

Article

Enhancing Infrared Photoluminescence Performance via Li^+ Substitution and Yb^{3+} Codoping in $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ Phosphor

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Abstract: Cr^{3+} -doped broadband infrared luminescent materials have attracted growing attention in consideration of their potential applications in phosphor-converted infrared light sources. However, discovering infrared-emitting luminescent materials with ultrabroadband emission and excellent thermal stability still remains a challenge. In this work, we report the significant improvement of infrared photoluminescence properties in $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor via Li^+ substitution and Yb^{3+} codoping. The prepared $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor can produce broad infrared emission over 650–1350 nm with a peak maximum at 898 nm under the excitation of blue light. Through the substitution of Li^+ for Na^+ , the maximum infrared emission peak can be tuned from 898 nm to 850 nm. When the Li^+ content is 0.5, the integrated infrared luminescence intensity of the obtained $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor increases by 4.2 times compared with that of the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor, and the luminescence thermal stability is also improved significantly (58.5%@100 °C). Moreover, Yb^{3+} codoping can simultaneously realize the characteristic infrared luminescence of Cr^{3+} and Yb^{3+} , resulting in a broadened spectral width due to efficient energy transfer from Cr^{3+} to Yb^{3+} . Finally, an ultrabroadband infrared light-emitting diode prototype is fabricated through a combination of the optimized $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$ phosphor with a commercial 490 nm LED chip, giving an infrared output power of 5.2 mW at 320 mA drive current. This work provides an effective way to optimize the infrared photoluminescence performance of Cr^{3+} -doped $\text{Na}_3\text{ScSi}_3\text{O}_9$ infrared phosphors.

Keywords: phosphor; Cr^{3+} - Yb^{3+} ; infrared luminescence; energy transfer; LEDs



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1. Introduction

Phosphor-converted infrared light-emitting diodes (LEDs) have aroused considerable attention owing to their appealing advantages over traditional infrared light sources, including their simple fabrication process, small size, low cost, and high luminescence efficiency [1–5]. These unique features give infrared LEDs broad application prospects in the fields of night vision, biomedical imaging, industrial nondestructive analysis, and so on [6–9]. As an indispensable component in phosphor-converted infrared LEDs, infrared-emitting phosphors play a crucial role in determining the overall luminescence performance of the final infrared LED devices [10]. In recent years, Cr^{3+} -activated broadband inorganic phosphor materials have attracted extensive attention in view of their superior infrared luminescence performance, including strong blue light absorption capability and tunable broadband emission in a weak octahedral crystal field [11–17]. Among them, Cr^{3+} -doped silicate-based broadband infrared phosphors usually show good physicochemical stability, low cost, and high luminescence efficiency [18–20], which enables them to be desirable light conversion materials for phosphor-converted infrared LEDs.

The infrared photoluminescence properties of Cr^{3+} -doped phosphors greatly depend on the surrounding crystal field environment where Cr^{3+} ions are located, which can exhibit narrowband and broadband emissions ascribed to the $\text{Cr}^{3+} {}^2\text{E} \rightarrow {}^4\text{A}_2$ and ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transitions,

respectively [21–23]. Recently, extensive research work has been devoted to improving the photoluminescence properties of these Cr^{3+} -doped infrared phosphors through ion substitution. For instance, Miao et al. successfully realized the tune of infrared photoluminescence of $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3:\text{Cr}^{3+}$ phosphor from a sharp-line emission at 695 nm to a broad emission band peaking at 750 nm by codoping Ga^{3+} ion [24]. Liu et al. synthesized $\text{Ga}_{2-x}\text{Sc}_x\text{O}_3:\text{Cr}^{3+}$ solid-solution phosphors, in which $\text{Ga}_{1.594}\text{Sc}_{0.4}\text{O}_3:0.006\text{Cr}^{3+}$ phosphor showed the best infrared photoluminescence performance with a high internal quantum efficiency (99%) [25]. Zhao et al. reported $\text{A}_2\text{MSbO}_6:\text{Cr}^{3+}$ phosphors ($\text{A} = \text{Ba}, \text{Sr}, \text{and Ca}$; $\text{M} = \text{Sc}, \text{In}, \text{Y}, \text{and Ga}$), whose maximum infrared emission peak could be tuned over 825–1010 nm through the precise modulation of composition [26]. Shao et al. presented the anionic F-substitution strategy to improve the infrared luminescence performance of the $\text{MgGa}_2\text{O}_4:\text{Cr}^{3+}$ phosphor, and a maximum external quantum efficiency (EQE) value of 60.6% was realized for the prepared $\text{Mg}_{1.2}\text{Ga}_{1.72}\text{O}_{3.8}\text{F}_{0.2}:0.08\text{Cr}^{3+}$ phosphor [27]. All the aforementioned research work gives great inspiration to design and develop Cr^{3+} -doped infrared broadband phosphors with tunable emission peaks.

On the other hand, for Cr^{3+} -doped infrared-emitting phosphors, the maximum emission peak is usually less than 900 nm and the full width at half maximum (FWHM) usually cannot exceed 200 nm, which greatly limits their practical applications for phosphor-converted superbroadband infrared LEDs [28,29]. To address these disadvantages, the Yb^{3+} codoping strategy has been reported to improve the spectral width and luminescence thermal stability of Cr^{3+} single-doped phosphors by making use of efficient energy transfer between Cr^{3+} and Yb^{3+} ions, which has been verified as an effective strategy to enhance infrared photoluminescence performance of these Cr^{3+} -doped phosphors. The representative works include $\text{Ca}_2\text{LuZr}_2\text{Al}_3\text{O}_{12}:\text{Cr}^{3+}, \text{Yb}^{3+}$ [30], $\text{Gd}_3\text{Sc}_{1.5}\text{Al}_{0.5}\text{Ga}_3\text{O}_{12}:\text{Cr}^{3+}, \text{Yb}^{3+}$ [31], $\text{Lu}_{0.2}\text{Sc}_{0.8}\text{BO}_3:\text{Cr}^{3+}, \text{Yb}^{3+}$ [32], $\text{CaTaO}_4:\text{Cr}^{3+}, \text{Yb}^{3+}$ [33], $\text{LiScP}_2\text{O}_7:\text{Cr}^{3+}, \text{Yb}^{3+}$ [34], and $\text{KYbP}_2\text{O}_7:\text{Cr}^{3+}$ phosphors [35]. However, developing novel infrared-emitting phosphors with long-wavelength broadband emission and excellent luminescence thermal stability still remains a challenge.

In this work, we reported the significant enhancement of infrared photoluminescence performance via Li^+ substitution and Yb^{3+} codoping in $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor. Broadband infrared emission with a spectral width of 234 nm and good luminescence thermal stability (66.8%@100 °C) can be achieved in the prepared $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}, \text{Yb}^{3+}$ phosphor. Moreover, infrared phosphor-converted broadband LEDs are constructed by combining $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}, \text{Yb}^{3+}$ phosphors with 490 nm LED chips, presenting a maximum infrared output power of 5.2 mW with a photoelectric conversion efficiency of 0.5% at 320 mA drive current.

2. Experimental Section

2.1. Synthesis

The $\text{Na}_{3-x}\text{Li}_x\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}, \text{Yb}^{3+}$ phosphors were synthesized by the high-temperature solid-state reaction method [35,36]. The starting powder raw materials of Na_2CO_3 (99.99%, Aladdin), Li_2CO_3 (99.99%, Aladdin), Sc_2O_3 (99.99%, Aladdin), SiO_2 (99.99%, Aladdin), Cr_2O_3 (99.99%, Aladdin), Yb_2O_3 (99.99%, Aladdin) were mixed and ground thoroughly for 30 min. After that, the mixed powders were sintered at 1150 °C for 5 h in air to obtain the final infrared phosphors.

2.2. Fabrication of Phosphor-Converted Infrared LEDs

The phosphor-converted infrared light sources were fabricated by combining an LED chip with the prepared $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}, 0.5\%\text{Yb}^{3+}$ phosphor. The HAAS 2000 photoelectric measuring system (350–1650 nm, EVERFINE, Shenzhen, China) was used to measure the light output power of the fabricated LEDs.

2.3. Characterization

A powder X-ray diffractometer was used to measure the phase purity and composition of the prepared phosphors (DMAX-2500PC, Rigaku, Tokyo, Japan). Field-emission scanning electron microscope (FE-SEM, JSM-7800F) (Edinburgh Instruments Ltd, Kirkton Campus, UK) was used to testify the microstructure and EDS elemental maps of the phosphors. An Edinburgh FLS1000 spectrofluorometer (Edinburgh Instruments Ltd, Kirkton Campus, UK) equipped with both continuous and pulsed xenon lamps was used to measure the infrared luminescence properties of the prepared phosphors, including photoluminescence excitation spectra, emission spectra, and luminescence decay curves. The temperature-dependent emission spectra were measured using a TAP02 high-temperature fluorescence test attachment (Edinburgh Instruments Ltd, Kirkton Campus, UK).

3. Results and Discussion

3.1. Structural Characterization of the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ Phosphor

Figure 1a depicts the crystal structure of the $\text{Na}_3\text{ScSi}_3\text{O}_9$ compound, which belongs to the orthorhombic lattice system with a $\text{P2}_1\text{2}_1\text{2}_1$ (No. 19) space group. There exist three distinct crystal sites for the Na^+ ions, which connect with four oxygen ions, five oxygen ions, and six oxygen ions to form $[\text{NaO}_x]$ polyhedra, respectively. In the meanwhile, four different crystallographic sites of Sc^{3+} and one crystallographic site of Si^{4+} also exist, which are linked to six oxygen ions and four oxygen ions to form the $[\text{ScO}_6]$ octahedron and $[\text{SiO}_4]$ tetrahedron, respectively. The crystal structure of the $\text{Na}_3\text{ScSi}_3\text{O}_9$ matrix can be formed through the ordered connections of these polyhedra. Considering the same chemical valence states of Cr^{3+} and Sc^{3+} and the similar ionic radii (when the coordination number is 6, the radius of the Cr^{3+} ion is 0.615 Å and the radius of the Sc^{3+} ion is 0.745 Å), the Cr^{3+} emitters prefer to occupy the position of Sc^{3+} in the $[\text{ScO}_6]$ octahedron in the $\text{Na}_3\text{ScSi}_3\text{O}_9$ host. The XRD patterns of the $\text{Na}_3\text{ScSi}_3\text{O}_9:x\%\text{Cr}^{3+}$ ($x = 0.5, 1, 2$, and 3) phosphors are given in Figure 1b. The XRD peaks of the obtained phosphors are consistent with the standard JCPDS card of the $\text{Na}_3\text{YSi}_3\text{O}_9$ crystal (No. 36-0127), which confirms that the as-synthesized phosphor has a pure phase and the doping of Cr^{3+} ions does not introduce any impurity phases.

The SEM and EDS elemental mapping images of the $\text{Na}_3\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ phosphor are displayed in Figure 1c. As shown in the SEM results, the sample is composed of irregular particles with uneven particle size distribution. The elemental mapping results clearly reflect that Na, Sc, Si, O, and Cr elements are uniformly distributed throughout the selected luminescent particle. The above results further reveal that the Cr^{3+} -doped $\text{Na}_3\text{ScSi}_3\text{O}_9$ infrared phosphor has been successfully synthesized.

3.2. Photoluminescence Properties of the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ Infrared Phosphor

Figure 2a shows the temperature-dependent infrared photoluminescence spectra of the prepared $\text{Na}_3\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ phosphor. As the test temperature increases from 25 to 200 °C, the infrared photoluminescence intensity exhibits a decreasing trend ascribed to the thermal quenching mechanism [36]. Moreover, as shown in Figure 2a, the spectral shape and emission peak stay almost unchanged as the test temperature gradually increases over 25–200 °C. The dependence of the infrared emission intensity on the temperature is given in Figure 2b. As the temperature increases to 100 °C, the integral emission intensity declines to 35.3% of the room temperature emission intensity, and the integral emission intensity decreases to <10% when the temperature reaches 200 °C, indicating that the luminescence thermal stability of the prepared $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor is very poor. Therefore, further optimization of the luminescence thermal stability of the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor is needed for practical applications. Figure 3 shows the Gaussian deconvolutions of the photoluminescence spectrum of the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor. The emission spectra can be decomposed into four Gaussian peaks in units of energy (cm^{-1}), which indicates that there exist four crystallographic sites for Cr^{3+} -emitting centers in the $\text{Na}_3\text{ScSi}_3\text{O}_9$ lattice.

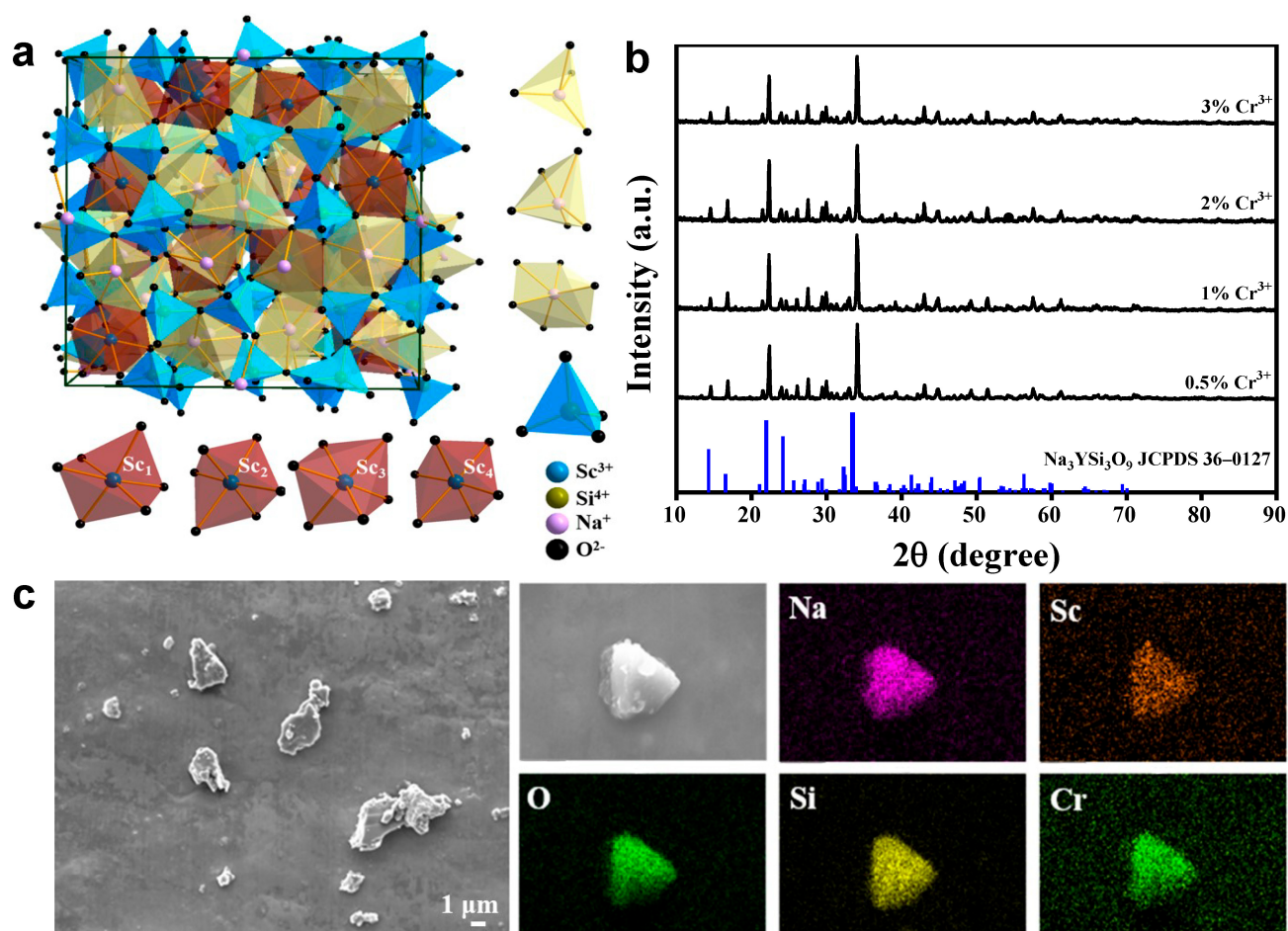


Figure 1. (a) Simulated crystal structure of the $\text{Na}_3\text{ScSi}_3\text{O}_9$. (b) XRD patterns of the $\text{Na}_3\text{ScSi}_3\text{O}_9$: $x\%\text{Cr}^{3+}$ ($x = 0.5, 1, 2$, and 3) phosphors. (c) SEM and EDS elemental mapping images of the $\text{Na}_3\text{ScSi}_3\text{O}_9$: $2\%\text{Cr}^{3+}$ phosphor.

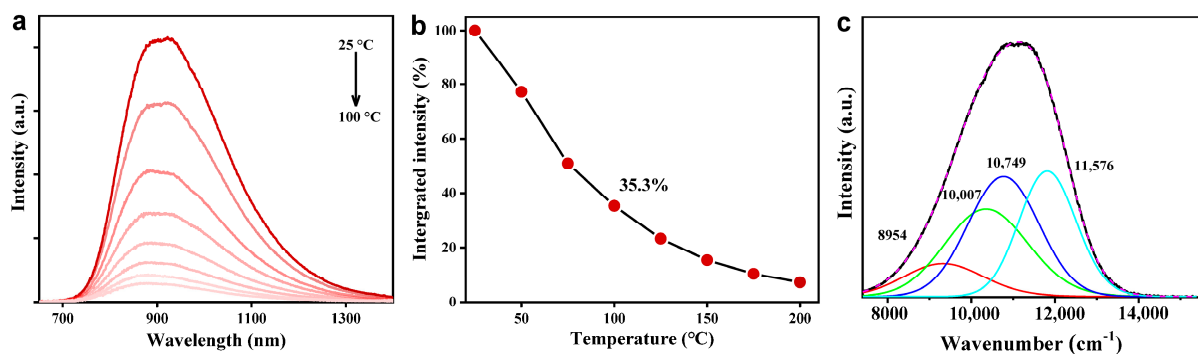


Figure 2. (a) Temperature-dependent infrared photoluminescence spectra of the $\text{Na}_3\text{ScSi}_3\text{O}_9$: $2\%\text{Cr}^{3+}$ phosphor. (b) Dependence of the infrared emission intensity on the test temperature. (c) The Gaussian peak fitting of the emission spectra of the $\text{Na}_3\text{ScSi}_3\text{O}_9$: $2\%\text{Cr}^{3+}$ phosphor.

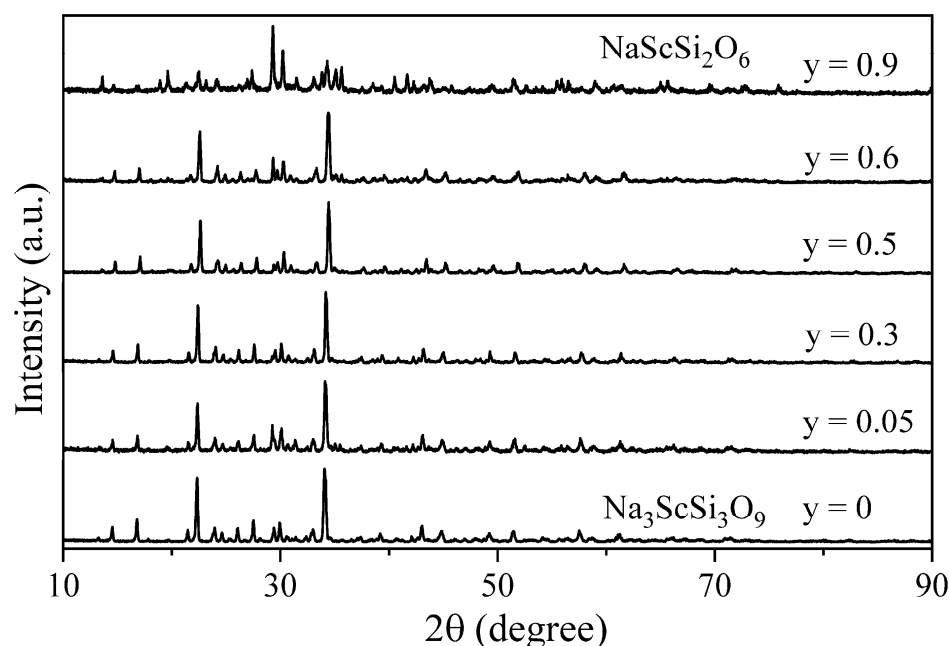


Figure 3. XRD patterns of the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ ($y = 0, 0.05, 0.3, 0.5, 0.6$, and 0.9) phosphors.

3.3. Structural Characterization and Photoluminescence Properties of the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ Phosphors

To improve the thermal stability of the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor, a series of $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphors with different Li^+ content were prepared and studied. Figure 3 presents the XRD patterns of the obtained $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ ($y = 0, 0.05, 0.3, 0.5, 0.6$, and 0.9) phosphors. It can be noted that the phase composition of the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor is consistent with that of $\text{Na}_3\text{ScSi}_3\text{O}_9$ when the content of Li^+ is less than 0.5 ($y \leq 0.5$). This indicates that the doped Li^+ ions successfully occupy the sites of Na^+ ions and no impurity phase can be formed. However, when $y > 0.5$, the $\text{NaScSi}_2\text{O}_6$ impurity phase starts to appear, and the main phase composition changes to the $\text{NaScSi}_2\text{O}_6$ compound when the y value reaches 0.9. Therefore, the content of Li^+ in $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor should be less than 0.5 from the perspective of phase composition.

The excitation spectra of the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:0.02\%\text{Cr}^{3+}$ ($y = 0, 0.05, 0.25$, and 0.5) phosphors are displayed in Figure 4a. Two excitation bands in the blue and red spectral regions are clearly observed, which can be ascribed to the $\text{Cr}^{3+} {}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ electron transitions, respectively [37]. The spectral shapes of the excitation spectra remain almost unchanged with varying Li^+ content, especially the blue excitation peak at around 489 nm. The photoluminescence emission spectra of the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ phosphors are shown in Figure 4b. Under the excitation of 489 nm, a significant enhancement in the infrared luminescence intensity and a blue shift of the emission peak can be observed with the increasing doping concentration of Li^+ . Compared with the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor, the emission intensity of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor is enhanced by ~ 4.2 times, and the peak emission shifts from 898 nm to 850 nm with an FWHM value of ~ 159 nm. The values of Dq/B are increased from 2.11 to 2.25 with the increase in the doping content of Li^+ , indicating that the surrounding crystal field environment experienced by Cr^{3+} ions shows an increasing trend.

The dependence of the integrated infrared luminescence intensity on the test temperature of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ phosphor is given in Figure 4c,d. The spectral shape and maximum emission peak wavelengths remain unchanged with the increase in the test temperature. When the test temperature increases to 100 °C, the integral emission intensity can keep 58.5% of the initial emission intensity at room temperature. As a result,

it can be seen that the substitution of Li^+ ions for Na^+ ions has a significant effect on the luminescence thermal stability of the prepared $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphors.

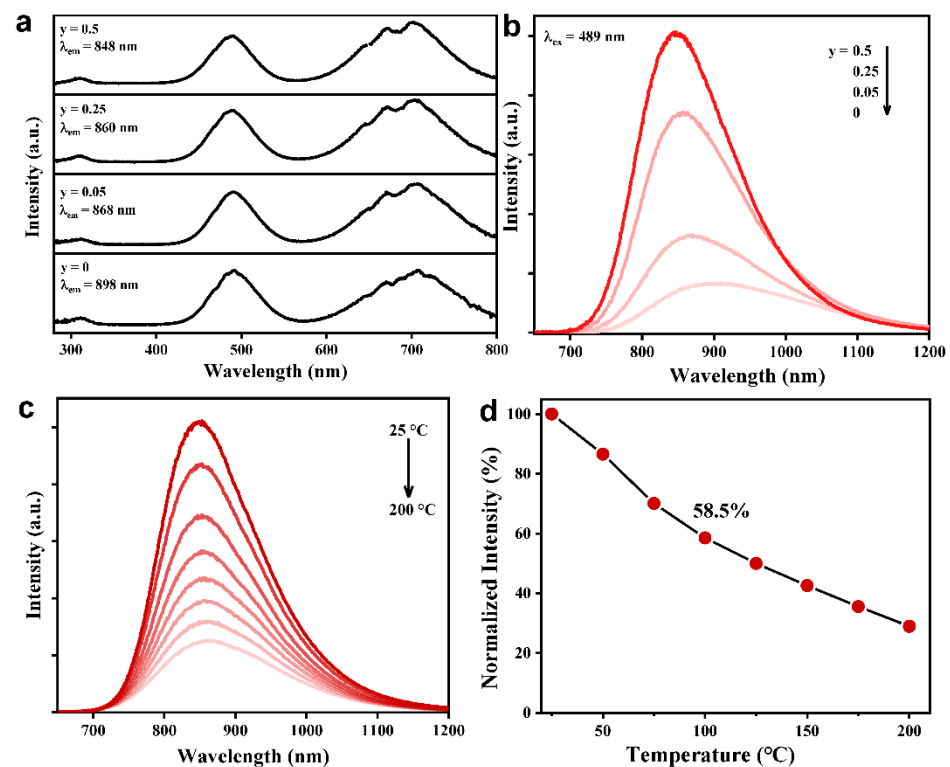


Figure 4. (a) Excitation spectra of the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ ($y = 0, 0.05, 0.25$, and 0.5) phosphors monitored at 898, 868, 860, and 848 nm, respectively. (b) Photoluminescence emission spectra of the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ ($y = 0, 0.05, 0.25$, and 0.5) phosphors upon 489 nm excitation. (c) Temperature-dependent infrared luminescence spectra of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ phosphor. (d) Dependence of the integrated infrared luminescence intensity on the test temperature.

3.4. Enhancing Infrared Photoluminescence Performance by Yb^{3+} Codoping

The infrared luminescence intensity and thermal stability can be improved by tuning the Na/Li stoichiometric ratio in the $\text{Na}_{3-y}\text{Li}_y\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor. However, the FWHM value of the obtained phosphor is still smaller than 200 nm and the maximum emission peak is less than 900 nm, which will limit the practical application for infrared LEDs. Therefore, a series of $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},z\text{Yb}^{3+}$ phosphors were synthesized by codoping Yb^{3+} . As presented in Figure 5a, all the XRD patterns of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},z\text{Yb}^{3+}$ phosphors agree well with the standard JCPDS card of the $\text{Na}_3\text{YSi}_3\text{O}_9$ crystal, which confirms that the synthesized phosphors are all pure phases and that the Cr^{3+} and Yb^{3+} codoping does not cause any impurities. Figure 5b exhibits the emission and excitation spectra of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ and $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$ phosphors, respectively. Under the excitation of 489 nm, the characteristic emission band of Cr^{3+} ions ascribed to the ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition can be clearly monitored. For $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$, an additional emission band is observed in the 950–1150 nm spectral range, which originates from $\text{Yb}^{3+} {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition [30]. Moreover, the spectral width of the emission spectrum of $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$ phosphor is significantly broadened. Moreover, it is noted that when monitored at 970 nm, the excitation spectrum of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$ phosphor shows the same spectral profiles with that of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ phosphor, which further proves the efficient $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer in the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$ phosphor.

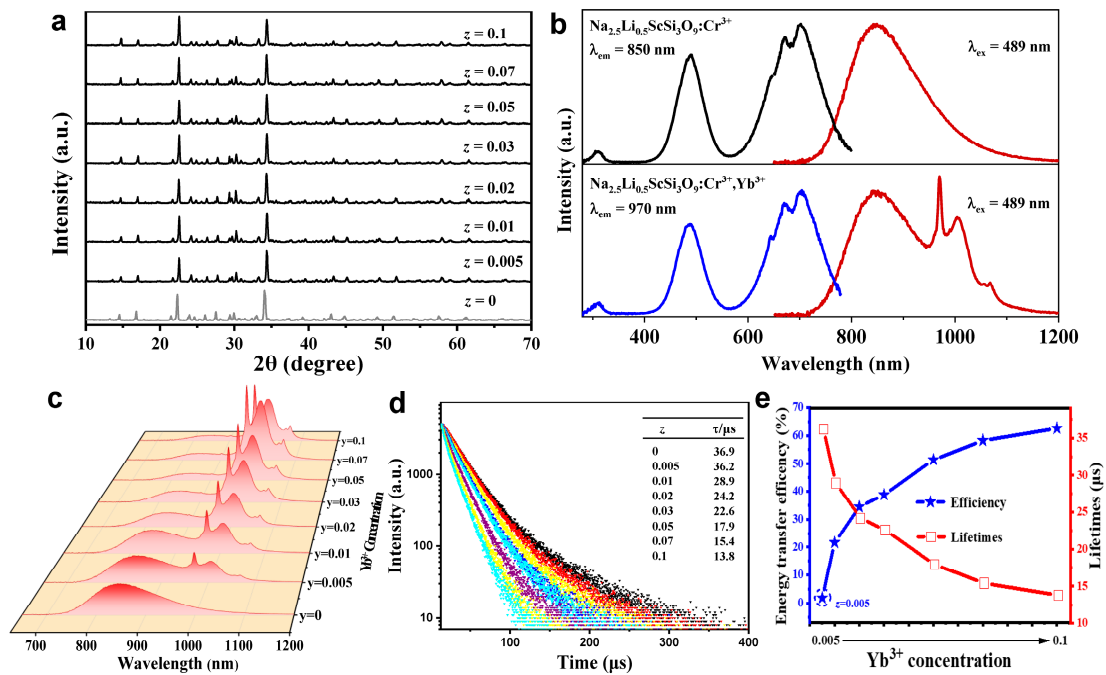


Figure 5. (a) XRD patterns of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},z\text{Yb}^{3+}$ phosphors. (b) Emission and excitation spectra of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}$ and $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$ phosphors. (c) Emission spectra of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},z\text{Yb}^{3+}$ ($z = 0, 0.005, 0.01, 0.02, 0.03, 0.05, 0.07$, and 0.1) phosphors upon 489 nm excitation. (d) Luminescence decay curves monitored at 850 nm with varying Yb^{3+} doping contents. (e) The lifetime and $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer efficiency as a function of Yb^{3+} doping contents.

The photoluminescence emission spectra of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},z\text{Yb}^{3+}$ phosphors upon 489 nm excitation are presented in Figure 5c. As the Yb^{3+} doping concentration increases, the luminescence intensity of Cr^{3+} gradually decreases. However, the infrared luminescence intensity of Yb^{3+} first increases monotonously and reaches the maximum when $z = 0.07$, then starts to decrease. Figure 5d gives the photoluminescence decay curves monitored at 850 nm with varying Yb^{3+} doping concentrations. The monoexponential equation can be used to fit the luminescence decay curves well [38]:

$$I(t) = I_0 + A \exp(-t/\tau) \quad (1)$$

where $I(t)$ represents the emission intensity at time t , A is the fitting constant, τ represents the lifetime. As shown in Figure 5d, the lifetimes of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},z\text{Yb}^{3+}$ phosphors monitored at 850 nm are determined to be $36.9, 36.2, 28.9, 24.2, 22.6, 17.9, 15.4$, and $13.8\text{ }\mu\text{s}$, respectively. The $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer efficiency (η) can be calculated by using the equation:

$$\eta = 1 - \tau_z/\tau_0 \quad (2)$$

where η is the energy transfer efficiency, τ_z and τ_0 are the lifetimes of the Cr^{3+} ions in the presence and absence of Yb^{3+} ions, respectively. The lifetime and $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer efficiency as a function of Yb^{3+} doping concentrations are shown in Figure 5e. The $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer efficiency (η) can reach 62.7% when the doping concentration of Yb^{3+} is increased to 10% .

Figure 6a,b depict the dependence of infrared luminescence spectra of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+},0.5\%\text{Yb}^{3+}$ phosphor on the test temperature upon blue light excitation. When the temperature increases from 25 to $200\text{ }^\circ\text{C}$, the infrared luminescence intensity decreases gradually, which is ascribed to the thermal quenching mechanism. When the temperature increases to $100\text{ }^\circ\text{C}$, the integral infrared luminescence intensity drops to 66.8% of room-temperature emission intensity, respectively (Figure 6c).

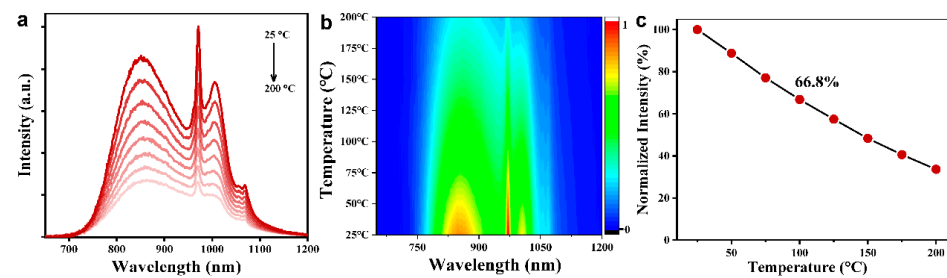


Figure 6. (a) Temperature-dependent infrared luminescence spectra of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}, 0.5\%\text{Yb}^{3+}$ phosphor. (b) The two-dimensional color map of temperature-dependent infrared luminescence spectra. (c) Dependence of the infrared emission intensity on the temperature.

3.5. Luminescence Properties of the Fabricated Phosphor-Converted Infrared LEDs

The phosphor-converted infrared emitters were assembled through the combination of the $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}, 0.5\%\text{Yb}^{3+}$ phosphor with a 490 nm LED chip. When the driving current is turned on, visible emission can be observed from the inside 490 nm LED chip, which can be fully covered by using a 650 nm long-pass filter, as shown in the insets in Figure 7a. Figure 7a displays the infrared emission spectra of the fabricated infrared LED under various drive currents. As the drive currents increase over 20–320 mA, the fabricated infrared LED shows a broad emission band in a wavelength range of 700–1100 nm, and the infrared luminescence intensity increases gradually. Meanwhile, the output power and photoelectric conversion efficiency of the fabricated infrared LED under various drive currents are given in Figure 7b,c. When the drive current increases over 20–320 mA, the infrared output power increases monotonously from 0.6 to 5.2 mW, while the photoelectric conversion efficiency declines from 1.2% to 0.5%. The decrease in conversion efficiency can be ascribed to the efficiency decrease in the 490 nm LED chip. Furthermore, the infrared luminescence performance of the assembled LEDs can be further improved through the optimization of the fabrication process. Therefore, the prepared $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}, \text{Yb}^{3+}$ phosphor shows a promising application for phosphor-converted infrared LEDs.

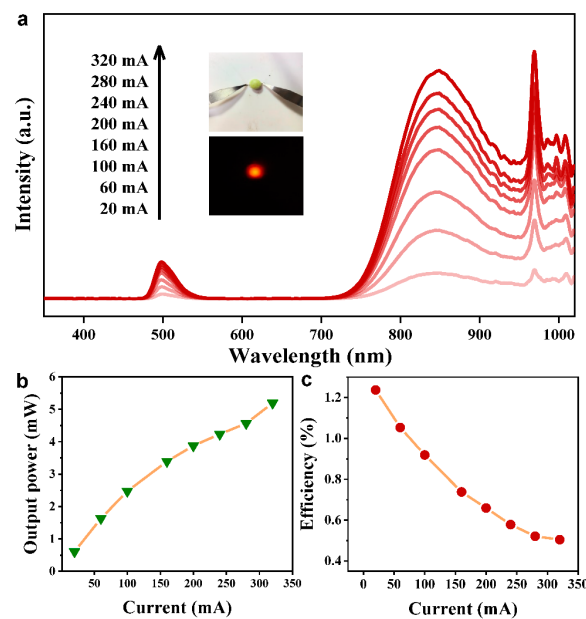


Figure 7. (a) Luminescence spectra of the fabricated infrared LED by combining $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:2\%\text{Cr}^{3+}, 0.5\%\text{Yb}^{3+}$ phosphor with a 490 nm LED chip at different drive currents. The insets present the fabricated infrared LED prototype device. (b,c) Output power and photoelectric conversion efficiency of the fabricated infrared LED under various drive currents.

4. Conclusions

In this work, we report that the infrared photoluminescence intensity, thermal stability, and spectral width can be significantly improved through Li^+ substitution and Yb^{3+} codoping in $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor. When the Li^+ content is 0.5, the integrated infrared luminescence intensity of the prepared $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor increases by 4.2 times in comparison with that of the $\text{Na}_3\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}$ phosphor. Meanwhile, thanks to the efficient $\text{Cr}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer, the optimized $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}, \text{Yb}^{3+}$ phosphor exhibits a broadened spectral width and good luminescence thermal stability, whose integral luminescence intensity at 100 and 125 °C can maintain 66.8% and 57.5% of room temperature emission intensity, respectively. An ultrabroadband infrared LED prototype device was assembled through the combination of the optimized $\text{Na}_{2.5}\text{Li}_{0.5}\text{ScSi}_3\text{O}_9:\text{Cr}^{3+}, \text{Yb}^{3+}$ phosphor and a 490 nm LED chip, which gives an infrared output power of 5.2 mW with photoelectric conversion efficiency of 0.5% at 320 mA drive current. Overall, this work provides new insights into the design and development of efficient, broadband, and thermally stable infrared-emitting phosphors for high-power infrared LEDs.

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