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# Optical absorption studies on the trapping states of CaS:Eu,Sm

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## Abstract

The optical absorption spectra of CaS:Eu,Sm at several concentrations of Eu (from 0 to 0.05 mol%) were examined to clarify the electron trapping mechanism for its photo-stimulated luminescence. Corresponding to the electron and hole trapping states, the difference between the absorption spectra after and before excitation was observed. The substructure of the infrared band of the absorption difference is eclipsed by the 4f–4f absorption of Sm<sup>3+</sup> ions in accordance with the photo-stimulation spectrum. In comparison of Sm<sup>3+</sup> with La<sup>3+</sup> in Eu co-doped CaS, it was inferred that the Sm<sup>3+</sup> ions are responsible for the storability of the traps instead of the direct capture of electrons as the previous investigators thought. Our results demonstrate that the Sm<sup>3+</sup> ions induce defects in their neighbourhood which act as the trapping centres but the Sm<sup>3+</sup> ions do not form Sm<sup>2+</sup> ions by trapping electrons.

## 1. Introduction

Photo-stimulable phosphors are a class of luminescent materials which attract the interest of many investigators due to their actual and potential commercial applications. The x-ray storage phosphor BaFBr:Eu<sup>2+</sup> [1], for example, is currently used for x-ray imaging. Another type of this class of phosphors is the rare-earth doubly doped alkaline earth sulphides, such as CaS:Eu,Sm [2, 3], SrS:Eu,Sm [4–6], CaS:Ce,Sm [7] and MgS:Ce,Sm [8]. They were conventionally used as infrared sensors [9] and expected to be developed as an erasable and rewritable optical memory medium [10]. A precise understanding to the mechanism for electron trapping in these crystals is important to the improvement of these materials and the associative devices.

Most investigators used to study the detrapping process via the stimulation spectra [1, 2, 5–9], *viz.*, the dependence of the stimulated luminescence intensity on the wavelength of the stimulating light. Apart from the influence by exhaustion of the stored energy in stimulation, the measurements of the stimulation spectra have to be performed on the samples with high radiative efficiency of the recombination and get rid of the region around the monitored wavelength of the luminescence. In this work, we examined the role of Sm ions in electron trapping in CaS:Eu,Sm by optical absorption spectra without the influence of the radiative efficiency and the limitation of the monitored wavelength. Some valuable information about

the optical storage was obtained from the absorption spectra; thereby we shall demonstrate a new mechanism for the trapping states in CaS:Eu,Sm.

## 2. Experiments

The powder samples CaS:Eu,Sm with different concentration of Eu and Sm were obtained by firing an intimate mixture of CaCO<sub>3</sub> (99.95%), Eu<sub>2</sub>O<sub>3</sub> (99.99%), SmF<sub>3</sub> (99.99%) and La<sub>2</sub>O<sub>3</sub> (99.99%) for two hours at 1100 °C in a sulfur atmosphere. The resulting powder samples were pressed into pellets (diameter 26 × 2 mm<sup>2</sup>) and then refired at 1000 °C for 1 hour in the same atmosphere. The samples were checked by x-ray powder diffraction using an XJ10-60F radiation diffractometer.

All optical measurements were carried out at room temperature. The experiments of photoluminescence and photostimulated luminescence were performed on a Spex Fluorolog-3 spectrofluorometer, in which a 500 W xenon lamp was used as excitation source and filtered by an excitation spectrometer. The irradiation on the samples at a single wavelength within ultraviolet and visible regions was done by the excitation spectrometer, whose slit width was set as large as possible to ensure that the samples are irradiated sufficiently. Filters were used to prevent the samples from possible undesired irradiation. The infrared stimulating light was provided by a 980 nm semiconductor laser, by which the stored energy in the sample was released resulting in the stimulated luminescence. In this way all the stimuable traps were emptied of electrons. For optical storage this means that the stored information is erased, thus the trapping state of the sample is denoted as the erased state below; after sufficient excitation at 260 nm or 470 nm the samples are in the stored state. Since most samples presented afterglow lasting for several seconds to minutes after excitation, the measurements on the stored samples were started after the samples had been kept in the dark free from any irradiation until the afterglow was exhausted.

The absorption spectra were measured on a Shimadzu UV-3101PC spectrometer. The system consists of an integrating sphere designed to gather and detect the diffused reflection light of the nontransparent solid sample, a photomultiplier as visible/UV and a PbS cell as near-infrared detectors and a halogen lamp for visible/near-IR and a deuterium lamp for UV light sources. In the measurement of IR stimulation spectrum, the infrared light was provided by a Shimadzu source. The sample was irradiated on an area as large as possible to insure a certain luminescence output would be detected while the stimulated luminescence would not decrease too fast with exhaustion of the stored energy for the measurement. The stimulated emission (640 nm) was detected by the emission spectrometer of the Spex. The slit width and scanning speed were properly selected so that the signal could be detected in a good resolution and low noise without exciting or stimulating it significantly. Both the Spex and Shimadzu were controlled by the personal computers in which all the measured spectra including the stimulation spectrum were calibrated for the spectral dependence of the light sources and response functions of the optical system.

## 3. Results and discussion

### 3.1. The infrared absorption band of the trapped electrons

In Eu and Sm doubly doped SrS or CaS, the Eu<sup>2+</sup> ions act as the efficient hole trapping centres [2, 4, 9] which serve to keep the holes spatially separated from the trapped electrons to avoid the undesired direct electron–hole recombination, so that the electrons are stimulated into conduction band from the traps and recombine with the holes at the Eu sites followed by the

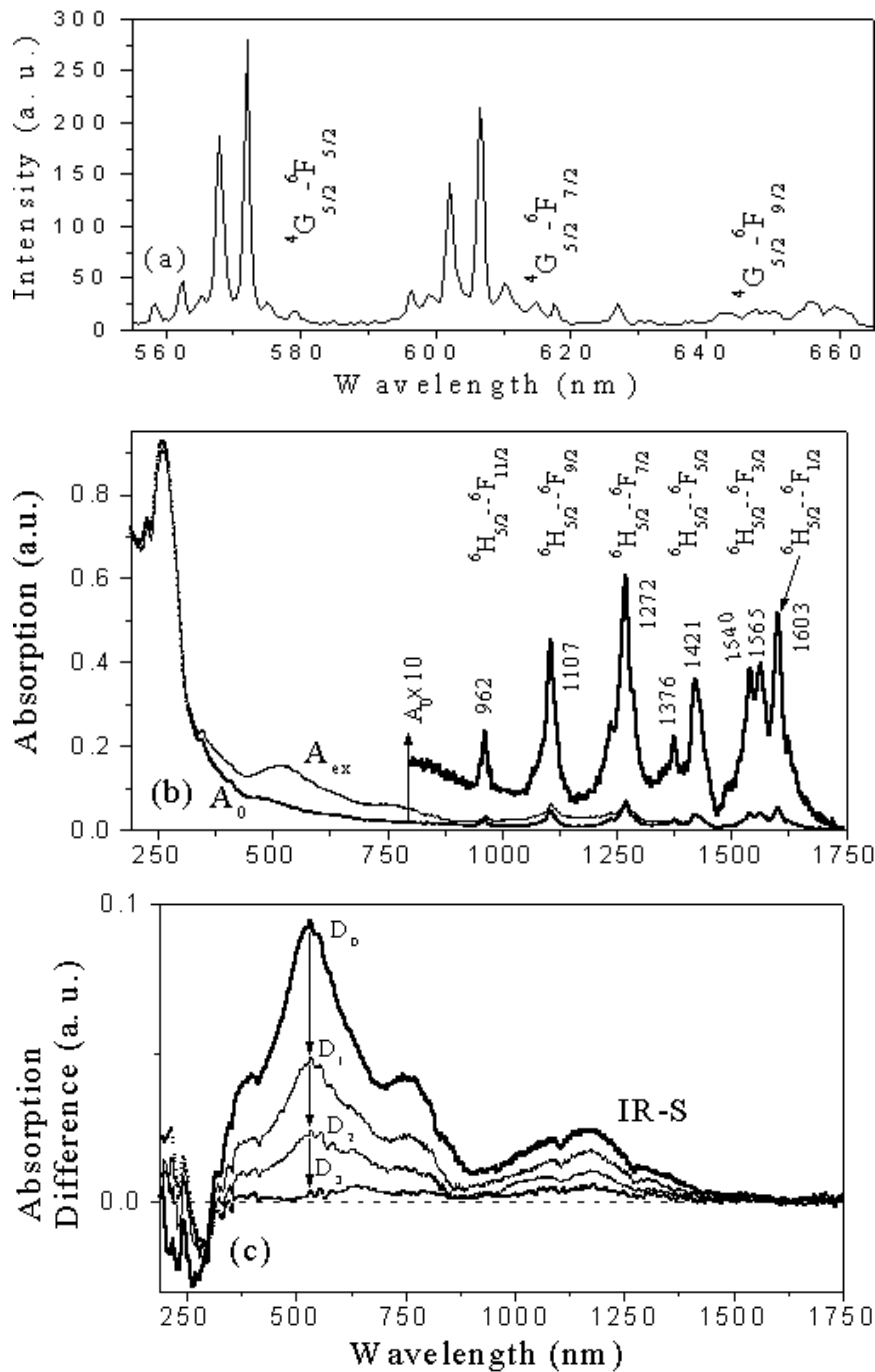
radiative 5d–4f transition of  $\text{Eu}^{2+}$ . The electron trapping is accompanied by generation of the same number of holes in the crystal. In order to examine the behaviour of the holes in the electron trapping process, we investigated the optical properties of CaS:Eu,Sm at several concentrations of Eu from 0 to 0.05 mol% while the concentration of Sm is constant at 0.2 mol%. If not particularly noted, hereafter the concentration of Eu is 0.05 mol% and that of Sm is 0.2 mol%.

For the samarium singly doped (0.2 mol%) CaS, after UV excitation a quite bright orange emission under the irradiation of the IR laser could be seen. The emission spectrum in figure 1(a) shows that the stimulated luminescence originates from the  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_J$  ( $J = 5/2, 7/2, 9/2$ ) transitions of  $\text{Sm}^{3+}$ . This suggests that the holes are trapped by  $\text{Sm}^{3+}$  ions or in the vicinity of the  $\text{Sm}^{3+}$  sites. There are many authors [2–8] who believed that the  $\text{Sm}^{3+}$  ions in alkaline earth sulphides act as electron traps and become  $\text{Sm}^{2+}$  after trapping electrons. Usually the positively and negatively charged centres are responsible for the electron and hole traps respectively. It seems unacceptable that one centre can trap either a hole or an electron. This model was first proposed by Keller *et al* [9] for the trapping process in IR stimutable phosphors SrS:Eu,Sm and SrS:Ce,Sm. But later they drafted another structure of the trapping state, owing to the difficulty of the  $\text{Sm}^{3+}$ – $\text{Sm}^{2+}$  model in explaining the stimulation by either infrared or visible light [11]. The electron trapped centre was written as  $(\text{Sm}^{3+})\text{--e}$ , as a modification of the mechanism for the electron trapping.

The optical absorption spectra of CaS:Sm after efficient IR stimulation (980 nm) and UV excitation (260 nm) are shown in figure 1(b). The strong absorption in the UV region corresponds to the interband absorption of the CaS host crystal. The absorption lines in the infrared region, which were not observed in undoped or Eu singly doped CaS, can be identified as the transitions from the ground state  ${}^6\text{H}_{5/2}$  to  ${}^6\text{F}_J$  ( $J = 1/2, 3/2\text{--}11/2$ ) within the  $4f^5$  configuration of  $\text{Sm}^{3+}$ . Their positions are in good agreement with the  $\text{Sm}^{3+}$  energy level diagram as reported previously [12, 13]. The two spectra in optically erased and stored states exhibit a remarkable difference. Their difference (subtraction of  $A_0$  from  $A_{ex}$ ) in figure 1(c) obviously results from the occupation of the electrons and holes of the energy levels of their traps in the stored state. Accompanied by the radiative transition from  $\text{Sm}^{3+}$  ions, an infrared band in the absorption difference occurs in the same region and has approximately the same peak position as the IR stimulation spectrum [2] of CaS:Eu,Sm. It can be assigned to the absorption stimulating the electrons from the trap level to the conduction band. This IR-stimulating band in the absorption difference will be denoted as the IR-S absorption band in the following sections.

### 3.2. The visible absorption bands of the trapped holes

The stored CaS:Sm was also found to be stimutable by visible light. The absorption difference decreases under the irradiation at the peak wavelength (530 nm) of the visible band as shown in figure 1(c), while the  $\text{Sm}^{3+}$  emission takes place and decays with the irradiating time. The sample looks grey after UV excitation, ascribed to the enhancement of the absorption to visible light; also it becomes white under sufficient exposure to visible or infrared light. We initially presumed that the electrons might be captured by the traps with two different depths, in view of the infrared and visible bands of the absorption difference. Thus, they were expected to decrease independently under the respective infrared and visible stimulation. But this presumption has been excluded because the infrared and visible stimulations have the same influence on the two bands of the absorption difference. By either infrared or visible stimulation, the infrared and visible bands decrease simultaneously almost at the same rate. They are related to each other in the optical storage. An identification of the visible band



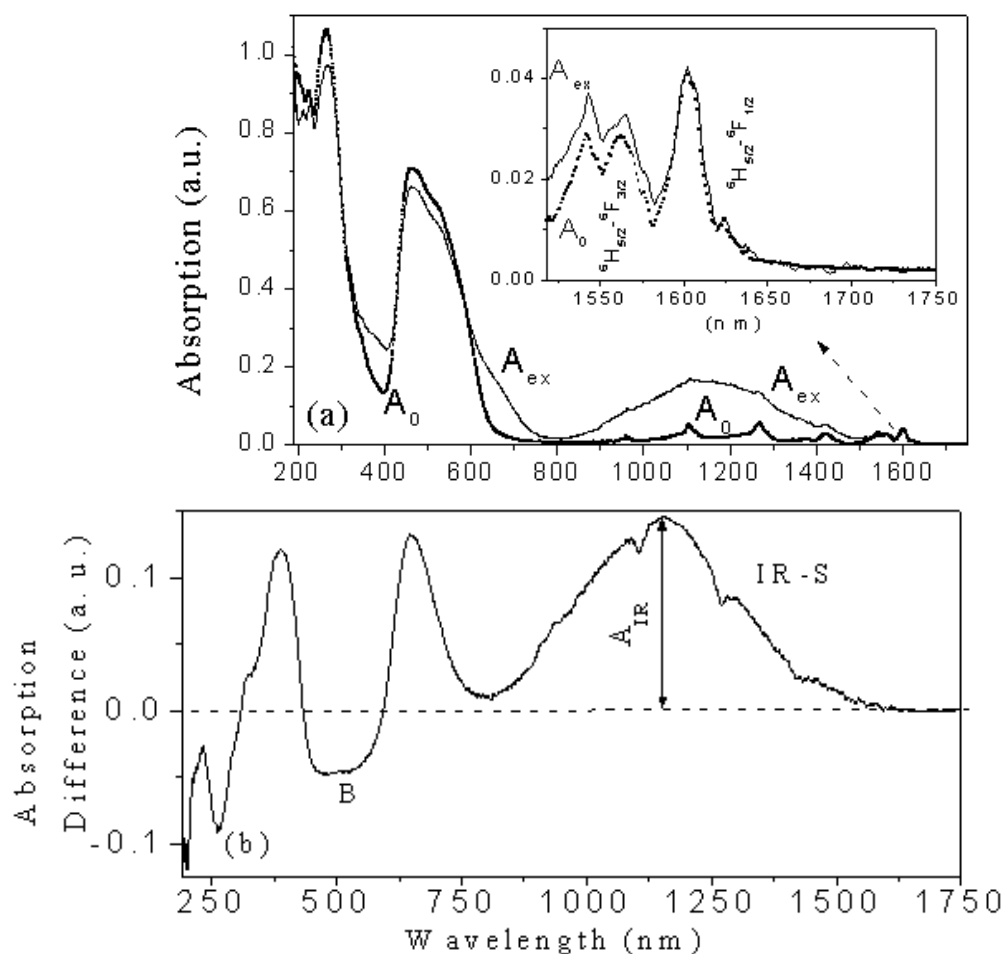
**Figure 1.** (a) Infrared (980 nm) stimulated emission spectrum of CaS:Sm after 260 nm excitation; (b) optical absorption spectra of CaS:Sm after strong stimulation at 980 nm ( $A_0$  in erased state) and excitation at 260 nm ( $A_{ex}$  in stored state); (c) the difference between the absorption spectra of the stored and erased CaS:Sm ( $D_0 = A_{ex} - A_0$ ), and the change of the absorption difference under 530 nm irradiation with a certain intensity. The stored sample was irradiated successively for 10 s ( $D_1$ ), 30 s ( $D_2$ ), 120 s ( $D_3$ ).

will be presented by comparing with the absorption difference of CaS:Eu,Sm in the following sections.

In the case of CaS:Eu,Sm, the strong absorption band predominantly distributed in the blue/green region results from the 4f–5d transition of  $\text{Eu}^{2+}$  (figure 2(a)). The absorption difference between the stored and erased states exhibits approximately the same line shape of the infrared band as that of CaS:Sm due to the same structure of the electron traps. But in the visible region they are quite different (figures 1(c) and 2(b)). Subsequent to 260 nm or 470 nm excitation, the IR stimulated luminescence spectrum presents a broad emission band centred at 640 nm arising from the 5d–4f transition of  $\text{Eu}^{2+}$ . The electron–hole recombination at the  $\text{Eu}^{2+}$  sites in the presence of  $\text{Eu}^{2+}$  (0.05 mol%) and  $\text{Sm}^{3+}$  (0.2 mol%) shows that the holes are trapped by the  $\text{Eu}^{2+}$  ions. Therefore the stimulated luminescence from  $\text{Eu}^{2+}$  suggests that the  $\text{Eu}^{2+}$  ions are more efficient than the  $\text{Sm}^{3+}$  ions in trapping holes. So the change of the absorption difference in the visible region from CaS:Sm to CaS:Eu,Sm can be ascribed to the fact that the holes are bound by different centres, i.e. the  $\text{Sm}^{3+}$  ions in CaS:Sm and  $\text{Eu}^{2+}$  ions in CaS:Eu,Sm. The holes may be trapped by these centres on their energy levels within the band gap. The hole detrapping transitions from these levels to the valence band, namely the reverse transitions of electrons from the valence band to the hole trapped levels, enhance the absorption in the corresponding wavelength region. This process has been described in detail for  $\text{F}^+$  centres in the MgO crystal [14].

To compare the behaviour of  $\text{Eu}^{2+}$  and  $\text{Sm}^{3+}$  ions in hole trapping, we lowered the Eu concentration with the expectation that their luminescence would be observed in the same crystal. The IR stimulated emission spectra subsequent to the respective 260 nm and 470 nm excitation on the initially erased sample CaS:Eu(0.02%),Sm(0.2%) are shown in figure 3(a) and their absorption difference in figure 3(b). The sharp lines on the background of the  $\text{Eu}^{2+}$  emission band in figure 3(a) have the same positions as those of CaS:Sm in figure 1(a). The IR-stimulated luminescence arises from both the  $\text{Sm}^{3+}$  and  $\text{Eu}^{2+}$  ions after the UV excitation. This also shows the existence of the  $\text{Sm}^{3+}$  ions in the stored state and that they are not changed into  $\text{Sm}^{2+}$ . We measured the excitation spectra of the emissions from  $\text{Sm}^{3+}$  and  $\text{Eu}^{2+}$  and the results are identical in principle to the previous investigators' [15, 16]. The  $\text{Eu}^{2+}$  ions are excited in the UV and blue/green regions, corresponding to the fundamental absorption of CaS and 4f–5d absorption of  $\text{Eu}^{2+}$  respectively. The  $\text{Sm}^{3+}$  excitation band occurs predominantly in the UV region. At 470 nm the  $\text{Eu}^{2+}$  ions can be excited efficiently yet the  $\text{Sm}^{3+}$  ions remain unexcited. Therefore all the holes are trapped by the  $\text{Eu}^{2+}$  ions and then the electron–hole recombination under IR stimulation takes place completely on  $\text{Eu}^{2+}$  ions followed only by their 5d–4f broad band emission. After the UV excitation by which the  $\text{Eu}^{2+}$  and  $\text{Sm}^{3+}$  ions are excited simultaneously, the holes can be trapped by these two types of hole trapping centre. Accordingly the stimulated luminescence spectrum exhibits both the 4f–4f line emission from  $\text{Sm}^{3+}$  and 5d–4f band emission from  $\text{Eu}^{2+}$ .

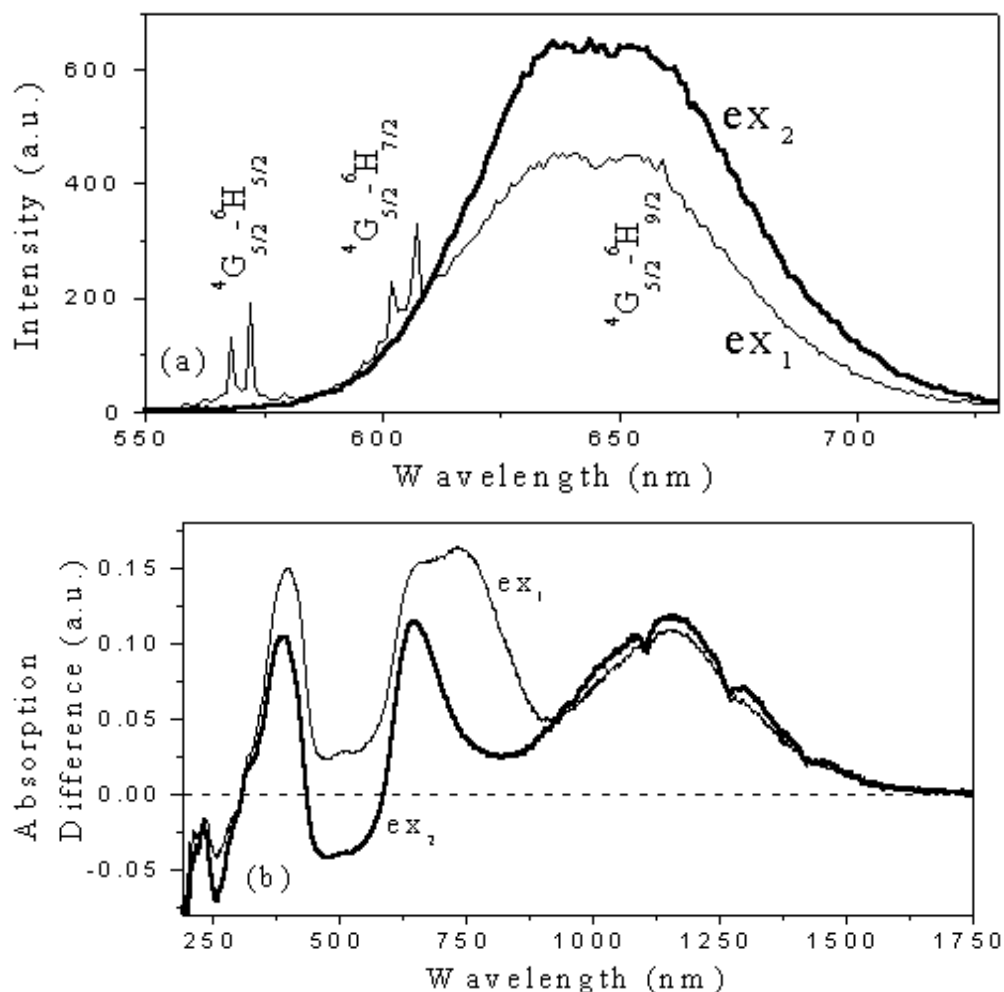
In the blue/green region the bottom B of the absorption difference of CaS:Eu,Sm (figures 2(b) and 3(b)) is similar to the inverse line shape of the 4f–5d absorption band of  $\text{Eu}^{2+}$ , which occurs in the same region. This means a decreased absorption of  $\text{Eu}^{2+}$  in the stored state after 470 nm excitation. We ascribed this to the loss of  $\text{Eu}^{2+}$  ions where the electrons are optically ionized and are then trapped by other centres, resulting in the formation of  $\text{Eu}^{3+}$  ions. This indicates that an electron is absent from the  $4f^7$  configuration of  $\text{Eu}^{2+}$ , or a hole occupies the  $4f^7$  ground state ( $^8S_{7/2}$ ) of  $\text{Eu}^{2+}$ . In stimulation the detrapped electrons enter the 5d orbit of  $\text{Eu}^{2+}$  from the conduction to form an excited states ( $4f^65d$ ) of  $\text{Eu}^{2+}$  ions [4]. Besides, it was suggested that in BaFBr: $\text{Eu}^{2+}$  the hole trapped  $\text{Eu}^{2+}$  ions may exist in another form of  $\text{Eu}^{2+}$ –hole complex [1], in which the hole binds a detrapped electron after stimulation to form an exciton with the hole and in the recombination the energy is transferred to the  $\text{Eu}^{2+}$



**Figure 2.** (a) Optical absorption spectra of CaS:Eu,Sm in erased ( $A_0$ , 980 nm stimulated) and stored ( $A_{ex}$ , 470 nm excited) states, inset: details of  ${}^6H_{5/2}-{}^6F_{3/2,1/2}$  lines of  $A_0$  and  $A_{ex}$ ; (b) absorption difference between the stored and erased states ( $A_{ex} - A_0$ ).

ion resulting in  $\text{Eu}^{2+}$  emission. For both of the two forms, the holes should occupy the energy levels within the band gap so that they can be trapped stably. In fact, the visible light at 470 nm is far from the energy of CaS interband absorption in the UV region (figures 1(b) and 2(a)). At this wavelength only the electrons on the levels within the band gap can be excited into the conduction band to transfer to the traps with the holes left behind in the band gap.

For the Sm singly doped CaS, however, it is not completely the same case as  $\text{Eu}^{2+}$  ions in CaS:Eu,Sm. After excitation, some of the  $\text{Sm}^{3+}$  absorption lines are partly immersed in the infrared stimulating absorption (figures 1(b), 2(a)). As the result of subtracting the absorption spectrum in the erased state from that in the stored state, the IR-S absorption bands of CaS:Sm and CaS:Eu,Sm exhibit several pits exactly at the peak positions of  $\text{Sm}^{3+}$  absorption lines, which become shallow with the decrease of the IR-S band to the longer wavelength. If we assumed that the valence or the number of  $\text{Sm}^{3+}$  ions is changed by trapping holes or electrons, similar to  $\text{Eu}^{2+}$  ions, we should also have observed the decrease of all the  $\text{Sm}^{3+}$  absorption lines with the same proportion. At the edge of the lower energy side of the IR-S absorption band, the pits are hard to see since the peak heights of the  $\text{Sm}^{3+}$  absorption lines concerned

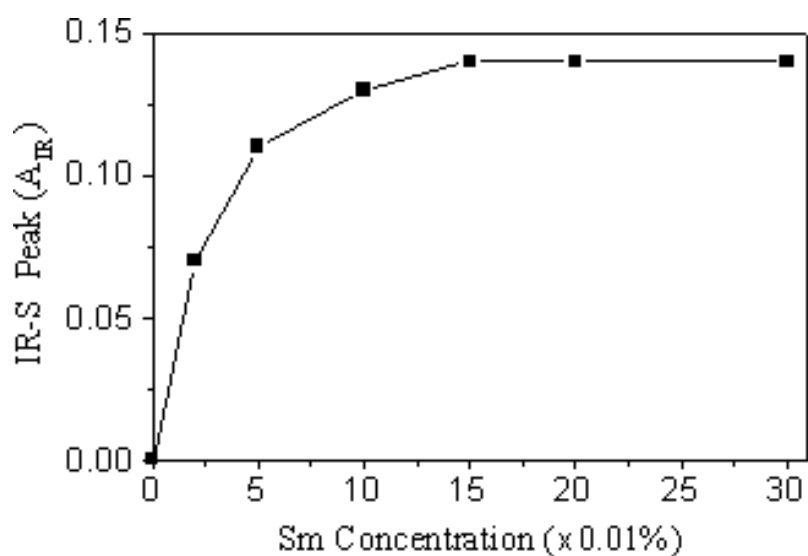


**Figure 3.** (a) The IR stimulated emission spectra of CaS:Eu(0.02%),Sm(0.2%) subsequent to the excitation at 260 nm ( $ex_1$ ) or 470 nm ( $ex_2$ ) and (b) the corresponding absorption difference.

( ${}^6H_{5/2} - {}^6F_{1/2}$ ,  ${}^6F_{3/2}$ ) are almost invariable during excitation. This suggests that the  $Sm^{3+}$  ions do not change in valence or number. Therefore the  $Sm^{3+}$  ions trap neither the holes to form  $Sm^{4+}$  nor the electrons to form  $Sm^{2+}$ .

It has been commonly admitted that substitution of a trivalent impurity cation for a divalent host cation may cause an additional host cation vacancy [14, 17–20], together with a coordinated anion trapping a hole and forming a V-type centre [14, 17], so that the  $Ca^{2+}$  vacancies induced by  $Sm^{3+}$  ions are most likely responsible for the hole traps in the absence of  $Eu^{2+}$  ions. The electron-hole recombination takes place at these V-type centres with the energy transfer to the nearby  $Sm^{3+}$  ions at some efficiency due to their short distance. On the other hand, another defect with a negative charge is required to be coordinated with the  $Sm^{3+}$  ions to preserve the electrical neutrality [18], which play the role of the electron capturing centres after excitation as will be demonstrated below. The configuration of a defect induced by an  $Al^{3+}$  ion in MgO [14, 17], for example, was described as  $Al^{3+} - O^2 - [Mg \text{ vacancy}] - O^-$ . In the case of CaS:Eu,Sm or CaS:Sm, it may be expressed as  $Sm^{3+} - S^2 - [Ca \text{ vacancy}] - S^-$ .



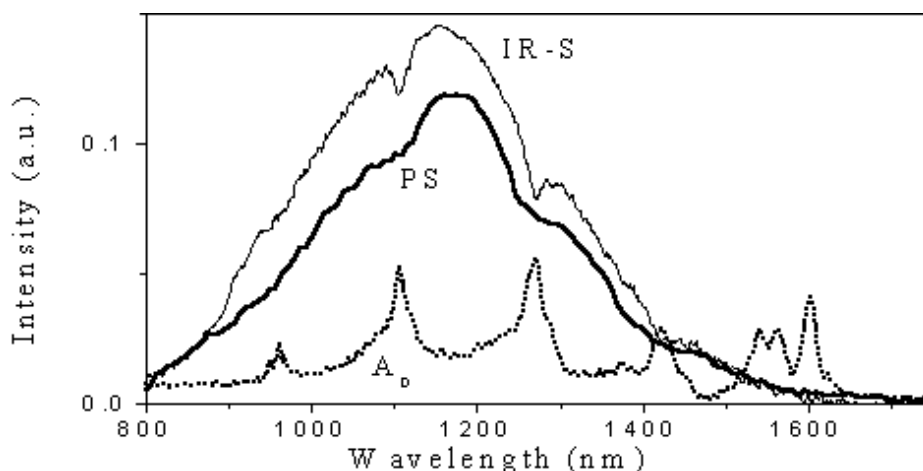


**Figure 4.** The dependence of the IR-S peak value ( $A_{IR}$ , figure 2(b)) of the absorption difference of CaS:Eu,Sm on Sm concentration. The Eu concentration is 0.05%.

### 3.3. The role of $Sm^{3+}$ ions in the trapping process

For CaS:Eu,Sm, the dependence of the peak height of the IR-S band on Sm concentration is plotted in figure 4. With respect to the association of the IR-S band with the trapped electrons, the absorption peak height  $A_{IR}$  reflects the population of the trapped electrons in saturated storage or the storing capacity of the materials, increasing with the concentration of Sm from 0 to about 0.1 mol%. This shows that the optical storage must be correlated with the incorporation of Sm ions. But this does not mean that the  $Sm^{3+}$  ions are simply the electron trapping centres. Substituting  $La^{3+}$  for  $Sm^{3+}$  at the same concentration in Eu co-doped CaS, we found that the afterglow of the sample increases significantly comparing with CaS:Eu and CaS:Eu,Sm. The afterglow arises from the thermal traps situated at a shallower position under the conduction band than the storing traps in CaS:Eu,Sm. For the thermal traps induced by  $La^{3+}$  in CaS:Eu,La, the  $La^{3+}$  ions would not be supposed to form  $La^{2+}$  by trapping electrons, since it is very difficult to get divalent lanthanum ions in the ordinary host lattices as we know. The Sm ions are responsible for the stability of the storage by deepening the trap level via the interaction with the trapped electrons, owing to the adjacent positions of the  $Sm^{3+}$  ion and the trapping centre as shown below.

The pits on the IR-S absorption band implies that the electron trap and the neighbouring  $Sm^{3+}$  ion influence each other in absorption to the incident light at the wavelengths where both the  $Sm^{3+}$  absorption and the IR-S absorption occur. For the optical absorption of an individual centre, it is reasonable to assume that each centre has a certain absorption area within which the incident light is absorbed at the relative possibility dependent on the distance from the centre and the wavelength of the incident light. Because of the short distance between the  $Sm^{3+}$  ion and the trapping centre, their absorption areas can be expected to overlap or coincide projectively along the incident light by sheltering each other, especially when they are bonded parallel to the incident light. If they were distributed without correlation at random in the crystal, they would be located too far away to shelter each other. The local area around the  $Sm^{3+}$  ion can be regarded as transparent for the incident light beyond the wavelength positions



**Figure 5.** Photo-stimulation spectrum (PS) of CaS:Eu,Sm by monitoring 640 nm emission in comparison with the IR-S band of the absorption difference and  $\text{Sm}^{3+}$  absorption lines  $A_0$  in figure 2.

of  $\text{Sm}^{3+}$  absorption lines, where the stimulating absorption of the trap is free from shelter by the  $\text{Sm}^{3+}$  absorption area. Thus the IR-S absorption of the trapping centre is only eclipsed by the  $\text{Sm}^{3+}$  ion at the wavelengths of its absorption peaks. The pits on the IR-S absorption band evidence that they are spatially correlated in pairs to form a complex, but the  $\text{Sm}^{3+}$  ion is not the trapping centre itself.

In correspondence with the IR-S absorption band, the photo-stimulation spectrum was expected to have a line shape with the same substructure eclipsed by  $\text{Sm}^{3+}$  absorption lines. In fact the IR photo-stimulation spectrum of CaS:Eu,Sm (PS in figure 5) was indeed found to present a similar band shape with several shoulders at the  $\text{Sm}^{3+}$  absorption positions consistent with but not as distinguishable as the pits of the IR-S absorption band. The indistinct substructure of the stimulation spectrum results from the lower resolution of the measurement. In the measurement, a faster scanning speed was chosen to overcome exhaustion of the stored energy in stimulated emission. A larger slit width of the Shimadzu for the infrared source was set to reduce the noise additionally caused by the loss of the stimulated luminescence in feeding into the Spex. Taking into account the nonradiative transition in the recombination, it can be understood that we have a lower signal to noise ratio for the measurement of the photo-stimulation spectrum.

The absorption spectra of powder sample was obtained on the Shimadzu via measurement of its diffused reflection light gathered in an integrating sphere without significant loss of the detected light. In addition, more information including the hole detrapping was obtained in the absorption difference as elucidated above. The substructure of the IR-S absorption band and the stimulation spectrum present evidence that the  $\text{Sm}^{3+}$  ions do exist in the vicinity of the trapping centres and keep their valence unchanged in the electron trapping process. The peak position of the IR-S absorption band (1155 nm) is close to the photo-stimulation spectrum in our measurement (1169 nm), and the previous report (1150 nm) [2] where its substructure was not found or was ignored by the authors.

In many crystals  $\text{Sm}^{2+}$  is also characterized by its optical transitions [21–24] between its ground states  $^7F_J$  ( $J = 0-6$ ) and excited states  $^5D_{0,1,2}$  within the  $4f^6$  configuration and even the sharp lines in its  $4f^6-4f^55d$  absorption at low temperature [25], different from the

$4f^7-4f^65d$  absorption of  $\text{Eu}^{2+}$  that exhibits only a broad band shape of the spectra (except for the phonon lines) in many host lattices. So far we have not found any characteristics of  $\text{Sm}^{2+}$  in the emission and absorption of  $\text{CaS:Eu,Sm}$  with various concentrations of Eu and Sm, nor did the previous investigators as far as we know. Nevertheless the optical storage capacity has to be associated with the existence of Sm ions as the concentration dependence of the IR-S peak height shows in figure 4. But the Sm ions do not have to capture electrons directly. They are most likely to combine the defects intimately to preserve the charge equilibrium in the local area and the electrical neutrality of the crystal with the substituting  $\text{Sm}^{3+}$  ion and the nearby  $\text{Ca}^{2+}$  vacancy, such as  $\text{O}^-$  or  $\text{S}^-$  centres, which act as the trapping centres. On the other hand, as a result of their short distance, the ionic interaction between the  $\text{Sm}^{3+}$  ion and the trapping centre may influence the position of the trap level. In this way the  $\text{Sm}^{3+}$  ions are involved in electron trapping and enable the traps to store electrons stably.

#### 4. Conclusions

In Sm doped or co-doped CaS, the optical absorption lines from the ground state  $^6\text{H}_{5/2}$  to  $^6\text{F}$  states within the  $4f^5$  configuration of  $\text{Sm}^{3+}$  were observed in the near-infrared region. In the same region the stimulating absorption of the trapped electrons occurs. The difference of the absorption spectra in optically stored and erased states arises from both the electron and hole trapping states after excitation. For  $\text{CaS:Sm}$  the Ca vacancies, which are induced by the substitution of the trivalent samarium ions for the divalent host cations, serve to trap the holes left behind by the UV excitation. For  $\text{CaS:Eu,Sm}$  the holes are found to be trapped by the  $\text{Eu}^{2+}$  ions, showing that they are highly efficient in hole trapping. The  $\text{Sm}^{3+}$  ions do not directly act as the trapping centres and their valence remains unchanged in the trapping process. They are responsible for the storable properties of the traps owing to their intimate combination with the trapping centres, which are formed by the defects around the trivalent rare-earth ions in the CaS crystal.

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