

Persistent luminescence mechanism of the $\text{CdSiO}_3\text{:Tb}^{3+}$ phosphors

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Abstract

The persistent luminescence mechanism of $\text{CdSiO}_3\text{:Tb}^{3+}$ materials was developed based on the band structure of the host, the $\text{R}^{2+/3+}$ energy level position therein, mainly determined by synchrotron radiation spectroscopy and trap depths, determined by thermoluminescence.

1. Introduction

The persistent luminescence materials have received special attention lately due to their significant applications in emergency signalization, micro defect sensing, optoelectronics for image storage, detectors of high energy radiation and thermal sensors. Despite the recent advances in the performance of these materials, the phenomenon mechanisms are still unclear, yet requiring multidisciplinary studies involving solid state sciences, materials engineering as well as new advanced spectroscopic methods. The most studied persistent luminescence phosphors contain Eu^{2+} as the emitting center [1,2]. In some systems, persistent luminescence is observed to originate from trivalent rare earths (R^{3+}), instead. Though the mechanism of Eu^{2+} persistent luminescence is more or less well established not much is known about the mechanism involving the other dopants, e.g. Tb^{3+} . This work describes the clarification of the unique persistent luminescence mechanism for Tb^{3+} in CdSiO_3 .

2. Experimental details

The materials were prepared with a solid state reaction at 950 °C with the R^{3+} (Eu^{3+} , Tb^{3+}) concentration of 1 mole-% of the cadmium amount. The electronic and defect energy level structures were studied with thermoluminescence (TL) and different synchrotron radiation (SR) spectroscopies: VUV-UV excitation and emission, XANES and EXAFS (HASYLAB, Hamburg, Germany). The photoluminescence measurements were also carried out in order to assist the development of the mechanism.

3. Results and discussion

3.1. Trap Depths

The thermoluminescence glow curve for the $\text{CdSiO}_3\text{:Tb}^{3+}$ phosphor shows two broad bands centered at ca. 70 and 200 °C. The curves were deconvoluted using the program TLanal v1.0.3 [3] and yielded three traps with energies from 0.6 to 0.75 eV supposed to be immediately below the bottom of the Conduction Band (CB) of CdSiO_3 .

3.2. Synchrotron Radiation Studies of $\text{CdSiO}_3\text{:R}^{3+}$

The X-Ray Absorption Spectroscopy measurements (XANES) indicated only the presence of Tb^{3+} . Besides, the Tb–O distances calculated based on EXAFS could be correlated with the calculated Cd–O distances. The VUV-UV excitation spectra for the Tb^{3+} doped material exhibited a sharp edge at ca. 235 nm (5.3 eV), corresponding to the excitation from the top of the Valence Band (VB) to the bottom of CB, e.g. the band gap energy E_g . For the Eu^{3+} doped

phosphor, a band at 250 nm was assigned to the $O^{2-}(2p) \rightarrow Eu^{3+}$ charge transfer (CT). Based on the energy of this CT band, the width of the VB as well as the position of the Eu^{2+} ion ground state in the $CdSiO_3$ band gap were estimated. With this information, and based on a previous empirical model, the position of the Eu^{3+} and, consequently, the $Tb^{3+} {}^7F_{0/6}$ ground states were approximated, too. The excited levels of Tb^{3+} are practically independent of the host and can be calculated readily to high accuracy based on the phenomenological simulations.

3.3. Persistent Luminescence and UV excited Spectroscopy of $CdSiO_3:Tb^{3+}$

The persistent luminescence spectra of $CdSiO_3:Tb^{3+}$, 120 seconds after ceasing the irradiation, shows the same profiles independent of the excitation (Fig. 1). The UV excited spectra have different spectral profiles under similar conditions suggesting that the emission with 306 nm excitation originates from an impurity ($Cd_2SiO_4:Tb^{3+}$?) with no persistent luminescence. Ar^+ laser excitation at 457 and 488 nm gave only the ${}^5D_4 \rightarrow {}^7F_J$ emission, but no persistent luminescence is observed, indicating that the 5D_4 level is below CB of $CdSiO_3$.

3.4. The mechanism of Tb^{3+} Persistent Luminescence in $CdSiO_3$

Based on the results obtained, a unique mechanism for the Tb^{3+} persistent luminescence (in $CdSiO_3$) was developed (Fig. 2). The irradiation promotes the electrons to the $4f^7 5d^1$ excited levels of Tb^{3+} well within the CB of $CdSiO_3$. These electrons are captured to CB and then trapped to a defect that can be an oxygen vacancy. The reverse process of freeing the electrons from the traps to the Tb^{3+} excited levels ($4f^8$ and $4f^7 5d^1$) via CB of $CdSiO_3$ precedes the radiative relaxation back to the $4f^8$ (7F_J) ground states of Tb^{3+} and the creation of the persistent luminescence.

4. Conclusions

The determination of the band gap energy, the $R^{2+/3+}$ energy level positions and the trap depths allowed the development of a credible persistent luminescence mechanism for Tb^{3+} in $CdSiO_3$ consistent with experimental observations. Further studies should be carried out to explain the persistent 5D_3 emission as well as the nature of the defects. A better refinement of the mechanism could also be achieved by simultaneous theoretical studies.

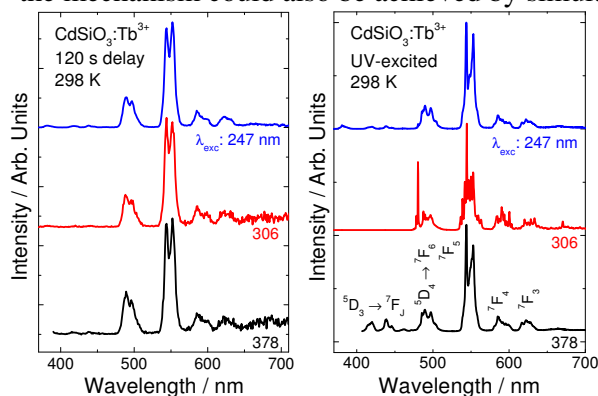


Figure 1. Persistent luminescence (left) and UV-excited (right) spectra of $CdSiO_3:Tb^{3+}$ under different excitations.

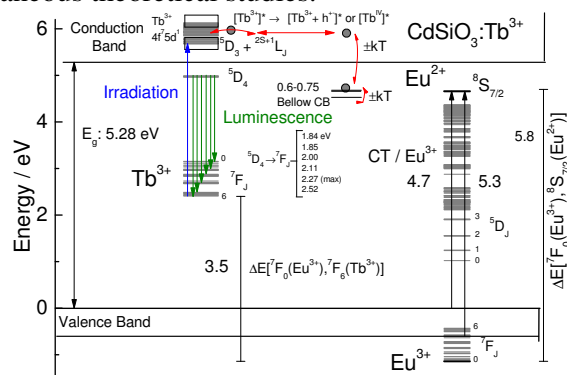


Figure 2. Persistent luminescence mechanism of the $CdSiO_3:Tb^{3+}$ phosphor.

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