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 (VUV) photons with energy lower than that of the band gap, were investigated by various methods: thermostimulated luminescence, photostimulated luminescence and optical absorption. The $CaF_2:Eu^{2+}$ thermoluminescence curves in the range of 60-330 K due to various types of trapped holes were the same after VUV- illumination as after x-irradiation. Thermoluminescence curves of Ce^{3+}-doped alkaline-earth fluorides created by VUV-illumination or x-irradiation were generally similar. However V_k thermoluminescence peaks were absent in VUV-illuminated $CaF_2:Ce^{3+}$ and $SrF_2:Ce^{3+}$ crystals. Creation of Ce^{2+} characteristic bands was observed in photostimulated luminescence spectra as well as in optical absorption spectra of vacuum ultraviolet illuminated or x irradiated Ce^{3+}-doped crystals. The proposed mechanism of creation of trapped hole and trapped electron defects by vacuum ultraviolet illumination involves charge transfer type transitions, in which the electron transfers from valence band to an impurity level, lying in the band gap. Comparison of all involved energies of transitions in the crystals investigated shows that the sum of all transition energies is less than that of the band gap by 1-3 eV. This energy difference can be considered as the energy of lattice relaxation around created Ce^{2+} or Eu^+ ions.

1. Introduction

Dense fluoride crystals doped with rare-earth ion are good materials for scintillators. Rare-earth ions in many crystals have a moderate decay time and high light output. The disadvantage of rare-earth doped scintillators is the slow component of decay time in micro; millisecond time scale. Slow components are related to recombinations of trapped electrons and holes. Besides the slow components, the trapped electrons and holes result in thermostimulated luminescence during subsequent heating.

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Creation of electron and hole defects in doped crystals by ultraviolet illumination was investigated in few papers [1,2]. Thermoluminescence curves produced by ultraviolet and by x-ray of $KBr:Eu^{2+}$ were similar, pointing on similar nature of the created defects [3]. However the processes of defect creation by ultraviolet light is still unclear.

The absorption, excitation, photostimulation spectra and thermoluminescence creation spectra of the single crystals CaF_2, SrF_2, BaF_2 doped with Ce^{3+} and $CaF_2:Eu^{2+}$ were studied in vacuum ultraviolet region up to 11 eV. Some previous results were published elsewhere [4].

2. Experimental

The alkaline-earth fluoride crystals were grown in vacuum in graphite crucible. PbF_2 as oxygen scavenger was added into the raw materials [1] .

Spectra in 4-11 eV range where measured with 1 meter normal incidence vacuum monochromator VMR2. For thermoluminescence studies the crystal was illuminated by light of VMF25 (25W hydrogen discharge lamp) dispersed by a VMR2 monochromator for a few minutes at 78 K. Heating rate was equal to 12 K/min. Photoluminescence spectra of peaks were corrected for emission spectrum of halogen lamp.

3. Results

Vacuum ultraviolet illumination creates several thermoluminescence peaks in all studied crystals doped with Eu^{2+} or Ce^{3+} (Fig.1). Thermo luminescence intensity decreased with decreasing of impurity concentration. Thermo luminescence glow curves were substantially the same after x-irradiation or after VUV illumination in $CaF_2:Eu^{2+}$.

Thermoluminescence peaks at 100-120 K belong to delocalisation of self-trapped holes - V_k centres in these crystals [5]. The thermoluminescence below room temperature of rare-earth doped alkaline-earth

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

fluorides associated with holes released from different traps [5,6] .

The main feature of Ce^{3+}-doped crystals is that the ratio of V_k peaks against other thermoluminescence peaks is considerably smaller in VUV illuminated crystals (see Fig.1). Obviously, the absence of V_k thermostimulated luminescence peaks in Ce^{3+}-doped crystals associated with presence of charge compensated interstitial fluorine ions.

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. The shape of thermoluminescence curves did not depend on VUV photon energy in CaF_2 and SrF_2. However, the V_k centres thermoluminescence peak appeared
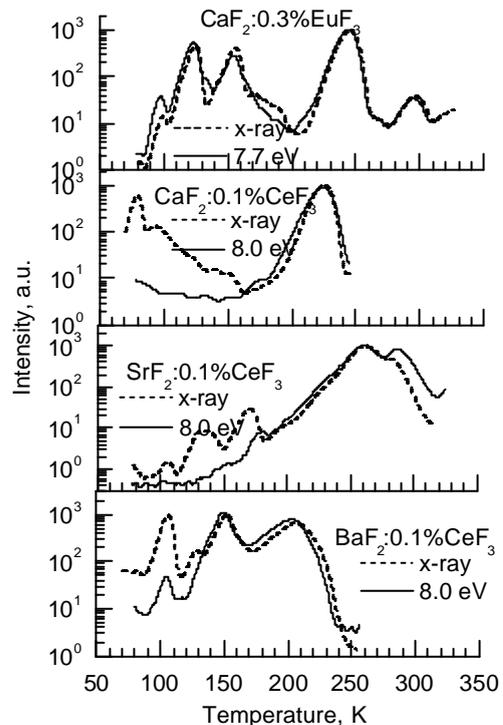
Fig.1 Thermostimulated luminescence curves of doped alkaline-earth fluoride crystals after x-ray irradiation or after vacuum ultraviolet illumination. Curves were normalised to equal maximal intensity. Thermoluminescence was measured at Ce^{3+} or Eu^{2+} emission bands.

when VUV photon energy exceeded the 7 eV in $BaF_2:Ce^{3+}$. Therefore, the free V_k centres created by photons with energies above 7 eV, while the trapped V_k centres in $BaF_2:Ce^{3+}$ created by photons with en-

ergies above 6 eV. We does not observe this effect in CaF_2 and in SrF_2, nevertheless, we may consider energy ≈ 1 eV as V_k centre optical binding energy on fluorine interstitials in all alkaline-earth fluoride crystals.

After x-irradiation or VUV-illumination at low temperature we observe the Ce^{3+} emission stimulated by red light (Fig. 2). Photostimulation spectra look very similar after x-ray irradiation or VUV illumination. During heating above 78 K the photostimulated luminescence decreased in the vicinity of appropriated thermoluminescence peaks. The intensity of luminescence drop to zero after heating to room temperatures in SrF_2 and BaF_2, however near 70-80% of initial intensity remains in CaF_2.
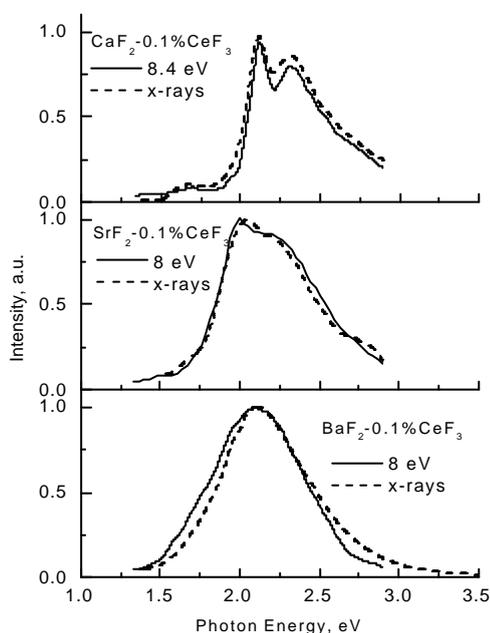
Fig. 2 Photostimulation spectra of Ce-doped alkaline-earth fluoride crystals exposed to x-irradiation or vacuum ultraviolet illumination at 78 K. Emission were recorded at Ce^{3+} bands.

New absorption bands were measured in VUV illuminated $CaF_2:Ce^{3+}$ and $BaF_2:Ce^{3+}$ crystals. In CaF_2 crystal significant part of the defects, created by x-ray or by VUV light, survives after heating up to room temperature (for x-ray see also [5]). Therefore we irradiate or illuminate the crystals at room temperature. The crystal becomes red in both cases. Several bands at 2.4 eV, 2.1 eV 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 $CaF_2:Ce^{3+}$ after γ-irradiation [7] or 308 nm (4.03 eV) two-photon laser illumination [8], which was attributed to absorption of Ce^{2+} ions.

The $BaF_2:Ce^{3+}$ crystal x-irradiated at 80 K shows broad absorption band at 2.3 eV (as those in photoluminescence spectrum see Fig.2) and at 3.4 eV. Both absorption bands were observed also after VUV illumination at 80 K.

Creation of thermoluminescence peaks in $CaF_2:Eu^{2+}$ was observed with photon energy above 5.8 eV. The creation spectra were similar for all three thermoluminescence peaks. The thermoluminescence below 200 K can be considerably suppressed by light with photon energies above 2.9 eV. Effectiveness of thermoluminescence suppression sharply rises above 2.9 eV up to 3.1 eV. Above 3.1 eV the effectiveness decreases due to the absorption of Eu^{2+}. We conclude that suppression of hole thermoluminescence peaks by photons with energy above 2.9 eV caused by photoionisation of Eu^+ centres.

4. Discussion

Experimental results undoubtedly show that as a result of vacuum ultraviolet illumination of doped alkaline-earth fluoride crystals the Ce^{2+} or Eu^+ ions as well as trapped hole centres are created. The defects are created by charge transfer transitions, when electrons transfer from valence band to impurity levels, which lie within band gap. However, in Ce-doped crystals electrons can transfer not only from valence band but also from levels of charge compensating fluorine interstitials.

For impurity ions, which are stable in valence state M^{n+} and $M^{(n-1)+}$, the charge transfer energy and photoionisation energy are related according to:

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

where E_g - band gap energy , E_{CT} - charge transfer energy for electron transition from top of valence band to M^{n+} level, E_{PI} - photoionisation energy for electron transfer from $M^{(n-1)+}$ level to bottom of conduction band [9]. The sum of Ti^{3+} photoionisation energy and charge transfer threshold to Ti^{4+} in Al_2O_3

[9] and YAlO$_3$ [10] is found to give approximately the band gap energy.

Table 1 Energies of photoionisation processes in doped alkaline-earth fluoride crystals. Eg - band-to-band transitions, E_{PI} – photo-ionisation energy for Ce^{2+} or Eu^{+}, E_{CT} - energy of transition from top of valence band to impurity level, obtained from the low-energy TSL creation edge. $\Delta E = E_g – E_{CT} - E_{PI} - \Delta E_i$. The binding energy of hole trapped on interstitial fluorine ion ΔE_i is taken 1.0 eV for Ce-doped alkaline-earth fluorides (see text).

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} Band gap energies were refined early in [11]
^{b} Ref.[12]
^{c} Ref. [13]

The appropriated energies are shown in Table 1. From the data of Table 1 one can see that the sum of experimental values is less than the band gap energies by values 1-3 eV. The additional energy may be lost during relaxation around the created Ce^{2+} or Eu^{+}. The effect of decreasing the energy distance between levels in the band gap and the bottom of conduction band is known for F centres in alkali halides [14]. We suppose that in the case of charge-transfer transitions the effect has to be more prominent, because the radii of Eu^{2+} or Ce^{3+} become considerably larger after trapping the electron.

5. Conclusion

The trapped electron and trapped hole defects were observed in alkaline-earth fluoride crystals doped with Eu^{2+} or Ce^{3+} by vacuum ultraviolet illumination with photon energy well below energy of band gap. Hole defects (V$_k$, V$_H$, V$_{kA}$), which are created by vacuum ultraviolet, are the same as those created by x-rays in Eu^{2+}-doped crystals. However, the V$_k$ were ineffectively created by vacuum ultraviolet in Ce^{3+}-doped CaF$_2$, SrF$_2$ crystals. Ce^{2+} electron trapped centres were identified in VUV illuminated or x-irradiated crystals by specific absorption and photostimulated luminescence bands.

We conclude that defects created by means of charge transfer type transitions, i.e. electrons from the valence band transfer to impurity levels, are in the band gap. In Ce^{3+}-doped crystals the transition started also from levels of charge compensating fluorine interstitials, which are $\approx$1 eV above the top of the valence band.

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