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Short communication

Controlled nucleation and crystal growth through nano SiO_2 for enhancing the orange luminescence of $(Sr,Ba)_3SiO_5$: Eu^{2+} in white LEDs application

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Abstract

To enhance the luminescence of $(Sr,Ba)_3SiO_5:Eu^{2+}$ for white light-emitting diodes, a new method for the synthesis of phosphor was developed. In the proposed method, the mixture of large and nano SiO_2 particles as a silica source was employed to control the nucleation and crystal growth of the material. The impurity phase $(Sr,Ba)_2SiO_4$, which easily coexisted with $(Sr,Ba)_3SiO_5$ was suppressed. Accordingly, the luminescence was enhanced significantly by the partial substitution of conventional SiO_2 with nano SiO_2. The improvement in crystallinity and morphology was examined with XRD and SEM. Moreover, the sintering temperature and the concentration of nano SiO_2 was optimized. The results show that appropriate amount of nano SiO_2 has pronounced effects on the nucleus formation and crystal growth, while excessive crystal seeds formed may hinder the growth of particles. A mechanism for this improvement was proposed.

Keywords: Luminescence; Phosphor; Nucleation; Nano SiO_2; LED

1. Introduction

White light-emitting diodes (WLEDs) show a number of advantages over conventional fluorescent lamps, incandescent bulbs, and cold cathode fluorescent lamp (CCFL) in terms of efficiency, reliability, long lifetime and eco-friendship, which pave way for their wide application in home lighting, outdoor decoration, traffic signal lamps, automobile lights, and the backlights of liquid crystal display (LCD) panels for mobile phones and TV sets, among others [1–6]. However, the WLEDs are mainly fabricated by coating yellow phosphors on blue InGaN chips at present, which have a poor color rendering index (CRI) due to the deficiency of a red component in the emission spectrum. Thus, a red phosphor is desired for improving the CRI of WLEDs [1–6].

$(Sr_{1-x}Ba_x)_3SiO_4:Eu^{2+}$ was a promising candidate for the application, whose emission peak could be tuned from about 580 to 600 nm with Ba^{2+} concentration varying from x=0 to 0.2 M [7–14]. Recently, several studies have focused on the synthesis and luminescence properties of $(Sr,Ba)_3SiO_5:Eu^{2+}$ [7–14]. However, the impurity $(Sr,Ba)_2SiO_4:Eu^{2+}$ easily coexists with the formation of $(Sr,Ba)_3SiO_5:Eu^{2+}$, which not only decreases luminous efficiency but also deteriorates emission color [11–14]. Wang's research demonstrated that $Sr_3SiO_5:Eu^{2+}$ tends to decompose into Sr_2SiO_4 and SrO during the cooling process and the decomposition could be restrained by a rapid cooling speed [11]. In order to enhance luminescence and improve particle morphology, the flux was widely applied in phosphor synthesis. However, the formation of Sr_2SiO_4 caused by the BaF_2 flux, during Sr_3SiO_5 synthesis was observed by Cheng et al. [12]. Nakamura et al. has explored the synthesis of

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$Sr_3SiO_5:Eu^{2+}$ by using two types of SiO_2 raw material [13]. The results show that the phosphor synthesized from fumed SiO_2 exhibits a much better performance than that from conventional SiO_2. In this work, conventionally employed micron size SiO_2 was substituted with nano SiO_2 in the synthesis of $Sr_3SiO_5:Eu^{2+}$ phosphor. The results showed that the luminescence was enhanced significantly by partial replacement of the comparatively large SiO_2 particles with nano SiO_2. The firing temperature and the concentration of nano SiO_2 were optimized.

2. Experimental

Samples were synthesized from $SrCO_3$ (99.9%), $BaCO_3$ (99.9%), Eu_2O_3 (99.99%), micron SiO_2 (99.9%, $D_{50}=20.461$ μm, BET surface area 0.958 m^2/g), nano SiO_2 (99.5%, $D\leq 20$ nm, BET surface area 185 ± 20 m^2/g) by a solid reaction at high temperature in the $H_2/N_2=25:75$ reduction atmosphere. The phases were identified by X-ray diffraction (XRD) analysis using a Rigaku D/Max-rB diffractometer. Particle morphology was characterized by using a JSM-6490LV scanning electron microscopy (SEM). The luminescence was measured by using a Hitachi F-4600 spectrometer.

3. Results and discussion

Fig. 1 presents the XRD patterns of $(Sr_{0.99}Eu_{0.01})_3SiO_5$ phosphors that were synthesized from the conventional SiO_2 source at different temperatures, compared with the standard XRD pattern of Sr_3SiO_5 (ICSD-418933) [15]. The phosphor synthesized at 1300 °C mainly consists of Sr_2SiO_4. As temperature increased from 1300 to 1400 and finally up to 1500 °C, the impurity Sr_2SiO_4 is reduced gradually and the pure phase of Sr_3SiO_5 occurs. Correspondingly, the luminescence intensity increased continuously with rising temperatures, as shown in Fig. 2 for those samples without nano SiO_2 doped. Moreover, the continuous increase in intensity of the main diffraction peak at $2\theta=30.61^\circ$ in Fig. 1 suggests that the crystallinity of phosphor improves with an increase of temperature.

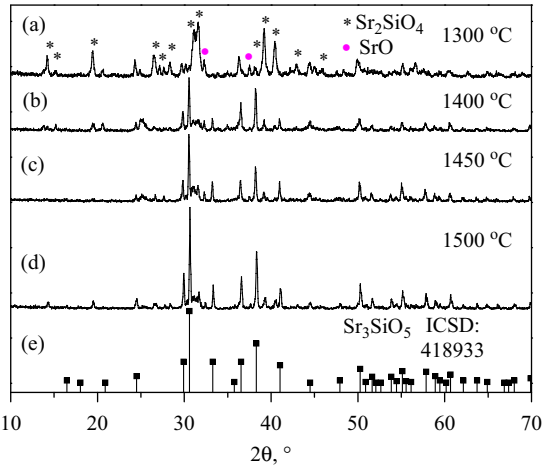

Fig. 1. The XRD patterns of $(Sr_{0.99}Eu_{0.01})_3SiO_5$ synthesized at 1300, 1400, 1450 and 1500 °C from micron SiO_2 by comparing with the standard ICSD 418933 [15].

In order to decrease the sintering temperature and enhance luminescence, we have tried to synthesize the $Sr_3SiO_5:Eu^{2+}$ phosphor by adopting NH_4Cl, KBr, H_3BO_3 and NaCl as fluxes. As shown in Fig. 3(a), the luminescence intensity of $(Sr,Ba)_3SiO_5:Eu^{2+}$ decreases and the emission peaks blue-shifts from 600 nm to 562 nm when the concentration of NH_4Cl is increased from 2.5 to 7.5 wt%. This is because the phases of $(Sr,Ba)_2SiO_4$ and $(Sr,Ba)Cl_2•H_2O$ are formed along with the formation of $(Sr,Ba)_3SiO_5$ phase, as revealed by the supplementary information in Fig. 1. Moreover, the impurities are increased with the content of NH_4Cl, which might quench the luminescence evidently. The out-side color of the $Sr_3SiO_5:Eu^{2+}$ phosphor synthesized by adopting KBr as a flux in natural light is virescent, as shown in SFig. 2, but the inner is orange. The Sr_2SiO_4 impurity caused by the KBr flux is also detected, as shown in SFig. 3, which is responsible for the decrease in luminescence and wavelength blue-shift as highlighted in Fig. 2(b). Besides, no positive effects are observed from the phosphors by adopting H_3BO_3 and NaCl as fluxes. To improve the luminescence property of the material, another strategy was envisaged, which proved quite beneficial.

The nano particles have large surface area to volume ratio and possess high surface potential, and can facilitate easy reactivity with other particles. Here, the nano SiO_2 was used to substitute the large SiO_2 particles. The concentration of nano SiO_2 was fixed at 0, 10%, 30%, 50% and 70% of the total weight of SiO_2. The phosphors were fired at 1400, 1450 and 1500 °C for 4 h, respectively in the H_2/N_2 reduction atmosphere. Their emission spectra are presented in Fig. 2(a)–(c). The optimal concentration for the nano SiO_2 at 1400 and 1450 °C are found 30%, with enhancement in the luminescence intensity of 106% and 61%, respectively, over the samples synthesized at the same condition without nano SiO_2 addition. When the temperature is 1500 °C, the luminescence intensities of samples doped with 10% and 30% nano SiO_2 are similar with each other. The intensity of the sample doped with 10% nano SiO_2 is 132% of that synthesized from large SiO_2 particles. Besides the enhancement of intensity, as shown in Fig. 2(a)–(c), the emission spectra red-shift from about 580 to 583 nm as the concentration of nano SiO_2 increases from zero to 30%. The redshift of emission spectra is beneficial for the improvement of CRI of WLEDs.

Fig. 2(d) summarizes the relative intensity of luminescence, achieved by integrating from 450 to 700 nm in emission spectra, as a function of nano SiO_2 concentration. Keeping the composition same, the luminescence intensity increases with an increase of temperature in the range of 1400–1500 °C, but the relative enhancement in quantity decreases when the content of nano SiO_2 is more than 30%. Moreover, the optimal content of nano SiO_2 required for phosphor synthesis also decreases with an increase of temperature. Mechanistically, it can be inferred that the appropriate amount of nano SiO_2 contributes to the formation of crystal nucleus, but too much nano SiO_2 doping will result in excess crystal seed formation. This overloaded doping may favor the competition among the crystal seeds to grow during the continuous reaction process at high temperature, ultimately hindering the growth of phosphor

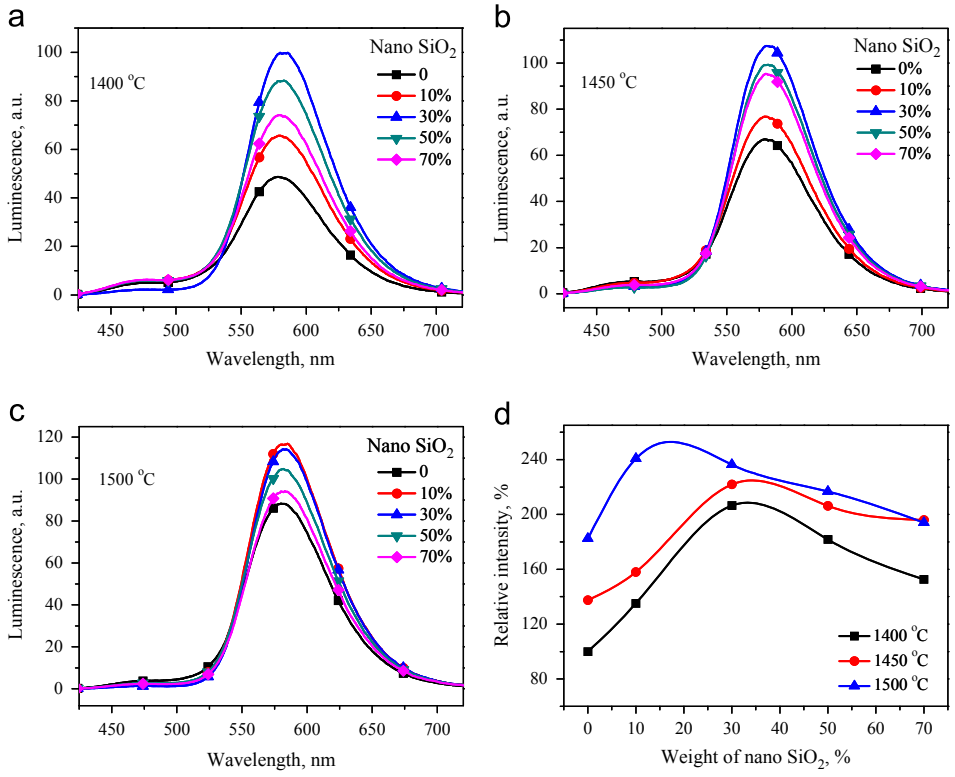

Fig. 2. The emission spectra of $(Sr_{0.99}Eu_{0.01})_3SiO_5$ synthesized at 1400 °C (a), 1450 °C (b) and 1500 °C (c) from with different contents of nano SiO_2, and their relative intensity as a function of nano SiO_2 concentration (d).

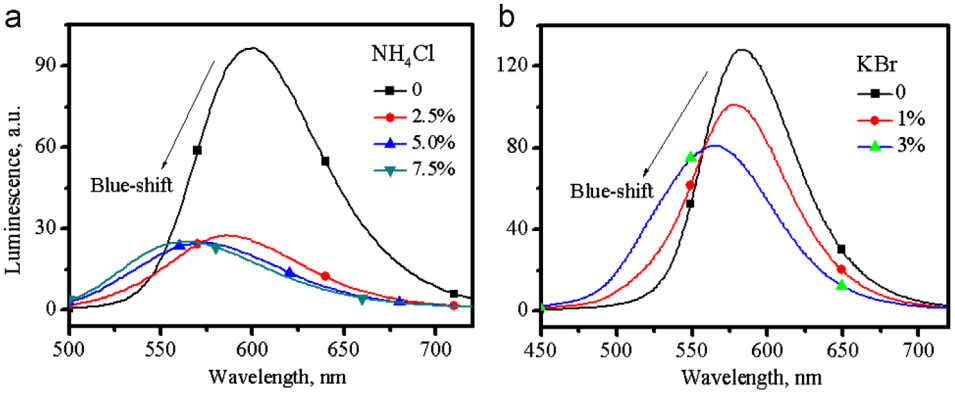

Fig. 3. Emission spectra of the phosphors $[(Sr_{0.85}Ba_{0.15})_{0.99}Eu_{0.01}]_3SiO_5$ and $(Sr_{0.99}Eu_{0.01})_3SiO_5$ synthesized by adding NH_4Cl and KBr as the flux for (a) and (b), respectively.

particles. This view is confirmed by the SEM pictures as shown in Fig. 4.

Fig. 4 displays the morphology of phosphor particles. The presence of small particles with rough surface in Fig. 4(a) suggest that the crystal grain does not grow well when there is no added nano SiO_2. However, the particle size grew significantly after doping 30% and 10% with nano SiO_2 at 1450 °C and 1500 °C, respectively, as displayed in Fig. 4(b) and (c). The particle size in Fig. 4(b) and (c) are similar to each other, but the particle surfaces in Fig. 4(c) are much smoother and cleaner than those in Fig. 3(b). The particles in Fig. 4(d) have clear profile and uniform shape, although they are not as large as those in Fig. 4(c). Practically, the uniform particles with a clean profile benefit to improve the final efficiency of WLED devices after packaging. The luminescence not only depends on particles size but also depends on their profile. These characters are clearly presented by the combinationa of Figs. 2 and 4.

Fig. 5 describes schematically the influence associated with large SiO_2 particles (a) and the mixture of large SiO_2 particles and nano SiO_2 (b) on the nucleation and crystal growth. As far as the point contact between the large $SrCO_3$ and SiO_2 particles is concerned, it is very hard to form a crystal nucleus for the hot-spot diffusive reaction. However, it is easy for nano SiO_2 which is absorbed on the surface of $SrCO_3$. Once the nucleus formed, the Helmholz free energy (F) of the system

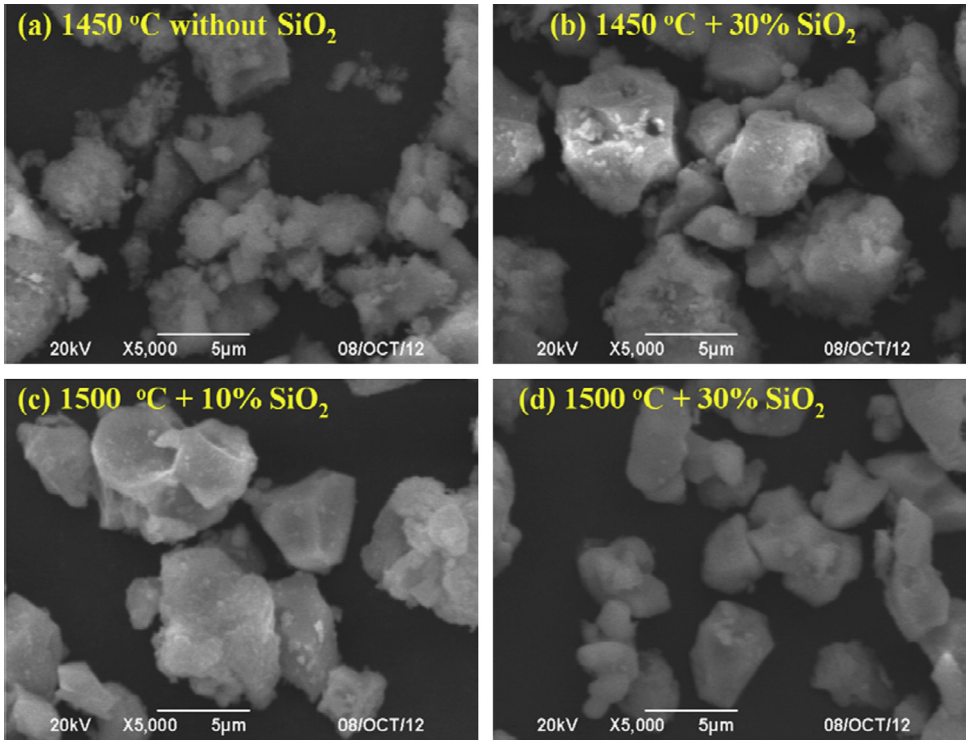

Fig. 4. The sintering temperature and the concentration of nano SiO_2 on the morphologies of $(Sr_{0.99}Eu_{0.01})_3SiO_5$ particles.

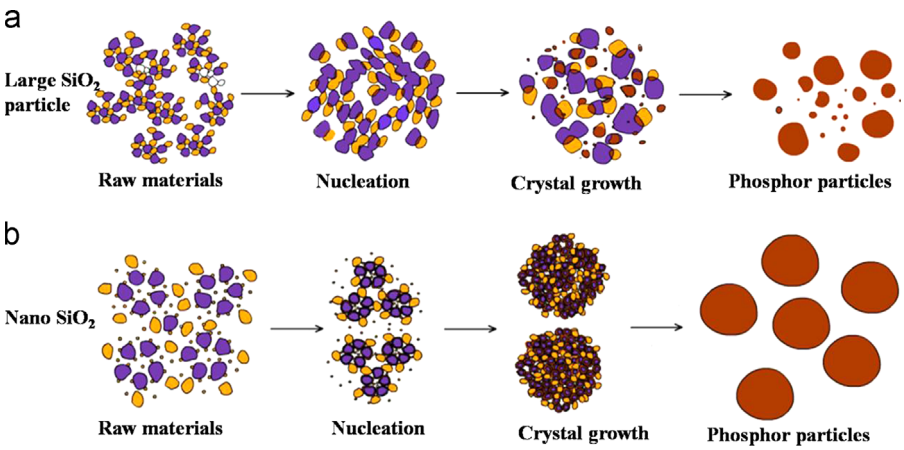

Fig. 5. The mechanism of the large SiO_2 particles (a) and the mixture of large SiO_2 particles and nano SiO_2 on the nucleation and crystal growth of the $Sr_3SiO_5:Eu^{2+}$ phosphor by reacting with $SrCO_3$.

which is defined as

$$\mathbf{dF} = -\boldsymbol{S}\mathbf{d}\boldsymbol{T} - \boldsymbol{P}\mathbf{d}\boldsymbol{V} + \boldsymbol{\mu}\mathbf{d}\boldsymbol{N},$$

will decrease evidently, where $\boldsymbol{S}$, $\boldsymbol{P}$, $\boldsymbol{\mu}$, $\boldsymbol{T}$, $\boldsymbol{V}$ and $\boldsymbol{N}$ present the entropy, pressure, chemical potential, temperature, volume and the number of particles, respectively. Accordingly, the grain will grow rapidly. Moreover, the numerous nucleus may surround a large particle to grow up and the small grain may aggregate together or merge into a large one. Herein, large grains with uniform shape are achieved, as shown in Fig. 4(d). But as for the raw material in large particle size, few tiny particles still exist, as seen from the particle distribution shown in SFig. 4. The nucleus will form preferentially from the tiny one and in turn grows into a large grain. However, most large particles have a low speed of reaction and the grain grows slowly. Thus, the small particles with irregular shape are obtained, as shown in Fig. 4(a).

According to above optimal results, the orange phosphor of $[(Sr_{0.85}Ba_{0.15})_{0.99}Eu_{0.01}]_3SiO_5$ was synthesized finally, by doping 20% nano SiO_2 and firing at 1500 °C for 6 h in the $H_2/N_2 = 25/75$ reduction atmosphere. The emission spectrum is given in Fig. 6(a), in which a broadband peaked at about 602 nm is observed. The correlated color temperature (CCT) of the phosphor is about 1615 K and the chromaticity coordinates is about CIE (0.5840, 0.4145). The relative position of the CIE coordinates in the chromaticity diagram of the phosphor is shown in Fig. 6(b), in contrast to the commercially available yellow phosphor of $YAG:Ce^{3+}$ and the blue phosphor of

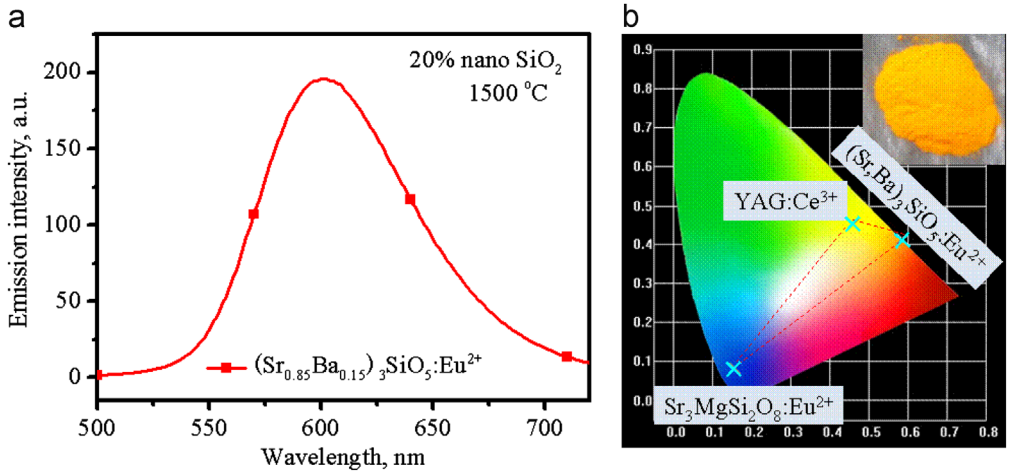

Fig. 6. Emission spectrum of $(Sr_{0.85}Ba_{0.15})_3SiO_5:Eu^{2+}$ c (a) and the relative position of color coordinates in chromatic diagram in contrast to the commercial yellow YAG:Ce^{3+} and the blue phosphor of $Sr_3MgSi_2O_8$: Eu^{2+} (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$Sr_3MgSi_2O_8:Eu^{2+}$. These parameters suggest that the phosphor is practically feasible to improve the CRI and decrease the CCT of WLEDs when used to package WLED devices.

4. Conclusion

In summary, a new method for the synthesis of $(Sr,Ba)_3SiO_5:Eu^{2+}$ phosphor was developed by adopting the mixture of large SiO_2 particle and nano SiO_2 as the silica source in synthesis, i.e., mixed with 10–30% nano SiO_2 into raw materials and suffered a high-temperature sintering at 1450–1500 °C for several hours in the H_2/N_2 reduction atmosphere. The luminescence was enhanced significantly by using this newly developed $(Sr,Ba)_3SiO_5:Eu^{2+}$ synthetic protocol. The fluxes were not applicable to the phosphor synthesis since other impurity phase induced. The luminescence intensity of $Sr_3SiO_5:Eu^{2+}$ doped with 30% nano SiO_2 synthesized at 1400, 1450 and 1500 °C was about 206%, 161% and 131% of that synthesized without nano SiO_2 addition at the same temperature. However, the relative enhancement rate caused by nano SiO_2 and the optimal content of nano SiO_2 required for phosphor synthesis decrease with an increase of firing temperature. From this viewpoint, it is necessary to take further theoretical and experimental studies to reveal the relationship among the number of crystal seeds, the speed of crystal growth, the content of nano SiO_2 and the firing temperature.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2013.04.017.

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