Decay behaviour of CaS phosphors activated by Ce$^{3+}$, Na$^+$ and Cu$^+$

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The nature of phosphorescence decay of calcium sulphide phosphors activated by Ce$^{3+}$, Na$^+$ and Cu$^+$ has been studied. The variation in the value of trap depth has been studied by UV excitation in phosphorescence decay. These results indicated that, the groups of traps studied have been associated directly with the activator (Ce$^{3+}$, Na$^+$ and Cu$^+$) in CaS by UV excitation. By peeling off procedure, as suggested by Bube [Phys Rev, 80 (1950) 655], three different trap depths have been obtained.

[Keywords: Phosphorescence decay, UV excitation, Trap depth]

1 Introduction

Alkaline earth sulphide phosphors have aroused much interest after the discovery of infrared stimulation and sensitized luminescence$^{1,2}$. Phosphorescence decay provides the most direct means of studying electron traps in luminescent materials. Decay studies, when combined with other experimental data, such as those obtained from glow curves of photoconductivity measurements, give useful insight into the type of kinetics involved in the luminescence process. Several research workers$^{3,4}$ have reported studies on CaS, SrS, and BaS phosphors doped with one or more impurity elements. The trivalent cerium ion is widely used as activator in a large variety of luminescent inorganic materials$^{5}$. Recently, more and more work is devoted to trivalent rare-earth, doped with different hosts, due to their potential device applications as opto-electronic compounds$^{6}$. The knowledge of defect, structures and its connection with distribution of energy levels in the band gap of solids is an important pre-requisite for thorough understanding of luminescence phenomenon. This note describes the results of the decay studies carried out on CaS, CaS:Ce$^{3+}$, CaS:Ce$^{3+}$ (Na$^+$) and CaS:Ce$^{3+}$ (Na$^+$) Cu$^+$ phosphor to study their decay characterization, energy transfer and the effect of charge compensation.

Experimental details — Preparation of phosphors - CaS phosphors have been prepared from CaSO$_4$ by reduction process. The reducing agent was AR grade carbon powder in proper proportion. The charge was fired in a central zone of Muffle furnace at 1000 °C for two hours. Then, it was pulverized in a dry atmosphere and stored, keeping in view the extreme purity as the main consideration in the preparation. The varying amount of cerium was added to the above mixture and the charge was fired, the prepared phosphor is denoted as CaS:Ce$^3$. By using sodium thioulsulphate, in proper proportion, as a flux and the charge was fired. The prepared phosphor is denoted as CaS:Ce$^3$(Na$^+$). The concentration of Ce and Cu was changed to optimize the lumen output and charge was fired and is denoted as, CaS:Ce$^3$(Na$^+$)Cu$^+$ phosphor. The details of phosphor preparation are almost the same as reported elsewhere$^{3,5,7,10}$.

Decay measurement — Decay has been observed at room temperature by using UV light source and detector unit. The detector unit consists of high voltage power supply, photo-multiplier tube (PMT), amplifier and X-Y recorder. Each sample was excited with ultraviolet radiation from an ac-operated UV lamp using 300 nm filter. To maintain excitation energy constant, a stabilizer was also used in conjunction with the lamp. The light emitted from phosphor was allowed to fall on the photo-multiplier...
Table 1 — Correlation coefficient and trap depths of phosphors

<table>
<thead>
<tr>
<th>Phosphors</th>
<th>Relative intensity</th>
<th>Total time of decay</th>
<th>Decay constant</th>
<th>Correlation coefficient (r)</th>
<th>Trap depths in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in arbitrary unit</td>
<td>(sec)</td>
<td></td>
<td></td>
<td>E1 (Slow)</td>
</tr>
<tr>
<td>CaS pure</td>
<td>34</td>
<td>330</td>
<td>0.84</td>
<td>0.99</td>
<td>0.73</td>
</tr>
<tr>
<td>CaS: Ce³⁺</td>
<td>80</td>
<td>780</td>
<td>0.91</td>
<td></td>
<td>0.76</td>
</tr>
<tr>
<td>CaS: Ce³⁺(Na⁺)</td>
<td>61</td>
<td>630</td>
<td>0.85</td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td>CaS: Ce³⁺(Na⁺)Cu⁺</td>
<td>66</td>
<td>645</td>
<td>0.91</td>
<td></td>
<td>0.70</td>
</tr>
</tbody>
</table>

Results and discussion — According to Randall & Wilkins\(^1\), the probability \(P\) of an electron escaping from the trap is given by:

\[
P = S \exp \left( \frac{-E}{KT} \right)
\]  

where \(S\) is the attempt to escape frequency, \(E\) the trap depth and \(T\) is the absolute temperature. Eq. (1) assumes that, the electrons free from the traps are not re-trapped, \(S\) and \(E\) are independent of temperature and non-radiative transitions are negligible for free electrons. For single trap level, the phosphorescence intensity decays as:

\[
I = I_o \exp (-pt)
\]  

where \(I_o = n_o p\)

\(n_o\) is the number of electrons in the trap of depth \(E\) at \(t=0\). If there is a distribution of trapping levels, the observed intensity will be due to the super-position of all the exponentials, then the form of the curve becomes:

\[
I = I_o \cdot 1^b
\]  

where \(b\) is the decay constant. The nature of the decay curves was investigated by plotting the logarithm of intensity, as a function of time. Non-linear curves were obtained for CaS. The relation between \(\log I\) and \(\log t\), however, was approximately linear (Fig. 1). The degree of linearity was estimated by calculating the correlation coefficient \(r\), the values of which are close to unity. These values are given in Table 1. A power law as suggested by Randall & Wilkins\(^1\) can represent such type of phosphorescence decay characteristics. They considered hyperbolic decay\(^3\) as the result of super-position of exponential corresponding to different traps. By peeling off procedure, as suggested by Bube\(^2\), it is to break-up the log \(I-t\) decay curve into three different components as shown in Fig. 2. Corresponding to these components, three different trap depths are obtained by using Eq. (1) and assuming \(S=10^7/s\) (here \(10^7/s\) for alkaline earth sulphide phosphors\(^5\)), at room temperature. The values of \(E\) and temperature, thus calculated, are presented in Table 1. The values of \(E\) later on termed as slow, middle and fast (Table 1).
The curve of CaS between log I and t is non-linear for CaS phosphor, while more non-linear for CaS:Ce⁺⁺, CaS:Ce⁺⁺(Na⁺) and CaS:Ce⁺⁺(Na⁺)Cu⁺.

The aggregation of monovalent charge Na⁺-Cu⁺ and absence of energy transfer from one activator to another. After energy transfer from Cu⁺ or monovalent pair Na⁺-Cu⁺ to Ce⁺⁺ is not possible due to Ce⁺⁺ ions, which are formed during UV-ray irradiation. Curie observed that, the trap group corresponding to about 0.68 eV is independent of activator concentration. These facts along with the results obtained in the present study are associated directly to the activation of UV irradiation. Therefore, it is apparent that, this particular group of traps is characteristic of the crystalline imperfections in the host lattice itself.

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References