

Luminescence behavior of Eu^{3+} in $\text{CaSiO}_3:\text{Eu}^{3+}(\text{Bi}^{3+})$ and $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}(\text{Bi}^{3+})$

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Abstract

$\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ were synthesized by the sol–gel method, and their structure and luminescence characteristics were investigated. The XRD results showed that the symmetry of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ structure, which is similar to the non-close-packing orthogonal structure of K_2SiO_4 is higher than that of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ perovskite structure belonging to the monoclinic system. From the excitation spectra of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, it can be seen that the main peaks located at 267 nm, 383 nm, 395 nm, 437 nm, 457 nm and 359 nm, which correspond to the charge transfer band of $\text{Eu}^{3+}-\text{O}^{2-}$, absorption transition of ${}^7\text{F}_{0.1}-{}^5\text{G}_1$, ${}^7\text{F}_{0.1}-{}^5\text{L}_6$, ${}^7\text{F}_1-{}^5\text{D}_3$ and ${}^7\text{F}_{0.1}-{}^5\text{D}_2$ of Eu^{3+} ions and ${}^3\text{P}_1-{}^1\text{S}_0$ of Bi^{3+} ions, respectively. When the $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ samples were excited with wavelength of 359 nm, the emission intensity of electronic dipole transition at 609 nm originated from ${}^5\text{D}_0-{}^7\text{F}_2$ of Eu^{3+} ions was stronger than magnetic dipole transition at 587 nm originated from ${}^5\text{D}_0-{}^7\text{F}_1$ of Eu^{3+} ions mainly due to the lower symmetry and the distortion of the structure. However, the opposite situation appeared in the emission spectrum of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$. In addition, the intensity comparison of each emission peaks between the emission spectra of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ showed that the energy transfer efficiency between Bi^{3+} ions and Eu^{3+} ions in $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ is apparently higher than that in $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$.

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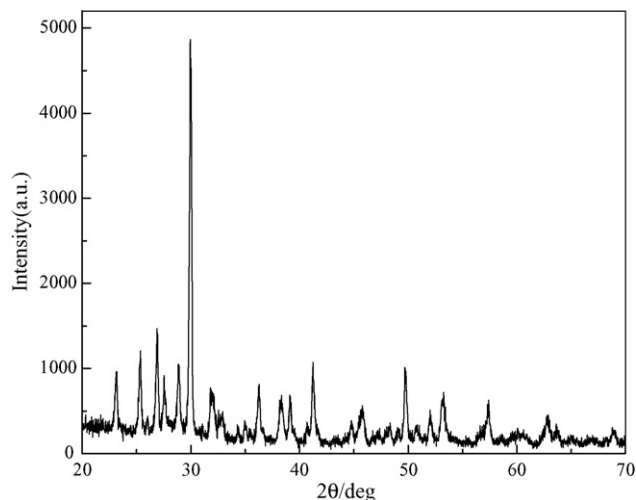
Keywords: Rare earth alloys and compounds; Sol–gel processes; Optical properties; Optical spectroscopy

1. Introduction

A study of the luminescence of rare earth solid state materials is an interesting research field in both rare earth physics and chemistry. Europium is a special element in the lanthanides: besides the common properties of rare earth elements, it exhibits the property of valence fluctuation, i.e., the valence state is divalent or trivalent, and it has different luminescence characteristics due to the different valences. The electron configuration of Eu^{3+} ions is $4f^6$. The red light emission of Eu^{3+} ions has been comprehensively applied in color television, panel display, cathode ray tube and many fluorescent powders of three primary colors [1–3]. Thus, it is necessary to study the luminescence

characteristic of Eu^{3+} ions for application. It is well-known that optical properties of rare earth luminescence materials are greatly influenced by the matrix. According to the free rare earth ion, electric dipole transitions between 4f energy levels are forbidden, which is the result of parity selection rules. However, when the rare earth ions are located in the lattices, parity selection rules is possibly out of work and then electric dipole transitions between 4f energy levels appear. It has been reported that Eu^{3+} ions exhibit favorable luminescent behavior in many matrixes [4–8]. In order to obviously show the effect of matrixes on the Eu^{3+} , Sr_2SiO_4 and CaSiO_3 were chosen as the matrixes of Eu^{3+} , and Bi^{3+} played the role of sensitizer ions. The samples of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ were synthesized by the sol–gel method. The structure and luminescence characteristics of the samples were investigated, and the relationship between the structure and luminescence properties was also discussed in this article.

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Fig. 1. XRD pattern of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$.

2. Experimental

The initial materials in this experiment included Eu_2O_3 (A.R.), ethanoic acid (A.R.), $\text{Bi}(\text{NO}_3)_3$ (A.R.), $\text{Ca}(\text{NO}_3)_2$ (A.R.) [$\text{Sr}(\text{NO}_3)_2$ (A.R.)], $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) (A.R.), HNO_3 (A.R.) and $\text{C}_2\text{H}_5\text{OH}$ (A.R.). The appropriate stoichiometric proportions of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ or $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ were weighed and their solution were mixed. The pure $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ were synthesized under the following conditions: the mol ratio of acetic acid and TEOS was 0.1; the bulk factor of H_2O and TEOS was 0.5; the mixed solution were laid in water bath at 65°C ; the precursors were presintered at 700°C for 3 h and sintered at 900°C for 4 h.

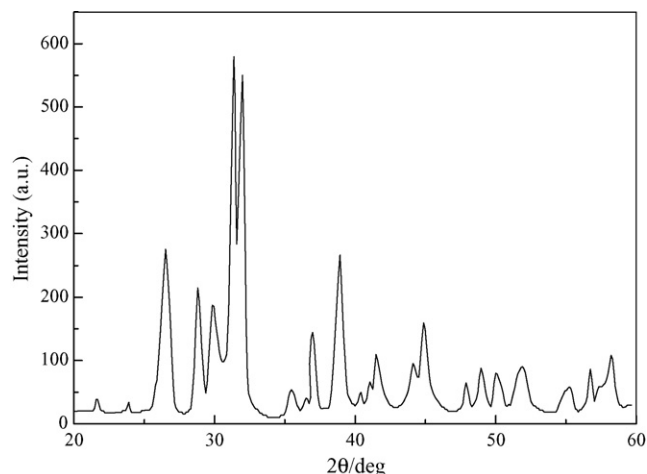
The structures of above samples were determined by a D/max-IIIc copper rotating-anode X-ray diffractometer. The emission and excitation spectra measurements were performed on the PE LS55 spectrometer.

3. Results and discussion

3.1. Crystal structure

3.1.1. Crystal structure of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$

The XRD pattern of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ was shown in Fig. 1 indicated that $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ sample has perovskite structure belonging to monoclinic system, and its space group is $P2_1/a$. Calculated by the XRD data, the sizes of the samples sintered at 900°C are around $2\ \mu\text{m}$. In the unit cell of perovskite CaSiO_3 , Si^{4+} ions locate at the center of monoclinic cube; O^{2-} ions locate at the six face centers of monoclinic cube; and Ca^{2+} ions located at the eight apex angles of cube. Octahedrons are formed by the Si^{4+} ions and their nearest neighbor O^{2-} ions, and their coordination number is six. Icosahedrons are constructed by Ca^{2+} ions and their nearest neighbor O^{2-} ions, and their coordination number is 12. The coordination numbers between Si^{4+} ions and Ca^{2+} ions are both eight. Because the doping content was low, the crystal structure did not change after doping the Eu^{3+} ions and Bi^{3+} ions. For the luminescence material of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, Eu^{3+} acts as the luminescence center and Bi^{3+} plays the role of sensitizer ions, which have been reported in our previous articles [9].

Fig. 2. XRD pattern of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$.

3.1.2. Crystal structure of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$

The sample of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ has the same structure with Sr_2SiO_4 (Fig. 2), which is similar to the non-close-packing orthogonal structure of K_2SiO_4 [10]. In this structure, Sr^{2+} ions locate at two kinds of unequivalent lattice sites, and their coordination numbers are 9 and 10, respectively. O^{2-} ions locate at three kinds of unequivalent lattice sites, and its space group is D_{2h} . Si^{4+} ions locate at the center of the oxygen tetrahedron. Therefore, it can be seen that the structure of Sr_2SiO_4 has the higher symmetry compared with that of CaSiO_3 . When the Eu^{3+} and Bi^{3+} are introduced into the Sr_2SiO_4 structure, they take the place of the Sr^{2+} . The crystal structure experienced no changes due to the low doping content of the Eu^{3+} ions and Bi^{3+} ions, which can be seen from Fig. 2. For the luminescence material of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, Eu^{3+} acts as the luminescence center and Bi^{3+} plays the role of sensitizer ions, which have been reported in our previous articles [10].

3.2. Luminescence characteristics

3.2.1. Excitation spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$

Excitation spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ were shown in Fig. 3. The monitoring wavelengths were 587 nm for $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and 609 nm for $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, respectively. From the excitation spectrum of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, Fig. 3(a), it can be seen that the main peaks located at 267 nm, 359 nm, 383 nm, 395 nm, 437 nm and 457 nm. The excitation peak of 267 nm corresponded to the charge transfer band of $\text{Eu}^{3+}-\text{O}^{2-}$, which was caused by the electrons transfer from 2p orbits of O^{2-} ions to 4f shells of Eu^{3+} ions. The excitation peak of 383 nm, 395 nm, 437 nm and 457 nm, respectively corresponded to the absorption transition of $^7\text{F}_{0,1}-^5\text{G}_J$, $^7\text{F}_{0,1}-^5\text{L}_6$, $^7\text{F}_1-^5\text{D}_3$ and $^7\text{F}_{0,1}-^5\text{D}_2$ of Eu^{3+} ions, in which the luminescent intensity of 395 nm was the strongest. In addition, there was another excitation peak located at 359 nm, which originated from $^1\text{S}_0-^3\text{P}_1$ of Bi^{3+} ions.

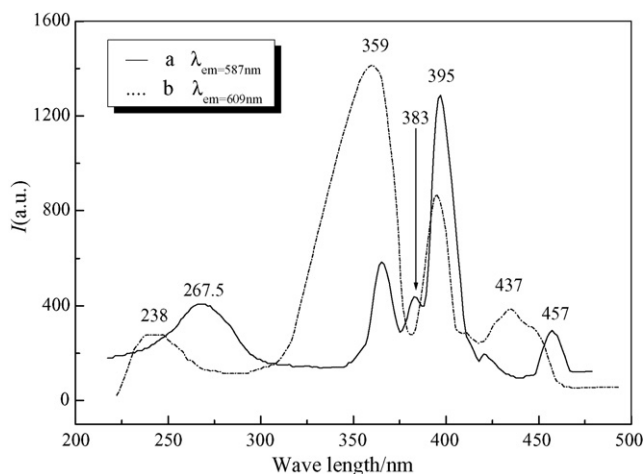


Fig. 3. Excitation spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$. (a) $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ (monitoring wavelength 587 nm) and (b) $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ (monitoring wavelength 609).

Compared with the excitation spectrum of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, the peaks located at 359 nm and 395 nm in the spectrum of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ (Fig. 3(a)) were almost at their original position. However, it can be seen that a red shift of the charge transfer band of $\text{Eu}^{3+}-\text{O}^{2-}$ appeared in the Fig. 3. The corresponding peak of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ shifted to the red side for about 30 nm. The reason for the red shift is that the electronegative difference between Eu^{3+} and O^{2-} in Sr_2SiO_4 is weaker than that in CaSiO_3 due to the stronger covalent characteristic of Sr_2SiO_4 . As a result, the electron transition energy between Eu^{3+} and O^{2-} decreases. That is to say, the electron of O^{2-} is prone to transfer to Eu^{3+} near them. Therefore, the charge transfer band of $\text{Eu}^{3+}-\text{O}^{2-}$ in the excitation spectrum of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ red shifted for about 30 nm.

It also can be seen that the peak located at 359 nm has the strongest intensity in Fig. 3. So the wavelength of 359 nm was chosen to detect the emission spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$.

3.2.2. Emission spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$

Emission spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ were shown in Fig. 4 with the excitation wavelength of 359 nm. When the samples were excited with wavelength of 359 nm, there were three emission peaks in the emission spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, i.e. 398 nm, 587 nm and 609 nm, originated from transition of $^3\text{P}_1-^1\text{S}_0$ of Bi^{3+} ions, $^5\text{D}_0-^7\text{F}_1$ and $^5\text{D}_0-^7\text{F}_2$ of Eu^{3+} ions, respectively.

$^5\text{D}_0-^7\text{F}_2$ of Eu^{3+} ions was forced electronic dipole transition and $^5\text{D}_0-^7\text{F}_1$ of Eu^{3+} ions was magnetic dipole transition. In particular, forced electronic dipole transition originated from $^5\text{D}_0-^7\text{F}_2$ of Eu^{3+} ions only appears when Eu^{3+} ions locates in non-reversion center lattices, and magnetic dipole transition originated from $^5\text{D}_0-^7\text{F}_1$ of Eu^{3+} ions only appears when Eu^{3+} ions locates in reversion center lattices. So the ratio

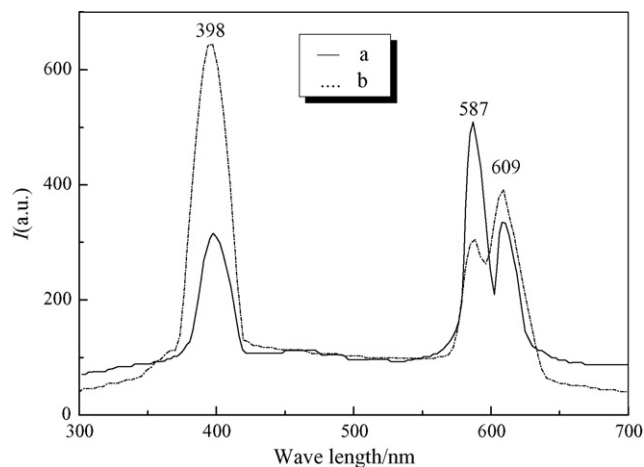


Fig. 4. Emission spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$. (a) $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and (b) $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$.

of emission intensity of these two peaks directly showed the symmetry of Eu^{3+} ions in crystal lattices [11,12]. According to Fig. 4(a), the emission intensity of the peak located at 587 nm was stronger than that at 609 nm. So it can be concluded that more Eu^{3+} ions located in reversion center lattices of the $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ structure. However, the opposite situation can be seen in the Fig. 4(b), which shows more Eu^{3+} ions located in non-reversion center lattices of the $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$. It is, may be, explained by the following two actions. According to the structure of CaSiO_3 and Sr_2SiO_4 , the Eu^{3+} and Bi^{3+} ions replaced Ca^{2+} or Sr^{2+} with the different valance, which resulted in the crystal lattice distortion after the doping process. On the other hand, the symmetry of Ca^{2+} in CaSiO_3 crystal structure was lower than that of Sr^{2+} ions in Sr_2SiO_4 crystal structure. Under the action of these two factors, Eu^{3+} ions deviated from symmetry center, and the deviation degree was higher than that in Sr_2SiO_4 . Therefore, the parity-forbidden transition of $4f-4f$ was mostly released in CaSiO_3 . As a result, the emission intensity of electronic dipole transition at 609 nm originated from $^5\text{D}_0-^7\text{F}_2$ of Eu^{3+} ions was stronger than magnetic dipole transition at 587 nm originated from $^5\text{D}_0-^7\text{F}_1$ of Eu^{3+} ions in CaSiO_3 crystal.

Compared with the emission intensity of $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, the emission intensity of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ located at 398 nm is about 50% lower, the emission intensity of the peak located at 587 nm was obviously enhanced, and the emission intensity of the peak located at 609 nm decreased appreciably. These results showed that Bi^{3+} ions transferred more energy to Eu^{3+} ions in $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ than that in $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$. That is to say, the energy transfer efficiency between Bi^{3+} ions and Eu^{3+} ions in $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ is apparently higher than that in $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$.

4. Conclusions

In summary, the luminescence characteristics of Eu^{3+} ions, such as emission intensity and efficiency, are strongly influenced by the structure of matrices. Through the investigation of the

excitation and emission spectra of $\text{Sr}_2\text{SiO}_4:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$ and $\text{CaSiO}_3:\text{Eu}_{0.08}^{3+}\text{Bi}_{0.002}^{3+}$, it can be concluded that the matrix of Sr_2SiO_4 with higher symmetry structure is more propitious to the luminescence characteristics of Eu^{3+} ions.

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