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Creation of trapped electrons and holes in alkaline-earth fluoride crystals doped by rare-earth ions

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Abstract

Defects in Ce^{3+} - and Eu^{2+} -doped alkaline-earth fluorides, created by vacuum ultraviolet (UV) photons at energies lower than at the bandgap, were investigated by various methods: thermostimulated luminescence, photostimulated luminescence and optical absorption.

The $\text{CaF}_2:\text{Eu}^{2+}$ thermoluminescence curves in the range of 60–330 K due to various types of trapped holes were the same after vacuum UV illumination as after x-irradiation. Thermoluminescence curves of Ce^{3+} -doped alkaline-earth fluorides created by vacuum UV illumination or x-irradiation were generally similar. However, V_k thermoluminescence peaks were absent in vacuum UV illuminated $\text{CaF}_2:\text{Ce}^{3+}$ and $\text{SrF}_2:\text{Ce}^{3+}$ crystals. This fact is obviously associated with the presence of charge-compensating fluorine interstitials in Ce^{3+} -doped crystals.

The creation of Ce^{2+} characteristic bands was observed in photostimulated luminescence spectra as well as in optical absorption spectra of vacuum UV illuminated or x-irradiated Ce^{3+} -doped crystals. The suppression of hole thermoluminescence peaks in $\text{CaF}_2:\text{Eu}^{2+}$ crystals by blue light is due to the photoionization of Eu^+ ions.

The proposed mechanism for the creation of trapped hole and trapped-electron defects by vacuum UV illumination involves charge-transfer-type transitions, in which the electron transfers from the valence band to an impurity level lying in the bandgap. Comparison of all energies involved of transitions in the crystals investigated shows that the sum of all the transition energies is less than that of the bandgap by 1.5–3.5 eV. This energy difference can be considered to be the energy of lattice relaxation around the created Ce^{2+} or Eu^+ ions.

1. Introduction

Dense fluoride crystals doped with rare-earth ions are good materials for scintillators. Rare-earth ions in many crystals have a moderate decay time and high-light output. The obvious disadvantage of rare-earth doped scintillators is that they have slow components of decay time on a micro or millisecond timescale. Obviously, slow components are related to recombinations of trapped electrons and holes. In addition to the slow components, the trapped electrons and holes result in thermally stimulated luminescence (TSL) during the subsequent heating.

The creation of electron and hole defects in the doped crystals by ultraviolet (UV) illumination has been investigated in a few papers [1–3]. The thermoluminescence curves produced by UV and x-rays of KBr:Eu²⁺ were similar, indicating the similar nature of the created defects [4]. This effect in KMgF₃:Eu was proposed for UV detection [5]. However, the processes of defect creation by UV light is still unclear.

Trivalent rare-earth ions in alkaline-earth lattice occupy Me²⁺ (Me–Ca, Sr, Ba) sites and so require some type of charge compensator for the extra positive charge. In crystals grown in the absence of oxygen, charge compensation is provided by an interstitial fluoride. Several charge compensation sites have been identified. Three common sites are the tetragonal centre, trigonal centre and cubic centres. In first and second of these sites, the charge compensation is local. Charge compensation may also be achieved by a remote interstitial fluoride [6].

We study the mechanism of creation of trapped electrons and holes by UV photons with an energy considerably lower than that of the band-to-band transitions. The absorption, excitation, photostimulation spectra and thermoluminescence creation spectra of the single crystals CaF₂, SrF₂, BaF₂ doped with Ce³⁺ and CaF₂:Eu²⁺ were studied in the vacuum UV region up to 11 eV. The transitions, which lead to defect creation, can be considered to be transitions of the valence-band electrons to impurity-ion levels located within the host bandgap. This process leaves holes in the host valence band. Previous results can be found in [7].

Such transitions are called as charge-transfer transitions. Charge-transfer absorption bands have been extensively studied in many crystals [8–11]. Charge-transfer luminescence was observed only in Yb³⁺-doped crystals [12]. For an impurity ion, which is stable in the valence states Mⁿ⁺ and M⁽ⁿ⁻¹⁾⁺ the charge-transfer energy and photoionization energy are related through

$$E_g = E_{CT} + E_{PI}, \quad (1)$$

where E_g is the bandgap energy, E_{CT} is the charge-transfer energy for electron transition from the top of the valence band to the Mⁿ⁺ level and E_{PI} is the photoionization energy for electron transfer from the M⁽ⁿ⁻¹⁾⁺ level to the bottom of conduction band [8]. In several oxide crystals the sum of the charge-transfer and photoionization energies are slightly less (by 0.5 eV) than the bandgap energy [8, 10]. This deviation can be thought to be due to uncertainties in bandgap values [10]. However, in the case of halide crystals we found that the deviation was 1–3 eV. We conclude that the lattice relaxation around the metal impurity ion M⁽ⁿ⁻¹⁾⁺, created after charge-transfer transition, is responsible for these deviations.

2. Experimental

The alkaline-earth fluoride crystals were grown *in vacuo* in graphite crucible. PbF₂ as an oxygen scavenger was added into the raw materials¹.

Spectra in the range of 4–11 eV was measured with a 1 m normal incidence vacuum monochromator VMR2. For thermoluminescence studies the crystal was illuminated by a

¹ Alkaline-earth fluoride crystals were grown in our laboratory by P Figura and V Ivashechkin.

VMF25 light (25 W hydrogen discharge lamp) dispersed by a VMR2 monochromator for a few minutes at 78 K. The heating rate was equal to 12 K min⁻¹. The creation spectra of the thermoluminescence peaks were corrected for spectral response of the monochromator and emission spectrum of the discharge lamp.

During studies of photostimulated luminescence or thermoluminescence, the crystals were irradiated by a W-anode x-ray tube with the parameters: 35 kV, 2–10 mA for 1–2 min through a 1 mm Al filter. The experimental setup included three grating monochromators: one for vacuum UV illumination and the other two monochromators were used for photostimulation and luminescence measurements. The photostimulation spectra were corrected for the spectral distribution of a halogen W-lamp with a known filament temperature as well as for the variable spectral width of a grating monochromator slit. The corrections for the spectral response of gratings were not made, but we use the central region of sensitivity for each grating, so that the correction for spectral response is not so significant.

New absorption bands were developed after the vacuum UV illumination of CaF₂:Ce³⁺ and BaF₂:Ce³⁺ crystals with unfiltered light from a deuterium discharge lamp with a quartz window or by hydrogen discharge lamp with a MgF₂ window. Lamps were directly attached to illuminating crystal or to a cryostat window. Quartz window have a high-energy edge near 7.9 eV and the deuterium lamp was able to colour the BaF₂:Ce³⁺ crystals. The MgF₂ window has an edge at 10.9 eV which is 1.3 eV less than the bandgap energy in CaF₂. The illumination of the CaF₂:Ce³⁺ crystal through 1–2 mm thick pure BaF₂ (edge 9.7 eV) led to a similar but several times weaker spectrum.

The presence of Eu³⁺ in the crystal was checked by measuring the sharp red lines under the vacuum UV illumination².

3. Results

3.1. Thermostimulated luminescence

Illumination by photons with energy levels several electron Volts lower than that of the bandgap creates several thermoluminescence peaks in all crystals doped with Eu²⁺ or Ce³⁺ studied (figure 1). The thermoluminescence intensity decreased as the impurity concentration decreased. The thermoluminescence glow curves were substantially the same after x-irradiation or after vacuum UV illumination in CaF₂:Eu²⁺. Thermoluminescence curve of Eu²⁺-doped BaFCl, BaFBr crystals were also similar after x-irradiation or after vacuum UV illumination [14].

The thermoluminescence peaks at 100–120 K refer to the delocalization of self-trapped holes; V_k centres in these crystals [15]. Thermoluminescence at lower temperatures may be considered to be recombination of closed pairs of the V_k centre; electron centre [16]. V_k centres trapped at interstitial fluoride or other defects become more stable [15]. Since the electron is very strongly trapped by the rare-earth ion, thermoluminescence below room temperature is associated with holes released from different traps [15, 17].

The main feature of Ce³⁺-doped crystals is that the ratio of the V_k peaks against other thermoluminescence peaks is considerably smaller in vacuum UV illuminated crystals (see figure 1). Obviously, the absence of V_k thermostimulated luminescence peaks in Ce³⁺-doped crystals is associated with the presence of charge-compensated interstitial fluorine ions.

Therefore, the self-trapped holes (V_k centres) are one of the primary products of photoionization processes during vacuum UV illumination.

² Most intensive absorption and excitation bands at 8.5 and 9.5 eV observed in CaF₂:Eu³⁺ were tentatively assigned to 4f–5d transition in Eu³⁺ by P Figura [13]. However, charge-transfer transitions are also possible. The charge-transfer transition energy for Eu³⁺ in fluorides was estimated to be near 8 eV [12].

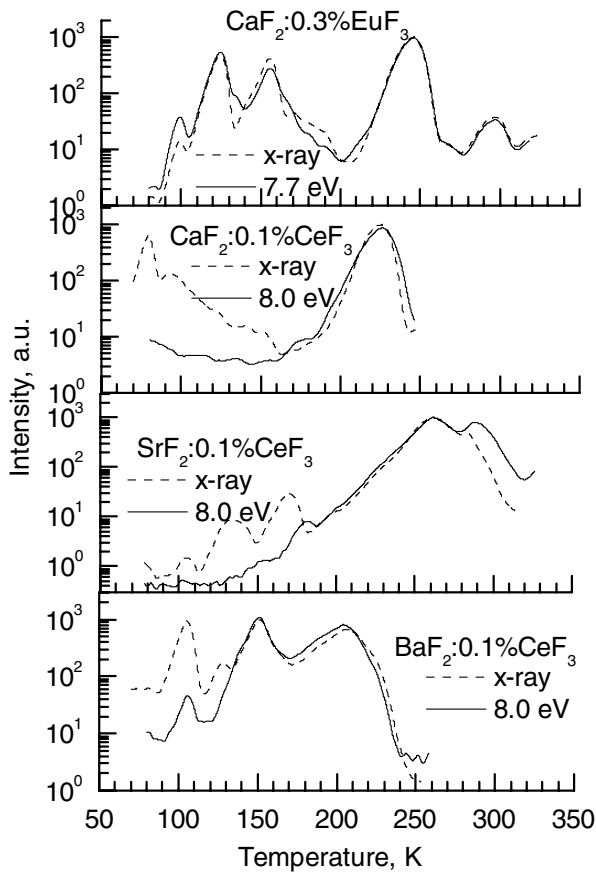


Figure 1. Thermostimulated luminescence curves of doped alkaline-earth fluoride crystals after x-ray irradiation or after vacuum UV illumination. Curves were normalized to equal maximal intensity. Thermoluminescence was measured at Ce^{3+} or Eu^{2+} emission bands.

The creation of thermoluminescence was observed when the photon energy was higher 6.2 eV in Ce^{3+} -doped BaF_2 , SrF_2 and higher 7.6 eV in CaF_2 (figure 2). The thermoluminescence creation spectra show a band, the maximum of which shifts to higher energies in a row of CaF_2 , SrF_2 , BaF_2 doped with Ce^{3+} . The shape of the thermoluminescence curves does not depend on the vacuum UV photon energy in CaF_2 and SrF_2 . However, the V_k -centre thermoluminescence peak appeared when the vacuum UV photon energy exceeded 7 eV in $\text{BaF}_2:\text{Ce}^{3+}$ (see figure 2). Therefore, the free V_k centres were created by photons with energies above 7 eV, whilst the trapped V_k centres in $\text{BaF}_2:\text{Ce}^{3+}$ were created by photons with energies above 6 eV. We not observe this effect in CaF_2 and in SrF_2 , nevertheless, we may consider energy levels of ≈ 1 eV as the V_k -centre optical binding energy on fluorine interstitials in all alkaline-earth fluoride crystals.

We also measured thermoluminescence in alkaline-earth fluoride crystals doped with 0.01% of Ce^{3+} or 0.001% Eu^{2+} . The shapes of the thermoluminescence curves were slightly different, in particular the V_k peak was relatively larger in $\text{SrF}_2:\text{Ce}^{3+}$ x-irradiated crystals. The intensity of the thermoluminescence peaks created by vacuum UV illumination decreases approximately in proportion to the rate of decrease of the impurity concentration. However, the similarity between thermoluminescence created by x-irradiation and that created by vacuum UV illumination was still present.

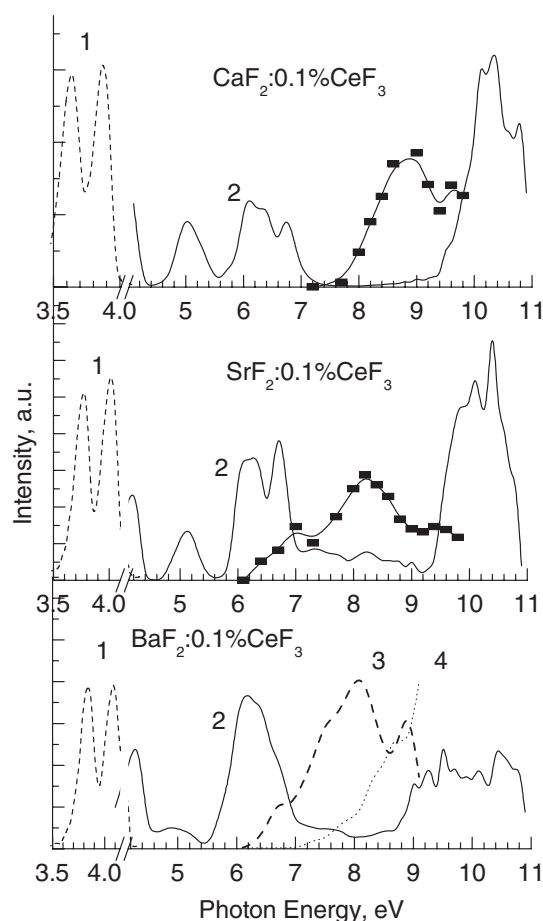


Figure 2. Emission (1), excitation (2) and thermoluminescence creation (3, 4) spectra of BaF_2 , SrF_2 and CaF_2 doped with 0.1 wt % of CeF_3 . Emission spectra were measured at 78 K, while excitation spectra were measured at 295 K. Thermoluminescence creation spectra for CaF_2 and SrF_2 are the same for all thermoluminescence peaks. Thermoluminescence creation spectra for BaF_2 were measured for 156 K (3) and 108 K (4) peaks.

3.2. Photostimulated luminescence

After x-irradiation or vacuum UV illumination at low temperatures, we observed Ce^{3+} emission stimulated by red light (figure 3). Photostimulation spectra look very similar after x-ray irradiation or vacuum UV illumination. Photostimulation spectrum of $\text{CaF}_2:\text{Ce}^{3+}$ (see figure 3 top plot) shows an obvious structure near 2 eV, which is similar to absorption bands of Ce^{2+} in CaF_2 [18]. The photostimulation spectra are broadened and the low-energy side of spectra are shifted to lower energies in the CaF_2 , SrF_2 and BaF_2 rows (see figure 3).

On heating above 78 K the photostimulated luminescence in the vicinity of the appropriated thermoluminescence peaks decreased. The intensity of the luminescence dropped to nil after heating to room temperature in SrF_2 and BaF_2 . However, almost 70–80% of the initial intensity remained in CaF_2 .

3.3. Optical absorption

The number of defects that can be created by vacuum UV illuminations is not that large and therefore we only measured new absorption bands in $\text{CaF}_2:\text{Ce}^{3+}$ and $\text{BaF}_2:\text{Ce}^{3+}$ crystals.

In CaF_2 crystal a significant part of the defects created by x-ray or by vacuum UV light, survives after heating to room temperature (for x-ray see also [16]). Therefore, we irradiate or

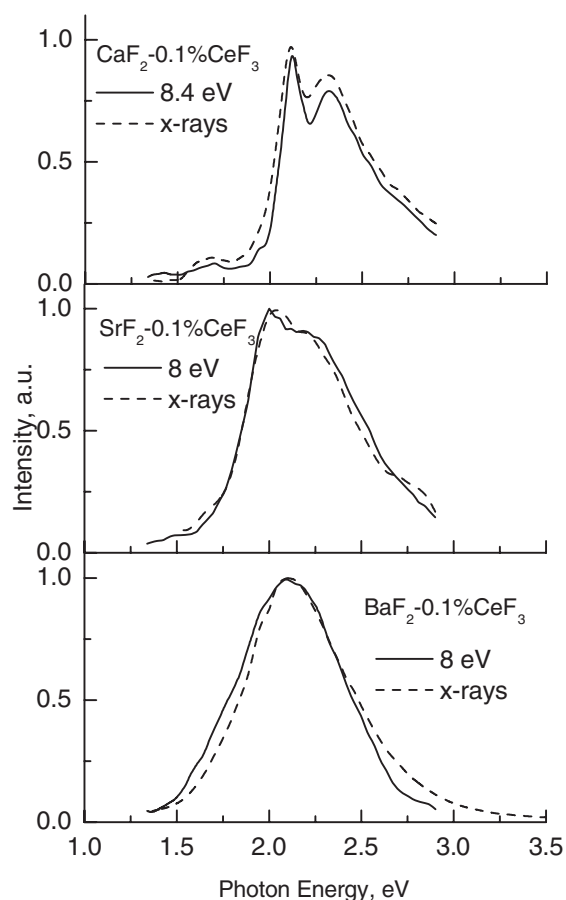


Figure 3. Photostimulation spectra of Ce-doped alkaline-earth fluoride crystals exposed to x-irradiation or vacuum UV illumination at 78 K. Emission were recorded at Ce^{3+} bands.

illuminate the crystals at room temperature. The crystal becomes red in both cases. Several bands at 2.4, 2.1 and 1.55 eV appeared during illumination. The absorption spectra in both cases were very similar. The coloration appeared when the photon energy was above ~ 8 eV. The absorption spectrum of the coloured crystal was similar to that observed in $\text{CaF}_2:\text{Ce}^{3+}$ after γ -irradiation [19] or 308 nm (4.03 eV) two-photon laser illumination [18], which was attributed to the absorption of Ce^{2+} ions.

The crystal $\text{BaF}_2:\text{Ce}^{3+}$ x-irradiated at 80 K shows a broad absorption band at 2.3 eV and a band at 3.4 eV (see figure 4). Both absorption bands were also observed after vacuum UV illumination at 80 K. The obvious difference between both absorption spectra connected with the absence of the V_k absorption band in the vacuum UV illuminated crystals (compare the BaF_2 TSL curves in figure 1). The V_k centres in BaF_2 have an absorption band with a maximum at 3.7 eV and a halfwidth of 1 eV [15].

It is surprising that there are no other bands above 2.5 eV in the photostimulation spectra, whilst in absorption spectra there are several intensive bands (see following sections). One may assume that the bands above 2.5 eV, which appeared in the absorption spectrum, belong to hole centres.

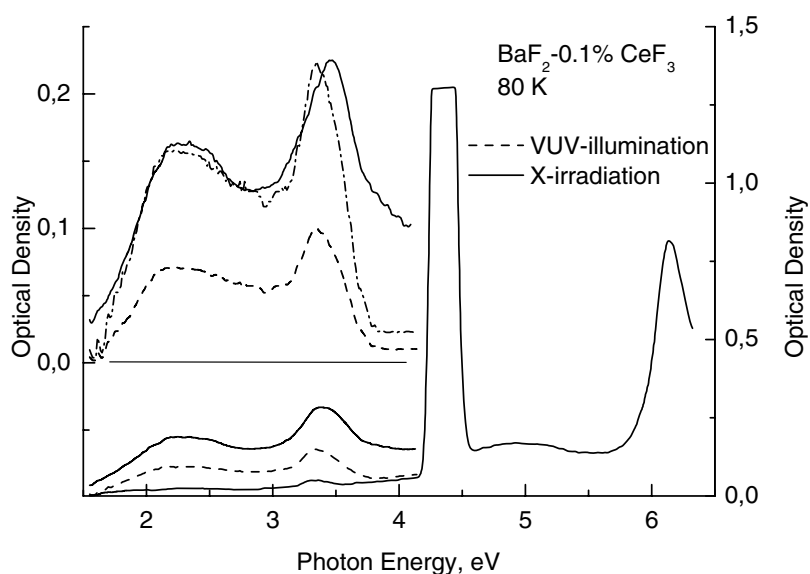


Figure 4. Absorption spectra of Ce-doped BaF_2 at 80 K before irradiation (lowest curve) and after x-irradiation or after illumination by vacuum UV. The zoomed low-energy side of the spectra were placed on left top part of the plot. Curve of vacuum UV illuminated crystal was increased and additionally shown (as dash-dot) for comparison with those of x-irradiated crystal. Crystal was illuminated by a vacuum UV light from a discharge deuterium light with maximal intensity at 7.7 eV and high-energy edge of the outlet window at 8 eV.

3.4. $\text{CaF}_2:\text{Eu}^{2+}$

Eu is introduced into the CaF_2 lattice in the form of divalent as well as trivalent ions. Crystals containing trivalent ions Eu^{3+} or both trivalent Eu^{3+} and divalent Eu^{2+} ions show very weak thermoluminescence after x-ray irradiation. Thus, we studied crystals containing only divalent Eu.

Two main absorption bands at 3.5 and 5.6 eV belong to $4f^7-4f^65d^1$ transitions split by the crystal field (figure 5). The excitation spectrum besides these bands also shows weak bands at 7.5 and 8.3 eV (see figure 5).

The creation of thermoluminescence peaks were observed at photon energies above 5.8 eV (see figure 5). The creation spectra were similar for all three thermoluminescence peaks.

We observe a photostimulated luminescence band at 2.1 eV with a low-energy edge at 1.5 eV for Eu^{2+} emission in x-irradiated or in vacuum UV illuminated crystals. The photostimulated luminescence observed can be completely bleached by 2.1 eV light at 80 K, but thermostimulated luminescence remains unchanged. Therefore, the observed photostimulated luminescence must be due to unknown electron traps. Unfortunately, Eu^{2+} emission was observed at 2.9 eV and so we cannot measure the photostimulation spectrum above 2.8 eV. Instead, we observed the suppression of the created thermoluminescence by a 2.5–3.5 eV light. Thermoluminescence below 200 K can be considerably suppressed by light at photon energies above 2.9 eV (see figure 5). The effectiveness of thermoluminescence suppression rises sharply in the range 2.9–3.1 eV. Above 3.1 eV the effectiveness sharply decreases with the absorption of Eu^{2+} (see figure 5). The thermoluminescence suppression spectrum becomes broader for lesser Eu^{2+} -concentration. Evidently, the decrease in the suppression spectra above 3.1 eV is associated with strong Eu^{2+} absorption. We conclude that suppression of hole

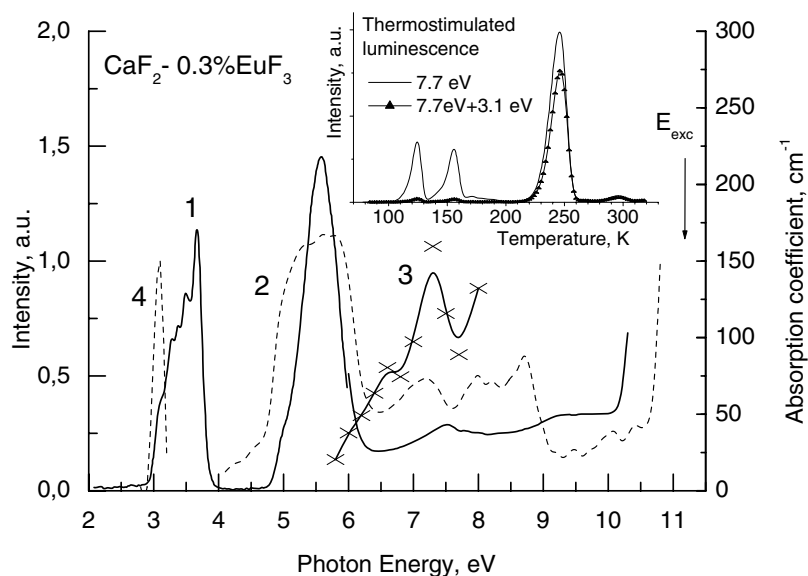


Figure 5. Absorption (1), excitation (2) and thermoluminescence creation (3) spectra of $\text{CaF}_2:0.3\% \text{EuF}_3$. Thermoluminescence suppression spectrum (4) shows 2.5–3.5 eV illumination of x-irradiated crystals at 80 K. As y ordinate we choose the ratio of the initial intensity of the 125 K thermoluminescence peak to the intensity of the peak after illumination.

thermoluminescence peaks by photons with energy levels above 2.9 eV is associated with the photoionization of Eu^+ centres.

The thermoluminescence peaks above 200 K were only slightly suppressed by 3 eV illumination (see figure 5). Therefore, the hole centres, which are responsible for 245 and 295 K thermoluminescence peaks, very ineffectively recombine with released electrons. It seems that thermoluminescence above 200 K is associated with uncharged hole centres. Stable X_3^- (halogen $_3^-$) uncharged hole centres have been found in alkali halides [20] and in $\text{CaF}_2:\text{Tm}^{3+}$ [21].

It should be pointed out that the photoionization of electrons from Eu^{2+} to conduction bands in CaF_2 begins at energy levels above 4 eV [6, 18], whilst the creation of self-trapped holes begins at above 5.8 eV (see figure 5).

4. Discussion

4.1. Hole centres

X-irradiation of alkaline-earth fluorides doped with trivalent rare-earth ions (RE^{3+}) at low temperatures leads to the creation of self-trapped hole centres and electrons trapped on rare-earth ions, RE^{2+} . Several types of self-trapped holes captured near RE^{3+} ions were designated as V_{kA} centres and those trapped on F^- interstitials were designated as V_H centres [15]. Self-trapped holes become mobile at 80–120 K in all alkaline-earth fluorides, while some types of V_{kA} centres are stable even at room temperature [15]. The peak temperatures of the glow curves of CaF_2 [17], SrF_2 and BaF_2 [22] below room temperature were not characteristic of the particular rare earth, but instead were common to all the trivalent rare-earth ions. Six or seven glow peaks were usually observed between 77 K and room temperature, and the

temperature at which they occurred were identical for each ion to within a few degrees. The centres proposed to be responsible for these effects involve different configurations of the F_2^- molecular ions [17]. Above room temperature, the glow peaks are specific to the added RE ions and do not show common peaks [22].

Experimental results show that in $CaF_2:Eu$ and $BaF_2:Ce$ vacuum UV creates the same hole thermoluminescence peaks as x-rays. The similarity of thermoluminescence curves (see figure 1) comes from the creation of holes by x-rays as well as by vacuum UV. However, V_k peaks are not created in Ce-doped CaF_2 , SrF_2 crystals by vacuum UV illumination while the other hole peaks are created (see figure 1). Obviously, inefficient V_k peak creation by UV photons in $BaF_2:Ce$ and the absence of V_k peaks in Ca and Sr fluorides associated with the presence of charge-compensating interstitial fluorine ions F^- .

4.2. Electron centres

Evidently, the photoluminescence spectra observed are due to transitions in Ce^{2+} ion (see figure 3). The appearance of photostimulated luminescence at low temperatures shows that the excited level is very close to the conduction band or lies within the conduction band. The sharpness of the photoluminescence bands in CaF_2 shows that the lowest excited level lies in the bandgap. However, in SrF_2 and, especially, in BaF_2 the photostimulated bands are smoothed out (see figure 3) and thus the excited states of Ce^{2+} in these crystals must lie in the conduction band. It is reasonable to assume, that the onset of the photostimulated luminescence spectrum can be considered to be the photoionization threshold from ground level Ce^{2+} to the bottom of the conduction band. The photoionization energies of Ce^{2+} from the spectra of figure 3 are estimated to be 1.9, 1.6, 1.4 eV in CaF_2 , SrF_2 , BaF_2 respectively.

We assume that thermoluminescence suppression (see figure 5) is related to the photoionization of Eu^+ ions. The released electrons are then recombined with hole centres leading to thermoluminescence reduction.

The 876, 975 and 1132 nm (1.42, 1.27 and 1.10 eV, respectively) bands which appeared in the heavy x-irradiated $KCl:Eu^{2+}$ crystals were attributed to the absorption of single valence Eu^+ ions [23, 24]. Possible shorter wavelength bands are hid by strong F and F-like bands. The emission bands at 480–500 nm (2.5–2.6 eV) developed in coloured or in x-irradiated Eu^{2+} doped KCl , $RbCl$, KJ crystals were attributed to the emission of Eu^+ ions [25].

4.3. Nature of observed transitions in the vacuum UV region

Experimental results show that because of the vacuum UV illumination of doped alkaline-earth fluoride crystals Ce^{2+} or Eu^+ ions in addition to trapped-hole centres are created. The thermoluminescence observed is caused by charge-transfer transitions, when electrons transfer from the valence band to impurity levels, that lie within the bandgap.

However, in Ce-doped crystals electrons can transfer not only from valence bands but also from charge-compensating fluorine interstitials. Illumination of $BaF_2:Ce^{3+}$ with 6–7 eV photons creates only V_{kA} and V_H hole centres (see figure 2). Above 7 eV self-trapped holes are also created. Similar behaviour was also observed in low doped $BaF_2:0.01\% CeF_3$. It seems, that due to 6–7 eV illumination the electron transfer from charge-compensating F^- interstitials to Ce^{3+} , while above 7 eV zone holes are created. Therefore, 1 eV can be considered as optical energy for releasing the V_k centre from F^- interstitials. The thermal stabilization energy for V_k centres trapped by interstitial fluorine F^- in $BaF_2:Tm^{3+}$ was estimated to be 0.6 eV [15]. It is known that the optical activation energy is higher than the thermal activation energy. Therefore, both energies are in agreement.

Illumination of $\text{CaF}_2:\text{Ce}^{3+}$ at 308 nm (4.03 eV) using a XeCl excimer laser, produces long-lived colour centres in the material [26]. The presence of these centres can be observed as the sample changes from its original transparent state to a reddish-brown colour. Quadratic dependence of the number of the created colour centres on the laser intensity can be interpreted in terms of two-photon process. Comparable flux illumination using the 337 nm (3.68 eV) output of a nitrogen laser, or the 355 nm (3.50 eV) output of the third harmonic of a Nd:YAG laser produces no coloration of the crystal. The spectral features of these colour centres correspond to the optical properties of divalent cerium ions at O_h sites in CaF_2 [26]. Our results agree well with the results given earlier in [26]. Indeed we observe the creation of defects in $\text{CaF}_2:\text{Ce}^{3+}$ by photons with energy levels above 7.6 eV (see figure 1). In [26] the crystal was coloured by two-photon total energy of 8.0 eV and was not coloured with two-photon energy of less than 7.4 eV.

The photoionization of Ce^{3+} in CaF_2 by 308 nm (4.03 eV) laser illumination has been reinvestigated for $\text{CaF}_2:\text{Ce}^{3+}$ and $\text{CaF}_2:\text{Ce}^{3+}, \text{Na}^+$ [6]. Illumination of the Ce-doped crystals with 308 nm (4.03 eV) laser light at room temperature produces colour centres by a two-photon process similar to those produced by x-irradiation or γ -irradiation. It was shown that a mechanism involving production of self-trapped holes can account for the photochemical processes in $\text{CaF}_2:\text{Ce}^{3+}$ and $\text{CaF}_2:\text{Ce}^{3+}, \text{Na}^+$ [6]. Schematically, the first photon initiated the transition from the valence band to the Ce^{3+} . The second photon absorbed by created self-trapped holes initiates the move of the hole away from Ce^{2+} [6]. However, we show, that the self-trapped hole and Ce^{2+} in $\text{CaF}_2:\text{Ce}^{3+}$ was created by a one-photon process.

In $\text{Y}_2\text{O}_3:\text{Eu}$ and $\text{La}_2\text{O}_3:\text{Eu}$, excitation into the charge-transfer states of Eu^{3+} leads partially to the dissociation of the charge-transfer state into Eu^{2+} and a free hole which may subsequently be trapped [27].

A similar type of transitions, followed by the creation of self-trapped holes, is known for CsI doped with Pb or Tl impurity [28–30]. Band-to-band transitions in pure CsI crystals are observed above 6.4 eV. For the impurity ions with trapped electrons, electron spectroscopy resonance spectra of V_k centres [28] and V_k -centre thermoluminescence peaks were observed [30]. It was concluded that the excitation of CsI:Tl by photons with 4.4–5.6 eV energy leads to the creation of trapped electrons and nonrelaxed holes. The higher the energy of the photons, the farther the trapped electron– V_k -centre distances [30]. The creation of free electrons and holes was observed in RbCl:Tl using photons with energy levels above 6.8 eV while band-to-band transitions begin at above 8.45 eV [31].

Photoionization of electrons from the Eu^{2+} level to conduction bands in alkaline-earth fluorides begins above 4 eV [18], when the photon energy falls into the second absorption band. In several alkali-halide crystals doped with Eu^{2+} photoionization also begins above 4.5 eV [1]. Our results show that transitions from the valence band to the Eu ion in CaF_2 begin above 5.8 eV (see figure 5). It is clearly seen from figure 5, that the energy difference between both types of transition is considerable. To observe charge-transfer transitions one needs to use vacuum UV illumination and this is why the creation of V_k centres has not been observed in Eu-doped alkali-halide crystals earlier [1].

4.4. Scheme of photoionization transitions

The energies of transitions between local impurity levels within bandgaps and delocalized zone states are related through the Born–Gaber thermodynamical cycle [8, 32]. The sum of the Ti^{3+} photoionization energy and the charge-transfer threshold to Ti^{4+} in Al_2O_3 [8] and YAlO_3 [32] is found to give approximately the bandgap energy of the host crystal (see (1)). The idea is rather simple: the charge transfer transition from the conduction band to the Ti^{4+} impurity

Table 1. Energies (in eV) of photoionization processes in doped alkaline-earth fluoride crystals. E_g is the band-to-band transition, E_{PI} is the photoionization energy for Ce^{2+} or Eu^{2+} , E_{CT} is the transition energy from the top of the valence band to the impurity level, obtained from the low-energy TSL creation edge. $\Delta E = E_g - E_{TSL} - E_{PI} - \Delta E_i$. Here the binding energy of holes trapped on interstitial fluorine ions ΔE_i is equal to 1.0 eV for BaF_2 (see text), we can also use this value for other Ce-doped crystals. ΔE can be considered as the energy differences between the unrelaxed and relaxed impurity-level positions.

Crystal	E_g (eV)	E_{CT} (eV)	E_{PI} (eV)	ΔE (eV)
$CaF_2:Ce^{3+}$	11.5 ^a	7.6	1.9	1
$SrF_2:Ce^{3+}$	10.9 ^a	6.2	1.6	2.1
$BaF_2:Ce^{3+}$	10.7 ^a	6.2	1.4	2.1
$CaF_2:Eu^{2+}$	11.5 ^a	5.8	2.9	2.8
$BaFBr:Eu^{2+}$	8.2 ^b	6 ^c	$\approx 0^c$	2.2
$BaFCl:Eu^{2+}$	9.1 ^b	6 ^c	$\approx 0^c$	3.1

^a Bandgap energies were refined earlier in [33].

^b [34].

^c [14].

level and photoionization transition from the created Ti^{3+} ion to the conduction band leads to an electron–hole pair. The sum of the experimental values in $Al_2O_3:Ti^{3+}$ and in $Lu_2O_3:Ce^{3+}$ is 0.5–0.6 eV lesser than the bandgap energy [8, 10]. This deviation is thought to be due to uncertainties in the bandgap value [10].

In $CaF_2:Eu^{2+}$ the electron transfer energy from the valence band to the Eu^{2+} level plus the photoionization energy of Eu^{2+} can be compared with the bandgap energy. In Ce-doped alkaline-earth crystals the transition energy from the level of the interstitial fluorine ion F_i^- , which is $\Delta E_i \simeq 1$ eV higher than the top of the valence band, to the Ce^{3+} level plus the transition energy from the created Ce^{2+} ion to the conduction band can be compared with bandgap energy. The appropriate energies are shown in table 1.

From the data of table 1 one can see that the sum of the experimental values is less than the bandgap energies by 1–3 eV. This discrepancy is more than in the case of oxides [8, 32]. Looking into all steps of the creation of defects: charge-transfer transition \rightarrow relaxation \rightarrow photoionization transition, one may conclude that the additional energy may be lost during the relaxation step. By other words, the unrelaxed levels of Ce^{2+} or Eu^{2+} lie deeper within the bandgap than the relaxed levels (figure 6). The effects of decreasing the energy distance between the level in the bandgap and the bottom of the conductivity band are well known for F centres in alkali halides [20]. The most intensive F and K absorption bands belong to transitions from the ground 1s state to excited 2p, 3p states, which lie within the bandgap. Lower intensive L bands belong to transitions to states within the conduction band. The energy distance between unrelaxed 2p states and the bottom of the conduction band in KCl is near to 0.7 eV, and during relaxation the distance is reduced to 0.1 eV. The effect can be associated with increasing the F-centre radius after excitation into 2p level. We suppose that in the case of charge-transfer transitions the effect are more prominent, because the radii of Eu^{2+} or Ce^{3+} become considerably larger after trapping the electron.

The relaxation energy in Eu^{2+} -doped crystals is definitely larger than the energy in Ce^{3+} -doped crystals (see table 1). It seems this is related to the fact that the ratio $R(Eu^{2+})/R(Eu^{3+})$ is sufficiently larger than the ratio $R(Ce^{2+})/R(Ce^{3+})$.

The charge-transfer transition is accompanied by an expansion of the metal–ligand bonds in the excited state, which gives rise to the observation of large Stokes shifts [12]. The decreasing of the energy difference between the impurity level and conduction band during

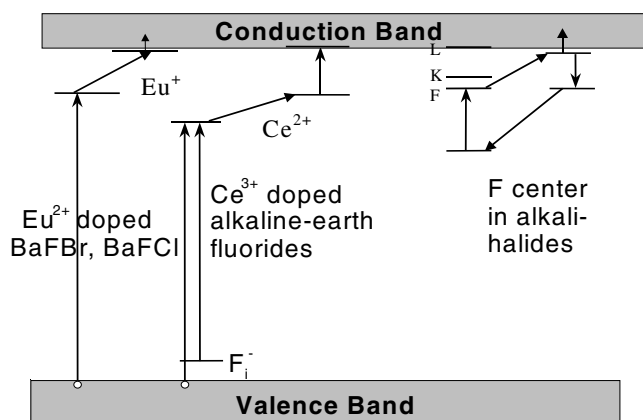


Figure 6. Scheme of creation of electrons and holes in doped crystals. Vertical arrows represent the optical transitions, inclined arrows represent the relaxation processes. The scheme of F-centre transitions in alkali halides [20] is shown for comparison.

relaxation can be considered as decreasing that between the two excited states of large systems which include impurity ions, surrounding anions and nearest lattice fragments.

5. Conclusion

The trapped-electron defects and the trapped-hole defects were observed in alkaline-earth fluoride crystals doped with Eu^{2+} or Ce^{3+} by vacuum UV illumination with photon energies well below the bandgap energy. The types of hole defects (V_k , V_H , V_{kA}) that are created by vacuum UV are the same as those created by x-rays in Eu^{2+} -doped crystals. However, the V_k centres were ineffectively created by vacuum UV in Ce^{3+} -doped CaF_2 and BaF_2 crystals. Ce^{2+} electron-trapped centres were identified in vacuum UV illuminated or x-irradiated crystals by specific absorption and photostimulated luminescence bands.

It was concluded that defects are created by means of charge-transfer-type transitions, when electrons from the valence-band transfer to an impurity level lying within the bandgap. In Ce^{3+} -doped crystals the transition started from levels of charge compensating fluorine interstitials, which lie ≈ 1 eV above the top of the valence band.

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