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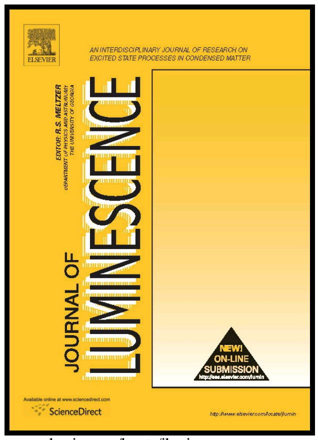

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The d-f luminescence of Eu^{2+}, Ce^{3+} and Yb^{2+} ions in $Cs_2MP_2O_7$ (M = Ca^{2+}, Sr^{2+})

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Abstract

The efficient narrow band emission of Eu^{2+} in $Cs_2MP_2O_7$ (M = Ca^{2+}, Sr^{2+}) is characterized by a large Stokes shift and a high quenching temperature which makes the material promising for application in warm white LEDs. The unusual Eu^{2+} luminescence properties were reported recently but an explanation for the peculiar behavior is lacking. In this paper we aim at providing new insights in the luminescence of the Eu^{2+} emission in $Cs_2MP_2O_7$ through measurements at cryogenic temperatures (down to 4 K) and by comparison with the d-f luminescence of Ce^{3+} and Yb^{2+} in the same host. The results reveal a sharp onset of the Eu^{2+} emission and excitation bands at 4 K. Usually the sharp onset for narrow excitation and emission bands coincide at an energy corresponding to the zero-phonon (purely electronic) transition, but for Eu^{2+} in $Cs_2MP_2O_7$ there is a large shift of 3500 cm^{-1} between the onsets, consistent with the large Stokes shift observed. The onset shift can be explained by emission from a lower energy distorted excited $4f^65d^1$ state. For Ce^{3+}, the f-d absorption bands are at energies expected based on the relation between the absorption energies for Eu^{2+} and Ce^{3+} reported by Dorenbos. Contrary to Eu^{2+}, the emission for Ce^{3+} shows a normal Stokes shift and therefore the emission bands are at much higher energies than predicted from the energy of the Eu^{2+} emission and the Dorenbos relations. Based on the present results the unusually large Stokes shift for the Eu^{2+} emission in $Cs_2MP_2O_7$ is assigned to a Jahn-Teller like deformation in the excited $4f^65d^1$ state of Eu^{2+} that is not present in the 5d state of Ce^{3+}.

Keywords: $Cs_2MP_2O_7$ (M = Ca^{2+}, Sr^{2+}), Lanthanide d-f luminescence, Stokes shift, Jahn-Teller deformation

1. Introduction

The optical properties of the Eu^{2+} ion ($4f^7$) have been thoroughly investigated [1–5] and the efficient luminescence of Eu^{2+} is widely applied, e.g. in fluorescent tubes, white light LEDs (wLEDs), displays, scintillators and anti-counterfeiting labels [6–10]. The emission and absorption spectra of Eu^{2+} are characterized by broad absorption and emission bands corresponding to transitions between the $4f^7$ ground state and the $4f^65d^1$ excited states. The energy level structure in the $4f^65d^1$ excited state is strongly influenced by covalency and crystal field splitting [8]. As a result, the d-f emission of Eu^{2+} can vary from the ultraviolet to the red spectral region, depending on the host lattice.

In phosphates Eu^{2+} ions typically show a violet or blue emission and emission wavelengths between 375 nm (for $Ba(PO_3)_2$:Eu^{2+}) and 505 nm (for $NaCaPO_4$:Eu^{2+}) have been reported [1]. However, recently an unusual red Eu^{2+} emission was reported for a Eu^{2+}-doped phosphate. In $Cs_2CaP_2O_7$ the d-f emission of Eu^{2+} is around 600 nm, while the absorption is in the usual blue-ultraviolet spectral region [11]. As a result, the Stokes shift of the emission is very large ($\Delta S > 6000$ cm^{-1}). The emission is further characterized by a high quantum yield and a high quenching temperature ($T_{0.5} \sim 600$ K), which is unexpected in combination with a large Stokes shift [8]. The special optical properties make $Cs_2CaP_2O_7$:Eu^{2+} promising as a red emitting phosphor in warm white LEDs, where a narrow band red emission is required to reduce efficiency loss that is inherent to the use of broad band red emitters. Broad band red emitters that are used to shift the color temperature of wLEDs into the desired warm white spectral region have a significant part of their emission between 630 and 700 nm where the eye sensitivity is low. This reduces the lumen/W efficiency [9].

The large Stokes shift and narrow band emission reported for Eu^{2+} in $Cs_2MP_2O_7$ (M = Ca^{2+}, Sr^{2+}) were discussed by Srivastava et al. [11]. Based on the narrow band emission ($\Gamma^{em} \sim 2000$ cm^{-1} at 80 K), normal emission lifetime ($\tau \sim 1$ μs) and high quenching temperature ($T_{0.5} \sim 600$ K) it was concluded that the large Stokes shift cannot be explained by anomalous emission from an Eu-trapped exciton state. In the past large Stokes shifts for Eu^{2+} emission have been explained by a trapped exciton emission, but in addition to a large Stokes shift, this emission is characterized by a large spectral width, longer lifetime and low quenching temperature [2]. Clearly, these characteristics are not observed for the Eu^{2+} emission in $Cs_2MP_2O_7$. An alternative explanation that was suggested in Refs. [11] and [12] involves distortions in the

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