**A Stable and Efficient Red-Emitting Color Converter Based on K$_2$SiF$_6$:Mn$^{4+}$ Phosphor-in-Glass Film for Next-Generation Laser-Excited Lighting and Display**

Shuaichen Si, Lin Huang, Xuejie Zhang, and Jing Wang*

Laser diodes (LDs) are expected to be the next-generation high luminance sources because of the unobvious “efficiency droop” phenomenon under high power. To achieve high-quality white lighting, red emission is essential for white lighting devices. K$_2$SiF$_6$:Mn$^{4+}$ (KSFM) is a highly suitable red phosphor for its strong broadband excitation in the UV and blue region and intense red emission at 631 nm. In addition, the ultranarrow emission makes it suitable for wide gamut displays. Herein, a stable and easily prepared red color converter, KSFM based phosphor-in-glass films on a coated sapphire substrate (CSA) is developed, which exhibits a high thermal conductivity of 32.02 W m$^{-1}$ K$^{-1}$. Compared with the KSFM phosphor, this KSFM–CSA composite shows an overall increase in thermal quenching and irradiation resistance abilities. A wide color gamut covering 128% of the National Television Standards Committee (NTSC) standard white LD (WLD) is fabricated by coupling a green-emitting CsPbBr$_3$ embedded glass plate and red-emitting KSFM–CSA with blue LDs. Furthermore, a high-quality WLD with a luminous flux (520 lm), luminous efficiency (93.0 lm W$^{-1}$), and color rendering index (CRI, 81.4) is achieved. With its excellent properties, the KSFM–CSA has great potential in high-power laser lighting and display.

1. Introduction

Currently, light-emitting diodes (LEDs) and laser diodes (LDs) have attracted significant attention and been regarded as the next-generation excitation sources because of their high luminous efficiency (LE), longevity, energy-saving feature, and environmental friendliness.$^{[1,2]}$ Especially the LDs, which are compact and free from the “efficiency droop” phenomenon, are more extensively used in the fields of automotive headlights, projectors, digital cinemas, laser TVs, large-screen splicing as well as optical wireless communication.$^{[3]}$

The most mainstream commercial white LDs (WLDs) are fabricated by the combination of blue LDs with a broad-band yellow-emitting Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG) phosphor. However, due to the drawback of the insufficient red component, commercial YAG-based device results in a high correlated color temperature (CCT) and a low color rendering index (CRI), making it difficult to obtain the ideal white light. The artificial cold white light has been reported to have negative effects on metabolism, sleep–wake, and mental alertness, which limits its applications in indoor lighting.$^{[4,5]}$

Therefore, it is necessary to develop suitable red-emitting phosphors to obtain high-quality WLDs. CaAlSiN$_3$:Eu$^{2+}$ (CASN) phosphor is regarded as an appropriate phosphor to remedy the red component in white lighting for its advantage in high efficiency and thermal stability. Recently, Liu et al. have fabricated CASN PiG films by combining phosphor with alumina ceramic substrate.$^{[6]}$ White light was achieved by simultaneously integrating blue LDs, CASN PiG films, and Lu$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (LuAG) PiG films with a high CRI value (88.6) and LE (153 lm W$^{-1}$). However, the CASN phosphor has serious photon reabsorption in green and yellow spectral regions, which reduces the output efficiency of WLDs. In addition, the glass powder will corrode the CASN phosphor and introduce luminescence
quenchers (i.e., Eu$^{3+}$) during the cosintering process. As an alternative, the Mn$^{4+}$-doped red-emitting fluoride phosphors have attracted more attentions, represented by $A_{x}Fx_{y}Mn^{4+}$ ($A = \text{Li, Na, K, Rb, Cs}; X = \text{Si, Ge, Sn, Ti, Zr, Hf}$). Among them, Mn$^{4+}$-doped potassium hexafluorosilicate phosphor ($K_{2}SiF_{6}:Mn^{4+}$, KSFM) shows strong broadband excitation in the wavelength ranging from UV to blue region, matching well with the commercial blue LEDs and LDs, and exhibits intense red emission at 631 nm with high photoluminescence quantum yield (PLQY). The appropriate emission can make up the red ingredient in the white lighting. KSFM has already been commercially implemented in LED lighting fields and shown to improve efficiency by $>10\%$ at $>90$ CRI, compared with CASN phosphors which have broad emission spectra. In addition, KSFM phosphor is also the most promising red phosphor for wide gamut displays because of the ultranarrow emission, outstanding luminescence efficiency, and super high color purity.

Another unavoidable issue in WLDs is to achieve satisfying thermal management due to the high input power density of LDs. As for KSFM phosphor, the poor thermal stability restricts its applications in laser-excited lighting and display. Single-crystal phosphor, phosphor ceramic, phosphor-in-glass (PiG), and PiG film are the alternatives to replace the common phosphor-in-silicone (PiS) for high drive applications, e.g., automobile headlights. Recently, KSFM single crystal phosphor and transparent ceramics, with high luminescence efficiency and thermal stability, have been reported successively. However, the complex fabrication process and high cost of single-crystal phosphor and phosphor ceramic limit their mass production. Furthermore, the relatively low thermal conductivity of the KSFM ceramic ($\approx 1.0 \text{ W m}^{-1}\text{ K}^{-1}$) and single crystal is not satisfied for high brightness applications.

In recent years, PiG film combining with a high thermal conductivity substrate (i.e., glass, sapphire, or aluminum) is regarded as a promising candidate to solve the issue above due to the superior heat dissipation ability, easy fabrication, and excellent efficiency. Peng et al. have sintered yellow YAG:Ce$^{3+}$ and red $3.5\text{MgO}:0.5\text{MgF}_{2}:\text{GeO}_{2}:\text{Mn}^{4+}$ (MFG:Mn$^{4+}$) PiG films tightly on a borosilicate glass plate and investigated their optical properties as color converters for high-power lighting. Park et al. have selected Al as the substrate to improve the thermal performance of the PiG films and a phosphor–Al composite (PAC) was fabricated by the SPS method. More importantly, Zheng et al. have directly sintered PiG films on a sapphire plate using the blade-coating technique and the composites showed excellent ability to withstand laser irradiation.

Sapphire, which is characterized by high transmittance ($>86\%$) and high thermal conductivity ($\approx 30 \text{ W m}^{-1}\text{ K}^{-1}$), is an ideal substrate material for LD devices with transmissive configuration which often leads to more compact designs. What is more, the surface of sapphire can be modified by coating the functional layers to improve the transmittance properties for varying demands of applications.

In this work, we manage to fabricate the KSFM PiG film onto the high thermal conductivity sapphire substrate by sintering and using glass powder ($\text{SnF}_{2}:\text{SnO–P}_{2}O_{5}$) with an ultralow Tg temperature ($166.1^\circ \text{C}$) as the inorganic encapsulating material to protect and bind the KSFM phosphor. A coated sapphire substrate (CSA), designed with an antireflection (AR) layer and a blue-pass filter (BP), is selected as a substrate for its high thermal conductivity and high transmittance. The thermal conductivity of the composite (named KSFM–CSA, $\approx 32.02 \text{ W m}^{-1}\text{ K}^{-1}$) is almost the same as the original CSA substrate. The microstructure and photoluminescence (PL) properties are studied in detail. In addition, the optical properties of the red composite materials can adjust by controlling the thickness of films and the ratios of KSFM to glass (KIG). Compared with the KSFM phosphor, the as-prepared KSFM–CSA composite shows large improvement in thermal stabilities: The relative integrated intensities increase from 80% to 86% at 500 K; the maximum tolerable power densities increase from 0.63 to 12.63 W mm$^{-2}$; the temperatures under their respective maximum power densities decrease from 258.3 to 134.7$^\circ \text{C}$; the saturated power densities under LDs excitation increase from 0.421 to 3.158 W mm$^{-2}$. As a proof-of-concept, an all-inorganic WLD is fabricated with the international commission on illumination (CIE) chromaticity coordinate (0.361, 0.345), CCT of 4356 K, and wide color gamut covering 128% of the national television standards committee (NTSC) standard by coupling a green-emitting CsPbBr$_{3}$-embedded glass plate and a red-emitting KSFM–CSA with blue LDs. Considering the improvement of CRI, yellow-emitting YAG phosphor is used to flourish the emitting spectra. The LE, CCT, CRI, and color drifts of the as-prepared WLDs are investigated in detail. All the results demonstrate that the KSFM–CSA composite is a promising candidate for use in high-power laser lighting and display.

2. Results and Discussion

2.1. Microstructural Characterization and Optical Properties

For clear representation, Figure 1a shows the photographs of the CSA plate, the KSFM–CSA under natural light and 365 nm UV lamp. The transmittance spectra of the sapphire substrate and the CSA are shown in Figure S1, Supporting Information. Thanks to the AR film, the transmittance of the CSA in the blue region is promoted from 85% to 95% compared with the sapphire substrate. Moreover, the reflectance of the yellow region is almost complete due to the existence of BP film, which causes the transparent blue appearance of the CSA. Both the AR and BP films are beneficial to improve the LE of WLDs. The KSFM–CSA appears faint yellow under natural light and bright red emission can be observed under 365 nm UV light. To prove that the KSFM phosphor remains intact in the glass matrix during the sintering process, the X-ray powder diffraction (XRD) patterns of the host glass, KSFM phosphor, and KSFM–CSA are shown in Figure 1b. For KSFM–CSA, there are no other phases except for the amorphous glass as well as crystalline KSFM phase which is identified with that of the KSFM phosphor (ICSD#64 763), indicating that the KSFM phosphor can maintain its structure during the sintering process. To study the microstructures of the composite, scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS) mapping, and EDS spectra are carried out, as shown in Figure 1c–2k and S2, Supporting Information. The shapes of the initial KSFM phosphor and host glass powder are cube morphology and irregular morphology, respectively.
The KSFM phosphor particles can be observed in the SEM images of KSFM–CSA and even keep their original morphology. The corresponding elemental regions of KSFM phosphor and glass matrix are distinct from each other, which is in accordance with the results of EDS spectra.

To further investigate the distribution of the KSFM phosphor particles in the glass matrix, we carry out a high-resolution real-time imaging study using a confocal laser scanning microscope (CLSM) with a 405 nm laser as the excitation light source, as shown in Figure 2. The red points represent the KSFM phosphor particles and the rest belongs to the glass matrix. From the 2D and 3D mapping images, we can observe that the KSFM phosphor particles are well distributed in the glass matrix.

In summary, the results of XRD, CLSM, SEM, and EDS spectra of the KSFM–CSA provide strong evidences that the KSFM phosphor particles remain intact during the cosintering process. It also demonstrates that the KSFM phosphors particles are uniformly distributed in glass matrix, which is beneficial for achieving color uniformity in LDs devices.

As shown in the inset of Figure 3a, the transmittance spectrum of the host glass shows high transmittance (>70%) in the range of 350–700 nm, indicating that the glass is an appropriate matrix for KSFM phosphor. The photoluminescence excitation (PLE) spectra of the KSFM–CSA and KSFM phosphor consist of two excitation bands centered at 350 and 450 nm arising from the $^4A_2 \rightarrow ^4T_1$ and $^4A_2 \rightarrow ^4T_2$ transition of Mn$^{4+}$ ions, respectively. As for PL spectra, the emission spectra consist of five sharp bands, centered at 609, 613, 631, 635, and 648 nm in the red spectra region. All these emission bands can be ascribed to different vibrational modes of $^2E \rightarrow ^4A_2$ transitions of Mn$^{4+}$ ions. The PL and PLE spectra of KSFM–CSA appear nearly identical with KSFM phosphor. The decay curves of the
Figure 2. a) Surface fluorescence distribution CLSM images and b) 3D reconstruction images of the KSFM–CSA sample excited by 405 nm laser, the KtG ratio of the KSFM–CSA is fixed at 2:3.

Figure 3. a) PL and PLE spectra of the KSFM phosphor and the KSFM–CSA, and transmittance spectrum of the host glass (green dash line); b) decay curves of the KSFM phosphor and the KSFM–CSA, the KtG ratio of the KSFM–CSA is fixed at 4:1.
KSFM–CSA and KSFM phosphor are shown in Figure 3b. The lifetimes of the KSFM–CSA and KSFM phosphor are calculated to be 8.1 and 8.6 ms, respectively. The decay curves of the two samples are almost the same. The PLQYs of the optimal KSFM–CSA and the KSFM phosphor are 59.1% and 94.0% under 450 nm excitation, respectively. We ascribe the drop to four main reasons: the first is that the glass matrix slightly absorbs incident excitation photons, which do not contribute emission photons, as proved by the transmittance spectrum of the host glass shown in Figure 3a; the second is that the emission photons from the KSFM phosphor particles are prevented by the host glass due to its transmittance is less than 100% in the red region; the third is the light scattering loss between the amorphous glass and the crystalline KSFM phosphor because of the mismatch refractive index; the fourth is the reduction of Mn⁴⁺ during the cosintering process due to the reduction environment of the glass matrix provided by Sn²⁺. The impurity ions (such as Mn³⁺, Mn²⁻) cause quenching either by energy transfer or metal–metal charge transfer which leads to a decrease in PLQY. Even though, it is hard to exclude there exists the interaction between the host glass and KSFM that could degrade the PL performance of KSFM. Fortunately, the KSFM–CSA sample still has a high PLQY of 59.1%, which is of great importance for its potential applications of LDs devices.

Both the thickness of the KSFM coating layer and KtG ratios have an impact on the optical properties of the KSFM–CSA samples. Here, we prepare a series of KSFM–CSA samples with different layer thicknesses and KtG ratios, shown in Figure 4b and S3c, Supporting Information, respectively. The cross sections of the KSFM–CSA samples with different layers from one to six are shown in Figure 4a. We can observe that the thickness of layers increases from 30 to 98 μm (Figure 4c). The PL spectra and the variation curve of integrated intensity under 450 nm excitation are shown in Figure 5a. The PL intensity of the samples increases from layers one to four, and then trends to equilibrium. This phenomenon can be ascribed to the optical path design of the spectrophotograph where the incident light radiates to the surface of the sample and the reflected light is detected by the detector. Due to the limitation of the penetration depth of incident light, the PL intensity approaches saturation with the increasing thickness of layers. The electroluminescence (EL) spectra, the integrated intensity of the blue and red emission, as well as the blue/red emission ratios with different layers under 1.0 W laser excitation, are shown in Figure 5b. With the increase in layer thickness, the red emission enhances first, then tends to be balanced, and finally decreases due to the hindrance of the thick layer. The blue emission decreases monotonously due to the enhanced absorption of the KSFM phosphor and the thick layer. The blue/red emission ratios gradually reduce, therefore, the CIE chromaticity coordinates shift from blue to red (Figure 5d), which is consistent with their actual illumination photographs (Figure 5c). Similar results can be observed when adjusting the KtG ratios of KSFM–CSA, as shown in Figure S3, Supporting Information. With the KtG ratios increasing, the red emission enhances, the blue emission decreases, and the CIE chromaticity coordinates shift toward the red emission region. In summary, we can adjust the optical properties of the red luminescent materials by controlling the thickness and KtG ratios, which is advantageous to the fabrication of LDs devices applied to different occasions.

2.2. Thermal Quenching and Resistance

Thermal performance is of vital importance for the color conversion materials used in high-power laser devices. To be more
persuasive, here, we compare the thermal quenching and irradiation-resistance ability to the blue laser of the KSFM phosphor and the KSFM–CSA. Figure S4, Supporting Information, presents the temperature-dependent PL spectra of KSFM phosphor and KSFM–CSA samples from 300 to 500 K. For both the materials, the Stokes and anti-Stokes emission regions (627–650 and 597–622 nm) are distinct and their intensities exhibit different variation trends with raising the temperature. The intensity of the KSFM phosphor rapidly drops due to nonradiative transitions above 400 K, whereas above 460 K as for the KSFM–CSA, shown in Figure 6. Due to the poor thermal quenching performance, the variation range of the KSFM phosphor is much larger than that of the KSFM–CSA. In addition, the relative integrated intensities of the KSFM phosphor, and the KSFM–CSA reach 80%, and 86% at 500 K, respectively. The high thermal conductivity of the CSA can account for the improved thermal quenching performance of the KSFM–CSA since high thermal conductivity of the CSA prevents the local overheating of the KSFM during the heating process. These results indicate that the KSFM–CSA can weaken the thermal quenching of the embedded phosphor and exhibits excellent thermal stability under high-temperature operation.

The ability of the color converter to withstand the exposure to high-power LDs, referred to as irradiation-resistance test, is a key factor in determining whether the material is suitable for application in high-power and high-brightness LDs devices. In this work, we use an infrared thermal imager to detect the
variations of surface temperature with increasing the incident power density. The KSFM phosphor is pressed to a plate before testing. The incident laser beam radiates directly to the surface of the materials and the distance between the laser and materials is \( \approx 2 \text{ cm} \). The spot size of the blue laser is fixed at 0.95 mm\(^2\). The temperatures on the surface of the KSFM phosphor and the KSFM–CSA as a function of incident laser power density are shown in Figure 7a. As shown in the figure, the temperature of the KSFM phosphor increases sharply, whereas the rising tendency is quite smooth of the KSFM–CSA. As for the KSFM phosphor, when the laser power density is increased from 0.05 to 0.32 W mm\(^{-2}\), the surface temperature merely rises from 27.7 to 65.5 °C. However, the temperature rapidly reaches 258.3 °C, when the laser power density is 0.63 W mm\(^{-2}\), and the surface of the phosphor is badly burned down (Figure 7b). The sharp increase in temperature can be explained as follow: due to the long lifetime of the excited state and relatively low absorption cross section for Mn\(^{4+}\) [26], the absorption is easy to reach saturation under the irradiation of laser and more light will be reflected or scattered in the phosphor grains, which leads to an increase in temperature. Unfortunately, the low thermal conductivity of the phosphor plate cannot dissipate the heat effectively and cause the accumulation of heat. Once the temperature increases, the thermal quenching increases and more heat is dumped in the phosphor, leading to a thermal runaway effect [14, 35]. This vicious circle will result in a sharp temperature rise and ultimately damage the phosphor. Concerning the KSFM–CSA, profiting from the super-high thermal conductivity (32.02 W m\(^{-1}\) K\(^{-1}\), details shown in Table S1, Supporting Information), the heat generated from laser radiation can be efficiently dissipated, and hence the temperature of the KSFM–CSA can be controlled within a smaller value. This, in turn, further reduces the thermal quenching and generates less heat. The surface temperature merely reaches 134.7 °C when the laser power density is 12.63 W mm\(^{-2}\). Meanwhile, there is no obvious distinction of the KSFM–CSA before and after radiation (Figure 7b). Furthermore, we carry out an irradiation-resistance time-dependent test of the KSFM–CSA with a fixed bluer laser power density of 10.52 W mm\(^{-2}\), presented in the inset of Figure 8a. With radiation time persisting from 0 to 10 s, the temperature of the KSFM–CSA sharply increases from 25.0 to 107.6 °C and then approximately keeps balance with continuous radiation extended to 5 min. Based on these results, the KSFM–CSA exhibits good performance in not only the outstanding heat dissipation capability, but also the excellent irradiation-resistance ability of the blue laser, and durability, which meet the demands of practical applications for laser lighting and display.

2.3. Optical Performance of the WLDS Device

The saturation behaviors of the KSFM phosphor and the KSFM–CSA under different excitation power densities are studied in detail. Figure 8 shows excitation power density-dependent EL spectra and luminous flux of the prototype laser lighting source devices based on KSFM phosphor and the KSFM–CSA, respectively. As shown in Figure 8b, the curve of the KSFM–CSA is below the one for the KSFM phosphor at low power density due to the lower PLQY of the KSFM–CSA. The saturated power density of the KSFM–CSA is 3.158 W mm\(^{-2}\), which is 7.5 times as large as the saturated power density of the KSFM phosphor (0.421 W mm\(^{-2}\)). In general, both thermal and optical saturation behaviors exist together in the KSFM phosphor and the KSFM–CSA under high laser fluence. As the optical saturation behavior is ascribed to the long lifetime of the excited state of Mn\(^{4+}\) ions, the optical saturation behavior can be thought to be the same in the KSFM phosphor and the KSFM–CSA. Therefore, the improved saturation behavior of the KSFM–CSA mainly comes from improved thermal saturation behavior, compared with the KSFM phosphor. These results indicate that increasing the thermal conductivity of the material is an effective approach to improve the saturation behavior of the KSFM phosphor.

The narrow-band red PL emission and good thermal stability make the KSFM–CSA an attractive candidate for LDs-based wide color gamut display. As a proof-of-concept experiment, we construct a WLDS based on the 441 nm blue LDs, the green-emitting CsPbBr\(_3\) embedded glass (full width at half maxima (FWHM) = 23 nm), and the red-emitting KSFM–CSA by stacking configuration (inset of Figure 9a). As expected, the EL spectra exhibit the completely isolated RGB emissive components, shown in Figure 9a. By controlling the thickness of CsPbBr\(_3\),
embedded glass and the KSFM–CSA, we obtain white light with the CIE chromaticity coordinate (0.361 and 0.345) and CCT of 4356 K. The calculated color gamut of the as-prepared WLD device can cover 128 % NTSC in CIE 1931 (Figure 9b), indicating that the KSFM–CSA is a promising narrow-band red luminescent material for LD-based display with stable luminescence performance.

The performances of the YAG–KSFM–CSA-based WLDs devices are studied in detail. To obtain a high-quality warm white light, it is necessary to enhance the red emission due to the deficiency of the red region of YAG. Here, KSFM phosphor layers with different thicknesses are printed on the YAG–CSA (1 layer) to prepare the multicolor YAG–KSFM–CSA (named 1Y+xR). The structure diagrams of the multicolor YAG–KSFM–CSA and the collimator integrated with samples are shown in Figure 10a. The high-power WLDs device consists of three parts: a power-adjustable blue fiber-optic laser, an optical fiber, and a spot size-adjustable collimator integrated with samples. With the increase in the KSFM layers, the red emission intensities of the WLDs enhance (Figure 10b). Meanwhile, the light tunes from cold white to warm white distinctly and the CIE chromaticity coordinates shift from (0.295, 0.258) to (0.453, 0.403), as shown in Figure 10c. The detailed optical performances of the as-fabricated WLDs under 1.0 W laser excitation are shown minutely in Table 1. As the thickness of the red layer increases, the LE of as-prepared WLDs decreases from 114.9 to 64.3 lm W$^{-1}$, and the CCT decreases from 10 173 to 2735 K. It is ascribed to the fact that more blue light is converted to red emission, and the spectral around the red region is not sensitive to the human eye, which leads to lower luminous flux. Benefiting from the supplementary red emission, the CRI of the WLDs increases from 68.3 to 87.2. Comprehensive considering all the optical parameters, a high-quality warm white light with a LE of 93.0 lm W$^{-1}$, a CCT of 3379 K, a CRI of 81.4
obtained by combining the 1Y + 3 R sample and blue LDs. This sample is selected for further detailed measurements.

To demonstrate the feasibility and efficiency of prepared WLDs in practical application, the EL, luminous flux, LE, CCT, Ra, and ΔE are measured prudentially under different laser power densities ranging from 1.05 to 7.37 W mm\(^{-2}\) (Figure 11). The emission intensity of the WLDs enhances monotonously with the incident power density increasing from 1.05 to 6.84 W mm\(^{-2}\) and then decreases slightly beyond a threshold, which can be ascribed to the luminous saturation behavior and thermal quenching effect under high power density. Moreover, when the laser power density is below 6.84 W mm\(^{-2}\), the Ra, CCT, and color drift of WLDs float slightly within limits. In a word, the YAG–KSFM–CSA composite in WLDs can withstand 6.84 W mm\(^{-2}\) laser irradiation and shows excellent stability, indicating the potential application in laser lighting.

To assess the durability of the as-prepared WLDs, an operating time-dependent aging test is studied at a fixed laser power density of 5.26 W mm\(^{-2}\), as shown in Figure S5, Supporting Information. Intriguingly, the YAG–KSFM–CSA sample can achieve thermal balance very quickly (within \(\approx 60 \text{ s}\)), giving stable LE, CCT, Ra, and color drift under long-term exposure to high-power blue LDs.

### 3. Conclusions

In this work, we successfully synthesize high thermal conductivity and good thermal resistance KSFM–CSA composite in a simple way. A glass powder with ultralow Tg temperature is used as an inorganic binder to protect KSFM phosphor. The optical properties of the KSFM–CSA composites can be adjusted precisely by controlling the KSFM coating thickness and KG ratios. Benefited by the high thermal conductivity \((\approx 32.02 \text{ Wm}^{-1}\text{K}^{-1})\), the KSFM–CSA exhibits good performance in thermal quenching, heat dissipation, irradiation-resistance of a blue laser, light saturation behavior, and durability, which meet the demands for high-power laser applications. By coupling a green-emitting CsPbBr\(_3\) embedded glass plate and a red-emitting KSFM–CSA with blue LDs, a WLD with the CIE chromaticity coordinate \((0.361, 0.345)\), CCT of 4356 K, and a wide color gamut covering 128% of the NTSC standard is fabricated. We expect that the KSFM–CSA is a promising narrow-band red luminescent material for LDs-based wide color gamut displays. As a proof-of-concept, we introduce yellow-emitting YAG phosphor additionally to obtained high color quality WLDs devices.

### Table 1. Optical performances of the as-fabricated WLDs devices under 1.0 W laser excitation.

| Samples       | LE [lm W\(^{-1}\)] | CIE (x, y)     | CCT [K] | CRI  |
|---------------|-------------------|----------------|---------|------|
| 1Y + 0 R      | 90.6              | (0.234,0.162)  | >12 000 | 72.2 |
| 1Y + 1 R      | 114.9             | (0.295,0.258)  | 10 173  | 68.3 |
| 1Y + 2 R      | 107.8             | (0.353,0.325)  | 4544    | 78.4 |
| 1Y + 3 R      | 93.0              | (0.401,0.389)  | 3379    | 81.4 |
| 1Y + 4 R      | 83.5              | (0.427,0.388)  | 3039    | 85.0 |
| 1Y + 5 R      | 64.3              | (0.453,0.403)  | 2735    | 87.2 |

Figures:

- Figure 10. a) The structure diagrams of the multicolor YAG–KSFM–CSA and the collimator integrated with samples; b) normalized EL spectra and c) CIE chromaticity coordinates of the as-fabricated WLDs devices with different layers under 1.0 W laser excitation, inset shows the corresponding photographs of WLDs in operation.

Table 1.
can be achieved for 1Y+3R samples, which are satisfactory values for transmission-configuration LD-driven lighting. The results shown in this work prove that the KSFM–CSA is a promising converter to realize wide color gamut displays and high color quality white light in LD devices. Moreover, encouraged by this work, we believe that major developments of LD lighting and display will be promoted.

4. Experimental Section

Materials: Precursor glass with a composition of 30SnF₂–40SnO–30P₂O₅ (in mol%) were prepared via a conventional melting–quenching method. The starting materials of SnF₂, SnO, and NH₄H₂PO₄ were weighted according to their stoichiometric ratio. The raw materials were then ground in an agate mortar for 20 min and sintered at 550°C for 10 min in a muffle furnace under an ambient atmosphere. The melt was poured into a graphite mold to cool down and then milled into powder using a ball grinder. The phosphor materials, such as YAG (Appotronics, Shenzhen, China) and KSFM (Looking long technology co. LTD, Shenzhen, China) are commercially available. The CSA plate (size of 14×0.3 mm²) was brought from Crystal-Optech (China). Terpineol (Aladdin, China, 95%), 2-(2-butoxyethoxy) ethyl acetate (Aladdin, China, 98%), and ethyl cellulose (Aladdin, China, 18–22 mPa s) were used as raw materials of organic solvent.

Fabrication of KSFM–CSA and YAG–KSFM–CSA Samples: The KSFM–CSA was prepared by screen-printing and sintering process. The viscous KSFM printing paste was obtained by fully mixing the glass powders, KSFM phosphors, and organic solvent in an agate mortar. The organic solvent was prepared by adequately mixing terpineol, 2-(2-butoxyethoxy) ethyl acetate, and ethylcellulose at 80°C for 10 h at 600 rpm. The K₁G ratios were designed to be 1:4, 2:3, 3:2, and 4:1, and the layer thickness was varied from 30 to 98 μm. Then, the prepared phosphor pastes were printed on the CSA substrates using a 250 meshes screen. Finally, the printed phosphor glass layers were sintered at 225°C for 10 min in a tube furnace under the N₂ atmosphere. The synthetic process of YAG–KSFM–CSA samples was similar to the description above. The only difference was that the KSFM layers were reprinted on the sintered YAG–CSA. The weight ratios of the YAG phosphor and KSFM phosphor to the glass powder were fixed at 1:1 and 4:1, respectively.

Fabrication of CsPbBr₃-Embedded Glass: CsPbBr₃-embedded glass with nominal compositions of 34B₂O₃–38SiO₂–4ZnO–5SrCO₃–8Cs₂CO₃–3PbBr₂–3NaBr (in mol%) was prepared by conventional melt-quenching method. The starting materials have been mixed carefully and then melted at 1200°C for 30 min in the ambient atmosphere. After poured into a preheated graphite mold, the glass melts were annealed at 460°C for 2 h to eliminate the inner stress. The controlled glass crystallization was proceeded by heating the as-prepared glass at 520°C for 10 h. Finally, the CsPbBr₃-embedded glass was cut and carefully polished for further purposes.

Characterization: The thermal diffusivity (α) was determined by the laser thermal conductivity meter (LFA-447, Netzsch). The specific heat capacity (c) was determined by the differential scanning calorimetry (DSC-204F1, Netzsch, Germany). The densities (ρ) of samples were measured using standard test methods for density and specific gravity (relative density).
of plastics by displacement (at 20 °C). The thermal conductivity can be calculated using the formula (1)

\[ \lambda = \rho \times c \times \alpha \]  

(1)

Phase purity was determined by laboratory XRD using a RIGAKU D-MAX 2200 VPC powder diffractometer operating with Cu Kα radiation. The microstructures of the KSFM-CSA samples were studied using a SEM (FEI/OLYMPUS/HKL-Quanta 400F) equipped with an EDS system. The distribution of the phonon particles in the KSFM-CSA sample was observed using a confocal laser scanning microscope (LSM 880, Carl Zeiss, Germany). The transmittance spectrum of the host glass was recorded using a UV–vis–NIR spectrophotometer (Cary 5000, Varian, America) equipped with a 450 W Xe lamp, a 150 W nF900 flash lamp, and a thermoelectrically cooled red-sensitive PMT. The surface temperatures of the KSFM phosphor and KSFM–CSA samples under different blue LD power densities were measured by an infrared (IR) thermal imager (Fluke Ti27, America).

Luminous properties of the constructed red LDs or WLDs, such as EL spectra, LE, CCT, CRI, CIE chromaticity coordinate were measured in an integrating sphere (Labsphere, America) of 25 cm diameter equipped with an ocean optics spectrophotometer (CDS – 600, Labsphere, America). The red or white LDs were fabricated by combining the corresponding samples and the blue laser (XD-450-HS-20W, Changchun new industry photoelectric technology, China). The blue laser consists of three parts: continuously tunable blue LDs, an optical fiber, and a collimator. The samples were integrated into the collimator. The optical power, as determined by the current input of the blue LDs, was measured using a power meter (Nova II display rohs, Ophir Photonics, Israel) equipped with a thermal sensor (30A-BB-18, Ophir Photonics, Israel). The spot size of the blue laser in the collimator was measured by a beam analyzer camera (BGS-USB-sensor (30A-BB-18, Ophir Photonics, Israel)).

The color drifts of the as-prepared WLDs were calculated using the formula (2)

\[ \Delta E = \sqrt{(u' - u'_)^2 + (v' - v'_)^2 + (w' - w'_)^2} \]  

(2)

where \( u' = 4x/(3 - 2x + 12y) \), \( v' = 9y/(3 - 2x + 12y) \) and \( w' = 1 - u' - v' \). Here, \( u' \) and \( v' \) are the chromaticity coordinates in the uniform \( u'v' \) color space, \( x \) and \( y \) are the chromaticity coordinates in the CIE 1931 color space, and \( o \) and \( t \) denote the chromaticity shifts at 1.05 W mm\(^{-2}\) laser power density and a given laser power density, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the National Key R&D Program of China (2018YFB0406800 and 2018YFB0406801), the Joint Funds of the National Natural Science Foundation of China and Yunnan Province (U1902222), NSFC (51772336, 51702373, and 11961145101), Key-Area Research and Development Program of GuangDong Province (2019B010926001), Guangzhou Science & Technology Project (202007020005, 201807010104 and 201802020033), Hunan High Level Talent Gathering Project (2019RS1077 and 2020RC5007) and China Postdoctoral Science Foundation (2020M672960).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

coated sapphire substrates, \( K_2 Si_F_6:M_n^{4+} \), laser diodes, phosphor-in-glass films

Received: May 26, 2021
Revised: September 16, 2021
Published online: November 25, 2021

[1] Y. Xu, L. H. Chen, Y. Z. Li, G. F. Song, Y. P. Wang, W. D. Zhuang, Z. Long, Appl. Phys. Lett. 2008, 92, 021129.
[2] B. Chandrajit, M. W. Merve, R. Bernhard, Adv. Opt. Technol. 2013, 66, 18.
[3] J. J. Wierier, J. Y. Tsao, D. S. Sizov, Laser Photonics Rev. 2013, 7, 963.
[4] Z. Chen, B. Wang, X. Li, D. Huang, H. Sun, Q. Zeng, Materials 2018, 11, 1792.
[5] H. Yuan, F. Massuyeyeu, N. Gautier, A. B. Kama, E. Faulques, F. Chen, Q. Shen, L. Zhang, M. Paris, R. Gautier, Angew. Chem. Int. Ed. 2020, 59, 2802.
[6] Z. H. Liu, P. Hu, H. J. Jiang, P. Sun, Y. F. Liu, Z. H. Luo, J. T. Xu, R. H. Huang, J. Jiang, Mater. Chem. C 2021, 9, 3522.
[7] J. Xu, Y. Yang, Z. Guo, B. Hu, J. Wang, B. Du, B. Liu, H. Ji, D. Hansen, O. B. Jensen, J. Eur. Ceram. Soc. 2020, 40, 4704.
[8] P. Huang, Y. Zhao, J. C. Wang, Y. R. Zheng, P. Yang, Q. Zheng, S. J. Gu, B. Y. Zhou, W. Jiang, L. J. Wang, J. Am. Ceram. Soc. 2020, 103, 4989.
[9] Y. Zhang, Z. Zhang, X. Liu, G. Shao, L. Shen, J. Liu, W. Xiang, X. Liang, Chem. Eng. J. 2020, 401, 125983.
[10] J. Xu, Y. Yang, Z. Jiang, B. Hu, X. Wang, H. Ji, J. Wang, Z. Guo, B. Du, C. Dam-Hansen, O. B. Jensen, Ceram. Int. 2021, 47, 15307.
[11] L. Huang, Y. Zhu, X. Zhang, R. Zou, F. Pan, J. Wang, M. Wu, Chem. Mater. 2016, 28, 1495.
[12] H. Lin, L. Yong, S. Shuaichen, B. Mikhail, W. Chengxin, W. Jing, Chem. Commun. 2018, 54, 11857.
[13] J. E. Murphy, F. Garcia-Santamaria, A. A. Setlur, S. Sista, SID 2015 DIGEST, 2015, 46, 927.
[14] J. D. Lin, Y. X. Lu, X. Y. Li, F. Huang, C. B. Yang, M. L. Liu, N. Z. Jiang, D. Q. Chen, ACS Energy Lett. 2021, 6, 519.
[15] S. Arjoca, E. G. Villora, D. Inomata, K. Aoki, Y. Sugahara, K. Shimamura, Mater. Res. Express 2015, 2, 055503.
[16] Y. Y. Zhou, C. K. Yu, E. H. Song, Y. J. Wang, H. Ming, Z. G. Xia, Q. Y. Zhang, Adv. Opt. Mater. 2020, 8, 2000976.
[17] J. Zhou, Y. Wang, Y. Chen, Y. Zhou, B. Milicic, L. Zhou, J. Yan, J. Shi, R. S. Liu, M. Wu, Angew. Chem. Int. Ed. 2021, 60, 3940.
[18] J. Wang, X. Tang, P. Zheng, S. Li, T. Zhou, R. J. Xie, J. Mater. Chem. C 2019, 7, 3901.
[19] Q. Yao, P. Hu, P. Sun, M. Liu, R. Dong, K. Chao, Y. Liu, J. Jiang, H. J. Jiang, Adv. Mater. 2020, 32, 1907888.
[20] R. Zhang, H. Lin, Y. Yu, D. Chen, J. Chen, Y. Wang, Laser Photonics Rev. 2014, 8, 158.
[21] X. J. Zhang, J. B. Yu, J. Wang, B. F. Lei, Y. L. Liu, Y. J. Cho, R. J. Xie, H. W. Zhang, Y. R. Li, Z. F. Tian, Y. Li, Q. Su, ACS Photonics 2017, 4, 986.
[22] J. Yu, S. Si, Y. Liu, X. Zhang, Y. Cho, Z. Tian, R. Xie, H. Zhang, Y. Li, J. Wang Li, J. Mater. Chem. C 2018, 6, 8212.
[23] X. J. Zhang, S. C. Si, J. B. Yu, Z. J. Wang, R. H. Zhang, B. F. Lei, Y. L. Liu, J. L. Zhuang, C. F. Hu, Y. J. Cho, R. J. Xie, H. W. Zhang, Z. F. Tian, J. Wang, J. Mater. Chem. C 2019, 7, 354.
[24] H. Yang, Y. Zhang, Y. Zhang, Y. Zhao, X. Liang, G. Chen, Y. Liu, W. Xiang, Chem. Eng. J. 2021, 414, 128754.
[25] S. X. Li, L. Wang, N. Hirosaki, R. J. Xie, Laser Photonics Rev. 2018, 12, 1800173.
[26] R. A. Osborne, N. J. Cherepy, Z. M. Seeley, S. A. Payne, A. D. Drobshoff, A. M. Srivastava, W. W. Beers, W. W. Cohen, D. L. Schlager, Opt. Mater. 2020, 107, 110140.
[27] J. Park, S. Cho, H. Kwon, Sci. Rep. 2018, 8, 17852.
[28] J. Park, J. Kim, H. Kwon, Adv. Opt. Mater. 2017, 5, 1700347.
[29] P. Zheng, S. Li, L. Wang, T. Zhou, S. You, T. Takeda, N. Hirosaki, R. J. Xie, ACS Appl. Mater. Interfaces 2018, 10, 14930.
[30] Y. Peng, Y. Mou, H. Wang, Y. Zhuo, H. Li, M. X. Chen, X. B. Luo, J. Eur. Ceram. Soc. 2018, 38, 5525.
[31] Y. Peng, Y. Mou, Y. Zhuo, H. Li, X. Wang, M. Chen, X. Luo, J. Alloys Compd. 2018, 768, 114.
[32] S. You, S. Li, P. Zheng, T. Zhou, L. Wang, L. Liu, N. Horisaki, F. Xu, R. J. Xie, Laser Photonics Rev. 2018, 13, 1800216.
[33] J. R. Oh, S. H. Cho, Y. H. Lee, Y. R. Do, Opt. Express 2009, 17, 7450.
[34] T. Senden, R. J. A. van Dijk-Moes, A. Meijerink, Light Sci. Appl. 2018, 7, 8.
[35] M. A. van de Haar, M. Tachikirt, A. C. Berends, M. R. Krames, A. Meijerink, F. T. Rabouw, ACS Photonics 2021, 8, 1784.