

Green $\text{EuAlO}_3:\text{Eu}^{2+}$ nanophosphor for applications in WLEDs



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ABSTRACT

Green-emitting aluminate nanophosphors fabricated by a pressure-assisted combustion synthesis ($P_0 = 1.4, 2.8$ and 3.4 MPa) and annealed in pure H_2 is reported. The XRD analysis indicates the formation of the EuAlO_3 orthorhombic phase. Transmission electron microscopy (TEM) shows coalesced irregular grains with lengths in the range of 35–140 nm. In addition, the nanophosphor synthesized at an initial pressure of 3.4 MPa produced the highest green luminescence centered at 530 nm, which was associated to $4f^7-4f^65d^1$ allowed transitions of the Eu^{2+} located into the $\text{EuAlO}_3:\text{Eu}^{2+}$ compound. A weak red emission peak corresponding to Eu^{3+} was also observed by cathodoluminescence. The CIE coordinates for green emission are $x = 0.2613$ and $y = 0.3892$, and the luminance produced from nanophosphors when they are excited with a commercial UV-396 nm LED ($8.0 \mu\text{W}$) was $285 \pm 4.3 \text{ Cd/m}^2$.

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1. Introduction

White light-emitting diodes (WLEDs) have attracted a lot of attention as an option for the next generation of lighting sources due to their potential to reduce the consumption of energy and to decrease pollution effects [1,2]. The common commercial WLEDs design typically involves a yellow phosphor excited with blue light coming from an InGaN-chip [2,3]. The combination of blue and yellow light produces white light of low color rendering index (CRI) due to a red emission deficiency [2], this configuration also show optical instability due to the halo phenomenon which has been observed under different output current [4]. To solve this problem, tricolor WLEDs based on red, green and blue phosphors has been proposed [1,5]. In the tricolor WLED design, three phosphors are dispersed on a transparent silicone, encapsulated and coupled with a blue or UV chip which excites the phosphors. The tricolor blend emission creates white light with high CRI ~ 90 [6]. For this reason, the development and optimization of red, green and blue phosphors is a challenge for materials science. Further, phosphor materials can also be used in field emission displays (FEDs) or in solid state illumination devices. During the last decades, the research on phosphors has been focused in the use of rare earths (REs) as dopants because they favor the fabrication of materials with good chemical and thermal stability [7]. Trivalent and divalent europium ions are usually used to produce the red and green emissions, respectively. The green luminescence can be

obtained particularly, when the Eu^{2+} ions are doping crystalline host lattices based on aluminates and, the green emission is attributed to the well known $4f^7-4f^65d^1$ allowed transition of the Eu^{2+} ions [8,9]. Oxide materials doped with Eu^{2+} and with strong green emission is desirable for the tricolor WLEDs because they are crystalline and show good chemical stability when they are integrated in WLEDs [7]. It has been demonstrated that the $\text{EuAlO}_3:\text{Eu}^{2+}$ lattice shows green emission under near UV excitation and it can be used as the green component in a tricolor WLEDs [10,11]. Some works reported the synthesis of orthorhombic $\text{EuAlO}_3:\text{Eu}^{2+}$ by the combustion synthesis starting from low atomic concentrations of Eu ($x = 5.0\text{--}20.0$ at.%), i.e., the starting materials have a non stoichiometric formula, and post-annealing in NH_3 or N_2 [10,11]. However, these methods have the disadvantages of long post-annealing time (>3 h) and the use of high temperatures (above 1100°C). To the best of our knowledge, the annealing in pure H_2 (which has a higher reduction capacity than ammonia) has not been explored to produce the $\text{EuAlO}_3:\text{Eu}^{2+}$. Besides as-synthesized powders starting from a ratio of Al/Eu 1:1 which is a high Eu content has not been explored. Thus, the aim of this work is: (1) to demonstrate that green-emitting $\text{EuAlO}_3:\text{Eu}^{2+}$ nanophosphors can be synthesized using a pressure assisted combustion synthesis and (2) to demonstrate that those nanophosphors could be useful for applications in WLEDs.

2. Experimental

Green-emitting nanopowders of europium aluminate $\text{EuAlO}_3:\text{Eu}^{2+}$ were prepared in two steps. In the first step, the as-synthesized

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powders were made through the pressure-assisted combustion synthesis (PACS) method, a detailed description of the method can be found in a previous report [12]. In the second step, the powders were annealed in a reducing atmosphere by using pure hydrogen for 1 h.

2.1. As-synthesized powders

All nitrates were purchased from Reaction, Puratronic, and Alfa Aesar and used without any additional treatment. Europium nitrate [$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ reaction 99.9%] and aluminum nitrate [$\text{Al}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ Puratronic 99.9965%] were dissolved in 25 ml of deionised water in such a way that a 1:1 M ratio of Al/Eu is obtained. Then, hydrazine [N_2H_4 Alfa Aesar 98.5%] was added in the mixture of nitrates. The precursor reaction was adjusted in order to obtain 1.5 g of as-synthesized powder samples. The oxidation fuel ratio (O/F) was 1 to reach the maximum of the heat of combustion [13]. The homogeneous blend of the nitrates and the hydrazine was put into a reactor, and then, it was pressurized with argon gas until the initial pressure P_0 is reached. Later, the temperature is gradually increased from the room temperature to 350 °C. A peak of pressure up to 7 MPa was observed around 290 °C which was the ignition temperature of the combustion synthesis. Three initial pressures using the PACS method were studied with argon gas: $P_0 = 1.4, 2.8$ and 3.4 MPa. As a result of this step europium aluminate powders with the EuAlO_3 phase and the $\text{Eu}(\text{OH})_3$ and the $\text{Eu}(\text{OOH})$ residual phases were obtained.

2.2. Reduction of the powders

The rapid in and rapid out process (RIRO) [10,11] was employed in pure H_2 atmosphere to reduce Eu^{3+} to Eu^{2+} . The as-synthesized powders are rapidly introduced in the hot zone in a tubular pre-heated furnace with a constant flow of reducing gas and maintained there for a short time. After this, the reduced powders were taken out of the hot zone. In our case, the as-synthesized were placed in a quartz crucible inside a tubular furnace and heated at a temperature of 1100 °C under constant flow (flow rate = 10 sccm) of ultra-high purity H_2 . The RIRO technique was applied during 1 h at 1100 °C for all samples. As a result of this step europium aluminate composed of mainly $\text{EuAlO}_3 \cdot \text{Eu}^{2+}$ and by the secondary phase of EuAl_2O_4 powders with strong green emission are obtained.

2.3. Characterization

All the powder samples were characterized by X-ray diffraction (XRD) in a Philips X'pert diffractometer with Cu $K\alpha$ ($\lambda = 0.15406$ nm) radiation. DRXWin software was used to estimate the percentages of the EuAlO_3 and EuAl_2O_4 phases. The estimation was made as follows: the sum of the areas under the diffraction peaks corresponding to each one of the XRD profiles was calculated. The total area was supposed to be 100%. Consequently, the percentage of each phase detected was calculated by dividing the sum of the area under peaks of the specifically phase EuAlO_3 or EuAl_2O_4 observed in the XRD pattern by the total area of the XRD pattern. Morphology of the as-synthesized and the reduced samples was analyzed by transmission electron microscopy (TEM) with a JEOL 2010 microscope at room temperature using 200 kV of accelerating voltage. Photoluminescence (PL) spectra were collected with a Hitachi FL-4500 spectrofluorometer. The photomultiplier tube was operated at 400 V for all measurements. Cathodoluminescence (CL) measurements were performed with a spectrometer consisting of a monochromator (Oriel MS260i) equipped with a thermoelectrically cooled CCD (Instaspec IV). The spectrometer was coupled through a quartz optical fiber to

an ultra-high vacuum (UHV) CL chamber equipped with a 10 keV electron gun (Kimball Physics). In order to measure the chromaticity coordinates and the luminance of the 3.4 MPa sample, pellets of 6.4 mm in diameter and 2.5 mm in thickness were made by applying 2.5 t of pressure on 270 mg of powder. The chromaticity coordinates and the luminance were taken by using a Konica Minolta CS-2000 spectroradiometer when the samples are irradiated with 380 nm and 396 nm UV-LEDs with a power of 8.0 μW . All measurements were obtained at room temperature.

3. Results and discussion

3.1. Structure and morphology

Fig. 1(a) compares the XRD patterns of the as-synthesized powders produced at different initial pressures from 1.4 to 3.4 MPa as is marked on the graph. The sample with 1.4 MPa of pressure had a mixture of europium hydroxides phases: EuOOH (JCPDS 18–0510), and $\text{Eu}(\text{OH})_3$ (JCPDS 83–2305) which are labeled with \blacktriangle and \bullet symbols on the XRD patterns, respectively. The EuAlO_3 orthorhombic phase (JCPDS 30–0012) was also detected in all samples with different pressures. The XRD pattern of the sample fabricated with 2.8 MPa shows mainly the presence of the EuOOH phase, and a lower content of the $\text{Eu}(\text{OH})_3$ and the EuAlO_3 phases. The reflection peaks observed in the XRD profile for the EuAlO_3 phase showed lower intensity than in the other samples. In contrast, for the 3.4 MPa sample the XRD showed mainly the presence of the EuAlO_3 phase, following the $\text{Eu}(\text{OH})_3$ phase and ultimately the EuOOH phase. In a previous work [10], the combustion synthesis method was used to create the EuAlO_3 as-synthesized powders but in that case no pressure was used and no europium hydroxide phases were obtained. In that work they started from $\text{Al}_2\text{O}_3 \cdot \text{Eu}^{3+}$ where the content of Eu was set at $x = 0.15$ at.% of Eu. In our case, the presence of europium hydroxide phases is related with the high quantity of the Eu used to start the chemical reaction (Al/Eu 1:1).

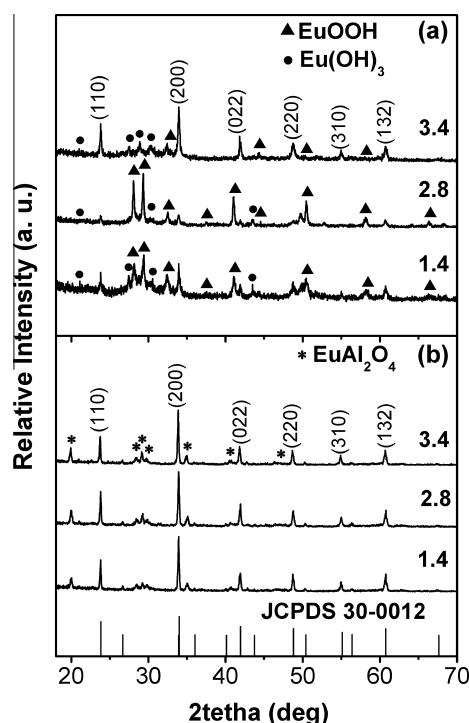


Fig. 1. XRD patterns of the (a) as-synthesized nanopowders and (b) the green-emitting nanopowders. The numbers correspond to the initial pressure in MPa.

Also, the introduction of pressure by the PACS method originated a decrease in the temperature of formation of the $\text{Eu}(\text{OH})_3$ and EuOOH phases. The standard pattern of the EuAlO_3 phase (JCPDS 30-0012) is plotted below the XRD patterns in vertical lines for comparison in Fig. 1(b). The calculated percentages of the EuAlO_3 orthorhombic phase observed for the as-synthesized samples were: 1.4 MPa sample (21.4%), 2.8 MPa sample (13.6%) and 3.4 MPa sample (76%). After the reduction treatment, the XRD analysis of the samples showed only the presence of two phases: mainly the orthorhombic EuAlO_3 and as a secondary phase the monoclinic EuAl_2O_4 , which is in agreement with the standard patterns of the JCPDS 30-0012 and JCPDS 74-0794 cards, respectively. The phase EuAl_2O_4 is identified by the * symbol on the XRD pattern for the sample with 3.4 MPa. The EuAlO_3 phase predominates because: (1) there is an excess of Eu and (2) a high temperature of annealing (1100 °C) was used [10]. In addition, a ratio of Al/Eu 1:1 was used, which is high compared with other reports where the Eu was used in lower amounts [10,11]. The estimated phase composition percentages of the mixture of the $\text{EuAlO}_3\text{:Eu}^{2+}$ and the EuAl_2O_4 were: 1.4 MPa (78%/22%), 2.8 MPa (70%/30%) and 3.4 MPa (72%/28%). The EuAl_2O_4 phase percentage can be increased if the precursors undergo a very long time (10–30 h) of reductive treatment, or by using a higher annealing temperature (1450 °C) under vacuum condition [14,15]. However, these experimental conditions are very expensive for mass production. The europium aluminate $\text{EuAlO}_3\text{:Eu}^{2+}$ powders studied in this work were produced with a very short time of annealing treatment (1 h); therefore this procedure could be an alternative for mass production. Fig. 2(a) shows the morphology of as-synthesized powders with the initial pressure of 3.4 MPa. The morphology showed clusters of coalesced irregular grains with average sizes located in the range of 14–130 nm. Fig. 2(b) shows the morphology of the 3.4 MPa sample after the reduction, the morphology consisted of coalesced grains with sizes in the range of 35–140 nm.

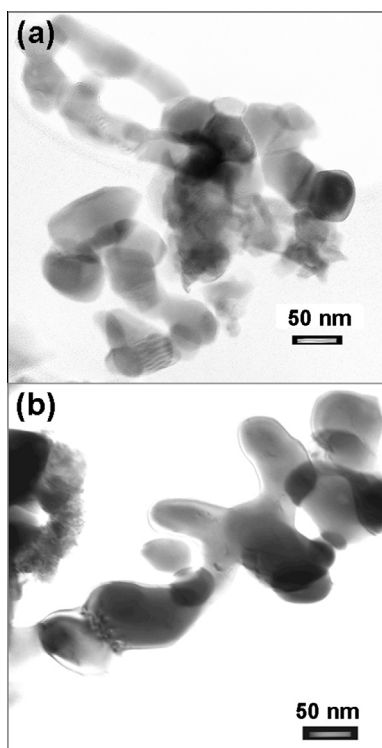


Fig. 2. TEM images of the (a) as-synthesized nanopowders and (b) reduced green nanophosphor produced with the initial pressure of 3.4 MPa.

3.2. Photoluminescence and cathodoluminescence

After the reduction treatment, the europium aluminates $\text{EuAlO}_3\text{:Eu}^{2+}$ showed green emission under near UV excitation. Fig. 3(a) illustrates the excitation spectra, from 250 nm to 500 nm, of the reduced powders produced with three different initial pressures. In all cases a broad band centered at 398 nm appeared (monitored at $\lambda_{\text{em}} = 530$ nm). This band is in agreement with the strong absorption of the Eu^{2+} ion from the $4f^7$ ground state to the $4f^65d^1$ excited state [8]. Moreover, our excitation spectra indicates that the green luminescence comes mainly from the $\text{EuAlO}_3\text{:Eu}^{2+}$, this conclusion is based in the fact that we did not observe the two excitation bands (380 and 460 nm) associated with the EuAl_2O_4 phase as reported by Meister et al. and Tezuka et al. [14,15]. Those groups also demonstrated that the green emission of EuAl_2O_4 is located around 515–520 nm, but in our case, the green emission of the europium aluminates powders is located at 530 nm and that emission is near of the emission at 538 nm of pure $\text{EuAlO}_3\text{:Eu}^{2+}$ observed by Hirata et al. [10]. It is possible that the EuAl_2O_4 compound contributes to green luminescence, however the emission may be overlapped with that of the $\text{EuAlO}_3\text{:Eu}^{2+}$ emission. In the EuAlO_3 compound, the Eu^{2+} ions are located into the same crystallographic A sites occupied by Eu^{3+} ions in the distorted perovskite structure ABO_3 [10]. Fig. 3(b) shows the emission spectra of the three reduced powder samples under excitation at 398 nm. The green emission is attributed to the $4f^7-4f^65d^1$ transition of the Eu^{2+} [8,9]. The reduced powder produced with the pressure of 3.4 MPa showed the highest emission intensity, followed by the 1.4 MPa sample and lastly the 2.8 MPa sample. A photograph of the green emission 3.4 MPa sample irradiated with a 380 nm UV LED is shown as inset in Fig. 3(b).

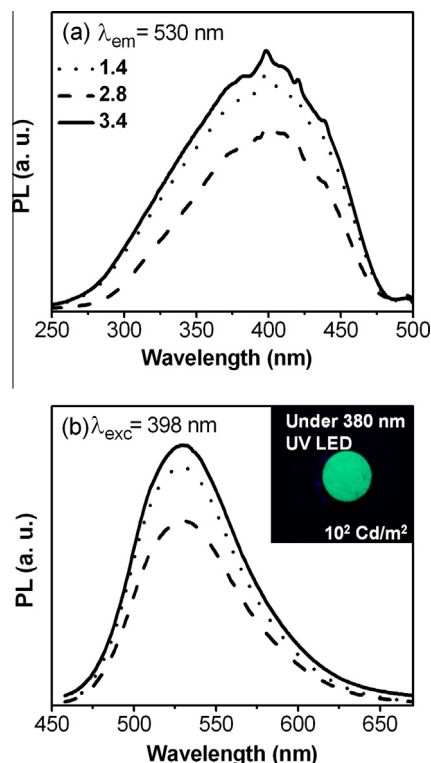


Fig. 3. (a) Excitation and (b) emission spectra of the green-emitting powders taken at room temperature. The numbers correspond to the initial pressure in MPa. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The initial amount of the EuAlO_3 phase (76%) of the 3.4 MPa sample is higher than those for the samples fabricated with 1.4 MPa (21.4%) and 2.8 MPa (13.6%). This fact suggests that the high initial amount of EuAlO_3 in the sample synthesized with 3.4 MPa could be a feature to obtain the highest green photoluminescence. The 2.8 MPa sample which contained the lowest amount of EuAlO_3 phase showed the lowest green luminescence intensity. Thus, we can conclude that the content of the EuAlO_3 phase in the as synthesized powders is essential to obtain better green luminescence. Furthermore, the $\text{Eu}(\text{OH})_3$ and the EuOOH europium hydroxides phases appear since their temperature range of formation using PACS technique is of 200–350 °C [16], but after the reduction treatment, the $\text{Eu}(\text{OH})_3$ and EuOOH phases are eliminated.

The cathodoluminescence (CL) spectrum of the reduced powder produced with the initial pressure of 3.4 MPa is shown in Fig. 4. A broad CL emission centered at $\lambda_{\text{CL}} = 535$ nm and a narrow peak at $\lambda_{\text{CL}} = 611$ nm with lower intensity were observed. The broad green emission band centered at 535 nm correspond to the $4f^7-4f^65d^1$ transition of Eu^{2+} [8,10], and the peak at 611 nm is attributed to the $^5D_0 \rightarrow ^7F_2$ level transitions of the Eu^{3+} ion [8]. As a proof of concept for applications in WLEDs, we measured the luminance (parameter related with brightness) produced by our phosphors when they are excited with commercial UV-LEDs. The values of luminance obtained after excitation were 100 ± 2.7 Cd/m² and 285 ± 4.3 Cd/m² for the 380 nm and 396 nm UV LEDs, respectively. Further, the CIE coordinate of the green emission for the sample fabricated with a pressure of 3.4 MPa was (0.2613, 0.3892) when it was excited with these UV-LEDs. It has been reported green emitting phosphors excited with deep UV light (147 nm) [17], other ones are excited with high voltages around 7 kV and other authors reported those phosphors excited with blue LEDs which produced luminance in the range of 40–100 Cd/m² [18,19]. Compared with those reports, our nanophosphor present an easier fabrication, higher luminance with lower energy of excitation and even intermediate voltage of excitation in order to get green emission by cathodoluminescence. Those results indicate that our nanophosphors have good potential for their use as green component in tricolor WLEDs.

The green emission observed after the photoluminescence measurements is associated to the characteristic Eu^{2+} ions transitions which mainly comes from the $\text{EuAlO}_3:\text{Eu}^{2+}$ compound [8,10,11]. Thus, the reduction of Eu^{3+} ions to Eu^{2+} for the case of the EuAlO_3 phase is at the surface and part of the bulk of the grains because of a weak red emission is also observed by cathodoluminescence (see Fig. 4), which is associated to the Eu^{3+} transitions, nonetheless mainly green emission by cathodoluminescence is observed. This

fact, makes us to suppose that the grains have a small inner core with EuAlO_3 phase in which the Eu^{3+} has not been converted into Eu^{2+} due to the very short time of the reduction treatment. The Eu^{3+} cathodoluminescence signal cannot come from the EuAl_2O_4 structure because of the oxidation state of the Eu in the EuAl_2O_4 matrix is Eu^{2+} [14]. In addition, the contribution of the green cathodoluminescence should come from the $\text{EuAlO}_3:\text{Eu}^{2+}$ phase, since we have a lower percentage of the EuAl_2O_4 phase (28%) compared with that for the EuAlO_3 phase (72%). Also the weak peak at $\lambda = 611$ nm, is attributed to the $^5D_0 \rightarrow ^7F_2$ transition of the Eu^{3+} ion. The emission spectrum of the reduced sample produced with initial pressure of 3.4 MPa (Fig. 3(b)) did not show Eu^{3+} ions transition peaks as in the case of the cathodoluminescence (CL) spectrum of the same sample. This is a consequence of the large energy difference between photons and electrons. For the case of the Photoluminescence measurements, the maximum excitation energy of photons ($\lambda_{\text{exc}} = 398$ nm) is $E_{\text{ph}} = 3.1$ eV, in contrast, electrons used in cathodoluminescence experiment have an energy of $E_{\text{CL}} = 4$ keV, then, there is difference of three orders of magnitude for the energy of excitation between photons and electrons. Hence, the electrons can penetrate and excite the Eu^{3+} ions contained in the $\text{EuAlO}_3:\text{Eu}^{2+}$ lattice. Furthermore, when the irregular grains are irradiated with electrons, the electrons penetrate up to tens of microns [20] and they can excite both ions: Eu^{3+} and Eu^{2+} , which are contained in the $\text{EuAlO}_3:\text{Eu}^{2+}$ nanophosphor. In a previous work [10] the $\text{EuAlO}_3:\text{Eu}^{2+}$ with orthorhombic structure phase is excited with electrons of similar energy (5 keV) as in this work, but in that case, only the CL red emission related to the Eu^{3+} transitions is observed and the green emission is only observed by Photoluminescence. In our case, both emissions (red and green) can be observed by exciting with electrons but not with photons, this fact suggest that our nanophosphor has a potential use for field emission displays (FEDs) applications.

4. Conclusions

Green-emitting nanopowders mainly composed of the $\text{EuAlO}_3:\text{Eu}^{2+}$ phase (72%) and a secondary EuAl_2O_4 phase (28%) were produced through a rapid method of two steps. The green photoluminescence and cathodoluminescence emissions are attributed to the $4f^7-4f^65d^1$ allowed transitions of Eu^{2+} that green emission comes mainly from the $\text{EuAlO}_3:\text{Eu}^{2+}$ phase. The sample fabricated with a pressure of 3.4 MPa showed the highest green luminescence centered at 530 nm, and the intensity of the emission is directly related with the content the EuAlO_3 phase in the as-synthesized powders before the reduction treatment. The green nanophosphors produced in this work could be useful as a phosphor for WLEDs due to their good luminance of 285 ± 4.3 Cd/m² when they are irradiated with a commercial UV-LED of 396 nm.

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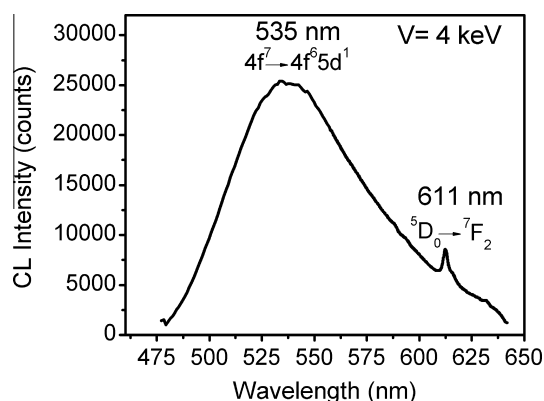


Fig. 4. Cathodoluminescence spectrum of the green nanophosphor synthesized with the initial pressure of 3.4 MPa.

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