CHARGE TRAPS IN Ce-DOPED CaF$_2$ AND BaF$_2$* 

W. DROZDOWSKI$^{a}$, K.R. PRZEGIĘTKA$^{a}$, A.J. WOJTOWICZ$^{a,b}$
AND H.L. OCZKOWSKI$^{a}$

$^a$Institute of Physics, Nicholas Copernicus University
Grudziądzka 5/7, 87-100 Toruń, Poland
$^b$Chemistry Department, Boston University
590 Commonwealth Ave., Boston, MA 02215, USA

(Received August 2, 1998)

Thermoluminescence of CaF$_2$:Ce, BaF$_2$, and BaF$_2$: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.

PACS numbers: 78.60.Kn, 73.50.Gr, 29.40.Mc

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: CaF$_2$:Eu and BaF$_2$. The former with its Eu$^{2+}$ luminescence peaking at $\approx 425$ nm is one of the brightest scintillators known today. Its very high quantum efficiency, however, contrasts with long decay time ($\approx 900$ ns [1]) and relatively low density. The latter is denser and exhibits very fast ($\approx 0.6$ ns) cross-over luminescence at 190 and 220 nm [2, 3], yet together with slow excitonic emission band peaking at $\approx 310$ nm (in pure CaF$_2$ there is no cross-over luminescence and the excitonic band peaks at $\approx 280$ 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 LuAlO$_3$:Ce and YAlO$_3$:Ce, a new way of improving...
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 LuAlO$_3$:Ce, comparing to its analogue YAlO$_3$:Ce. Although the traps are shallower in YAlO$_3$:Ce, the glow curves of both materials look quite similar. The only significant difference is an additional, very strong peak in LuAlO$_3$:Ce at $\approx 500$ 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 LuAlO$_3$:Ce and the decay time in YAlO$_3$: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 (Oh) 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 CaF$_2$:Ce,Mn irradiated at room temperature: Ce$^{3+}$ ions in cubic (Oh) and tetragonal (C$_4v$) sites, responsible for TL below $\approx 430$ 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 $\approx 400$ 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 $\approx 280$ 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 CaF$_2$: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 CaF$_2$:Ce, BaF$_2$, and BaF$_2$: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 CaF$_2$:0.01%Ce, CaF$_2$:0.1%Ce, BaF$_2$, and BaF$_2$: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 (CaF$_2$:0.01%Ce), 60.9 mg (CaF$_2$:0.1%Ce), 50.2 mg (BaF$_2$), and 148.5 mg (BaF$_2$: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 $\beta$-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 CaF$_2$:Ce, 30 s for BaF$_2$:Ce, and 45 s for BaF$_2$.

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 BaF$_2$ is the excitonic emission due to the $e^- + V_K$ recombination. In case of Ce-doped crystals the Ce$^{3+}$ 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 Ce$^{3+}$ 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:

\[
I(T) = \sum_{i=1}^{N} n_0 i s_i \exp\left(-\frac{E_i}{k_B T}\right) \exp\left[-\frac{s_i}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E_i}{k_B T}\right) dT\right]
\]

(I denotes the TL intensity, $N$ — the number of peaks, $T$ — the temperature, $\beta$ — 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
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

$$\delta T = \beta \delta t$$  \hspace{1cm} (2)

has been assumed, where $\delta T$ is the difference between the temperature of the sample and of the heating element (so-called thermal lag), $\beta$ — the heating rate, and $\delta t$ — an additional fitting parameter. Since reasonably high values of $\delta t$ have been derived from the fitting procedure (4.3 s for CaF$_2$:0.01%Ce and BaF$_2$:0.2%Ce, 3.9 s for CaF$_2$:0.1%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 CaF$_2$: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 CaF$_2$:Ce, BaF$_2$, and BaF$_2$: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 CaF$_2$:0.01%Ce will be discussed later. Although the glow curves of both CaF$_2$: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 BaF$_2$:Ce resembles to some extent that in CaF$_2$: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 BaF$_2$ and CaF$_2$, 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):

$$E_{\text{BaF}_2:\text{Ce}} = 0.82E_{\text{CaF}_2:\text{Ce}} + 0.99.$$  \(3\)

Interestingly, since the band gap $E_g = 12.2$ eV in CaF$_2$ and $E_g = 10.6$ eV in BaF$_2$ \[18\], it seems that the trap depths scale with the band gaps:

$$\frac{E_{\text{BaF}_2:\text{Ce}}}{E_{\text{CaF}_2:\text{Ce}}} \approx \frac{E_g,\text{BaF}_2:\text{Ce}}{E_g,\text{CaF}_2:\text{Ce}}.$$  \(4\)
TABLE I

Parameters of traps in CaF$_2$:Ce ($T_{\text{max}}$ — temperature, at which the glow curve peaks, $E$ — trap depth, $s$ — frequency factor, $n_0$ — initial trap concentration; each value of $T_{\text{max}}$ 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$^{-1}$).

<table>
<thead>
<tr>
<th>Trap</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$:</td>
<td>$T_{\text{max}}$ [K]</td>
<td>330</td>
<td>384</td>
<td>412</td>
<td>478</td>
</tr>
<tr>
<td>E [eV]</td>
<td>0.85</td>
<td>1.00</td>
<td>-</td>
<td>0.73</td>
<td>1.41</td>
</tr>
<tr>
<td>0.01%Ce</td>
<td>$\ln s$</td>
<td>28.3</td>
<td>28.4</td>
<td>-</td>
<td>18.3</td>
</tr>
<tr>
<td>$n_0$</td>
<td>$1.6 \times 10^5$</td>
<td>$3.0 \times 10^6$</td>
<td>-</td>
<td>$8.8 \times 10^5$</td>
<td>$4.0 \times 10^4$</td>
</tr>
<tr>
<td>CaF$_2$:</td>
<td>$T_{\text{max}}$ [K]</td>
<td>-</td>
<td>377</td>
<td>397</td>
<td>417</td>
</tr>
<tr>
<td>E [eV]</td>
<td>-</td>
<td>0.98</td>
<td>0.86</td>
<td>0.75</td>
<td>1.40</td>
</tr>
<tr>
<td>0.1%Ce</td>
<td>$\ln s$</td>
<td>-</td>
<td>28.2</td>
<td>23.0</td>
<td>18.4</td>
</tr>
<tr>
<td>$n_0$</td>
<td>-</td>
<td>$9.8 \times 10^6$</td>
<td>$1.7 \times 10^7$</td>
<td>2.5 $\times 10^7$</td>
<td>5.0 $\times 10^5$</td>
</tr>
</tbody>
</table>

Fig. 3. Major trap depths in BaF$_2$:Ce vs. major trap depths in CaF$_2$:Ce (circles — points based on parameters from Tables I and II, solid line — fit).
Parameters of traps in BaF$_2$ and BaF$_2$:Ce ($T_{\text{max}}$ — temperature, at which the glow curve peaks, $E$ — trap depth, $s$ — frequency factor, $n_0$ — initial trap concentration; each value of $T_{\text{max}}$ 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$^{-1}$).

<table>
<thead>
<tr>
<th>Trap</th>
<th>i</th>
<th>ii</th>
<th>iii</th>
<th>iv</th>
<th>v</th>
<th>vi</th>
<th>vii</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{max}}$ [K]</td>
<td>345</td>
<td>–</td>
<td>405</td>
<td>–</td>
<td>441</td>
<td>489</td>
<td>–</td>
</tr>
<tr>
<td>$E$ [eV]</td>
<td>0.80</td>
<td>–</td>
<td>0.61</td>
<td>–</td>
<td>0.55</td>
<td>0.69</td>
<td>–</td>
</tr>
<tr>
<td>$\ln s$</td>
<td>25.0</td>
<td>–</td>
<td>15.2</td>
<td>–</td>
<td>11.7</td>
<td>13.6</td>
<td>–</td>
</tr>
<tr>
<td>$n_0$</td>
<td>$6.1 \times 10^6$</td>
<td>–</td>
<td>$1.7 \times 10^6$</td>
<td>–</td>
<td>$2.1 \times 10^6$</td>
<td>$2.5 \times 10^6$</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trap</th>
<th>viii</th>
<th>ix</th>
<th>x</th>
<th>xi</th>
<th>xii</th>
<th>xiii</th>
<th>xiv</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{max}}$ [K]</td>
<td>–</td>
<td>597</td>
<td>–</td>
<td>659</td>
<td>–</td>
<td>705</td>
<td>–</td>
</tr>
<tr>
<td>$E$ [eV]</td>
<td>–</td>
<td>1.54</td>
<td>–</td>
<td>2.26</td>
<td>–</td>
<td>2.28</td>
<td>–</td>
</tr>
<tr>
<td>$\ln s$</td>
<td>–</td>
<td>27.7</td>
<td>–</td>
<td>37.6</td>
<td>–</td>
<td>35.3</td>
<td>–</td>
</tr>
<tr>
<td>$n_0$</td>
<td>–</td>
<td>$5.6 \times 10^6$</td>
<td>–</td>
<td>$1.7 \times 10^6$</td>
<td>–</td>
<td>$3.1 \times 10^5$</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trap</th>
<th>i</th>
<th>ii</th>
<th>iii</th>
<th>iv</th>
<th>v</th>
<th>vi</th>
<th>vii</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{max}}$ [K]</td>
<td>338</td>
<td>390</td>
<td>–</td>
<td>436</td>
<td>–</td>
<td>–</td>
<td>504</td>
</tr>
<tr>
<td>$E$ [eV]</td>
<td>0.75</td>
<td>0.94</td>
<td>–</td>
<td>1.00</td>
<td>–</td>
<td>–</td>
<td>1.12</td>
</tr>
<tr>
<td>$\ln s$</td>
<td>23.8</td>
<td>26.0</td>
<td>–</td>
<td>24.5</td>
<td>–</td>
<td>–</td>
<td>23.3</td>
</tr>
<tr>
<td>$n_0$</td>
<td>$6.0 \times 10^5$</td>
<td>$4.9 \times 10^5$</td>
<td>–</td>
<td>$9.0 \times 10^4$</td>
<td>–</td>
<td>–</td>
<td>$7.9 \times 10^5$</td>
</tr>
</tbody>
</table>

The glow curve of undoped BaF$_2$ differs from those of Ce-doped samples. The lowest temperature peak is also visible in the curves of BaF$_2$:0.2%Ce and CaF$_2$:0.01%Ce (in CaF$_2$: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 $\approx 0.8$ 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 BaF$_2$ glow curve has no distinct structure and the calculated trap parameters are less reliable. The peaks above $\approx 550$ K may be due to Ce-independent intrinsic electron traps. The calculated parameters of all traps detected in undoped and Ce-doped BaF$_2$ are summarized in Table II.

4. Conclusions

Our measurements show that there are more traps in CaF$_2$:Ce than reported so far. The trap distribution in BaF$_2$: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.

Acknowledgments

This work has been supported by the Committee for Scientific Research, Poland (project no. 2 P03B 049 14), Nicholas Copernicus University, and ALEM Associates (Boston, USA). Thanks are due to Dr. T.M. Piters (Universidad de Sonora, Mexico) for the fitting procedure, which we have been using in the glow curve analysis.

References