

CHARGE TRAPS IN Ce-DOPED CaF_2 AND BaF_2 *W. DROZDOWSKI^{a†}, K.R. PRZEGIĘTKA^a, A.J. WOJTOWICZ^{a,b}
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Thermoluminescence of $\text{CaF}_2\text{:Ce}$, BaF_2 , and $\text{BaF}_2\text{:Ce}$ irradiated at room temperature is reported. X-ray induced emission spectra of the samples show that both excitonic (due to $e^- + V_K$ recombination) and Ce^{3+} $d-f$ luminescence may contribute to thermoluminescence signal. The simple Randall-Wilkins model is used to deconvolute glow curves into seven to eight first-order peaks. Parameters of all traps are calculated and correlations between peaks in the curves of the examined materials are discussed.

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1. Introduction

The scintillation properties of undoped and rare earth (RE) doped alkaline earth fluorides have been studied by many investigators. Two materials are particularly attractive: $\text{CaF}_2\text{:Eu}$ and BaF_2 . The former with its Eu^{2+} luminescence peaking at ≈ 425 nm is one of the brightest scintillators known today. Its very high quantum efficiency, however, contrasts with long decay time (≈ 900 ns [1]) and relatively low density. The latter is denser and exhibits very fast (≈ 0.6 ns) cross-over luminescence at 190 and 220 nm [2, 3], yet together with slow excitonic emission band peaking at ≈ 310 nm (in pure CaF_2 there is no cross-over luminescence and the excitonic band peaks at ≈ 280 nm). Although it seems that the favorable properties of these two materials could be combined in RE-doped BaF_2 , such attempts have not given satisfactory results so far [4, 5].

With the papers of Bartram et al. [6] and Wojtowicz et al. [7, 8] on light yield and thermoluminescence of $\text{LuAlO}_3\text{:Ce}$ and $\text{YAlO}_3\text{:Ce}$, a new way of improving

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the properties of scintillators has appeared. One of the important conclusions of these papers is the responsibility of electron traps for the 35% light loss in $\text{LuAlO}_3:\text{Ce}$, comparing to its analogue $\text{YAlO}_3:\text{Ce}$. Although the traps are shallower in $\text{YAlO}_3:\text{Ce}$, the glow curves of both materials look quite similar. The only significant difference is an additional, very strong peak in $\text{LuAlO}_3:\text{Ce}$ at ≈ 500 K (heating rate $\beta = 1$ K/s). The 1.7 eV deep electron trap responsible for this peak contributes predominantly to the scintillation light loss. The existence of shallower traps in both samples does not affect the room temperature light yield, but changes the scintillation time profiles: the rise time in $\text{LuAlO}_3:\text{Ce}$ and the decay time in $\text{YAlO}_3:\text{Ce}$ are prolonged. All these results make it clear that improvement of the crystal growth procedures aimed at eliminating the traps would give us brighter and faster scintillators.

Thermoluminescence of undoped and RE-doped alkaline earth fluorides has already been investigated. Merz and Pershan [9] have recorded glow curves ranging from 80 to 450 K for thirteen RE^{3+} ions in CaF_2 and roughly estimated the depths of all traps. According to the model they have proposed, irradiation at liquid nitrogen temperature reduces trivalent rare earths in cubic (O_h) sites to divalent state and produces self-trapped hole centers (so-called V_K centers). During heating, diffusion of such a center towards a divalent RE site and recombination with its additional electron results in thermoluminescence (TL) emission. Ratnam and Banerjee [10] have distinguished two types of electron traps involved in TL of $\text{CaF}_2:\text{Ce},\text{Mn}$ irradiated at room temperature: Ce^{3+} ions in cubic (O_h) and tetragonal (C_{4v}) sites, responsible for TL below ≈ 430 K ($\beta = 0.5$ K/s), and deep intrinsic traps stabilized by lattice imperfections caused by Ce-activation. The same material with various concentrations of cerium and manganese has been examined extensively by Jassemnejad, McKeever and co-workers [11–13]. For CaF_2 doped with cerium only, a strong peak at ≈ 400 K ($\beta = 2$ K/s) has been associated with $e^- + V_K$ type recombination of electrons released from cubic Ce^{2+} ions with perturbed V_K centers, while a composite peak at 550–600 K with recombination of trigonal (C_{3v}) photochromic (PC) centers with interstitial fluorine atoms (a PC center is a divalent RE ion, here Ce^{2+} , with an electron trapped at the nearest-neighbour anion vacancy in [111] direction). Both processes result in the excitonic emission at ≈ 280 nm. The additional presence of Ce^{3+} $d-f$ luminescence in TL emission spectra has been explained by radiative energy transfer from the $e^- + V_K$ recombination to Ce^{3+} ions. In disagreement with Ratnam and Banerjee [6], tetragonal Ce^{3+} ions have been excluded from contributors to TL of $\text{CaF}_2:\text{Ce}$. Shi et al. [14] have studied the temperature dependence (in the range from 10 to 350 K) of the excitonic luminescence decay time in BaF_2 . They have associated the peculiarities of the $\tau(T)$ curve with the existence of four traps due to impurities or defects in the lattice. The trap depths have been calculated as 0.08, 0.22, 0.29, and 0.41 eV.

In this communication the glow curves of $\text{CaF}_2:\text{Ce}$, BaF_2 , and $\text{BaF}_2:\text{Ce}$ above room temperature are analyzed. The emphasis is laid on deconvolution of these curves into single peaks, calculation of trap parameters and comparison of trap distributions in these materials.

2. Materials and experiments

The crystals of CaF₂:0.01%Ce, CaF₂:0.1%Ce, BaF₂, and BaF₂:0.2%Ce were grown by Optovac Inc. (North Brookfield, MA, USA) using the Bridgman method. The cerium concentrations are those added to the melt (in mole %). No significant contamination by oxygen was observed and the samples were not subjected to any chemical reducing procedure. Polished \approx 1 mm thick samples with masses of 35.7 mg (CaF₂:0.01%Ce), 60.9 mg (CaF₂:0.1%Ce), 50.2 mg (BaF₂), and 148.5 mg (BaF₂:0.2%Ce) were examined.

The glow curves between 300 and 770 K were recorded with a RISO TL/OSL System, model TL/OSL-DA-12 [15], at three heating rates of 1, 2, and 5 K/s. To irradiate the samples, 196 keV β -rays from a Sr/Y-90 radioactive source were used. The measurements were conducted in argon atmosphere and an interference filter U-340 was mounted in the system to reject any undesirable emissions (mainly the thermal radiation of the sample and the heating element). In order to get distinct glow peaks and, on the other hand, not to exceed the sensitivity limits of the reader, the following irradiation times were chosen: 3 s for CaF₂:Ce, 30 s for BaF₂:Ce, and 45 s for BaF₂.

Radioluminescence was measured with a standard set-up consisting of an X-ray tube operated at 35 kV and 25 mA, a monochromator (SpectraPro-500 by Acton Research Corporation) and a photomultiplier (R928 by Hamamatsu).

3. Results and discussion

Radioluminescence spectra of the samples are shown in Fig. 1. The band of undoped BaF₂ is the excitonic emission due to the $e^- + V_K$ recombination. In case of Ce-doped crystals the Ce³⁺ $d-f$ luminescence dominates, but a contribution of the excitonic band is also visible. Assuming that the same recombination processes lead to radioluminescence and thermoluminescence, both above-mentioned emissions (excitonic and Ce³⁺ $d-f$) may contribute to the TL signal (see the transmission curve of the U-340 filter used in TL measurements, dotted line in Fig. 1).

Representative glow curves of the samples, recorded at the heating rate of 2 K/s, are presented in Fig. 2. Similar curves (with maxima shifted to different temperatures) have been obtained at other heating rates. In spite of the composite structure of all curves, characteristic asymmetry of the major peaks is visible. This fact suggests that the simple TL model of Randall and Wilkins [16] with the first-order kinetics may be used to analyze the data. Indeed, satisfactory results have been achieved in deconvoluting any of the glow curves into seven to eight separate peaks (Fig. 2). This has been done by fitting the following expression (based on the Randall–Wilkins formula) to experimental points:

$$I(T) = \sum_{i=1}^N n_{0i} s_i \exp\left(-\frac{E_i}{k_B T}\right) \exp\left[-\frac{s_i}{\beta} \int_{T_0}^T \exp\left(-\frac{E_i}{k_B T}\right) dT\right] \quad (1)$$

(I denotes the TL intensity, N — the number of peaks, T — the temperature, β — the heating rate, n_0 — the initial concentration of filled traps, E — the trap depth, s — the frequency factor, and k_B — the Boltzmann constant). The

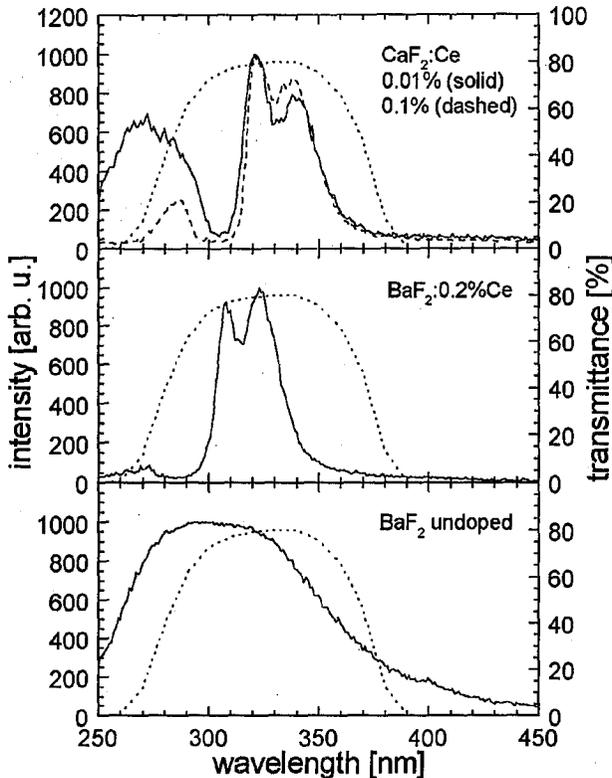


Fig. 1. X-ray excited emission spectra of $\text{CaF}_2:\text{Ce}$, BaF_2 , and $\text{BaF}_2:\text{Ce}$ (solid and dashed lines — radioluminescence, dotted lines — transmittance of the U-340 filter).

preliminary input values for the fitting procedure have been chosen by trial and error. For higher reliability of the fits, three curves at different heating rates have been proceeded simultaneously, which has also enabled to take non-ideal heat transfer into consideration. A linear relation

$$\delta T = \beta \delta t \quad (2)$$

has been assumed, where δT is the difference between the temperature of the sample and of the heating element (so-called thermal lag), β — the heating rate, and δt — an additional fitting parameter. Since reasonably high values of δt have been derived from the fitting procedure (4.3 s for $\text{CaF}_2:0.01\%\text{Ce}$ and $\text{BaF}_2:0.2\%\text{Ce}$, 3.9 s for $\text{CaF}_2:0.1\%\text{Ce}$, and 2.2 s for BaF_2), the Hoogenstraaten heating rate method has not been used to find the trap parameters. This method is sensitive to higher thermal lags and in such cases it decreases trap depths and frequency factors [17].

The glow curves of $\text{CaF}_2:\text{Ce}$ show a rich variety of peaks grouped in two regions. Following the interpretations of Jassemnejad and McKeever [11], the first region (peaks II–V) may originate in thermal activation of electrons from cubic Ce^{2+} ions and its composite structure is possibly due to different localization of these ions in relation to perturbed V_K centers. The second region (peaks VI–X)

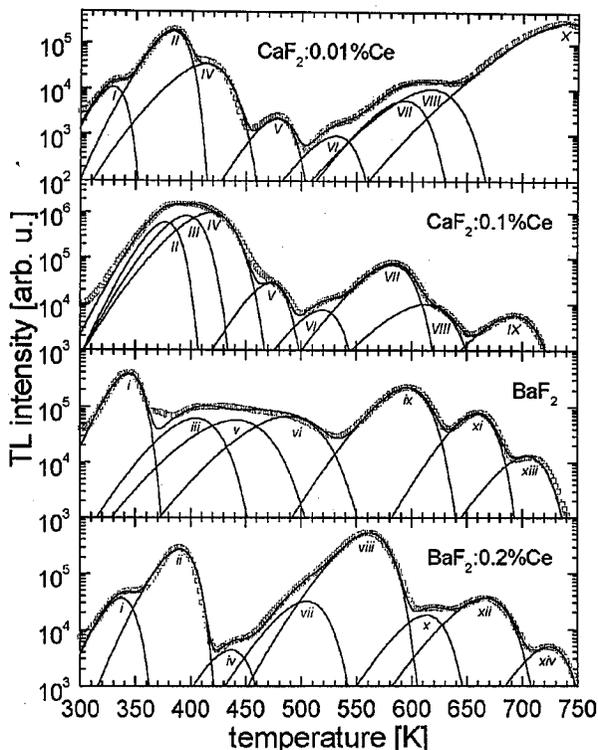


Fig. 2. Glow curves of CaF₂:Ce, BaF₂, and BaF₂:Ce measured at 2 K/s (squares — experimental points, solid lines — fits).

may involve PC centers and/or intrinsic electron traps. An additional peak (denoted as I) in CaF₂:0.01%Ce will be discussed later. Although the glow curves of both CaF₂:Ce samples are not so much similar, the deconvolution into single peaks has shown that most of the trap depths and frequency factors are the same (Table I). Generally, larger content of cerium increases the TL intensity, but there are some unexplained changes in relative initial trap concentrations, which cause the differences in the glow curve shapes.

The distribution of traps in BaF₂:Ce resembles to some extent that in CaF₂:Ce, but the second region starts 50–80 K lower and it is difficult to determine its limits (particularly to which region the peak denoted as iv belongs). To compare the trap depths in Ce-doped BaF₂ and CaF₂, the following correlation between the major peaks has been assumed: I–i, II–ii, VII–viii, IX–xii. For depths in eV a relationship has been found (Fig. 3):

$$E_{\text{BaF}_2:\text{Ce}} = 0.82E_{\text{CaF}_2:\text{Ce}} + 0.09. \quad (3)$$

Interestingly, since the band gap $E_g = 12.2$ eV in CaF₂ and $E_g = 10.6$ eV in BaF₂ [18], it seems that the trap depths scale with the band gaps:

$$\frac{E_{\text{BaF}_2:\text{Ce}}}{E_{\text{CaF}_2:\text{Ce}}} \approx \frac{E_{g,\text{BaF}_2:\text{Ce}}}{E_{g,\text{CaF}_2:\text{Ce}}}. \quad (4)$$

TABLE I

Parameters of traps in $\text{CaF}_2:\text{Ce}$ (T_{\max} — temperature, at which the glow curve peaks, E — trap depth, s — frequency factor, n_0 — initial trap concentration; each value of T_{\max} and n_0 is given for curves measured at 2 K/s; n_0 is in the same units as TL intensity and s is in s^{-1}).

Trap		I	II	III	IV	V
$\text{CaF}_2:$ 0.01%Ce	T_{\max} [K]	330	384	—	412	478
	E [eV]	0.85	1.00	—	0.73	1.41
	$\ln s$	28.3	28.4	—	18.3	32.3
	n_0	1.6×10^5	3.0×10^6	—	8.8×10^5	4.0×10^4
$\text{CaF}_2:$ 0.1%Ce	T_{\max} [K]	—	377	397	417	473
	E [eV]	—	0.98	0.86	0.75	1.40
	$\ln s$	—	28.2	23.0	18.4	32.5
	n_0	—	9.8×10^6	1.7×10^7	2.5×10^7	5.0×10^5
Trap		VI	VII	VIII	IX	X
$\text{CaF}_2:$ 0.01%Ce	T_{\max} [K]	532	592	618	—	740
	E [eV]	1.43	1.64	1.38	—	1.77
	$\ln s$	29.1	29.8	23.5	—	25.2
	n_0	2.1×10^4	1.4×10^5	3.1×10^5	—	1.0×10^7
$\text{CaF}_2:$ 0.1%Ce	T_{\max} [K]	519	579	599	689	—
	E [eV]	1.43	1.60	1.38	2.09	—
	$\ln s$	29.9	29.8	23.6	32.7	—
	n_0	1.5×10^5	1.7×10^6	3.0×10^5	1.5×10^5	—

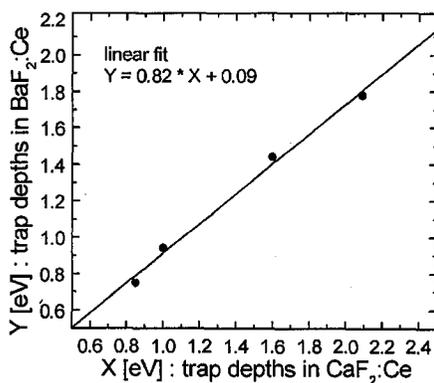


Fig. 3. Major trap depths in $\text{BaF}_2:\text{Ce}$ vs. major trap depths in $\text{CaF}_2:\text{Ce}$ (circles — points based on parameters from Tables I and II, solid line — fit).

TABLE II

Parameters of traps in BaF₂ and BaF₂:Ce (T_{\max} — temperature, at which the glow curve peaks, E — trap depth, s — frequency factor, n_0 — initial trap concentration; each value of T_{\max} and n_0 is given for curves measured at 2 K/s; n_0 is in the same units as TL intensity and s is in s⁻¹).

BaF ₂ undoped							
Trap	i	ii	iii	iv	v	vi	vii
T_{\max} [K]	345	—	405	—	441	489	—
E [eV]	0.80	—	0.61	—	0.55	0.69	—
$\ln s$	25.0	—	15.2	—	11.7	13.6	—
n_0	6.1×10^6	—	1.7×10^6	—	2.1×10^6	2.5×10^6	—
Trap	viii	ix	x	xi	xii	xiii	xiv
T_{\max} [K]	—	597	—	659	—	705	—
E [eV]	—	1.54	—	2.26	—	2.28	—
$\ln s$	—	27.7	—	37.6	—	35.3	—
n_0	—	5.6×10^6	—	1.7×10^6	—	3.1×10^5	—
BaF ₂ :0.2%Ce							
Trap	i	ii	iii	iv	v	vi	vii
T_{\max} [K]	338	390	—	436	—	—	504
E [eV]	0.75	0.94	—	1.00	—	—	1.12
$\ln s$	23.8	26.0	—	24.5	—	—	23.3
n_0	6.0×10^5	4.9×10^6	—	9.0×10^4	—	—	7.9×10^5
Trap	viii	ix	x	xi	xii	xiii	xiv
T_{\max} [K]	562	—	614	—	666	—	724
E [eV]	1.44	—	1.75	—	1.78	—	2.66
$\ln s$	27.5	—	30.8	—	28.6	—	40.5
n_0	1.3×10^7	—	4.3×10^5	—	1.0×10^6	—	1.1×10^5

The glow curve of undoped BaF₂ differs from those of Ce-doped samples. The lowest temperature peak is also visible in the curves of BaF₂:0.2%Ce and CaF₂:0.01%Ce (in CaF₂:0.1%Ce it may be hidden under much stronger Ce-related peaks). The most likely interpretation of this peak is the existence of a ≈ 0.8 eV deep electron trap not influenced by RE-doping. During the TL readout, electrons released from this trap recombine with perturbed V_K centers. The 350–550 K area of the BaF₂ glow curve has no distinct structure and the calculated trap parameters are less reliable. The peaks above ≈ 550 K may be due to Ce-independent intrinsic electron traps. The calculated parameters of all traps detected in undoped and Ce-doped BaF₂ are summarized in Table II.

4. Conclusions

Our measurements show that there are more traps in CaF₂:Ce than reported so far. The trap distribution in BaF₂:Ce is in some respects similar. The intensities of the glow curves are high enough to suspect that all the traps reported in this paper decrease the scintillation light yield of the examined materials. Most of the traps are related to cerium ions, nevertheless traps not introduced by rare earths

have also been detected. Thus a more complex model than the one proposed by Jassemnejad and McKeever [11] would be needed to explain all the details of our experiments. Measurements of thermoluminescence of CaF_2 and BaF_2 doped with other RE ions will be an interesting continuation of this research.

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