

Influence of Ce³⁺ Ions on the Near Infrared Emission of Eu²⁺-doped Ca₃Sc₂Si₃O₁₂

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The luminescence properties of double-doped with Eu²⁺ and Ce³⁺ ions Ca₃Sc₂Si₃O₁₂ have been studied for the first time. The Eu²⁺ ions in Ca₃Sc₂Si₃O₁₂ exhibit a NIR emission with a maximum at about 840 nm, which is located in the highest spectral response region of c-Si photovoltaic solar cells. Upon the introduction of Ce³⁺ ions into the lattice the Ce³⁺ 4f → 5d band at 445 nm appears in the excitation spectra for the Eu²⁺ NIR emission, indicating to the presence of energy transfer between Ce³⁺ and Eu²⁺ ions. The co-doping with Ce³⁺ ions is also followed by local distortions of the Eu²⁺ environment and inhomogeneous broadening of the Eu²⁺-related spectral bands. It was found that the relative intensity of the higher-energy Eu²⁺ 4f⁷ → 4f⁶5d excitation band at 360 nm decreases with the increase of Ce³⁺ concentration. This unusual observation is ascribed to photoionization of Eu²⁺ ions, electron trapping on defects and subsequent non-radiative relaxation.

Keywords: Phosphors, Luminescence, Eu²⁺, Energy transfer.

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1. INTRODUCTION

Recently, some of us have reported that Eu²⁺-doped garnet of composition Ca₃Sc₂Si₃O₁₂ exhibits a broadband emission in the 720-1100 nm region with a maximum at about 840 nm, which is due to the 4f⁶5d → 4f⁷ transition of Eu²⁺ ions occupying Ca positions in the crystal lattice [1]. To our knowledge, this is the only observation of a near infrared (NIR) 4f⁶5d → 4f⁷ emission of Eu²⁺ ions in any compound. The large crystal-field splitting of 4fⁿ-15d configurations of lanthanide ions is a prominent feature of crystals with the garnet structure, and this factor is expected to be responsible for the unusually long-wavelength position of the Eu²⁺ emission in Ca₃Sc₂Si₃O₁₂ [1]. In the crystal structure of this compound, all the Ca atoms are coordinated by eight oxygen atoms forming a dodecahedron (D₂ point symmetry) with four long Ca-O distances of 2.51 Å and four short Ca-O distances of 2.40 Å, whereas Sc atoms occupy octahedral positions [2].

In first sight NIR emitting Eu²⁺-doped phosphors of the garnet family may be of interest for photovoltaic applications. It is accepted that the mismatch between the incident solar spectrum and the spectral response of crystal silicon (c-Si) solar cells (see Fig. 1) is one of the main reasons for their limited efficiency (~ 29 %) [3]. Taking into account that the NIR emission of Eu²⁺-doped Ca₃Sc₂Si₃O₁₂ is located in the highest spectral response region of c-Si and its excitation spectrum contains broad bands with maxima at about 358 and 524 nm [1], one can suppose that an optimized material may be used to convert the short-wavelength part of sunlight (300-550 nm) into the NIR emission, thereby increasing the efficiency of c-Si photovoltaic solar cells. One of evident shortcomings of this material is a low absorbance between 400 and 500 nm, meanwhile, as one can see from Fig. 1, the contribution of photons with wavelengths in the 400-500 nm spectral region to the total solar energy is quite essential.

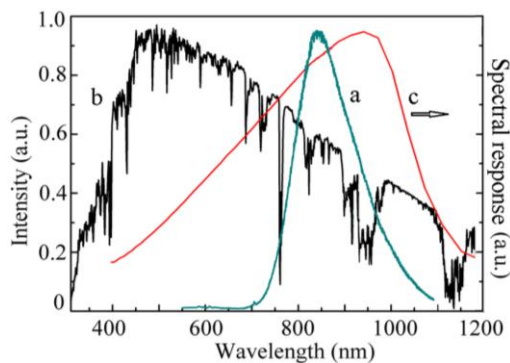


Fig. 1 – Comparison of (a) emission spectrum of Ca₃(1-*y*)Eu₃*y*Sc₂Si₃O₁₂ (*y* = 0.01), (b) incident solar spectrum (AM1.5 G) and (c) spectral response of c-Si

It is known that Ca₃Sc₂Si₃O₁₂ doped with Ce³⁺ ions is one of the most promising phosphors for light emitting diodes because of its favorable luminescent properties and a weak thermal quenching of luminescence [4]. Several groups of authors have studied the luminescent properties of Ce³⁺ ions in Ca₃Sc₂Si₃O₁₂ upon excitation in the range from 100 to 500 nm [1, 4-6]. It was found that at room temperature Ce³⁺-doped Ca₃Sc₂Si₃O₁₂ shows a broadband emission with a maximum at 505 nm and a shoulder at about 550 nm. Since this emission is efficiently excited by photons in the 400-500 nm region, co-doping with Ce³⁺ ions may be a possible way to improve the properties of Ca₃Sc₂Si₃O₁₂:Eu²⁺ as a down-converter of sunlight. In this communication, we report on the influence of Ce³⁺ ions on the luminescence properties of Eu²⁺ in this compound.

2. EXPERIMENTAL

Polycrystalline samples of nominal composition Ca₃(1-*x-y*)Ce₃*x*Eu₃*y*Sc₂Si₃O₁₂ (*x* = 0, 0.0001, 0.0005,

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0.001, 0.005, 0.01; $y = 0.01$) were prepared by solid state reaction method. Starting mixtures of high-purity CaCO_3 , SiO_2 , Sc_2O_3 and $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Ce}$) were fired at a temperature of about 1300°C for 4 h. The specimens were cooled, mortared to insure homogeneity and fired twice at 1300°C for 4 h in a reducing medium of CO . The final products were checked by X-ray diffraction (XRD) using a Shimadzu LabX XRD-6000 automated diffractometer. Morphological investigations were carried out by scanning electron microscopy (SEM) on a TESCAN VEGA 3 electron microscope. Diffuse reflectance spectra of the samples were measured on a Perkin-Elmer Lambda-9 spectrophotometer. The emission and excitation spectra were recorded at 77 K and room temperature using a Fluorolog 3-22 (Horiba Jobin Yvon) spectrofluorometer equipped with a xenon lamp. Measurements were performed in the range of 220-1200 nm with the use of a Hamamatsu R928P photomultiplier as a detector in the 400-850 nm region and a liquid nitrogen cooled InGaAs infrared detector (800-1200 nm).

3. RESULTS AND DISCUSSION

The synthesis procedure resulted in the formation of colored polycrystalline materials, moreover, their color changed with the Ce^{3+} concentration. XRD patterns of the final products with $x = 0-0.005$ were well matched with JCPDS File No 72-1969 for $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, although the presence of small amounts of impurity phases (Sc_2O_3 , Ca_2SiO_4) was also detected. The typical XRD pattern is presented in Fig. 2.

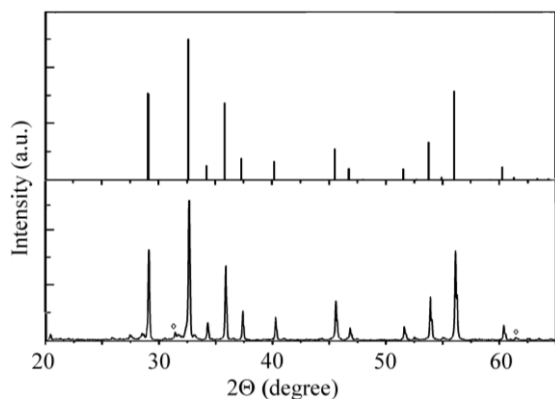


Fig. 2 – Comparison of X-ray diffraction pattern of as-prepared $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0.001$; $y = 0.01$) with the JCPDS data (File No 72-1969) as a reference. Peaks from the impurity phase (Sc_2O_3) are denoted by the symbols (°)

The XRD pattern of sample with the nominal value of $x = 0.01$ revealed more significant amounts of the impurity phases. Besides this, the intensity of the Eu^{2+} NIR emission of this sample was found to be significantly lower than those of the other samples. These data are in line with the results reported previously for Ce^{3+} -doped $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ [4-6]. In particular, Shimomura et al. [4] have found out that in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ Ce^{3+} ions tend to occupy the Ca dodecahedral positions and, probably due to the difference between the formal charges of Ce^{3+} and Ca^{2+} ions, only limited amounts of Ce^{3+} can be introduced into the crystal lattice. Since no charge compensating agents were used for the synthesis, one can

expect that in all the samples under study the majority of the Ce^{3+} ions are present in the form of locally uncompensated $\text{Ce}_{\text{Ca}}^{\bullet}$ centers. The positive excess charge of these centers is distantly compensated by intrinsic point defects, such as calcium vacancies and Ca^{2+} ions on the scandium sites.

As an example, the SEM photograph of the $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0.001$; $y = 0.01$) sample is presented in Fig. 3. As can be seen, the phosphor is composed of slightly agglomerated particles with smooth faces. The size of particles varies from 3 to $15\ \mu\text{m}$.

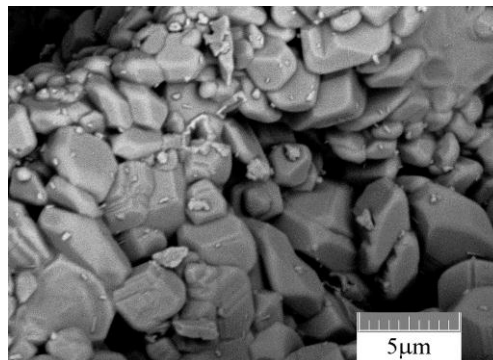


Fig. 3 – SEM photograph of $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0.001$; $y = 0.01$)

Kubelka-Munk-transformed diffuse reflectance spectra in the visible region of the non-doped with Ce^{3+} and double-doped $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0.005$; $y = 0.01$) samples are compared in Fig. 4. It is seen that both the spectra contain a broad absorption band with a maximum at about 524 nm caused by $4f^7 \rightarrow 4f^65d$ transitions of Eu^{2+} [1]. The introduction of Ce^{3+} ions into the crystal lattice leads to the appearance of a strong absorption band at 445 nm, which should be attributed to the lowest-energy $4f \rightarrow 5d$ transition of Ce^{3+} ions occupying the Ca dodecahedral positions [4-6].

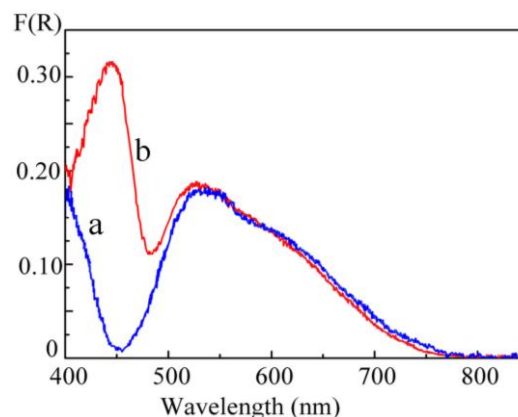


Fig. 4 – Kubelka-Munk-transformed diffuse reflectance spectra of (a) $\text{Ca}_{3(1-y)}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($y = 0.01$), (b) $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0.005$; $y = 0.01$)

The influence of Ce^{3+} concentration on the excitation spectra of $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0-0.005$; $y = 0.01$) for the NIR emission is shown in Fig. 5. The spectra consist of broad bands in the 300-800 nm range with maxima at ~ 360 , 445 and 524 nm. It is clear that

the bands at 360 and 524 nm are due to excitation of the Eu^{2+} ions via transitions from the $4f^7(^8\text{S}_{7/2})$ ground state to the components of the $\text{Eu}^{2+} 4f^65d$ configuration [1], while the band at 445 nm is caused by $4f \rightarrow 5d$ transition of Ce^{3+} ions. It should be also noted that the intensity of the latter band for the samples with $x = 0.0001$ and 0.0005 is very low.

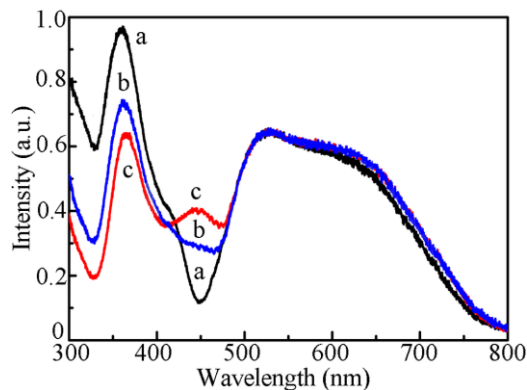


Fig. 5 – Influence of Ce^{3+} concentration on the excitation spectra of the Eu^{2+} emission in $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($y = 0.01$): a) $x = 0$; b) $x = 0.001$; c) $x = 0.005$. The spectra were recorded at 293 K for the emission at 830 nm and normalized at 525 nm

From comparison of the excitation spectra for the Eu^{2+} emission in $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0-0.005$; $y = 0.01$), the following observations can be made:

a) The excitation band at 445 nm appears in the spectra upon introduction of Ce^{3+} ions into the crystal lattice, its intensity increases with increasing Ce^{3+} concentration, supporting the presence of energy transfer between Ce^{3+} and Eu^{2+} ions;

b) The higher-energy $\text{Eu}^{2+} 4f^7 \rightarrow 4f^65d$ excitation band undergoes some shift towards the longer wavelengths with increasing Ce^{3+} concentration. At room temperature, the position of its maximum changes from 358 nm for $x = 0$ to 365 nm for $x = 0.005$. The relative intensity of this band decreases markedly with the increase of Ce^{3+} concentration.

The energy transfer between Ce^{3+} and Eu^{2+} ions has been observed in a number of inorganic compounds, including alkaline earth silicates $\text{Li}_2\text{SrSiO}_4$ [7], $\text{Ca}_2\text{Mg}_{0.5}\text{AlSi}_{1.5}\text{O}_7$ [8]. This phenomenon is typically ascribed to an electric multipolar interaction between these ions, although because of strong overlap of the Ce^{3+} -emission and Eu^{2+} -excitation bands in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ the radiative energy transfer (reabsorption) may be also of importance. The decrease in relative intensity of the UV Eu^{2+} excitation band with increasing the Ce^{3+} -content (Fig. 5) implies the appearance of additional non-radiative process. It should be noted that this excitation band, in contrast to the visible one, does not show any fine structure at 77 K. This fact may be explained by photoionization of the Eu^{2+} ions upon excitation in this region. Indeed, in Ref. [1] the energy gap between the bottom of the conduction band and the lowest-energy $\text{Eu}^{2+} 4f^65d$ state was estimated to be some tenths of eV, so that $\text{Eu}^{2+} 5d$ states involved in the $4f^7 \rightarrow 4f^65d$ transitions at ca. 360 nm lie in the conduction band of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$. Thus, photoionization of Eu^{2+} ions, electron delocalization process, its

trapping on defects and subsequent non-radiative relaxation are expected to be responsible for the luminescence quenching. Note that since the contribution of photons with wavelengths in the 400-500 nm spectral region to the total solar energy exceeds 15 %, whereas that of photons with wavelengths less than 400 nm amounts to about 5 % (see Fig. 1), the Ce^{3+} co-doping of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Eu}^{2+}$ allows one to increase an efficiency of converting the short-wavelength part of sunlight (300-550 nm) into the NIR emission.

Hamilton et al. [9] have studied an electron trapping following photoionization of Ce^{3+} ions in yttrium aluminum garnet (YAG) by means of optical-absorption and fluorescence spectroscopies. It was found that the back-transfer of excitations from traps to the cerium ions in YAG is a slow and inefficient, i.e. an essential part of cerium ions returns non-radiatively to the ground state. These authors have also supposed that oxygen vacancies participate in this process. In the double-doped $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, other types of defects may also promote non-radiative relaxation to the Eu^{2+} ground state. Since the relative intensity of the UV excitation band decreases steadily with increasing cerium concentration, Ce^{3+} ions seem to be involved either directly or indirectly in this process. Beck et al. [10] studied mechanisms of electron trapping upon photoionization of Sm^{2+} ions in CaF_2 and found out that dominant electron traps are small clusters of Sm^{3+} ions. Taking into account that Ce^{3+} ions at the Ca dodecahedral sites in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ have a positive charge compared to the regular lattice, the capture of electrons from the conduction band by these centers cannot be excluded. Note that Ce ions in the low oxidation state (+2) have been found quite stable at room temperature in some alkaline earth fluorides (CaF_2 , BaF_2) [11, 12]. Although the high stability of Ce^{2+} in the alkaline earth fluorides may be exceptional phenomenon, it is not unreasonable to assume the formation of transient or even quasi-stable Ce^{2+} centers in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$.

To analyze the reasons for the red shift of the higher-energy $\text{Eu}^{2+} 4f^7 \rightarrow 4f^65d$ excitation band with the increase of Ce^{3+} concentration, emission and excitation spectra of the double-doped samples were also recorded at liquid nitrogen temperature. As shown earlier in Ref. [1], at 77 K the NIR emission band of Eu^{2+} ions in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ is narrowed and a fine structure is observed in the spectrum. The onsets of both the excitation and emission spectra for $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Eu}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0.005$; $y = 0.01$) at 77 K are presented in Fig. 6. It is seen that the mirror symmetry at about 769 nm is observed, indicating that this feature is a zero-phonon line (ZPL) of the $\text{Eu}^{2+} 4f^65d \rightarrow 4f^7$ transition. Stokes and anti-Stokes vibronic replicas are present at about 245 and 501 cm^{-1} from the ZPL, suggesting a coupling with a $\sim 245 \text{ cm}^{-1}$ local vibrational mode. Note that the obtained emission spectrum is very similar to that of single-doped with $\text{Eu}^{2+} \text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ [1], and no distinct changes in the spectrum were observed upon varying the excitation wavelength in the 350-750 nm region. Thus, one can conclude that no significant influence of Ce^{3+} on the surrounding of the Eu^{2+} ions was revealed in these experiments.

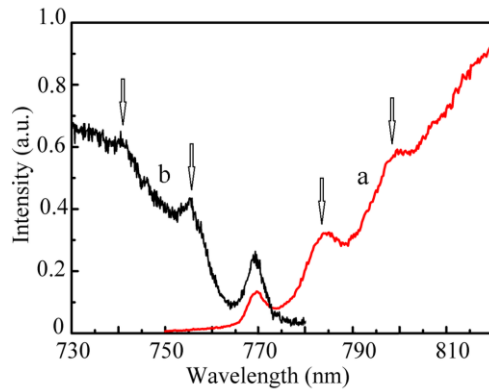


Fig. 6 – Emission and excitation spectra of $\text{Ca}_{3(1-x-y)}\text{Ce}_{3x}\text{Ce}_{3y}\text{Sc}_2\text{Si}_3\text{O}_{12}$ ($x = 0.005$; $y = 0.01$) at 77 K. The emission spectrum (a) was recorded upon excitation with $\lambda_{\text{exc}} = 520$ nm and the excitation spectrum (b) was obtained for the emission at 830 nm. Arrows indicate the positions of the vibronic replicas

The red shift of the higher-energy $\text{Eu}^{2+} 4f^7 \rightarrow 4f^65d$ excitation band with the increase of Ce^{3+} concentration can be ascribed to the formation of several kinds of Eu^{2+} centers with slightly different crystal field parameters and the emission spectra of which do not differ much. In other words, the introduction of Ce^{3+} ions into the crystal lattice leads to slight deformations of the Eu^{2+} environment and the distortions of different geometries cause the inhomogeneous broadening of the spectral

bands. An additional manifestation of the Ce^{3+} -induced inhomogeneous broadening is some redshift of long-wavelength tail of the visible band in the excitation spectra of the double-doped samples (see Fig. 5).

4. CONCLUSIONS

The luminescence properties of double-doped with Eu^{2+} and Ce^{3+} ions $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ have been studied. The Eu^{2+} ions in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ exhibit the NIR emission in the range of 720-1100 nm, which is located in the highest spectral response region of c-Si photovoltaic solar cells. Upon the introduction of Ce^{3+} ions into the crystal lattice the $\text{Ce}^{3+} 4f \rightarrow 5d$ excitation band at 445 nm appears in the excitation spectra for the NIR emission of Eu^{2+} ions, its relative intensity increases with increasing Ce^{3+} concentration, indicating to the presence of energy transfer between Ce^{3+} and Eu^{2+} ions. This allows one to increase an efficiency of converting the short-wavelength part of sunlight (300-550 nm) into the NIR emission. The co-doping with Ce^{3+} ions is also followed by local distortions of the environment of Eu^{2+} ions. This causes the inhomogeneous broadening of the Eu^{2+} excitation bands. It was shown that the relative intensity of the higher-energy $\text{Eu}^{2+} 4f^7 \rightarrow 4f^65d$ excitation band decreases with the increase of Ce^{3+} concentration. Photoionization of Eu^{2+} ions, electron trapping on defects and subsequent non-radiative relaxation to the Eu^{2+} ground state $^8S_{7/2} (4f^7)$ are expected to be responsible for this observation.

Вплив іонів Ce^{3+} на інфрачервоне випромінювання $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, легованого іонами Eu^{2+}

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Досліджено люмінесцентні властивості $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, легованого іонами Eu^{2+} та Ce^{3+} . Іони Eu^{2+} в $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ демонструють випромінювання з максимумом при 840 нм, яке локалізовано в області найвищої спектральної чутливості кремнієвих (c-Si) фотоелектричних елементів. При введенні іонів Ce^{3+} в кристалічну ґратку в спектрі збудження інфрачервоного випромінювання Eu^{2+} з'являється смуга з максимумом при 445 нм (перехід $4f \rightarrow 5d$ в Ce^{3+}), що вказує на наявність переносу енергії між іонами Ce^{3+} та Eu^{2+} . Це також супроводжується локальними деформаціями найближчого оточення Eu^{2+} та неоднорідним уширенням відповідних смуг випромінювання та збудження. Встановлено, що відносна інтенсивність смуги збудження люмінесценції Eu^{2+} при 360 нм (перехід $4f^7 \rightarrow 4f^65d$) зменшується зі збільшенням концентрації Ce^{3+} . Це незвичайне спостереження приписується фотоіонізації іонів Eu^{2+} , захопленню електронів на дефектах та наступною безвипромінювальною релаксацією в основний стан.

Ключові слова: Люмінофори, Люмінесценція, Eu^{2+} , Перенос енергії.

Влияние ионов Ce^{3+} на инфракрасное излучение $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, активированного ионами Eu^{2+} В.П. Доценко¹, И.В. Березовская¹, И.В. Затовский², С.С. Смола¹, Н.П. Ефрюшина¹¹ Физико-химический институт им. А.В. Богатского НАН Украины,
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Исследованы люминесцентные свойства $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, активированного ионами Eu^{2+} и Ce^{3+} . Ионы Eu^{2+} в $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ демонстрируют излучение с максимумом при 840 нм, которое находится в области наибольшей спектральной чувствительности кремниевых (с-Si) фотоэлектрических элементов. При введении в решетку ионов Ce^{3+} в спектре возбуждения инфракрасного излучения Eu^{2+} появляется обусловленная переходом $4f \rightarrow 5d$ ионов Ce^{3+} полоса при 445 нм, что указывает на наличие переноса энергии между Ce^{3+} и ионами Eu^{2+} . Введение ионов Ce^{3+} также сопровождается локальными искажениями ближайшего окружения ионов Eu^{2+} и неоднородным уширением соответствующих полос люминесценции и возбуждения. Установлено, что относительная интенсивность полосы возбуждения люминесценции Eu^{2+} при 360 нм (переход $4f^7 \rightarrow 4f^65d$ в ионах Eu^{2+}) уменьшается с увеличением концентрации ионов Ce^{3+} . Это наблюдение приписывается фотоионизации ионов Eu^{2+} , захвату электронов на дефектах и последующей безызлучательной релаксации в основное состояние.

Ключевые слова: Люминофоры, Люминесценция, Eu^{2+} , Перенос энергии.**REFERENCES**

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