Thermally stimulated conductivity and evaluation of some parameters of CaS:Pr phosphors

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1 Introduction
Calcium sulphide phosphors have great potential as a broad band light source in both powder and thin film luminescent devices. Intense broad band fluorescence observed in CaS: Cd both by optical and electrical excitation had further rejuvenated the interest of research workers. Calcium sulphide activated with rare earth makes it magnetically susceptible and find use in audio video thin film.

In thermally stimulated conductivity (TSC) or photo conductivity (PC) ionizing radiation may be used as the exciting source, but one detects the thermally or optically stimulated relaxation back to equilibrium by monitoring the freed charges during their passage through the de-localised excited states (i.e. conduction band for electron or valence band for holes).

In the above process, the perturbation is usually the absorption of energy from ionized radiation and the stimulated relaxation back to equilibrium by monitoring the emission of luminescence from the system during the transition of the freed charges back to the ground state.

The emitted luminescence at which the system returns to in equilibrium, as seen in a characteristic luminescence versus time curve is the effect of doping in forming the trap level and their degeneracy. This observation is quite intriguing as determined by thermo-luminescence (TLS) studies. Thermally stimulated conductivity has an edge over TLS, as TSC accounts for both radiative and non-radiative transition, while TLS accounts only for radiative one.

2 Theoretical Considerations
Randall and Wilkins considered a simple model for production of TL based on the thermally stimulated release of \( n \) electrons from a descrete trapping at energy \( E \) and characterized by a frequency factor \( \tau \). This is equivalent of assuming a single value for trap capture cross-section. With the above constraint \( n_0 \) (Est) can be simply written as \( n(t) \) and under the condition of negligible retrapping and quasi-equilibrium TL intensity is given by:

\[
i(T) = A \exp \left[ -\frac{E}{KT} - \frac{1}{\beta \tau_0} \int_0^T \exp \left( -\frac{E}{KT} \right) dT \right] \tag{1}
\]

where \( A \) is a constant involving the product of charge mobility, free lifetime and depth of penetration of charge, i.e. \( n_0 \), \( E \) trap-depth, \( K \) Boltzmann constant, \( T \) the absolute temperature, \( \beta \) heating rate, \( \tau_0 \) the inverse of trap frequency factor. The rate at which the trapped charge is released can be expressed in terms of total charge \( q \) at traps and a relaxation time \( \tau \) by:
\[
\frac{dq}{dt} = -\frac{q}{\tau}\quad \ldots (2)
\]

When the sample is warmed at a linear rate, \( q \) is a function of temperature and time, and the solution of Eq. (2) is:

\[
q = q_0 \exp \left( -\frac{\int dt}{\tau} \right)\quad \ldots (3)
\]

The thermally stimulated current is simply the rate of release of charge:

\[
i = \frac{dq}{dt} = -\frac{q_0}{\tau} \exp \left( -\frac{\int dt}{\tau} \right)\quad \ldots (4)
\]

The release of charge from temperate must overcome energy barrier (trap energy \( E \)) and the jumping probability per unit time is proportional to \( \exp(-E/KT) \). The relaxation time \( \tau \) is interpreted as the average time required for the jump or the reciprocal of the probability and is given by:

\[
\tau = \tau_0 \exp \left( \frac{E}{KT} \right)\quad \ldots (5)
\]

since for a uniform heating rate \( T = T_0 + \beta t \), combining Eqs (4) and (5) one can get:

\[
i(T) = \frac{q_0}{\tau_0} \exp \left[ -\frac{E}{KT} - \frac{1}{\beta T_0 \tau_0} \exp \left( -\frac{E}{KT} \right) \right] dt\quad \ldots (6)
\]

\[
= A \exp \left[ -\frac{E}{KT} - \frac{1}{\beta T_0 \tau_0} \exp \left( -\frac{E}{KT} \right) \right] dt\quad \ldots (7)
\]

2.1 Evaluation of \( E, \tau_0 \), and \( \tau \)

Two methods have been used for evaluation of \( E, \tau_0 \), and \( \tau \). According to Garlic-Gibson (14) the lower temp. tail of Eq. (7) is given by:

\[
\ln i = C - \frac{E}{KT}\quad \ldots (8)
\]

\( E \) can be evaluated from the linear plots of Eq. (8), but in case there is no sharp rise in \( i(t) \) versus \( T \) curves (Fig. 1) this method is not suitable.

In the derivation of Eq. (7):
2.2 Cowell and Woods curve fitting method

Substitution of $x = E/KT$ and $dx = -E/KT^2 \, dt$ in Eq. (7) and approximation yields:

$$i(x) = A \exp[-x - B(-x)^2 x^{-2}] \quad \text{... (12)}$$

If this is differentiated and equated to zero, maximum of the curve is given by:

$$B' = \frac{\exp x^*x^{-3}}{x^* + 2} \quad \text{... (13)}$$

where $x^* = E/KT_m$ and $B'$ is the approximate value of $B$ obtained by replacing the approximation of Eq. (12) by an equality sign. Eqs (12) and (13) are used for curve fitting technique. The value of $T_m$ is obtained from the experimental curve. Bucci plot method is used to calculate approximate value of $E'$ of $E$. With $T_m$, this leads to an approximate value of $x^*$. This value is inserted in Eq. (12). The factor $A$ is used as an adjustable parameter to normalize the theoretical curve with the experimental one at the maximum, that is:

$$A = \frac{i(x^*)}{\exp[-x^* - B'\exp(-x^*).x^{-3}]} \quad \text{... (14)}$$

Any error in the initial value of $E'$ chosen is indicated by a failure to obtain a good fit between the experimental and the theoretical curves. If the fit is not good, a new value of $E'$ is chosen and the procedure is repeated, until an excellent fit is obtained. The value of $E$ corresponding to this fit is taken to be the correct value of $T_m$, which can be calculated from the value of $B$ obtained. An advantage of Cowell and Woods method is that the value of $A$ is also obtained from it, from which one can get initial density of filled traps.

3 Experimental Details

Polycrystalline samples of calcium sulphide phosphors were obtained using solid-state reaction between praseodymium oxide (99.99 % purity, Fluka, A.G., Switzerland) and calcium sulphate (May & Baker, 99.99 % pure) using sodium sulphate and sodium thiosulphate as fluxes by heat treatment technique in the reducing atmosphere of carbon-dioxide. Various parameters were changed to optimise the luminescence. After heat treatment the melt was pulverised quickly and ground into a fine powder. Crystalization of powder was checked by taking X-ray diffraction powder photograph of each sample. All the samples were found to be of proper crystallization. The samples were pressed to form pellets of 3.1 cm diameter and 1 mm thickness. Each pellet containing 500 mg of phosphor material is sintered for 30 min and cooled in the dark. The pellets were then excited by unfiltered mercury radiation from Phillips 125 W 240 V mercury lamp for 10 min and the phosphor pellets were allowed to decay their light for 30 min. The parallel plate capacitor type cell was fabricated by the usual technique keeping one electrode transparent.

The heating chamber consists of heating coil in the form of a cord wound over an aluminium hollow cylinder. The heating cord was connected with a high wattage low resistance in series, kept away from the container and connected to an autotransformer. The voltage was adjusted to achieve the desired heating rate. The capacitor was enclosed in a heating chamber and linear heating rate of 1 °C per min was used. TSC measured with Keithly solid state electrometer. The current feeder was adjusted every 2.5 min to the desired heating rate. TSC curves were plotted. TSC rises to peak and decreases to almost 10-20 times at a temperature around 330 K. The whole experiment...
Table 1 - Evaluated values of activation energy/trap depth \((E)\) \(\tau_0\), \(\tau_{300}\), \(\tau_m\) and attempt to escape frequency by Bucci plot method

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Act.Conc. per 10 g of CaSO(_4)</th>
<th>Trap depth (eV)</th>
<th>(\tau_0) (s)</th>
<th>(\tau_{300}\times10^2) (s)</th>
<th>(\tau_m\times10^7) (s)</th>
<th>Attempt to escape frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSD2</td>
<td>0.0004</td>
<td>0.7150</td>
<td>2.00\times10^9</td>
<td>2.03</td>
<td>6.35</td>
<td>5.10\times10^9</td>
</tr>
<tr>
<td>TSD3</td>
<td>0.0006</td>
<td>0.6970</td>
<td>3.43\times10^9</td>
<td>1.77</td>
<td>4.7</td>
<td>2.92\times10^8</td>
</tr>
<tr>
<td>TSD4</td>
<td>0.0008</td>
<td>0.7098</td>
<td>1.6\times10^9</td>
<td>1.33</td>
<td>5.25</td>
<td>6.17\times10^7</td>
</tr>
<tr>
<td>TSD5</td>
<td>0.0012</td>
<td>0.7850</td>
<td>2.15\times10^9</td>
<td>3.22</td>
<td>5.78</td>
<td>4.65\times10^7</td>
</tr>
<tr>
<td>TSD6</td>
<td>0.002</td>
<td>0.6885</td>
<td>4.15\times10^10</td>
<td>1.52</td>
<td>5.92</td>
<td>2.41\times10^8</td>
</tr>
<tr>
<td>TSD7</td>
<td>0.003</td>
<td>0.7596</td>
<td>4.53\times10^10</td>
<td>2.54</td>
<td>5.92</td>
<td>2.21\times10^8</td>
</tr>
<tr>
<td>TSD8</td>
<td>0.004</td>
<td>0.7146</td>
<td>1.41\times10^9</td>
<td>3.94</td>
<td>9.93</td>
<td>7.09\times10^8</td>
</tr>
<tr>
<td>TSD9</td>
<td>0.008</td>
<td>0.7698</td>
<td>2.78\times10^10</td>
<td>3.42</td>
<td>7.93</td>
<td>3.60\times10^9</td>
</tr>
<tr>
<td>TSD10</td>
<td>0.012</td>
<td>0.6742</td>
<td>9.63\times10^9</td>
<td>1.99</td>
<td>4.55</td>
<td>1.04\times10^8</td>
</tr>
</tbody>
</table>

Table 2 - Evaluated values of activation energy/trap depth \((E)\) \(\tau_0\), \(\tau_{300}\), \(\tau_m\) and \(N_0\) (initially filled traps) using Cowell & Woods method

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Act.Conc. per 10 g of CaSO(_4)</th>
<th>Trap depth (eV)</th>
<th>No. of (Initially filled traps)</th>
<th>(\tau_m) (K)</th>
<th>(\tau_0) \times10^9 (s)</th>
<th>(\tau_{300}) \times10^3 (s)</th>
<th>(\tau_m) \times10^7 (s)</th>
<th>Attempt to escape frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSD2</td>
<td>0.0004</td>
<td>0.7150</td>
<td>1.52\times10^{15}</td>
<td>313.0</td>
<td>1.96</td>
<td>1.91</td>
<td>6.07</td>
<td>5.10\times10^9</td>
</tr>
<tr>
<td>TSD3</td>
<td>0.0006</td>
<td>0.6989</td>
<td>1.40\times10^{15}</td>
<td>315.5</td>
<td>4.18</td>
<td>2.16</td>
<td>5.74</td>
<td>2.39\times10^8</td>
</tr>
<tr>
<td>TSD4</td>
<td>0.0008</td>
<td>0.7098</td>
<td>1.34\times10^{15}</td>
<td>310.5</td>
<td>1.8</td>
<td>1.52</td>
<td>6.02</td>
<td>5.37\times10^8</td>
</tr>
<tr>
<td>TSD5</td>
<td>0.0012</td>
<td>0.7850</td>
<td>9.06\times10^{14}</td>
<td>318.0</td>
<td>2.23</td>
<td>3.34</td>
<td>5.99</td>
<td>4.48\times10^8</td>
</tr>
<tr>
<td>TSD6</td>
<td>0.002</td>
<td>0.6895</td>
<td>8.04\times10^{14}</td>
<td>311.5</td>
<td>4.68</td>
<td>1.72</td>
<td>6.30</td>
<td>2.13\times10^8</td>
</tr>
<tr>
<td>TSD7</td>
<td>0.003</td>
<td>0.7596</td>
<td>1.66\times10^{14}</td>
<td>315.5</td>
<td>4.28</td>
<td>2.41</td>
<td>5.69</td>
<td>2.33\times10^8</td>
</tr>
<tr>
<td>TSD8</td>
<td>0.004</td>
<td>0.7086</td>
<td>2.77\times10^{14}</td>
<td>315.5</td>
<td>1.67</td>
<td>2.47</td>
<td>6.24</td>
<td>5.99\times10^8</td>
</tr>
<tr>
<td>TSD9</td>
<td>0.008</td>
<td>0.7688</td>
<td>0.94\times10^{14}</td>
<td>315.5</td>
<td>3.19</td>
<td>2.66</td>
<td>6.17</td>
<td>3.13\times10^8</td>
</tr>
<tr>
<td>TSD10</td>
<td>0.012</td>
<td>0.6762</td>
<td>1.61\times10^{15}</td>
<td>318.0</td>
<td>1.26</td>
<td>2.60</td>
<td>5.99</td>
<td>7.93\times10^8</td>
</tr>
</tbody>
</table>

was repeated for all the samples. No. sample gives two peaks. There was no hope of further rise of the currents. Hence the temperature was not increased further.

4 Results and Discussion

Typical plots of (TSC) are shown in Fig. 1. The following are the main conclusions drawn on the basis of qualitative analysis of (TSC) curves.

1. The TSC at room temperature (300 K) is found to decrease with increase in activator concentration in the beginning and further increases with increase in concentration. It is minimum for the sample No. TSD\(_6\) having activator concentration of 0.002 mg per 10 gm of calcium sulphate.

2. Initially the TSC peaks are found to decrease with increase in activator concentration and then increase with increase in concentrations. Peak temperature were found in the range from 311.0 to 318.0

3. The calculated value of density of initially filled traps also shows similar variations. It is least for sample No. TSD\(_6\).

4. Attempt to escape frequency factor was found different for different samples. This is the reciprocal of lifetime \((\tau_0)\) of an electron at a particular trap at a high temperature. The substances are supposed to be in the atomic state at this temperature. This life time comes out to be in the range \(10^{-9}-10^{-10}\) sec or attempt to escape frequency factor in the range \(10^8-10^9\). This factor was taken constant by the workers following the methods of Gross-Weiner, Garlic-Gibson and Randall and Willkins. The trap depth is found to be in the range 0.69-0.78 eV. This
factor was assumed as constant by many research workers in TSL measurements. This is the most important conclusion of this work and superiority of Bucci-Fischi and Cowell-Woods curve fitting technique over others, such as Gross-Weiner, Garlick Gibson, and Randall and Wilkins technique. Attempts to escape frequency factor varies from $10^8$ to $10^9/s$ while Randall and Wilkins had assumed it to be $10^7/s$.  

5. Evaluated values of trap depths, attempt to escape frequencies, $\tau_0$, $\tau_m$ and $\tau_{500}$ are shown in Table 1 and Table 2. The decrease in initial value of TSC can be understood by using Wapenaar and Schoonman\textsuperscript{15} model. According to this model activator site is capable of capturing hole and electron both, radiatively or non-radiatively. The hole may be converted to $\text{Pr}^{4+}$. This trapping may release energy radiatively showing luminescence. This reduces the hole conductivity thus decreasing net conductivity. The energy level of the trapped carrier is 0.7 eV above the valence band. Thermal excitation of electrons from valence band to this site will further create a hole in valence band, which gives rise to TSC by increase in temperature. This converts $\text{Pr}^{4+}$ further into $\text{Pr}^{3+}$.

References