Multiple thermoluminescence glow peaks and afterglow suppression in CsI:Tl co-doped with Eu$^{2+}$ or Yb$^{2+}$

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Abstract. CsI:Tl is a widely utilized scintillator material with many desirable properties but its applicability is limited by persistent afterglow. However, effective afterglow suppression has been achieved by co-doping with divalent lanthanides. The present report is concerned with observation of multiple thermoluminescence glow peaks in CsI:Tl,Eu and CsI:Tl,Yb, attributed to varying distributions of charge-compensating cation vacancies relative to divalent lanthanide co-dopants, and the subsequent modification of these distributions by repeated observations. It is observed that Yb$^{2+}$ provides a slightly shallower electron trap than Eu$^{2+}$, and that it can occupy a face-centered position by virtue of its relatively small ionic radius; the latter observation is confirmed by electrostatic calculations. It is also found that repeated observation of thermoluminescence in these materials has a modest adverse effect on afterglow suppression.

1. Introduction

Afterglow suppression in scintillator material CsI:Tl, co-doped with various divalent rare-earth ions, has been investigated extensively, as described in several previous publications.$^5,6,7,8,9,10,11,12$ Thermoluminescence measurements$^5,6$ of CsI:Tl revealed glow peaks at 60K, 90K and 120K, attributable$^{13,14}$ respectively to thermally-activated tunneling recombination, the onset of V$_K$-center mobility, and thermal ionization of electrons from Tl$^0$. It has also been established that radiative recombination occurs at Tl sites, where the emitting state is (Tl$^+$ + STE),$^6$ and that Tl$^+$ is unstable in CsI.$^{15}$ In the present work, repeated measurements are found to modify the distribution of glow peaks while preserving their overall intensity.

2. Sample preparation

Single crystals 10 mm in diameter and 35 mm long, subsequently sliced into samples 2.5 mm thick, were grown by the vertical Bridgeman method at RMD. Two samples were employed in the present investigation: sample SC8-1#3 with 0.2% Tl and 0.2% Eu in the starting material, and sample SC66A-1#2 with 0.2% Tl and 0.1% Yb in the starting material. However, the proportions of dopants incorporated in the finished crystal samples varied substantially from one sample to another and within each sample.
3. Experiment.
Radioluminescence and thermoluminescence measurements were performed at the University of Connecticut on the single-crystal samples of co-doped CsI:Tl,Eu and CsI:Tl,Yb prepared at RMD. The branching ratio of electron hole pairs that contribute either to scintillation or thermoluminescence was determined by employing a common apparatus for both measurements. An electron Van de Graaff accelerator operated at a beam voltage of 1.0 MeV and a beam current of 1.0 µA was employed as a primary radiation source, with a thin copper target that served as a point source of ~0.5 MeV gamma rays. Each sample was mounted in turn on a heated pedestal monitored by a thermocouple and cooled by flowing nitrogen gas through a heat exchanger. Luminescence was conducted to a photomultiplier by a shielded optical fiber. Samples were irradiated for four minutes at reduced temperatures to record radioluminescence and then subjected to a temperature ramp of +25°C per minute at an enhanced gain setting to record thermoluminescence. These two steps were repeated alternately several times for each sample, with varying results.

Figure 1. Light output of an as-received sample of CsI:Tl, irradiated at -63°C and subsequently heated to 280°C with a temperature ramp of +25°C/min.

Figure 2. Light output of the same sample of CsI:Tl,Eu as in Figure 1, during the third irradiation at -124°C and the third temperature ramp of +25°C/min to 280°C.
Three distinct glow peaks are observed after the first irradiation of CsI:Tl, Eu, as shown in Figure 1. The highest-temperature peak near 100°C, which is broader than the others, probably contains multiple components. After the third irradiation, the highest temperature peak has disappeared and a new peak has appeared at lower temperature, as shown in Figure 2. A similar transformation occurs in CsI:Tl, Yb. Multiple glow peaks are attributed to the varying proximity of charge-compensating cation vacancies to the co-dopant. Presumably, cation vacancies can migrate at the elevated temperatures (≤ 280°C) achieved during thermoluminescence by changing places with neighboring cations, and the total energy of the sample is reduced by their increased proximity to divalent co-dopant cations. The effect of a nearby charge-compensating cation vacancy on the co-dopant trap depth can be approximated by Coulomb interaction of the excess charges involved in their unperturbed lattice positions, diminished by the dielectric constant of the medium. Accordingly, it can be calculated from the formula

\[ \Delta E_n = \frac{e^2/a_0}{\kappa (a/a_0) \sqrt{\left( \alpha_n^2 + \beta_n^2 + \gamma_n^2 \right)}} \]  

where \( e^2/a_0 = 27.2 \text{ eV} \), \( \kappa = 6.31 \), \( a = 4.56 \text{ Å} \), \( a_0 = 0.529 \text{ Å} \), and \( \alpha_n, \beta_n \) and \( \gamma_n \) are integers denoting the position of the charge-compensating cation vacancy relative to the europium or ytterbium impurity in units of the lattice parameter. The parameters \( \kappa \) and \( a \) are, respectively, the dielectric constant and lattice parameter of CsI. Values of \( \Delta E_n \) calculated from Eq. (1) are listed in Table 1. The rate of thermal ionization in a glow peak corresponding to a trap depth \( E \) is given by the formula

\[ p = s \exp\left(-E/k_B T\right), \]  

where \( T \) is in degrees Kelvin. The value of the pre-exponential factor \( s \) determines the temperature width of the thermoluminescence glow peak. If one assumes that \( s \) is approximately the same for all traps, based on the observation that the temperature widths of the various glow peaks are comparable, it follows that the trap depths and temperatures for successive glow peaks are related by

\[ \frac{\Delta E_n}{E_{\infty}} = \frac{\Delta T_n}{T_{\infty}}. \]  

Table 1. Values of \( \Delta E_n \) for CsI:Tl, Eu and CsI:Tl, Yb, calculated from Eq. (1)

| \( n \) | \( (\alpha_n,\beta_n,\gamma_n) \) | \( 1/\sqrt{\left( \alpha_n^2 + \beta_n^2 + \gamma_n^2 \right)} \) | \( \Delta E_n \) (eV) | \( T_{\infty}+\Delta T_n \) (K) | \( T_{\infty}+\Delta T_n \) (K) |
|---|---|---|---|---|---|
| 1 | (±1,0,0), (0,±1,0), (0,0,±1) | 1.0 | -0.500 | 233 | 163 |
| 2 | (±1,±1,0), (±1,0,±1), (0,±1,±1) | 0.707 | -0.354 | 303 | 233 |
| 3 | (±1,±1,±1) | 0.577 | -0.289 | 334 | --- |
| 4 | (±2,0,0), (0,±2,0), (0,0,±2) | 0.5 | -0.250 | --- | --- |
| 5 | (±2,±1,0), (±2,0,±1), (±1,±2,0), (0,±2,±1), (±1,±1,0), (0,±1,±2) | 0.447 | -0.224 | --- | --- |
| 6 | (±2,±1,±1), (±1,±2,±1), (±1,±1,±2) | 0.408 | -0.204 | 375 | --- |
One can then infer the values of $E_\infty$ and $T_\infty$ in the absence of a charge-compensating cation vacancy from Eq. (3) and Table 1, which also lists the approximate temperatures of observed glow peaks. The trap depths for isolated co-dopants are inferred to be $E_\infty \approx 1.00$ eV for Eu$^{2+}$/Eu$^{2+}$ and $E_\infty \approx 0.84$ eV for Yb$^{2+}$/Yb$^{2+}$.

4. Anomalous Thermoluminescence Glow Peak in CsI:Tl,Yb

![Figure 3](image.png)

Figure 3. Light output of a sample of CsI:Tl,Yb during the fourth irradiation at -125°C and the fourth temperature ramp of +25°C/min to 150°C. The glow peak at -70°C is anomalous.

The scintillation and thermoluminescence of CsI:Tl,Yb during the fourth irradiation and temperature ramp of the present investigation are shown in Figure 3. The most prominent thermoluminescence glow peak at -70°C (203K) is anomalous in that it doesn’t fit Equation (1) and Table (1). This anomalous peak is attributed to Yb$^{2+}$ in the face-center position with a cation vacancy in the adjacent cell. That situation can occur in CsI because the ionic radius of Yb$^{2+}$ is smaller than that of Eu$^{2+}$ and substantially smaller than that of Cs$^+$. The radius of the face-center position in undistorted CsI is given by the formula

$$r_{FC} = a \sqrt{2} - r_{i^-},$$

where $a$ is the lattice parameter of CsI, $a = 4.56$ Å, and $r_i$ is the ionic radius of iodine minus with six-fold coordination, $r_i = 2.20$ Å. It follows that $r_{FC} = 1.02$ Å. Note that the undistorted face-centered position in CsI can accommodate Yb$^{2+}$ but not Eu$^{2+}$, and was established to be more stable than the body-centered position.

5. Hole Traps

In the present experiment, light emission is observed at temperatures as high as ~100 °C. However, it has been shown that V$_{i}$-centers trapped at Tl$^+$ ions or cation vacancies become unstable at much lower temperatures. Accordingly, it is inferred that two or more cation vacancies must stabilize a trapped V$_{i}$-center pending its combination with an electron ionized from a divalent co-dopant and the subsequent radiative recombination of the resulting exciton at a thallium site.
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