Luminescence of Divalent Ytterbium in Ca_2SiS_4.

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Abstract

The luminescence of ytterbium doped calcium thiosilicate is studied. Excitation and emission spectra are presented and related to an energy level scheme. A comparison with divalent europium in the same host is carried out.

1. Introduction

Calcium thiosilicate is one of the most interesting host for divalent europium within the class of sulfides [1]. It provides two different Ca^{2+}-sites for which the Eu^{2+} can substitute. The Eu^{2+} emission spectrum contains two maxima, one peaking at 560nm and one at 660nm, and each peak can be related to a crystallographic site [2]. From the well documented trends in the behaviour of different rare earth ions doped in the same host material, interesting luminescent properties are expected to occur for Yb^{2+} doped Ca_2SiS_4 [3].

2. Experimental details

Ca_2SiS_4 was prepared by solid state reaction and doped with Yb (concentrations at%: 0.1% and 1%), as well as with Eu, Sm and Tm for comparison, as these are the divalent ions for which 5d-4f luminescence is most likely to be observed. XRD was used for checking phase composition. Photoluminescence excitation and emission spectra and thermal quenching profiles were obtained using a helium cryostat in a steady state photoluminescence spectrometer (Edinburgh Instruments FS 920).

3. Results and discussion

For Sm and Tm, the emission spectrum is dominated by 4f-4f emission from the trivalent state of these ions.

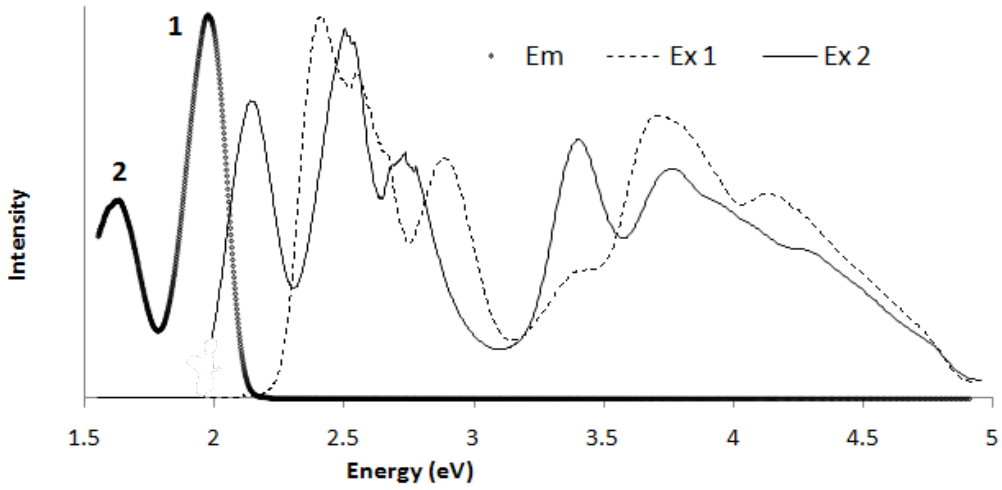

Figure 1: Excitation (Ex1 monitored at peak1, Ex2 at peak 2) and emission spectrum (at 70K) of $Ca_2SiS_4:Yb^{2+}$

Ytterbium in Ca_2SiS_4 does exhibit 5d-4f luminescence, but this emission is seriously quenched at room temperature. Therefore, all spectra presented in this work are recorded at low temperature.

3.1. Emission and excitation spectra

The emission spectrum of $Ca_2SiS_4:Yb^{2+}$ consists of two peaks, as is the case for Eu^{2+} in the same host. In **Figure 1**, the emission peak with the shortest wavelength (1.97eV; 630nm) is labeled "1". The one with the longer wavelength (1.62eV; 765nm) is labeled "2". The emission peaks for Eu^{2+} in the same host are found at 2.21eV (560nm) and 1.88eV (660nm). In contrast with the case of $Ca_2SiS_4:Eu^{2+}$, the excitation spectrum of $Ca_2SiS_4:Yb^{2+}$ reveals clear and resolved substructure. From these data, an energy level scheme for Yb^{2+} in this material is proposed.

3.2. Temperature dependent behaviour

The thermal quenching temperature (**Figure 2**) of Yb^{2+} in calcium thiosilicate is around 230K, considerably lower than 470K for Eu^{2+} in the same host. This is attributed to the lower activation energy for Yb^{2+} to excite the 5d electron to conduction band states. [4,5].

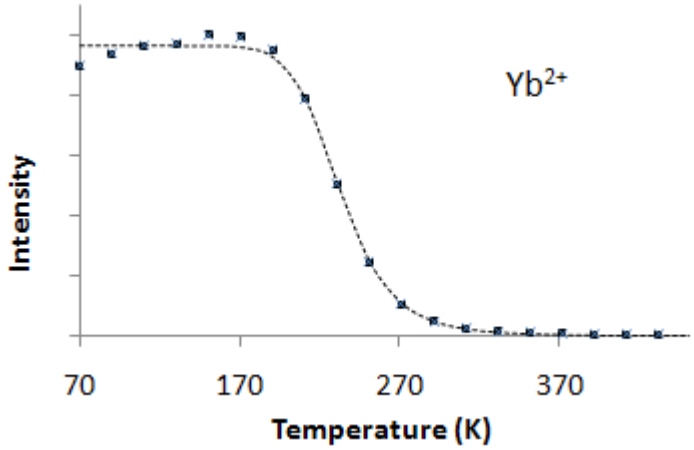

Figure 2. Thermal quenching behaviour of Yb2+ in Ca2SiS4.

Both emisson peaks have a distinctly different quenching behaviour, which is analysed in detail and compared with the quenching of Eu^{2+}-luminescence in the same material.

3.3. Decay time measurements

Decay time measurements are performed. The decay profile at 70K can be approximated by a double exponential, in which the shortest wavelength peak (1 in Figure 1, 1.97eV; 630nm) has the longest lifetime and the longest wavelength peak (2 in Figure 1, 1.62eV; 765nm) has the shortest lifetime.

References

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