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# Temperature effects of $Ce^{3+}$ emissions from $Gd_2SiO_5:Ce$ and their high excitation states<sup>☆</sup>

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## Abstract

In the range 15–453 K temperature dependence of  $Ce^{3+}$  emissions at 450 nm under UV–VUV excitations is presented. Possible origins of two new emission bands at 582 and 651 nm have been discussed. The strong excitation states in 3–30 eV are also analyzed. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:**  $Ce^{3+}$  emission;  $Gd_2SiO_5:Ce$ ; Temperature effect; Electronic states

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## 1. Introduction

Ce-doped  $Gd_2SiO_5$  (GSO:Ce) crystal is a promising scintillator with a high absorption coefficient, high luminescence output, fast decay time (20–60 ns) and excellent hardness ( $10^9$  rad) [1]. Its applications on  $\gamma$ -detector of positron emission computed tomography and position sensitive detectors have been studied [2]. On the other hand, GSO:Ce is also a good physical system for studying energy transfer from  $Gd^{3+}$  to  $Ce^{3+}$  [3]. This indicates an effective

sensitization of  $Ce^{3+}$  luminescence by  $Gd^{3+}$  ions. Further researches are aimed at luminescence properties under different conditions and their mechanism. Luminescence mechanism is being studied [4]. A single exponential decay of the  $Ce^{3+}$  luminescence was obtained when the excitation energy ( $Ex$ ) is less than 6.1 eV ( $Ex < Eg$ ). However, the excitation with energy greater than 6.1 eV ( $Ex > Eg$ ) gets results in nonexponential decay [5–7]. In this paper, the temperature dependence of GSO:Ce luminescence at UV(3.5 eV)–VUV(6.5 eV) excitation is presented.

## 2. Experimental

The used samples were crystal fibers with a diameter of 500  $\mu$ . The crystal fibers of GSO:Ce

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(0.25%) were grown by the Laser Heated Pedestal (LHP) method [8] in air and are transparent. The growth is seedless, the orientation of the crystal is therefore random. The emission spectra of GSO:Ce in 15–300 K were recorded by a FF500 Monochromator at excitation with the third harmonic (355 nm) of a YAG:Nd laser. The excitation spectra of GSO:Ce luminescence at 450 nm in 3–30 eV and temperature dependence of emission spectra above RT at excitation with VUV (189 nm) were performed at the SUPERLUMI Station in HASYLAB of DESY, Germany. The resolution of excitation monochromator is upto 0.007 nm. A position sensitive detector (MCP) was used to measure emission spectra.

### 3. Experimental results and analysis

Emission spectra of  $\text{Ce}^{3+}$  in GSO:Ce at UV (355 nm) excitation are shown in Fig. 1. At 15 K the emission spectra can be decomposed into two bands peaked at 416 and 454 nm from  $5d \rightarrow 4f$  ( $^2F_{5/2}$ ) and  $5d \rightarrow 4f$  ( $^2F_{7/2}$ ) transitions of  $\text{Ce}^{3+}$ , respectively. (The  $^2F_{5/2}$  and  $^2F_{7/2}$  levels are ground states split by ‘spin-orbit’ coupling and separated by  $2000 \text{ cm}^{-1}$ .) At room temperature they combine in one broad band peaked at 435 nm with FWHM of 91 nm. Temperature dependence of the integrated intensity of the emission spectra (as shown in Fig. 1) indicates that there is no thermal quenching, i.e. the integrated intensity does not decrease, as temperature varies

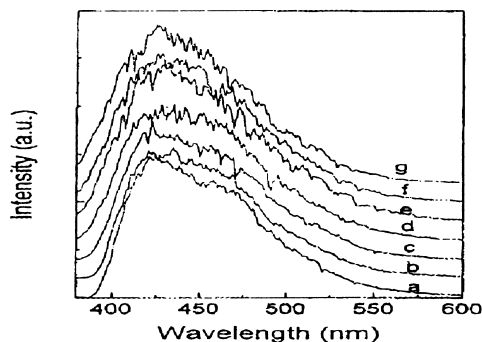


Fig. 1. Temperature dependence of  $\text{Ce}^{3+}$  emission from GSO:Ce at 355 nm excitation (a) 15, (b) 50, (c) 100, (d) 150, (e) 200, (f) 250 and (g) 300 K.

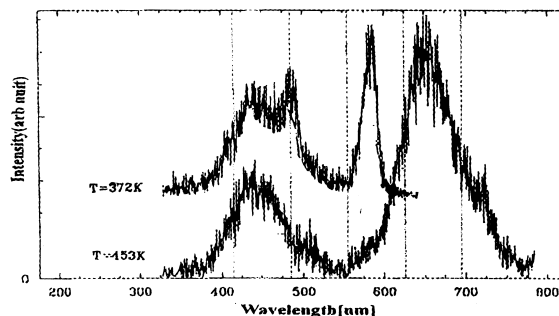


Fig. 2. Emission spectra of  $\text{Ce}^{3+}$  in the GSO:Ce under excitation with 189 nm above RT (a) 372 and (b) 453 K.

from 15 to 300 K, instead the integrated intensity slightly increases. This is probably due to the thermal shift of the absorption band. Red shift of  $4f \rightarrow 5d$  absorption band makes the absorption at 355 nm somewhat increase with rising temperature.

As shown in Fig. 2, under VUV (189 nm)-excitation temperature dependence of the emission spectra from  $\text{Ce}^{3+}$  in GSO:Ce above room temperature is very interesting. Besides a broad band peaking at 440 nm, two new strong bands peaking at 484 and 582 nm with FWHM 22 nm appeared at 372 K, which were absent in Fig. 1. When the temperature increases to 453 K the two new bands almost disappeared. Meanwhile, another wide band peaked at 651 nm with FWHM 80 nm occurred. This novel result was not reported before.

In the excitation spectra of  $\text{Ce}^{3+}$  emission (450 nm) from GSO:Ce at 6 K (Fig. 3) there are three

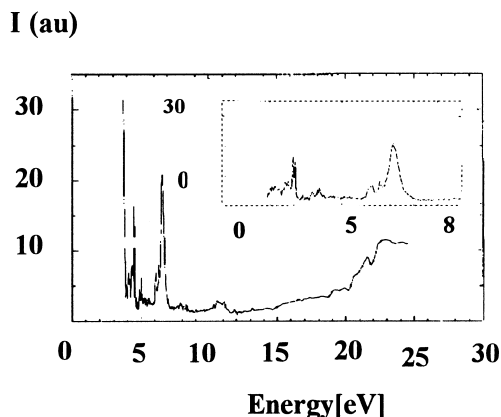


Fig. 3. Excitation spectra of  $\text{Ce}^{3+}$  emission at 450 nm from the GSO:Ce at 6 K.

kinds of strong excitation states centered at 4.5, 6.5 and 22.5 eV. The former is a very narrow band with double peaks at 4.48 and 4.52 eV corresponding to  $^8S_{7/2} \rightarrow ^6I$  transitions intra 4f configuration of  $Gd^{3+}$ . The later is a very broad band with a peak at 22.5 eV corresponding to excitation of  $Gd^{3+}$  5p 5d core electrons.

The excitation band at 6.5 eV has two satellite peaks at 6.13 and 6.27 eV, which are assigned to the edge absorption of energy gap because the  $E_g$  of GSO is 6.1 eV or the transition of 4f $\rightarrow$ 6s of  $Ce^{3+}$ . The excitation in the range of 4.93–6.0 eV was assigned to the photoionization of  $Ce^{3+}$  in GSO:Ce [3]. The main peak at 6.5 eV is ascribed to the transition between valence band and conduction band.

#### 4. Discussion

What is the origination of two new emission bands at 582 and 651 nm?

There are two possible considerations. In the first, the 582 nm band is assumed to be from the emission of the second kind of  $Ce^{3+}$  centers, and the 651 nm band may ascribe to related Charge Transfer State (CTS). In GSO:Ce there are two nonequivalent  $Gd^{3+}$  sites with nine and seven coordinates, respectively, which can be responsible for the two types of  $Ce^{3+}$  centers as  $Ce^{3+}$  replaces  $Gd^{3+}$  in the lattice. Besides the emissions from  $Ce^{3+}$  centers (called  $Ce^{3+}$  I) mentioned above, Suzuki et al. [3] also observed the emission at 550 nm from the second type of  $Ce^{3+}$  centers (called  $Ce^{3+}$  II) having absorption band at 300 and 378 nm. Under excitation with 355 nm we can't see the 550 nm band from  $Ce^{3+}$  II in Fig. 1. But at 189 nm (VUV) excitation one might see all emissions from  $Ce^{3+}$  I and  $Ce^{3+}$  II centers via energy transfer from host GSO to  $Ce^{3+}$ . The wavelength of  $Ce^{3+}$  II emissions assumed here is longer than that of Suzuki's report [3]. It is probably due to red shift of the emission band at higher temperature (372 K).

The CTS state related to  $Ce^{3+}$  II might be caused by the charge transit from  $O^{2-}$  in GSO to  $Ce^{3+}$  and changed into  $O^-$  and  $Ce^{2+}$ . The CTS usually has configuration coordinate deflection from that of  $Ce^{3+}$  II and locates above the excited state of  $RE^{3+}$  as

well as overlap with high vibration states of  $RE^{3+}$  excited state, so that excited electrons of  $Ce^{3+}$  II can easily come into the CTS at higher temperature and produce 651 nm new emission with a wide band. Meanwhile, the 582 nm emission of  $Ce^{3+}$  II should be decreased. This is the case in Fig. 1.

In the second, the 582 and 651 nm emissions are ascribed to some defects (or impurity). The defect centers can be excited by the photon with energy higher than 6.1 eV corresponding band gap ( $E_g$ ) of GSO via energy transfer from host to the defect centers, which can emit 582 and 651 nm bands. At least two different types of defects in the GSO and energy transfer exist from one to another. Their transfer probability corresponding from the 582 nm band to the 651 nm band was increased with rising temperature by means of the assistance of phonons.

#### 5. Conclusions

The luminescence of  $Ce^{3+}$  in GSO:Ce has no temperature quenching from 15 to 453 K under UV(355 nm)–VUV(189 nm) excitations.

New emission bands at 581 and 652 nm probably originated from either  $Ce^{3+}$  II centers and related CTS or some defect centers.

The efficient excitation at 6.5 eV narrow band and a wide band peaking at 22.5 eV are related to the transition between the 'valence-conduction' bands and mixing states of  $Gd^{3+}$  5p 5d core levels, respectively.

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