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FFFECT OF TRACE Bi 3+ ON LUMINESCENCE OF Ce 3+ IN Cas:Ce, Bi

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We have measured the excitation spectra, time resolved luminescence spectra and decay curves of the sample CaS:Ce,Bi. The effect of trace Bi on Ce luminescence and on the resonat transfer among Ce ions in CaS:Ce,Bi are discussed.

## 1. INTRODUCTION

Cerium doped calcium sulfied is a green cathodoluminophors whose energy efficiency is as high as 20%. In order to improve further the luminescent properties of this material, to choise available sensitizers is important. For this purpose, the energy transfer of inter- and internal centers in CaS:Ce,Bi is investigated in this work.

## 2. EXPERIMENTAL

The samples with various dopant concentrations were prepared by the solid sulfurizing flux method reported elsewhere 1. The excitation and emission spectra were measured by a MPF-4 Fluorescence Spectrophotometer. The 266nm fourth hammonic pulses, with a half power width of 10ns and the repetition frequency of 5Hz, of a YAG laser were used to excite the sample in luminescence decay and the time resolved spectra measurements. The signals were recorded by a Bx-530 type Boxcar Integrator.

## 3. RESULTS AND DISCUSSION

The excitation spectrum of  ${\rm Bi}^{3+}$  emission in CaS:Bi consists of mainly three bands peaked at 280nm, 310nm and 410nm respectively. The last two are characteristic excitation bands of  ${\rm Bi}^{3+}$ ion. For CaS doped with  ${\rm Ce}^{3+}$  and trace  ${\rm Bi}^{3+}$ , in the excitation spectrum of  ${\rm Ce}^{3+}$  emission (monitoring at 570nm), compared with the excitation spectrum of  ${\rm Ce}^{3+}$  emission in CaS:Ce $^{3+}$ , two

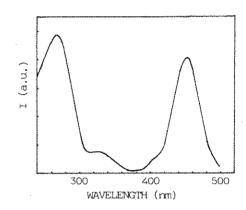


FIGURE 1 Excitation spectrum of Ce $^{3+}$  emission in CaS:Ce, Bi (Ce $^{3+}$ :  $5X10^{-4}$ , Bi $^{3+}$ :  $5X10^{-3}$ ; monitoring wavelenth: 570nm)

additional bands peaked at about 310nm and 410nm, which belong to  ${\rm Bi}^{3+}$ , are observed (Fig. 1). It is a direct experimental evidence that the excitation energy may be transferred from  ${\rm Bi}^{3+}$  to  ${\rm Ce}^{3+}$ .

The life time of  $\mathrm{Ce}^{3+}$  excited state is less than 1  $\mathrm{ps}^2$ . The luminescence decay curve of  $\mathrm{Bi}^{3+}$  in CaS:Bi is composed of two components with the time constants of about 50  $\mathrm{ps}$  and 370  $\mathrm{ps}$  respectively, when the  $\mathrm{Bi}^{3+}$  concentration being  $\mathrm{5X10}^{-4}$ . In CaS:Ce,Bi, the decay of  $\mathrm{Bi}^{3+}$  emission becomes faster, with a fast-component of 12  $\mathrm{ps}$  and a slow-component, 35  $\mathrm{ps}$ . In the sample we have found that the decay of  $\mathrm{Ce}^{3+}$  emission is

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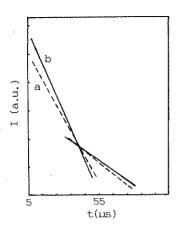


FIGURE 2
Decay curves of CaS:Ce,Bi for
(a) emission of Ce at 570nm and
(b) emission of Bi at 447nm

the same as that of  ${\rm Bi}^{3+}$ , having a fast decay constant, 15  $\mu {\rm s}$ , and a slow one, 33  $\mu {\rm s}$ , as shown in Fig. 2. As increasing the concentration of  ${\rm Bi}^{3+}$ , the decay for both  ${\rm Bi}^{3+}$  and  ${\rm Ce}^{3+}$  becomes faster. All these results imply that the excited energy absorbed by  ${\rm Bi}^{3+}$  is transferred to  ${\rm Ce}^{3+}$  and this energy transfer process is a nonradiative event.

Fig. 3 shows the time resolved emission spectra of CaS:Ce,Bi. An interesting result is obtained that the intensity of sub-bands of the  ${\rm Ce}^{3+}$  emission changes differently with the delay time. As we know, these two sub-bands are due to the recombination from the same excited state(5d) of  ${\rm Ce}^{3+}$  to its different ground states  ${}^2F_{5/2}$  and  ${}^2F_{7/2}$ , respectively. The explanation of above results is given by proposing an idea of resonat transfer taking place only between the

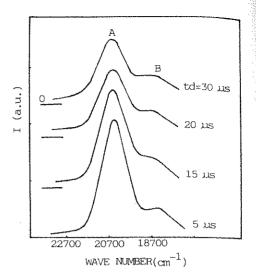


FIGURE 3 Time resolved spectra of CaS:Ce,Bi

transition  $5d^{-2}F_{5/2}$  which results in sub-band A. Both the Bi<sup>3+</sup> and Ce<sup>3+</sup> ions can be excited by the host excitation. Consequently, Bi<sup>3+</sup> should compete with Ce<sup>3+</sup> in getting the excitation energy from the host. On the other hand, we believe that the co-dopant Bi<sup>3+</sup> probably may also affect the internal energy transfer among Ce<sup>3+</sup> ions. The effect of trace Bi<sup>3+</sup> on Ce<sup>3+</sup> luminescence and on the resonat transfer among Ce<sup>3+</sup> ions is discussed.

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