

SLOW COMPONENTS OF THE EMISSION DECAY IN FLUORIDE CRYSTALS DOPED WITH Ce^{3+}

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Spatially separated defects created by photons with energies 6–8 eV in alkali-earth fluoride crystals doped with cerium are investigated with the help of thermoluminescence. Measuring the spectra of creation of V_k and H peaks of thermostimulated luminescence in $BaF_2:Ce^{3+}$, we demonstrate that photons with energies higher than 6 eV induce H centers (self-trapped holes captured by interstitial F ions), whereas the formation of self-trapped holes begins on exposure to photons with energies greater than 7 eV. The influence of photoionization on the Ce^{3+} luminescence in BaF_2 , SrF_2 , CaF_2 , and CeF_3 crystals is investigated in the range of photon energies 4–8 eV. An exponential Ce^{3+} -emission decay was observed for excitation energy lying in the range 4–6 eV. Slow and fast decay components were observed under excitation by photons with energies higher than 6 eV. We believe that the slow and fast components are due to the tunnel recombination of trapped electrons with hole centers.

INTRODUCTION

Both cerium fluoride crystals and other crystal matrices activated with cerium are promising materials to be used in transient scintillators. Many crystals doped with Ce^{3+} ions have a decay time in the range of several tens of nanoseconds and high luminous efficiency. A disadvantage of scintillators with cerium dopant is the slow decay component with characteristic decay time of about a microsecond. Obviously, the slow component is caused by recombination processes. We studied slow Ce^{3+} -emission decay components caused by the photoionization with 6–9 eV photons in CaF_2 , SrF_2 , and BaF_2 crystals doped with cerium and in CeF_3 crystals.

Detailed studies of photoionization in fluoride and oxide crystals with cerium dopant [1–3] are concentrated on the elucidation of the reasons for the lack of laser generation in such crystals. The formation of color centers was detected in $CaF_2:Ce^{3+}$ pumped by an excimer laser (308 nm) to the lowest $4f-5d$ Ce^{3+} band. The color centers were Ce^{2+} ions. The initial absorption increased quadratically with the laser radiation intensity, thereby pointing to a two-photon process [2]. The authors concluded that the laser excitation causes the photoionization of cerium through the intermediate $5d$ -state. An electron enters the conduction band and is captured by the other Ce^{3+} ion [2].

More recently, it was determined that the 308-nm pumping of $CaF_2:Ce^{3+}$ at 80 K leads only to the displacement of an interstitial charge-compensating F ion from the (001) site to the neighboring (111) site [3]. Coloring of $CaF_2:Ce^{3+}$ and Na⁺ crystals was observed at 80 K, and coloring of $CaF_2:Ce^{3+}$ crystals – at temperatures higher than 80 K. The authors concluded that holes were formed in a photochemical process. The initial stage can be represented as the electron transfer from the valence band to the Ce^{3+} energy level. The authors assumed that the first photon produces a Ce^{2+} ion and a hole on an interstitial F (H center). The second photon, absorbed by the H center, caused the separation of defects [3]. Nevertheless, we do not exclude the possibility of coloring of crystals through the two-photon absorption ($4 + 4 = 8$ eV). We have shown that the single-photon excitation produces holes in BaF_2 , SrF_2 , and CaF_2 crystals doped with Ce^{3+} when photon energies are higher than 6 eV.

DETAILS OF THE EXPERIMENT

The spectra in the range 4–10 eV were measured with the use of a VMR2 vacuum monochromator. The emission spectra were recorded with an MDR2 diffraction monochromator. To study the thermoluminescence of crystals, they were illuminated by a VMF25 hydrogen discharge lamp through a VMR2 monochromator for several minutes at a temperature of 78 K. The recorded spectra were corrected for the spectral efficiency of the monochromator and for the lamp spectrum.

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TABLE 1. Luminescence Bands and Decay Times for the Crystals Studied at 78 K

Crystal	E_{cm} , eV	τ_{rad} , ns	τ_{fast} , ns	τ_{slow} , μ s
CaF ₂ :Ce ³⁺	3.63, 3.87	40	80	1.6
SrF ₂ :Ce ³⁺	3.78, 4.02	36	70	1.6
BaF ₂ :Ce ³⁺	3.83, 4.09	28	60	1.6
CeF ₃	4.09, 4.3	15	20	1.5

Note. Here τ_{rad} are decay times recorded under 4–6 eV excitation, and τ_{fast} and τ_{slow} are the fast and slow decay times observed under 6–9 eV excitation.

The photoluminescence decay was measured by the single-photon method with a time-to-number converter in CAMAC. The duration of an excitation pulse was about 10 ns. The excitation pulse decayed by a hyperbolic law. To extract the proper decay time from the experimental curve, the procedure of convolution calculation was used.

The crystals were grown in vacuum with addition of 0.1 or 0.01 wt. % CeF₃ and necessary amounts of PbF₂ or CdF₂ deoxidizer to eliminate oxygen. The absence of oxygen was checked through the absence of the absorption and the luminescence characteristic of oxygen defects.

RESULTS

Generally, the phenomenon of photoionization in crystals is taken to mean the delocalization of captured charge carriers – electrons and holes. Released electrons or holes can be captured by other traps, and holes are rapidly self-trapped at low temperatures. Thus, the photoionization process can be investigated using the reaction products – induced defects. We investigated Ce³⁺ photoionization in several crystals, studying the radiation-induced recombination of the induced defects – the thermostimulated luminescence. A number of induced defects can recombine just after their creation. This leads to the appearance of slow components of Ce³⁺ emission.

Luminescence and Excitation Spectra

Two narrow Ce³⁺-luminescence bands correspond to transitions from the lowest 5*d* state to the 4*f*⁴ – ²F_{7/2}, ²F_{5/2} split ground state (see Table 1 and Fig. 1). The emission spectra were almost identical at room temperature and 78 K. In the excitation spectra, bands with maxima at about 4.2 and 5 eV and the group of bands at about 6.5 eV were observed. The first two bands are usually attributed to transitions on the 5*d* state split by a crystal field.

The last group of bands can be associated with transitions to the 6*s* state, by analogy with the explanation of the 6.5–8.5 eV excitation bands in LaF₃:Ce³⁺ [13], though the mechanism of charge transfer – the electron transfer from the valence band to the cerium energy level – is not excluded for these energies [13]. The relative intensity of the excitation band at about 5 eV decreases when going from CaF₂ to BaF₂, whereas the relative intensity of the group of bands at 6.5 eV increases. A similar behavior of the 5-eV band was also observed in the absorption spectra. The edge of the excitation spectrum at about 9 eV correlates with the edge of the exciton absorption spectrum. The relative intensity of Ce³⁺-emission excitation within the limits of exciton and interband transitions decreases when going from CaF₂ to BaF₂.

Obviously, the efficiency of the exciton energy transfer to cerium ions decreases when going from compact to less compact lattices. A plateau in the range 7–9 eV was also observed, which was the least pronounced for CaF₂. According to this, the thermoluminescence induced by 7–9 eV photons has the least intensity in CaF₂ crystals.

Thermoluminescence Induced by VUV Radiation

Several peaks of the thermostimulated luminescence were induced in alkali-earth fluoride crystals doped with cerium after exposure to photons with energies greater than 6 eV. Temperatures of thermoluminescence peaks upon UV illumination and on exposure to x-ray radiation were close in value (Fig. 2). Luminescence curves at temperatures between 140–300 K agree well with the curves registered on exposure to x-ray radiation. The relative intensity of low-temperature peaks of the thermostimulated luminescence at 80–120 K was much less in crystals illuminated by UV radiation.

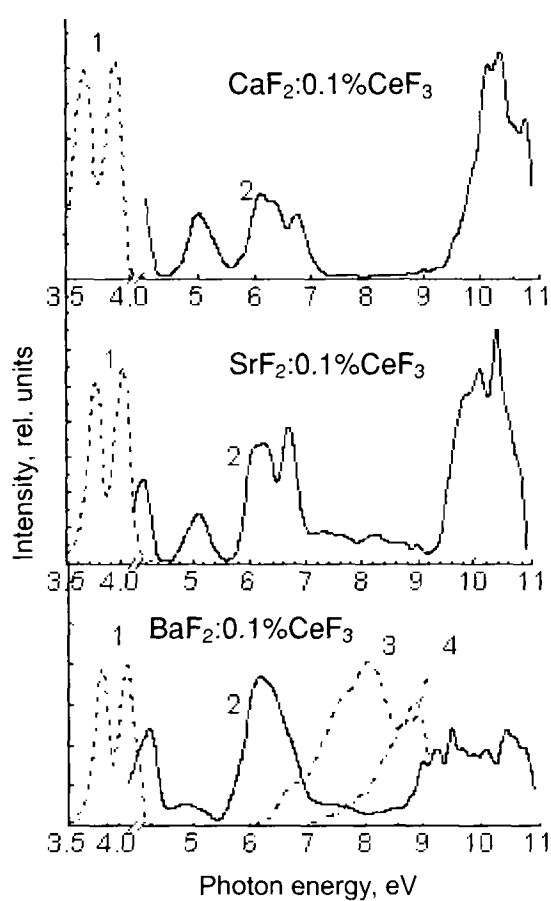


Fig. 1

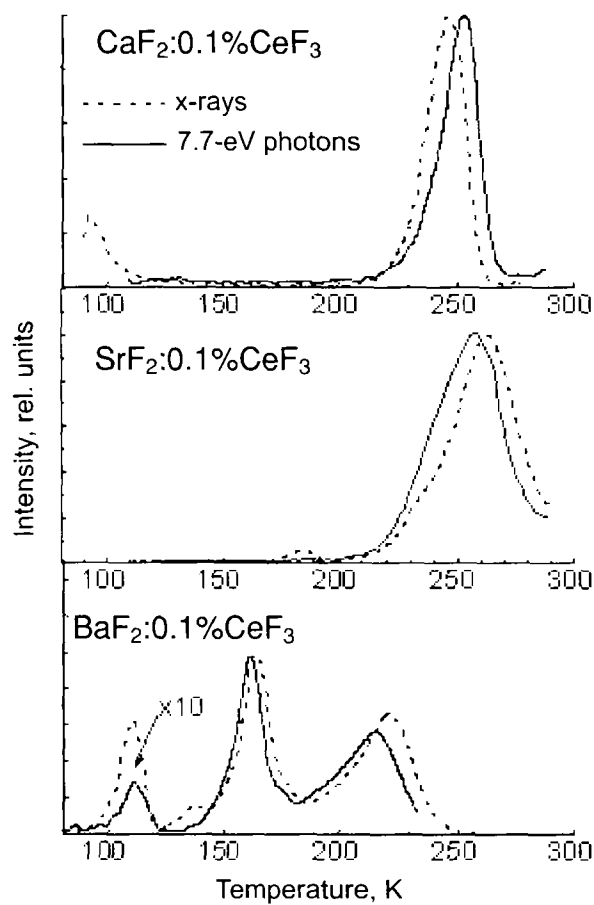


Fig. 2

Fig. 1. Luminescence (1), excitation (2), and thermoluminescence initiation (3 and 4) spectra of BaF_2 , SrF_2 , and CaF_2 crystals doped with 0.1 wt. % CeF_3 . The luminescence spectra were measured at 78 K, the excitation spectra – at 295 K, and the thermoluminescence initiation spectra – for peaks at 166 (3) and 112 K (4).

Fig. 2. Thermoluminescence curves for alkali-earth fluoride crystals doped with Ce^{3+} , stimulated by x-ray radiation and 7.7-eV VUV radiation. The curves are normalized for comparison. The peak intensity of BaF_2 at 112 K, induced by 7.7-eV photons, was multiplied by a factor of 10. The emission was measured in the region of the high-energy Ce^{3+} band.

The induced thermoluminescence was best studied in $\text{BaF}_2:\text{Ce}^{3+}$ crystals. Three peaks at 112, 166, and 220 K with comparable intensities were observed for crystals on exposure to x-ray radiation. The relative intensity of the peak at 112 K was 20 times less for crystals illuminated by the UV radiation (Fig. 2). The initiation spectra of the peaks at 166 and 220 K differ strongly from the initiation spectrum of the peak at 112 K. The peaks at 166 and 220 K were induced under illumination by photons with energies greater than 6 eV. The curve of the peak initiation spectrum reaches its maximum at 8 eV and then decreases. In contrast to this, the peak at 112 K is excited under illumination by photons with energies greater than 7 eV. The curve of the initiation spectrum of the peak at 112 K grows steadily with increase in the photon energy (Fig. 2). A similar behavior of the initiation of thermoluminescence peaks was also observed in $\text{BaF}_2:0.01\% \text{CeF}_3$, though the relative intensities and the temperatures of peaks differed slightly from those in $\text{BaF}_2:0.1\% \text{CeF}_3$ crystals.

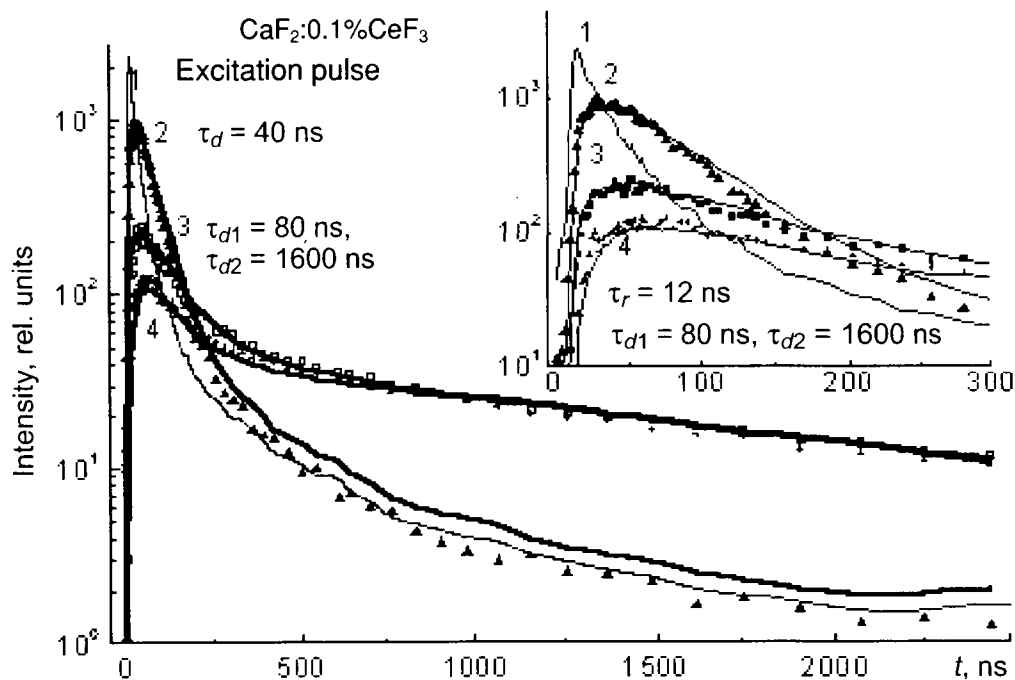


Fig. 3. 3.87-eV Ce^{3+} -emission decay in $\text{CaF}_2:\text{Ce}^{3+}$. Curve 1 is for the lamp excitation pulse; symbols near the curves are for excitation energies of 4.3 (2), 6.4 (3), and 7.2 eV (4). Curves 2–4 were calculated based on the convolution of the excitation pulse and the exponential components. For curve 4, it was necessary to add a 12-ns rise component to fit the experimental data.

Slow Components of Ce^{3+} Luminescence

The decay curve of BaF_2 , SrF_2 , and CaF_2 crystals doped with Ce^{3+} excited by photons with energies less than 6 eV consists of separate exponents with times given in Table 1. The decay times were identical for both emission bands. The decay times remained unchanged upon cooling to 12 K, and were designated as radiation times (Table 1). Above 6 eV, the decay curve contains fast and slow components. It should be noted that the decay times for the fast component were nearly doubled compared to the radiation times. The decay curve at times in the range 0.4–3 μs is not well described by a single exponent; the curve is better described by a hyperbolic law. The decay curve remained unchanged when the temperature decreased from 78 to 12 K.

CeF_3 crystals with various impurity concentrations were also investigated. The impurity concentration in CeF_3 crystals can be checked from the ratio of the 4.1-eV band intensity to the intensity of the 3.5-eV wide band caused by the near-impurity emission of cerium ions [11]. The slow decay components of the unperturbed cerium-ion emission at 4.1 eV were identical in crystals with different impurity concentrations (Fig. 3). This demonstrates that the slow decay component is caused by intrinsic defects rather than by impurity ones.

DISCUSSION

Thermoluminescence

Alkali-earth fluoride crystals doped with rare-earth ions (RE^{3+}) create self-trapped holes of different types and electrons captured by rare-earth ions on exposure to x-ray radiation. Self-trapped holes captured on RE^{3+} are called V_{LA} centers, and holes captured by a charge-compensating interstitial fluoride F^- ion are called V_{H} or simply H centers [5]. Self-

trapped holes themselves become mobile in all alkali-earth fluorides at temperatures 80–120 K. Some types of V_{KA} centers are stable even at room temperatures [5]. Ce^{2+} ions and other ions of RE^{2+} are stable below 400–500 K.

Temperatures of thermostimulated luminescence peaks in CaF_2 crystals are approximately identical for all rare-earth ions rather than characteristic of a specific RE^{3+} ion [6]. Six or seven thermostimulated luminescence peaks were usually observed between 77 K and room temperature. Their temperatures were identical for all ions to within several degrees. For most ions, a large peak was observed at about 300 K. Centers initiating thermoluminescence peaks include molecular F_2^- ions of various configurations [6]. Hence, the thermoluminescence that we observed in crystals doped with cerium below room temperatures is associated with the delocalization of trapped holes and their migration to electron centers.

Recently, the two main thermostimulated luminescence peaks at 90 and 130–140 K in pure LaF_3 and crystals doped with rare-earth RE^{3+} have been attributed to the annealing of halide defects, such as H and V_K centers, in alkali halides [12].

The thermostimulated luminescence peaks recorded after illumination by VUV radiation are similar to peaks induced on exposure to x-ray radiation. This means that UV radiation also leads to the formation of trapped holes and trapped electrons. Hole centers of V_{KA} and H types are induced under illumination by 6–7 eV photons. Self-trapped holes and V_K centers are also induced when photon energies are greater than 7 eV. The process proceeds with comparable efficiencies in BaF_2 crystals with 0.1 and 0.01% cerium, which excludes the impurity ion transfer to neighboring pairs. It is most likely that 6–7 eV electrons are transferred from charge-compensating interstitial F fluoride ions to cerium Ce^{3+} under illumination, whereas band holes are formed when the photon energy is greater than 7 eV. Thus, an energy of 1 eV can be considered as the optical bond energy of a hole on a fluoride F interstice. The estimated thermal energy of hole stabilization on the interstitial fluoride is 0.6 eV in $BaF_2:Tm^{3+}$ [5]. It is well known that the optical activation energy is always greater than the thermal one. Therefore, we believe that an optical bond energy of 1 eV is a fairly reasonable value.

The possibility of formation of Ce^{4+} ions in alkali-earth fluoride crystals was discussed, but was not proved experimentally. Apparently, the energy required for an electron to be transferred from a cerium ion to the conduction band is too high due to the high ionization potential of a Ce^{3+} ion. The detection of self-trapped holes of several types near RE^{3+} in alkali-earth fluoride crystals on expose to x-ray radiation means that the hole localization on a rare-earth ion is more favorable energetically than the formation of a Ce^{4+} center. Probably, for this reason the energy of transitions from the valence band to the cerium ion level is smaller than the energy of transitions from the cerium ion level to the conduction band.

Luminescence Decay

It was assumed that the excitation of cerium ions in LaF_3 and CeF_3 crystals by photons with energies higher than 6.5 eV led to the photoionization of an electron from the cerium level to the conduction band and its subsequent capture by traps [7]. The slow components of cerium luminescence are associated with the electron release from traps [7]. We established that the duration of the slow component does not depend on a temperature below 12 K, which demonstrates the tunnel character of charge-carrier return to cerium. We believe that the exposure of a crystal by photons with energies higher than 6 eV leads to the electron transfer from the $2p$ band of the fluoride energy level to the cerium energy level. The hole formed is rapidly self-trapped. The electron from the formed Ce^{2+} ion tunnels to a neighboring self-trapped hole and then recombines. The recombination energy is sufficient for the excitation of $4f-5d$ transitions of trivalent cerium Ce^{3+} . The recombination rate determines the fast and slow decay components. Probably, self-trapped holes captured on the nearest fluoride interstices produce the fast luminescence component, whereas holes captured on far-removed interstices determine the slow decay component.

Simple Model

It is very attractive to explain transitions between the valence band, the impurity energy level, and the conduction band using the simplified electrostatic model [9, 10]. Detailed analysis of the Born–Haber-type cycle and experimental tests showed that the sum of the Ti^{3+} threshold photoionization energy and the energy of charge transfer to Ti^{4+} is approximately equal to the energy of the forbidden band in the Al_2O_3 crystal [9]. The concept is rather simple: successive electron transfer from the valence band to the Me^{n+} energy level and the photoionization of the electron from the created $Me^{(n-1)+}$ energy level to the conduction band leads to the formation of an electron in the conduction band and a hole in the valence band. The sum of experimental quantities is slightly less than the forbidden band width [9]. In our case, the energy of electron transition from the valence band to the cerium Ce^{3+} energy level plus the energy of transition from the Ce^{2+} energy level to the conduction

band should be equated to the forbidden band width. The threshold of creation of V_k centers in $BaF_2:Ce^{3+}$ is equal to 7 eV (Fig. 1). The forbidden band width in BaF_2 is equal to 10.6 eV [5]. Proceeding from these values, the electron photoionization energy from the Ce^{2+} energy level can be evaluated as 3.6 eV. Several weak absorption bands in the IR region centered at 0.88, 1.09, and 1.49 eV and the strong band at 2.5 eV were attributed to the Ce^{2+} ion absorption in CaF_2 [3]. The depth of location of energy levels of lanthanide ions relative to the bottom of the conduction band can be estimated from the energy of $4f-6s$ transitions in a free ion [10], which yields 2.5 eV for bivalent cerium. Taking 2.5 eV as the threshold energy of electron transfer from the Ce^{2+} energy level to the conduction band, we obtain the value $7 + 2.5 = 9.5$ eV, whereas the forbidden band width is equal to 10.6 eV. Thus, the rule stated in [9] is obeyed in $BaF_2:Ce^{3+}$ to within 1 eV.

CONCLUSIONS

The photoionization in alkali-earth fluoride crystals doped with Ce^{3+} on exposure to 6–10 eV photons begins with the electron transition from the $2p F^-$ valence band to the cerium energy level. Subsequent tunnel recombination of the electron from the created Ce^{2+} energy level with a trapped hole in the form of V_k or H centers leads to the appearance of fast and slow Ce^{3+} -luminescence decay components. The remaining charges cause the appearance of thermostimulated luminescence peaks caused by the thermal hole release.

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