

# Photo and electroluminescence from terbium doped zinc sulfide films deposited by spray pyrolysis

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Undoped, silver doped and silver-terbium doped zinc sulfide photoluminescent thin films have been prepared by the spray pyrolysis technique. The crystalline structure of the deposited films is hexagonal wurzite, in all cases. The films have a preferential growth with the (0 0 2) direction perpendicular to the surface of the substrate. In general, the relative chemical compositions show that the films are formed by a zinc rich ZnS material. The photoluminescent excitation measurements are in agreement with the optical transmission results indicating that the excitation mechanism is related to electron–hole pair generation across the ZnS band gap. The photoluminescent spectra show the typical bands associated with the transition from the  $^5D_4$  level to the  $^7F_6$ ,  $^7F_5$ ,  $^7F_4$  and  $^7F_3$  levels of the  $Tb^{3+}$  ions. The emission spectra for the undoped and silver doped films show the well known self-activated emission, centered at 460 and 490 nm, respectively. The dependence of the emission intensity on the temperature shows an energy activation of 0.1 eV for competitive non-radiative transitions. Electroluminescent devices using silver-terbium doped zinc sulfide films as active layer show emission spectra similar to those observed in photoluminescence measurements but with a reduced intensity.

## 1. Introduction

II–VI semiconductors doped with rare earth ions have been extensively studied for electroluminescent applications [1]. Suitable doping with rare earth ions provides the possibility to have luminescent emission in almost all the visible wavelength range [2]. However, most of them are trivalent, so to dope zinc sulfide (ZnS) the resulting valence mismatch should be removed by co-doping with a charge compensatory element [3]. There are several reports where co-doping with alkaline metals (lithium) [4], noble metals (copper) [5] or halide ions (chlorine and fluorine) [6] have been shown to be successful to obtain the required charge compensation. On the other hand, due to their large ionic radii it is difficult to incorporate these kind of ions (rare earth) as substitutional impurities instead of the cations, mainly in ZnS, without distorting the surrounding crystal structure [7].

Rare earth doped zinc sulfide has been prepared in the form of single crystals [8], powders [9] and thin films prepared by several methods, e.g. electron beam evaporation [10], thermal evaporation [11] and MOCVD [12]. The rare earth impurities have been incorporated during crystal or thin film growth or by post-deposition diffusion [13]. It has been observed that firing of the start material at 1250 °C in a  $N_2$ - $CS_2$  gas stream is necessary to obtain an optimal incorporation of the rare earth impurities [14]. Recently, deposition of rare earth ion doped zinc oxide and tin oxide films by spray

pyrolysis was reported [15], which is considered as a cheaper and easier technique for thin film deposition. There are several reports about deposition of luminescent films prepared by this technique [16–18]. Also, there is a report where the preparation of MISIM type electroluminescent devices is described with the active layer (ZnS:Mn) deposited by spray pyrolysis showing optoelectronic characteristics similar to those reported for the best cases [19]. The spray pyrolysis technique has also been used for deposition of pure zinc sulfide using thiourea complexes [20] or an organometallic zinc compound [21], but for other non-luminescent applications.

In this work we report the photoluminescent characteristics of silver-terbium doped, hereafter terbium doped, zinc sulfide films prepared by the spray pyrolysis process using a pneumatic nozzle, without any post-deposition firing or annealing process. It should be noted that silver was used as a charge compensatory co-dopant, we also show that the application of these films as the active layer in the preparation of MISIM electroluminescent devices is possible.

## 2. Experimental

The films were deposited by the spray pyrolysis technique using a pneumatic nozzle. The apparatus used for depositions has been reported elsewhere [22].

The starting solution was 0.1 M of zinc acetate and *n-n* dimethylthiourea dissolved in a mixture of 4 parts of deionized water and 1 part of isopropyl alcohol. Glacial acetic acid was added to obtain a complete dissolution of the starting materials and to adjust the pH of the solution to a value of 2.5. Doping of the start solution was achieved by adding  $\text{AgNO}_3$  and  $\text{TbCl}_3$  in a concentration of 10 at % for both materials. Undoped zinc sulfide films, silver doped zinc sulfide films and terbium doped ZnS films, using silver as a co-dopant in the latter case, were made at different substrate temperatures within the range from 450 to 570 °C in 20 °C steps. Filtered air was used as the carrier gas with a flow rate of 10 l min<sup>-1</sup> which was kept constant. The solution flow rate was kept constant at 12 ml min<sup>-1</sup>. The deposition time was 10 min, in all cases. The substrate–nozzle distance was 30 cm. The substrates were pyrex glass slices of 1 × 2.5 cm<sup>2</sup>. The substrate heater was a molten tin bath and the back surfaces of the substrates, in contact with this bath, were covered with a graphite film to obtain a uniform temperature and to avoid tin contamination of the prepared samples.

Films deposited, for all conditions, were characterized by means of X-ray diffraction measurements with a Siemens D500 X-ray diffractometer. For selected samples, relative chemical composition measurements were performed by energy dispersive spectroscopy (EDS) using an Oxford Link Pentafet System. The thickness of the deposited films was measured with a Dektac IIA profilometer. Optical transmission spectra, with air in the reference beam, were obtained with a double beam Shimadzu 260 UV-Vis spectrophotometer in the wavelength range from 250 to 900 nm. The photoluminescence characteristics, excitation and emission spectra, were obtained with a Spex Fluoromax spectrofluorometer sensitive in the range from 200 to 850 nm. The excitation light was produced with a xenon lamp. The dependence of the emission intensity on temperature, during measurement, was analysed in the range from 140 to 290 K with the sample placed on a cold finger at a pressure of 0.133 Pa. This system has quartz windows and two optical fibers were coupled to the spectrofluorometer, one for excitation and the other to collect the emitted light. To evaluate the possible application of these films to the preparation of MISIM type electroluminescent devices, these were prepared using a glass substrate coated with a transparent conductive contact of antimony doped tin oxide deposited by r.f. sputtering with a sheet resistance of 20 Ω/□. The insulating films were of aluminium oxide with a thickness of 200 nm prepared by ultrasonic spray pyrolysis [23]. The ZnS:Tb,Ag active layer was deposited at a substrate temperature of 510 °C with a thickness of about 500 nm.

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for terbium doped zinc sulfide films deposited at substrate temperatures of 510 °C and 570 °C. It can be observed that the crystalline structure of the film deposited at 510 °C is wurzite hexagonal. The magnitude of the peak associated with the reflection on the (0 0 2) family planes indicates

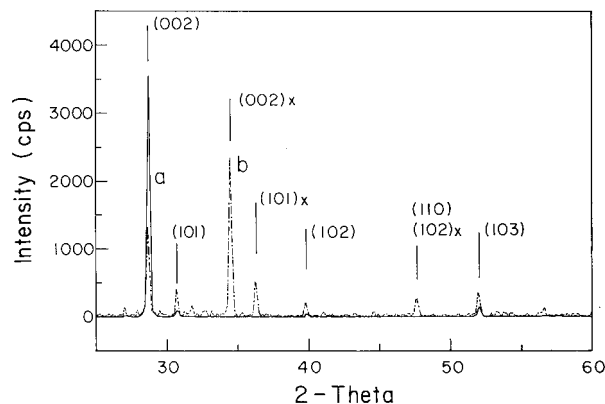


Figure 1 X-ray diffraction spectra for ZnS:Tb,Ag films deposited by spray pyrolysis at substrate temperatures of (a) 510(-) and (b) 570 (-) °C.

preferential growth of the crystalline structure with the (0 0 2) plane parallel to the surface of the substrate. On the other hand, this spectrum shows several small features associated with reflection on other families of crystalline planes. The undoped samples and the silver doped samples have the same crystalline structure with preferential growth with the (0 0 2) planes parallel to the surface of the substrate. It can be inferred from this that the incorporation of Tb and Ag atoms does not strongly affect the crystalline structure of the host material. Using the Scherrer expression it was possible to calculate the grain size of the crystallites resulting in a value of 44 nm, which is of the same order of magnitude for all films deposited at the same  $T_s$ . The X-ray spectra for films deposited at substrate temperatures lower than 570 °C, show that the deposited films have the wurzite crystalline structure, meanwhile the X-ray spectrum for the film deposited at the highest  $T_s$  used (570 °C), Fig. 1b, shows that the deposited material is a mixture of separated phases of zinc sulfide and zinc oxide, the latter has hexagonal crystalline structure (zincite) with the same space group  $P6_3mc$ . The growth of this ZnO phase is explained by the high substrate temperature used in this case. At such a high substrate temperature there is a competition between the zinc oxide and the zinc sulfide growth.

There are several reports which show the transformation of metallic sulfides to metallic oxides by annealing at atmospheric pressure at relatively high temperature. These results indicate that zinc oxide growth takes place for depositions at higher substrate temperatures. However, the zinc oxide phase also shows a preferential growth with the *c-axis* perpendicular to the surface of the substrate. The main result indicates that when using substrates temperatures lower than 570 °C, it is possible to deposit terbium doped zinc sulfide films having the wurzite hexagonal crystalline structure co-doping the deposited material with silver impurities, for charge compensation.

Table I shows the result of the relative chemical composition analyses for selected samples. It is observed that in all cases the zinc atomic per cent is higher than the sulfur atomic per cent. This trend is commonly observed in metallic oxides and sulfides prepared by the spray pyrolysis process [22]. For the silver doped sample the amount of silver incorporated in the deposited films is

TABLE I Relative chemical composition of zinc sulfide films deposited by spray pyrolysis

Sample	$T_s$ (°C)	Zn(at %)	S(at %)	Ag(at %)	Tb(at%)
Undoped	510	58	42	–	–
Silver doped	510	59	38	3	–
Terbium doped	450	56	41	1	2
Terbium doped	510	59	39	1	1

higher than in the terbium doped films. In the latter case, the silver and terbium incorporated concentrations have similar values. The absence of chlorine indicates that atomic terbium is incorporated in the deposited films. There are several reports in which doping the spraying solution with chlorides results in the incorporation of atomic chlorine or as a molecular impurity [24,25]. However, in those cases the depositions were made at lower substrate temperatures than that used in the present work. In general, when chlorides are used as start materials, the chlorine concentration incorporated in the deposited films decreases as the substrate temperature increases. This is an important result because chlorine doped zinc sulfide shows a blue photoluminescent emission, called self-activated emission normally observed in zinc sulfide, which is due to a luminescent center formed by the association at nearest neighbor sites of a doubly ionized zinc acceptor vacancy defect and the ionized impurity donor; this complex is written as  $(V_{Zn}-Cl_s)^-$  with an effective negative charge. In the present work, therefore, the self-activated emission due to chlorine impurities in ZnS should be neglected. However, it is also known that silver impurities alone, or in combination with other impurities (such as Cl), produce a specific luminescent band characteristic of the activator, in the present case the silver atoms. This band is also called the self-activated luminescence emission band.

Fig. 2 shows the optical transmission spectra in the wavelength range from 250 to 900 nm, for the undoped (2a), silver doped (2b) and terbium doped (2c) zinc sulfide films deposited at a substrate temperature of 510 °C. In the two latter cases, the absorption edge occurs at a wavelength of about 340 nm, which is associated with absorption corresponding to the energy band gap of

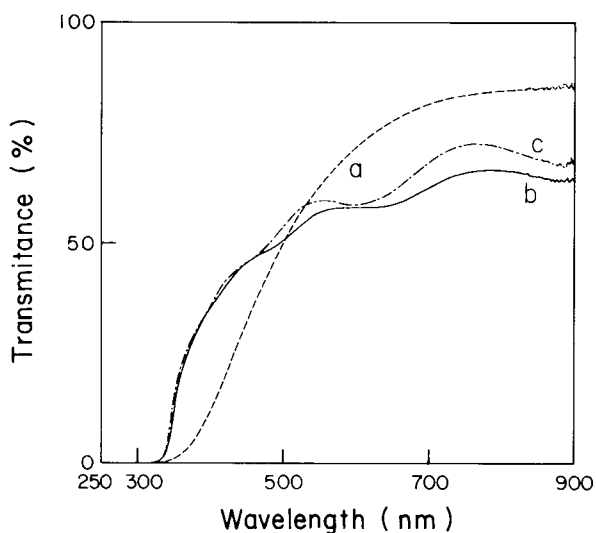


Figure 2 Optical transmission spectra for (a) undoped, (b) silver doped and (c) terbium doped zinc sulfide films prepared at 510 °C.

the zinc sulfide ( $E_g \cong 3.5$  eV), giving rise to the generation of electron-hole pairs. Nevertheless, the absorption edge of the undoped sample shows a small shift toward longer wavelengths. This is associated with the different thickness of the deposited films, since the thickness of the silver doped and terbium doped samples are similar (450 nm), meanwhile the thickness of the undoped sample is of the order of 900 nm. On the other hand, Fig. 3 shows the photoluminescent excitation spectrum for the terbium doped zinc sulfide sample deposited at 510 °C. This spectrum has a peak located at about 340 nm, which corresponds to photon absorption through the energy band gap, in agreement with the optical transmission spectra. These results might indicate that the main contribution to the excitation spectrum is due to the absorption through the energy band gap.

Silver doped zinc sulfide films deposited at substrate temperatures higher than 490 °C show a broad band photoluminescent emission, using an excitation wavelength of 340 nm, centered at about 490 nm, as is shown in Fig. 4a. It should be remarked that the intensity of this emission is of the same order of magnitude as that observed for the terbium doped zinc sulfide films. It is well known that silver impurities incorporated in ZnS show blue photoluminescent emission located at about 490 nm or at 630 nm, depending on the incorporation of other kinds of impurities and annealing temperature. In the present case, if silver is incorporated alone the observed self-activated emission is associated with a complex luminescent center like  $(V_{Zn}-Ag_{Zn})^-$ . Fig. 4b shows the photoluminescent spectrum for an undoped zinc sulfide film deposited at  $T_s = 510$  °C. This spectrum is formed for a wide band centered at about 460 nm, which corresponds to the self-activated emission associated with a complex luminescent center. This self-activated emission is observed in ZnS when it is doped with certain metallic impurities, called activators, such

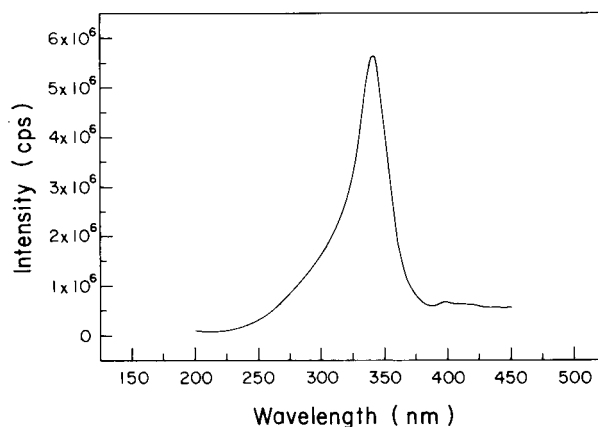


Figure 3 Photoluminescence excitation spectrum for zinc sulfide films. The peak corresponds to electron-hole pair generation.

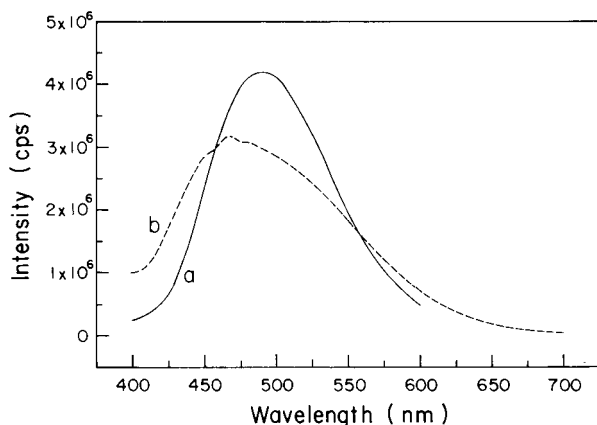


Figure 4 Photoluminescence spectra from (a) silver doped (—) and (b) undoped (---) doped zinc sulfide films prepared at  $T_s = 510^\circ\text{C}$  for an excitation wavelength of 340 nm.

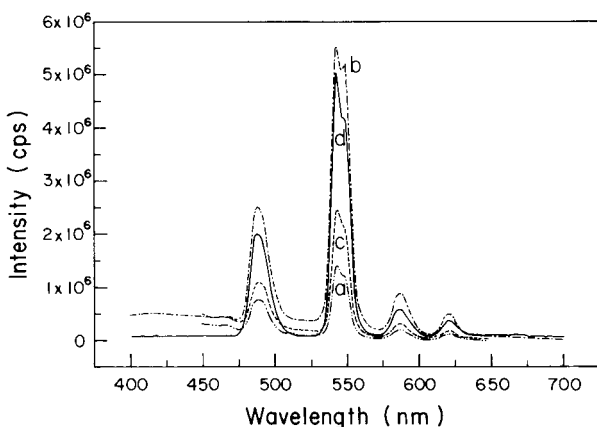


Figure 5 Photoluminescent emission spectra from terbium doped zinc sulfide films deposited at (a) 470 (---), (b) 510 (---) and (c) 550  $^\circ\text{C}$  (---), using an excitation wavelength of 340 nm. The electroluminescent spectrum (figure d, —) from a MISIM type device with an active layer of ZnS:Tb,Ag prepared at 510  $^\circ\text{C}$  is also shown.

as: Cu, Ag, Au, and with other impurities, called co-activators, such as: Cl, Br, I, Al, Ga, In, etc. Probably, in the present case, there is an unintentional doping of the deposited films to produce this self-activated emission. It should be remarked that this emission is located at a different wavelength to the emission due to the pyrex glass substrates, which is located at 420 nm.

Fig. 5 shows the photoluminescent emission spectra for terbium doped zinc sulfide films deposited at 470, 510 and 550  $^\circ\text{C}$ , for films with similar thickness. In all cases the characteristic emissions from the  $\text{Tb}^{3+}$  ion located at 487, 542, 585 and 618 nm are observed. These emissions correspond to the transition from the  $^5\text{D}_4$  level to the  $^7\text{F}_6$ ,  $^7\text{F}_5$ ,  $^7\text{F}_4$  and  $^7\text{F}_3$  levels, respectively. These results indicate that the terbium impurities are being incorporated in a suitable ionization state ( $\text{Tb}^{3+}$ ) to produce the typical emission spectra of that trivalent rare earth ion. The highest peak in the emission spectra is a band located at about 542 nm and shows a double contribution. This double contribution is well defined for samples deposited at low temperature, meanwhile, for samples deposited at high temperature the contribution on the side of longer wavelength decreases in comparison with that at 542 nm. This behavior is explained taking into account that when a trivalent rare earth ion is placed in a host material the spherical symmetry of the free ion is destroyed, and as a

result the spectroscopic levels split under the influence of the asymmetric electric field produced by other impurities or other defects in the crystal [26]. If the magnitude of splitting is considered as an indication of the quality of the crystalline host, then the absence of splitting in the spectra, for samples deposited at higher substrate temperature ( $< 570^\circ\text{C}$ ) indicates a high quality crystalline host. This result is in agreement with the results of the X-ray diffraction characterization. The emission intensity is of the same order of magnitude for samples deposited in the substrate temperature range from 450 to 550  $^\circ\text{C}$ , meanwhile, for samples deposited at higher substrate temperatures (570  $^\circ\text{C}$ ) the overall intensity decreases. This decrease is associated with the damage effect on the zinc sulfide crystallinity caused by the growth of the zinc oxide phase at that substrate temperature, as observed from the X-ray measurements. It should be noted that terbium doped zinc oxide films deposited by spray pyrolysis using the same deposition conditions do not show any photoluminescent emission. However, although the general form of these spectra is similar, it appears that all these spectra are composed of the emissions from two different centers, one contribution, the main one, associated with the typical emission from the terbium ions and the other very extended with a low intensity, which can be associated with silver doping giving rise to the self-activated emission observed in zinc sulfide. The absence of a marked blue band emission indicates that the majority of the silver atoms are acting as charge compensators resulting in an increased intensity due to the terbium ions.

Fig. 6 shows the dependence on temperature, during measurement, in the range from 140 to 290 K, of the emission intensity for the 542 nm wavelength, using an excitation wavelength of 341 nm, for a terbium doped zinc sulfide film deposited at 510  $^\circ\text{C}$ . This curve shows

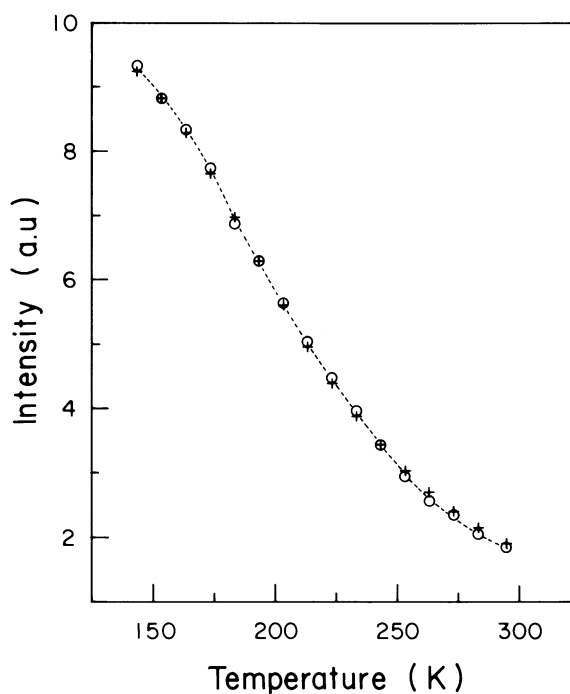


Figure 6 Dependence of the 542 nm wavelength emitted intensity on the temperature, during measurement. The dashed line (open circles) is the best fit to the experimental data.

that the photoluminescent intensity at 140 K is higher than that at room temperature by a factor of about 5. The decreasing behavior is described by the relation.

$$I(T) = I_o[1 + C \exp(-E_a/kT)]^{-1} \quad (1)$$

The dashed line (or open circles) corresponds to the best fit to the experimental data, where  $I_o = 10.35$  and the activation energy  $E_a$  has the value of 0.1 eV. The constant  $C$  has a value of 160. The calculated activation energy value of the non-radiative transitions, due to the crossover of the energy potential curves of the excited and ground states is higher than values obtained for photoluminescent centers associated with localized states generated by other kinds of incorporated impurities, where the vibronic spectrum of the lattice of the host material has a strong effect. It is clear that the variation of the intensity of the emitted light could be considered small, which is explained because the rare earth sites form stable complexes and there is a slight influence from the host crystal environment and the emitted light is associated with intra-atomic electronic transitions inside the impurities, as is expected for rare earth ions in which the external electronic shell screens the crystal effect on the electronic levels of the ion.

Fig. 5d shows the electroluminescent (EL) spectrum for a device of the MISIM type using a terbium doped zinc sulfide film deposited at 510 °C as the active layer. The EL spectrum, obtained for an a.c. applied voltage  $V_p = 90$  V with a frequency of 15 kHz, shows four peaks associated with the transitions between the intra-atomic electronic levels of the  $Tb^{3+}$  ions, from the  $^5D_4$  level to the  $^7F_6$ ,  $^7F_5$ ,  $^7F_4$  and  $^7F_3$  levels. However, in the EL case the intensity of the emission is lower than that obtained in photoluminescence. This can be explained by taking into account that for EL devices the optimum rare earth concentration is higher than that used for bulk crystals showing photoluminescent emission.

#### 4. Conclusions

The photoluminescent characteristics of undoped, silver doped and terbium doped zinc sulfide films deposited by spray pyrolysis have been studied. All deposited films show the wurzite hexagonal crystalline structure, with the (0 0 2) direction perpendicular to the surface of the substrate. From the optical transmission and the excitation spectra, the photoluminescent emission is primarily excited by the generation of electron-hole pairs across the energy band gap of the zinc sulfide, with a maximum optical absorption at 341 nm. The photoluminescent emission spectra of the undoped and silver doped samples show the well known self-activated emission observed in ZnS with maxima located at 460 and 490 nm, respectively. Meanwhile the emission spectra for the terbium doped zinc sulfide films show the typical photoluminescent emissions associated with the electronic transitions from the  $^5D_4$  level to the  $^7F_6$ ,  $^7F_5$ ,  $^7F_4$  and  $^7F_3$  levels of the  $Tb^{3+}$  ions. The highest intensity is observed for the sample prepared at a substrate temperature of 510 °C. The activation energy of the non-radiative transitions has a value of 0.1 eV. The electroluminescent emission spectra is similar to that of

photoluminescent emission, although less intense. The results obtained indicate that it is necessary to make depositions with different concentrations of silver nitrate and terbium chloride added to the spraying solution to obtain the best doping concentration, resulting in the highest photoluminescent emission.

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