technique.

Although CL was discovered more than 30 years ago, many features of CL mechanism are still not well understood. In particular, the real lattice configuration of the initial state for CL transition is under discussion (see, e.g., Ref. [5]). In order to get some insights into this problem, in the present work the influence of local environment around the core-hole on the excitation spectra and kinetics of CL has been studied for so-called extrinsic (impurity) CL. If some alkali or alkaline earth halide crystal (e.g., SrF$_2$ or CaF$_2$) which does not have intrinsic CL is doped with a heavier metal ion (e.g., Ba$^{2+}$), then the radiative recombination of the valence electrons with holes created in the uppermost $np$ levels of the impurity ion (5$p$ levels of Ba$^{2+}$) can become possible. Of course, such extrinsic CL is observed if the spectrum of these transitions is in the optical transmission region of the host crystal. The excitation threshold of the impurity CL coincides with the energy separation between the impurity $np$-level and the bottom of the conduction band.

It is well known that crystals with the fluorite structure (CaF$_2$, SrF$_2$, and BaF$_2$) undergo a phase transition from cubic fluorite to orthorhombic PbCl$_2$ structure at high pressure. Thus, if Ba$^{2+}$ ions are incorporated into the SrF$_2$ or CaF$_2$ host having smaller lattice parameter than BaF$_2$, the strong local stress around the Ba$^{2+}$ ions can result in the appearance of a local phase transition. Accordingly, the local environment of the Ba$^{2+}$ ions in these hosts can become very different from that in BaF$_2$ and can remarkably modify the properties of Ba$^{2+}$-related impurity CL in SrF$_2$ and CaF$_2$ compared to those of intrinsic CL in BaF$_2$. The conventional experimental technique for studying local environment of atoms in solids is extended X-ray absorption fine-structure (EXAFS) spectroscopy which provides, in particular, data on interatomic distances and coordination numbers, i.e., can directly indicate whether the local phase transition takes place.

In the present work the local structure around the Ba$^{2+}$ ions in SrF$_2$:Ba(1%) and CaF$_2$:Ba(1%) crystals has been studied using EXAFS technique. The obtained data were compared with the results of first-principles calculations of the local structure distortions around the Ba$^{2+}$ ions in SrF$_2$:Ba and CaF$_2$:Ba solid solutions. The excitation spectra and kinetics of extrinsic CL in SrF$_2$:Ba and CaF$_2$:Ba were measured using synchrotron radiation. Finally, the observed spectral and kinetic properties of extrinsic CL in SrF$_2$:Ba and CaF$_2$:Ba are analyzed taking into account the results of EXAFS measurements and first-principles calculations.
II. EXPERIMENTAL DETAILS

The EXAFS measurements were carried out on station 7.1.13 of synchrotron radiation source (SRS) at Daresbury Laboratory with an electron beam energy of 2 GeV and the maximum storage ring current of 250 mA in multibunch mode. The incident radiation was monochromatised using a double-crystal Si(111) monochromator. Experiments were performed at 300 K at the Ba $L_{III}$ edge (5.247 keV) in the energy range 5.15–5.62 keV (the upper boundary was limited by the proximity of the Ba $L_{II}$ edge). The EXAFS data were collected in transmission mode using two ion chambers filled with He+Ar gas mixtures that gave 20% and 80% absorption of incident radiation.

The oscillatory EXAFS function $\chi(k)$ was extracted from the absorption curve $\mu x(E) = \ln(I_0/I)$ (where $E$ is the energy of radiation) in the normal way. After removing the pre-edge background, splines were used to extract the smooth atomic part of the absorption $\mu x_0(E)$, and the dependence $\chi = (\mu x - \mu x_0)/\mu x_0$ was calculated as a function of the photoelectron wave vector $k = [2m(E - E_0)/h^2]^{1/2}$. The energy origin $E_0$ was taken to be the position of the inflection point on the absorption edge. The edge steps ranged from 0.012 to 0.019. For each sample direct and inverse Fourier transforms with modified Hanning windows were used to extract the information about the first three shells from the experimental curve $\chi(k)$. The distances $R_j$, coordination numbers $N_j$, and Debye-Waller factors $\sigma_j^2$ for each shell as well as the energy origin correction $\delta E_0$ were simultaneously varied to obtain the minimum root-mean-square deviation between the experimental and calculated $k^2\chi(k)$ curves. The number of fitting parameters (8) was usually about half of the number of independent data points ($N_{\text{ind}} = 2\Delta k a R/\pi = 14–17$). The accuracy of the fitting parameters was estimated from the Fisher information matrix. To increase this accuracy, additional constraints (equal energy corrections $\delta E_0$ for all shells) and known relations between coordination numbers for the fluorite structure were used. FEFF software was used to calculate the dependence of the backscattering amplitude and phase, the central-atom phase shift and the mean free path of a photoelectron on its wave vector.

The excitation spectra and decay kinetics of CL were measured on station 3.1 of SRS. This setup is equipped with 1-meter Seya-Namioka primary monochromator and the excitation photon energy range of 5–35 eV. Luminescence was detected by fast photomultiplier tube XP2020Q via interference filter 204.0 nm having bandpass (FWHM) 20 nm and peak transmission 17.5%. The setup had no secondary monochromator for emission spectra measurements in deep UV region. Standard time-correlated single-photon counting was used for time-resolved measurements in a single-bunch mode operation of the SRS.

It is necessary to add that the experimental investigation of the Ba-impurity luminescence in SrF$_2$:Ba and CaF$_2$:Ba is not a simple task because of rather low concentration of Ba in our samples and high intensity of other emissions spectrally overlapping with impurity CL, in particular, emissions from self-trapped excitons of the host crystals and from uncontrolled impurities (mainly of rare-earth ions). Due to this fact the excitation spectra of impurity CL were measured as time-resolved excitation spectra within the short (~1 ns) time window immediately following the SR excitation pulse, thus corresponding to detection of the fast component of luminescence. Additionally, as CL in BaF$_2$ is temperature-independent up to 850 K (Ref. [17]) and other unfavorable kinds of luminescence exhibit considerable thermal quenching upon heating, all measurements related to impurity CL were carried out at increased temperature of $T = 455$ K.

For luminescence measurements, BaF$_2$, SrF$_2$:Ba(1.0 mol.%), and CaF$_2$:Ba(1.0 mol.%) single crystals were cleaved just prior to their installation into the sample chamber. Before the EXAFS measurements the samples were powdered, sieved and the powder was rubbed into the surface of adhesive tape. From 5 to 8 layers of the tape were used for recording of EXAFS spectra.

III. RESULTS AND DISCUSSION

A. First-principles calculations

First-principles calculations of the local structure of SrF$_2$:Ba and CaF$_2$:Ba solid solutions were performed within the density-functional theory in the local density approximation (LDA) using the ABINIT software. The pseudopotentials needed for calculations were constructed using the OPIUM program or borrowed from.

TABLE I. Structural relaxation around Ba atoms in CaF$_2$:Ba and SrF$_2$:Ba solid solutions. The experimental Ba–X distances (in Å) obtained from the EXAFS data analysis are compared with interatomic distances calculated from first principles and interatomic distances in undoped CaF$_2$ ($a = 5.4712$ Å) and SrF$_2$ ($a = 5.8000$ Å) host materials.

| Shell | EXAFS experiment | First-principles calculations | Distances in host materials |
|-------|------------------|-------------------------------|-----------------------------|
| Ba–F  | 2.568(24)        | 2.581                         | 2.369                       |
| Ba–Ca | 3.946(31)        | 3.942                         | 3.869                       |
| Ba–F  | 4.582(51)        | 4.586                         | 4.536                       |
| Ba–F  | 2.633(17)        | 2.628                         | 2.511                       |
| Ba–Sr | 4.105(91)        | 4.139                         | 4.101                       |
| Ba–F  | 4.779(40)        | 4.832                         | 4.809                       |
| Ba–F  | 2.685(14)        | —                             | 2.685                       |
| Ba–Ba | 4.384(14)        | —                             | 4.384                       |
| Ba–F  | 5.141(14)        | —                             | 5.141                       |

CaF$_2$:Ba solid solutions were performed with 1-meter Seya-Namioka primary monochromator and the excitation photon energy range of 5–35 eV. Luminescence was detected by fast photomultiplier tube XP2020Q via interference filter 204.0 nm having bandpass (FWHM) 20 nm and peak transmission 17.5%. The setup had no secondary monochromator for emission spectra measurements in deep UV region. Standard time-correlated single-photon counting was used for time-resolved measurements in a single-bunch mode operation of the SRS.

It is necessary to add that the experimental investigation of the Ba-impurity luminescence in SrF$_2$:Ba and CaF$_2$:Ba solid solutions was performed with 1-meter Seya-Namioka primary monochromator and the excitation photon energy range of 5–35 eV. Luminescence was detected by fast photomultiplier tube XP2020Q via interference filter 204.0 nm having bandpass (FWHM) 20 nm and peak transmission 17.5%. The setup had no secondary monochromator for emission spectra measurements in deep UV region. Standard time-correlated single-photon counting was used for time-resolved measurements in a single-bunch mode operation of the SRS.

First-principles calculations of the local structure of SrF$_2$:Ba and CaF$_2$:Ba solid solutions were performed within the density-functional theory in the local density approximation (LDA) using the ABINIT software. The pseudopotentials needed for calculations were constructed using the OPIUM program or borrowed from.
Ref. 18. The local structure of the solid solutions was modeled with CaF$_2$ and SrF$_2$ supercells containing 3×3×3 FCC unit cells in which one of 27 metal atoms was substituted by the Ba atom. The cut-off energy was 30 Ha (816 eV); the integration over the Brillouin zone was performed on the 4×4×4 Monkhorst-Pack mesh. Interatomic distances in the local environment of the Ba atom, corrected for the systematic errors in the lattice parameter determination for undoped CaF$_2$ and SrF$_2$ in the LDA, are presented in Table 1.

As the possibility of the local phase transition into the orthorhombic phase is also discussed in this work, we performed the first-principles calculations for the 1×2×1 supercell of the $Pnma$ phase of CaF$_2$:Ba and SrF$_2$:Ba, in which one Ca(Sr) atom was substituted by the Ba atom. The calculations showed that the energy of this phase exceeds that of the fluoride phase with the same Ba content by 54 meV per formula unit for CaF$_2$:Ba and by 69 meV for SrF$_2$:Ba. The atomic coordinates obtained in these calculations were used for simulating the theoretical EXAFS spectra for the orthorhombic phase.

The energy band structure of BaF$_2$ and its solid solutions was calculated in both the LDA and one-shot $GW$ approximations first without taking into account the spin-orbit coupling of the Ba$(5p)$ states and then was corrected for the spin-orbit splitting. The details of such calculations are described in Ref. 19. The calculated LDA band gaps for 3×3×3 supercells of CaF$_2$:Ba and SrF$_2$:Ba are 7.29 and 7.03 eV, respectively; the LDA band gap of BaF$_2$ is 6.69 eV. In all three compounds, the bottom of the conduction band is at the Γ point and the top of the valence band is at the X point of the Brillouin zone. In the LDA approximation, the energy separations between the top of the Ba$^{2+}$(5p) band and the conduction band edge are 14.13, 14.81, and 15.22 eV in BaF$_2$, SrF$_2$:Ba, and CaF$_2$:Ba, respectively. The calculated spin-orbit splitting of the Ba (5p) states in BaF$_2$ is 2.05 eV. In order to take into account the many-body effects, the $GW$ corrections to the positions of the valence and conduction bands in undoped CaF$_2$ and SrF$_2$ as well as to the position of the Ba$^{2+}$(5p) band in BaF$_2$ were calculated. After taking into account the many-body effects and spin-orbit splitting of the Ba(5p) states, the final energy separations between the top of the Ba$^{2+}$(5p) band and the conduction band edge are 17.35, 18.23, and 18.73 eV in BaF$_2$, SrF$_2$:Ba, and CaF$_2$:Ba, respectively.

B. EXAFS data

In order to determine the local environment of the Ba$^{2+}$ impurity, EXAFS spectra were analyzed. Typical Fourier-filtered EXAFS spectrum $k^2\chi(k)$ for the CaF$_2$:Ba sample and its best theoretical fit are shown in Fig. 1. The best agreement between the experimental and calculated data was obtained for a model in which the Ba ions substitute for the Sr or Ca ions in the fluorite structure. Interatomic distances for three nearest shells obtained from the EXAFS data analysis, the data calculated from known lattice parameters of undoped host crystals and the results of first-principles calculations for CaF$_2$:Ba and SrF$_2$:Ba solid solutions are given in Table 1. It is seen that for BaF$_2$ the interatomic distances obtained from the EXAFS data analysis agree well with the X-ray data. For SrF$_2$:Ba and CaF$_2$:Ba solid solutions the nearest Ba--F distances are shorter than in BaF$_2$, but are always much longer than interatomic distances in host crystals. The distances obtained from first-principles calculations agree with the experimental interatomic distances in solid solutions. The coordination numbers are close to 8, 12, and 24 for all samples, as expected for the fluoride structure.

On the other hand, the comparison of the experimental EXAFS spectrum with the theoretical one simulated for the orthorhombic phase shows that the spectra are very different (Fig. 2). So, we can conclude that the local phase transition from cubic fluorite to orthorhombic PbCl$_2$ structure that could be induced by the strong local stress in the host around the impurity ions is absent in CaF$_2$:Ba and SrF$_2$:Ba samples.

As for the Debye-Waller factors, the comparison has shown that in solid solutions these factors are close to those in BaF$_2$ (for example, $\sigma_d^2 = 0.0144(25)$ Å$^2$ in BaF$_2$ and 0.0181(81) for CaF$_2$:Ba for the first shell). We can conclude that the possible off-centering of the impurity Ba ion is absent in solid solutions, and so the impurity occupies the on-center position at the site.

The obtained EXAFS results show that the impurity Ba$^{2+}$ ions substitute for Sr$^{2+}$ and Ca$^{2+}$ ions in SrF$_2$:Ba and CaF$_2$:Ba in an on-center position. The solid solutions do not undergo any local phase transition that could be induced by the strong local stress around the impurity ions. On the other hand, as the nearest Ba--F distances in SrF$_2$:Ba and CaF$_2$:Ba are shorter compared to undoped
BaF$_2$, one can expect a faster decay of CL in SrF$_2$:Ba and CaF$_2$:Ba than in BaF$_2$ because of increased overlap of respective wave functions.

C. Luminescence spectroscopy

The results of our EXAFS studies and first-principles calculations have shown that the crystal structure (symmetry) around Ba$^{2+}$ ions does not change for the case of impurity Ba$^{2+}$ ions and so, one should not expect noticeable changes of the shape of emission spectra of the impurity CL in CaF$_2$:Ba and SrF$_2$:Ba compared to that of intrinsic CL in BaF$_2$ (such a behavior of emission spectra of impurity and intrinsic CL was observed, in particular, in Ref. 20 for the system Rb$_{1-x}$Cs$_x$F). As was mentioned above, because of the low concentration of Ba in our samples the intensity of the impurity CL from SrF$_2$:Ba and CaF$_2$:Ba was rather low compared to that of other emissions observed from these crystals. However, the inspection of emission spectra obtained for CaF$_2$:Ba and SrF$_2$:Ba has shown the presence of a weak featureless band (shoulder) with a maximum at about 220 nm at the high-energy part of the emission spectrum, which can be associated with the impurity CL. Further investigations of excitation spectra and decay times of this band (spectrally selected by interference filter) in the time-resolved mode, which are described below, evidently show that the fast luminescence observed from the studied SrF$_2$:Ba and CaF$_2$:Ba crystals is indeed due to the impurity CL.

The CL excitation spectra measured in the region 16–32 eV for three investigated samples are shown in Fig. 3. In BaF$_2$ the excitation of electrons from the Ba$^{2+}$ (5p) core band to the conduction band starts at 18.1 eV, in agreement with previous data. The thresholds of the impurity CL excitation spectra in SrF$_2$:Ba and CaF$_2$:Ba, when electrons are excited from the Ba (5p) level of the impurity ion, are shifted to higher energy by $\sim$0.5–1 eV. These data are in reasonable agreement with the above results of first-principles calculations for the energy separation between the top of the Ba$^{2+}$ (5p) band and the conduction band edges in BaF$_2$, SrF$_2$:Ba, and CaF$_2$:Ba.

The case of CaF$_2$:Ba and SrF$_2$:Ba differs from that of Rb$_{1-x}$Cs$_x$F described in Ref. 20. In the latter system the host crystal (RbF) possesses intrinsic CL, i.e. the Rb (4p) core holes do not undergo fast Auger decay and accordingly the migration of these holes towards the nearby Cs$^+$ ions leads to the appearance of Cs (5p) related impurity CL. For small concentrations of Cs$^+$ the intensity of Cs (5p) impurity CL under the creation of Rb (4p) core holes can be rather strong compared to the intensity of Cs (5p) impurity CL under direct creation of Cs (5p) holes because of the strong absorption by the host crystal. As a result, the well pronounced excitation threshold of Cs (5p) impurity CL in Rb$_{1-x}$Cs$_x$F for small values of $x$ coincides with the edge of transitions from the host Rb (4p) band to the conduction band. In contrast to that, in SrF$_2$:Ba and CaF$_2$:Ba the Ca (3p) and Sr (4p) core holes possess very fast ($10^{-14} - 10^{-15}$ s) Auger decay right after their creation which prevents the possibility of noticeable migration of these holes towards Ba$^{2+}$ ions. Accordingly, the excitation spectrum of impurity CL in SrF$_2$:Ba and CaF$_2$:Ba should correspond to the spectrum of holes creation directly on the impurity Ba (5p) level, and the excitation threshold of Ba (5p) impurity CL in SrF$_2$:Ba and CaF$_2$:Ba corresponds to the edge of transitions from the Ba (5p) impurity level to the conduction band.

Undoped BaF$_2$ (Fig. 3, curve a) shows well-known broad excitation bands correlated to the absorption spectrum of BaF$_2$, which was extensively discussed in previous papers. In SrF$_2$:Ba and CaF$_2$:Ba the impurity Ba$^{2+}$ center should be considered as a strongly localized electronic system. This means that for electronic
transitions between the impurity Ba (5p) levels and the conduction band the momentum conservation law is not important and only the energy conservation law should be taken into account. In this case the shape of the absorption (excitation) spectrum will reflect the features of the density of states in the conduction band rather than the features of band-to-band transitions at specific points of the Brillouin zone as is the case for the BaF$_2$ crystal. The CL excitation spectra in SrF$_2$:Ba and CaF$_2$:Ba show a rather rich structure with several relatively narrow peaks and dips. Although narrow dips at $\sim$22.6 and $\sim$23.7 eV in SrF$_2$:Ba and at $\sim$28.0 eV in CaF$_2$:Ba definitely correspond to maxima in absorption (and reflection) spectra of the host crystals and are related to the creation of the core (cation) excitons, the structure between the excitation thresholds and the above mentioned narrow dips corresponds to the features of absorption by impurity Ba$^{2+}$ ions. It should be mentioned here that the reflection/absorption spectra of SrF$_2$ and CaF$_2$ do not have any pronounced structure in the spectral range 18–22 eV for SrF$_2$ and 18–24 eV for CaF$_2$ (Ref. 20), i.e. the host crystals are relatively transparent for exciting radiation in these spectral ranges. Only at photon energies corresponding to the excitation of core excitons the competition of strong absorption by the host crystal and weaker absorption by impurity Ba$^{2+}$ ions is responsible for well-pronounced features in the impurity CL excitation spectra.

Fig. 4 shows the CL decay curves for BaF$_2$, CaF$_2$:Ba, and SrF$_2$:Ba. In contrast to Ba-doped crystals, the measurements for undoped BaF$_2$ were performed at $T = 300$ K with an excitation energy $E_{ex} = 30$ eV, where the decay time of CL in BaF$_2$ has its maximum value. The fitting of the decay curve for BaF$_2$ with a single exponent gives the value of decay time equal to 0.79±0.01 ns. It is easily seen that CL decay time for SrF$_2$:Ba and CaF$_2$:Ba is remarkably longer in comparison with BaF$_2$ and is equal to 0.98±0.01 ns. The measurements have revealed that CL decays in CaF$_2$:Ba and SrF$_2$:Ba do not show any remarkable changes both with temperature (in the temperature range 200–450 K) and excitation energy (20–32 eV). In the case of BaF$_2$ the decay time slightly decreases with temperature above 300 K. This fact might be explained by an increase with temperature of the band mobility of Ba (5p) core holes in BaF$_2$ resulting in an increase of the migration losses and accordingly in acceleration of decay.

In contrast to intrinsic CL, when the uppermost core hole can migrate in the crystal, one of the features of the impurity CL is that for small concentrations ($\sim$1%) of impurity ions the core hole created at this ion is strongly localized on this ion and is not movable. In the case of Ba$^{2+}$-related impurity CL in SrF$_2$ and CaF$_2$ the impurity Ba (5p) levels lie well above the uppermost core band of the host crystal (by $\sim$5 eV in SrF$_2$ and by $\sim$10 eV in CaF$_2$ (Ref. 21)). Accordingly, thermally activated migration of the Ba (5p) core hole via the host uppermost core band is also not possible. Moreover, as already mentioned above, the Ca (3p) and Sr (4p) core holes cannot show noticeable migration because of very fast Auger decay.

In spite of the fact that the nearest interatomic Ba–F distance is shorter in CaF$_2$:Ba and SrF$_2$:Ba in comparison with BaF$_2$ and hence the probability of CL transitions $F^-$ (2p)$\rightarrow$Ba$^{2+}$ (5p) should be higher due to the expected increase of the overlap of the F (2p) and Ba (5p) wave functions, the decay kinetics in BaF$_2$ is remarkably faster. One explanation for this discrepancy may be the possible mobility of the Ba (5p) core holes in BaF$_2$ (in contrast to SrF$_2$:Ba and CaF$_2$:Ba), which can lead to non-radiative recombination of the holes at the crystal surface.

On the other hand, the overlap of wave functions of the Ba$^{2+}$ (5p) and F$^-$ (2p) band states and accordingly
the probability of optical transitions between these states is determined not only by the Ba–F distance but mainly by the shape of respective wave functions. In order to estimate the corresponding probabilities of optical transitions, first-principles calculations of spectra of the imaginary part of the dielectric function $\varepsilon_2$ for transitions from the completely filled Ba (5p) band to unoccupied states of the valence band were performed for BaF$_2$ and 2x2x2 supercells that model the CaF$_2$:Ba and SrF$_2$:Ba solid solutions. Although these spectra (Fig. 5) are absolutely hypothetical, nevertheless they allow estimating the probability of optical transitions between the Ba (5p) band and the valence band for wave functions corresponding to the electronic states in real crystals. It is seen that in solid solutions the averaged probability of these transitions is much smaller than in undoped BaF$_2$. This result agrees with slower CL decay observed in the solid solutions and so can also serve as its explanation. It should be noted that the absorption coefficients calculated using the $\alpha(\omega) = (2\omega/c)\{(1/2)[(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1]\}^{1/2}$ equation from the complex dielectric function $\varepsilon_1 + i\varepsilon_2$ for transitions between the Ba (5p) band and the valence band are of comparable magnitude with the absorption coefficients for allowed optical transitions between the Ba (5p) band and the conduction band and so can explain the very fast kinetics of CL.

As was indicated above, we obtained experimentally that decay times of impurity CL in SrF$_2$:Ba and CaF$_2$:Ba are roughly the same. This observation is also in line with our conclusion that the CL transition probability is not directly related to the Ba–F interatomic distance. As can be seen from Fig. 5, depending on the photon energy, the transition probability in SrF$_2$(Ba) can be either larger or smaller than that in CaF$_2$(Ba). We can propose that the particular recombination processes in two our samples are such that their transition probabilities are close, and so the closeness of the two decay times is just a coincidence.

It is necessary to mention that the obtained results of first-principles calculations are far evaluative because the detailed calculations should take into account the excitonic effects and additional relaxation of the F ions around the Ba ion that captured the core hole. According to Ref. 24 in BaF$_2$ the displacement of the nearest F ions towards the Ba ion with the core hole can be as large as 0.24 Å. Because of strong lattice distortion associated with this relaxation, the probability of Ba (5p) core hole decay can change significantly.

IV. CONCLUSIONS

In the present work spectral and kinetic properties of extrinsic crossluminescence (CL) in SrF$_2$:Ba and CaF$_2$:Ba are compared with those of intrinsic CL in BaF$_2$ and are analyzed taking into account EXAFS data obtained at the Ba $L_{\text{III}}$ edge and results of first-principles calculations. EXAFS studies have shown that the nearest Ba–F interatomic distances in SrF$_2$:Ba and CaF$_2$:Ba are shorter than in undoped BaF$_2$, but are always much longer than the Ca(Sr)–F distances in the host lattices. The local structure analysis indicates that the impurity Ba ions substitute for host Ca(Sr) ions in the on-center positions. The Ba–F distances obtained for SrF$_2$:Ba and CaF$_2$:Ba from EXAFS data are very close to those obtained from first-principles calculations. The solid solutions do not undergo any local phase transition from cubic fluorite to orthorhombic PbCl$_2$ structure that could be induced by the strong local stress in the host around the impurity ions.

It was shown that spectral and kinetic properties of CL related to radiative decay of Ba (5p) core hole depend remarkably on the local environment of Ba$^{2+}$ ions in the host crystal. The shift of the CL excitation threshold to higher energies correlates well with the results of first-principles calculations for SrF$_2$:Ba and CaF$_2$:Ba solid solutions. The CL decay time was revealed to be longer in SrF$_2$:Ba and CaF$_2$:Ba than in BaF$_2$ in spite of expected acceleration of decay with decreasing Ba–F distance in SrF$_2$:Ba and CaF$_2$:Ba due to the assumed increase of the overlap of wave functions. This discrepancy was associated with the mobility of the Ba (5p) core hole in BaF$_2$, which recombines non-radiatively at some defect states (e.g. at the surface of the crystal). The slower CL decay in SrF$_2$:Ba and CaF$_2$:Ba solid solutions can also be associated with decreasing the probability of optical transitions between the Ba (5p) states and the valence band predicted by first-principles calculations for solid solutions. The latter hypothesis needs further justification by taking into account the excitonic effects and additional relaxation of the F ions around the Ba ion containing the core hole.

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