

Persistent Luminescence of Pr³⁺ in CdSiO₃

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INTRODUCTION

Persistent luminescence materials have lately received special attention due to their versatile applications in emergency signalization, micro defect sensing, and optoelectronics for image storage; as detectors of high energy radiation and pressure/temperature sensors. Despite the recent advance made in boosting the performance and discovery of mechanisms, the development of red emitting nanocrystalline materials still poses a challenge also to the more fundamental studies and interpretation [1]. Red persistent luminescence from Pr³⁺ has previously been related to a "intervalence charge transfer" model [2]. In this work, a new red emitting material, CdSiO₃:Pr³⁺, is studied and an alternative mechanism is proposed for the Pr³⁺ persistent luminescence.

RESULTS AND DISCUSSION

The CdSiO₃:Pr³⁺ materials were prepared in air with a solid state reaction at 950 °C with the Pr³⁺ concentration of 0.1, 1 and 10 mole-% of the Cd amount. The X-ray powder diffraction confirmed the presence of the metasilicate phase without orthosilicate impurities.

The Pr³⁺ ion in CdSiO₃ can be excited into two overlapping bands: below 250 and at 305 nm (Fig. 1, left). The bands are assigned to the host absorption and the 4f²→4f¹5d¹ transitions of Pr³⁺, respectively. The low intensity of the latter, compared to the 4f²→4f² transitions above 425 nm, indicates that the 4f¹5d¹ levels are in the host's conduction band (CB). Persistent luminescence is not observed upon excitation at the ³H₄→³P₀ transition because the ³P₀ level is below the bottom of CB.

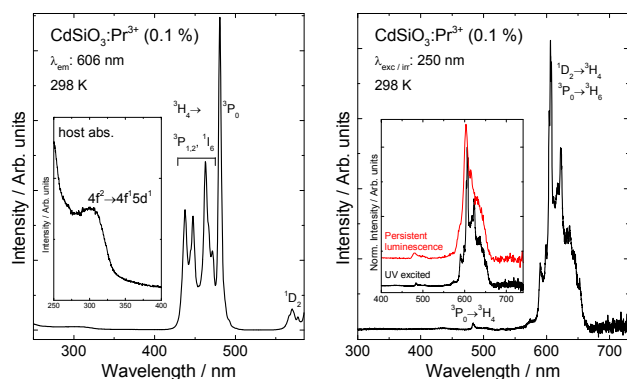


Fig. 1. Excitation (left) and emission (right) spectra of CdSiO₃:Pr³⁺.

The emission from CdSiO₃:Pr³⁺ consists of the Pr³⁺ transitions at 483 (³P₀→³H₄) and from 585 to 660 nm (both ³P₀→³H₆ and ¹D₂→³H₄) (Fig. 1, right). The weakness of the blue-green emission is due to cross-relaxation coupling the ³P₀→¹D₂ relaxation with the ³H₄→³H₆ excitation. This process is strong even at low (0.1 %) Pr³⁺ concentration due to the presence of Pr³⁺ - Pr³⁺ pairs in the CdSiO₃ host [3]. The persistent luminescence spectrum is similar to the UV excited one.

The thermoluminescence (TL) glow curve (Fig. 2) for CdSiO₃:Pr³⁺ shows three broad bands centered at ca. 90, 160 and 365 °C. With the aid of the program TLanal v1.0.3 [4], the TL curve was deconvoluted which yielded four traps with energies from 0.67 to 1.1 eV supposed to be immediately below the bottom of CB of CdSiO₃.

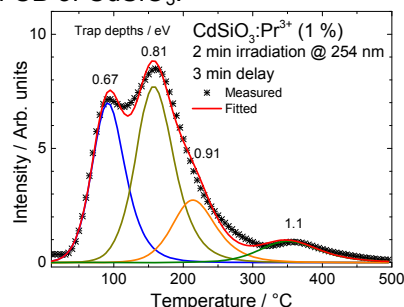


Fig. 2. Deconvolution of the TL glow curve of CdSiO₃:Pr³⁺.

CONCLUSIONS

The CdSiO₃:Pr³⁺ shows a nearly pure red emission due to the quenching of the blue-green emission (cross-relaxation). A close to ideal trap structure was identified, yielding both strong RT persistent luminescence and good energy storage. Finally, a new mechanism is proposed challenging the "intervalence charge transfer" model.

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