Efficient broadband near-infrared phosphor $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ for solar-like lighting

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ABSTRACT For healthy lighting, daily lighting that considers both visible light and near-infrared (NIR) light is necessary. However, at ~900 nm, the extensively used solar-like phosphor-converted light-emitting diodes (pc-LEDs) are limited by a lack of high-performance NIR luminescent materials. We report a broadband NIR phosphor $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ with a double perovskite-type structure, thus simultaneously demonstrating high luminescence efficiency and good thermal stability. Under 550-nm excitation, $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ demonstrates broadband NIR emission centered at ~890 nm with luminescence internal/external efficiencies of 82.0%/35.7%, respectively. Furthermore, the luminescence integrated intensity at 430 K remains at ~66.4% of the initial intensity. We successfully fabricated pc-LED devices using a 465-nm-sized blue chip and other commercial phosphors, presenting a relatively complete solar-like spectrum from blue to NIR light and is expected to be used in solar-like lighting.

Keywords: broadband near-infrared, double-perovskite, $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$, pc-LEDs, solar-like spectrum

INTRODUCTION

The concept of healthy lighting has attracted considerable attention in recent years. The spectrum of healthy lighting sources should be as close to the solar spectrum as possible, including visible and near-infrared (NIR) regions [1–3]. Common lighting sources, which contain visible light regions, meet brightness requirements but fail in multiple health-related requirements. NIR light (700–1400 nm) has the merits of low absorption and low scattering to biological tissue and is favorable for improving the activity of biological molecules by enhancing the immunity of the human body [4–7]. Therefore, for both animals and plants, daily lighting that considers both visible and NIR light is necessary. Artificial all-spectrum solar sources are a promising solution for healthy lighting, ecological simulation, and other fields. Currently, the light sources used to simulate sunlight primarily include carbon arc, halogen, and Xe lamps. Carbon arc lamps produce toxic gases. The spectrum of the halogen lamp is considerably different from the solar spectrum. Moreover, the Xe lamp has high luminous intensity, excellent spectral continuity but delayed luminescence with high cost [8–11]. However, phosphor-converted light-emitting diodes (pc-LEDs) have excellent energy efficiency, long service life, and low cost. Thus, for healthy lighting, pc-LEDs are now used to

fabricate solar-like light sources.

The visible region of the solar spectrum can be achieved by commercial phosphors excited by blue LED chips. To meet the requirements of broad-spectrum emission and high efficiency of pc-LEDs, the NIR region usually requires using high-performance NIR luminescent materials doped with Cr^{3+} ions [12–21]. Zeng *et al.* [22] reported Cr^{3+} -doped double perovskite $\text{La}_2\text{MgZrO}_6$, demonstrating broadband NIR emission centered at 825 nm with ~58% luminescence internal quantum efficiency (IQE). Double perovskite $\text{Cs}_2\text{AgInCl}_6$ presents a broadband NIR emission peak at 1010 nm by incorporating Cr^{3+} in a weak crystal field environment [23]. Furthermore, gallate magnetoplumbite $\text{LaMgGa}_{11}\text{O}_{19}$ phosphor demonstrates broadband NIR emission peak at 770 nm with 45% luminescence external efficiency via the multi-site occupation of Cr^{3+} [24]. Although these materials are suitable for the NIR region, the reported emission bands are primarily distributed in the 700–850 nm range or >1000 nm. The lack of high-performance phosphors close to 900 nm will result in a large deviation between the artificial and actual solar spectra.

This study describes the design and development of Cr^{3+} -doped double perovskite $\text{Sr}_2\text{ScSbO}_6$ NIR luminescence phosphor with high luminescence efficiency and excellent resistance to luminescence thermal quenching. Cr^{3+} ions are placed in a weak crystal field environment using antimonate double-perovskite as a host. Under ultraviolet (UV) or visible light excitation, $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ exhibits broadband NIR emission centered at ~890 nm with full width at half maximum (FWHM) of ~130 nm. The IQE/external quantum efficiency (EQE) of $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ at room temperature is 82.0%/35.7%. At ~430 K, the luminescence intensity remains 66% of that at 80 K. We successfully fabricated pc-LEDs devices with a relatively complete solar-like spectrum from 400 to 1100 nm by combining a 465-nm-sized blue chip and other commercial phosphors, which is expected for use in healthy lighting and sunlight simulation.

EXPERIMENTAL SECTION

Materials and preparation

$\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ phosphors were synthesized by conventional high-temperature solid-state reaction. Strontium carbonate (SrCO_3 , 99.99%), scandium oxide (Sc_2O_3 , 99.5%), antimony pentoxide (Sb_2O_5 , 99.99%) and chromium sesquioxide (Cr_2O_3 , 99.99%) were stoichiometrically weighed and evenly ground in

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an agate mortar. Then, the ground powders were pre-calcined at 800°C for 3 h in a box furnace. After being cooled to room temperature, the samples were extracted and then ground before being calcined at 1500°C for 8 h. Finally, the sample was allowed to naturally cool at room temperature before being ground into fine powders for subsequent measurements.

Characterization

X-ray diffraction (XRD) patterns of $\text{Sr}_2\text{ScSbO}_6 \cdot x\% \text{Cr}^{3+}$ phosphors were collected on a diffractometer (Bruker Corporation, DE) with Cu K α radiation (40 kV and 35 mA, $\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 15° – 65° for phase identification. Rietveld refinements were performed using Fullprof Suite using XRD patterns measured from 5° to 120° in step scan mode [25]. Particle morphology and energy-dispersive X-ray spectroscopy (EDS) analyses were performed using a scanning electron microscope (SEM, JEOL JSM-6510A). The diffuse reflectance (DR) spectra were recorded using a UV-visible-NIR spectrophotometer (UH4150, Hitachi) with BaSO_4 as a standard. The steady photoluminescence (PL) spectra were measured using a fluorescence spectrophotometer (FLS920, Edinburgh) with a Xe lamp as the radiating source. The photoluminescence quantum efficiency at room temperature was measured by absolute PL quantum yield spectrometer (Hamamatsu, C11347).

LED device fabrication

LED devices were obtained using the following method. First, at a mass ratio of 5:1:1, the prepared phosphors and commercial phosphors were mixed and stirred with Dow Corning (OE-6550) A and B components. Then, the mixed glue was coated on a 465-nm-sized blue-light chip (Sanan Optoelectronics) and then cured at 80°C for 1 h. The spectra of LED devices were recorded using a linear Si charged coupled device array detector (Ocean Optics, Sony ILX511B 2048 pixels, USB2000+). The measuring voltage and current were 3.6 V and 300 mA, respectively.

RESULTS AND DISCUSSION

Perovskite materials have potential applications in photo-detectors and LEDs because of their flexible structure and excellent photoelectric properties [26]. Considering a simple

perovskite oxide with the chemical formula ABO_3 , cation A is larger than cation B. Cation A is 12-fold coordinated, whereas cation B is six-fold coordinated with oxygen anions. The corner-sharing octahedra form the skeleton of the structure in which the smaller B cation occupies the center position. The crystal structure of perovskite is extremely flexible; however, certain rules must be followed to ensure structural stability [27]. Compared with a single cubic perovskite system, adding multiple B/B' cations in double perovskite compounds primarily affects the physical properties and crystal structure. In 1963, Patterson *et al.* [26] reported that multiple perovskite compounds, including $\text{Sr}_2\text{ScSbO}_6$, exhibit high-temperature superconductivity, high magnetoresistance, and other properties. In 2013, Ray *et al.* [28] discussed the phase transition process of $\text{Sr}_2\text{ScSbO}_6$ at different temperatures. However, a double perovskite structure skeleton composed of both B and B' octahedra will produce a certain distortion because of different ionic radii compared with a single perovskite structure skeleton composed of a single B octahedron. The $[\text{BO}_6]$ octahedron is squeezed in various manners in $\text{Sr}_2\text{ScSbO}_6$, causing the regular octahedron to tilt and leading to the crystal system transition from cubic ($Fm\bar{3}m$) to monoclinic ($P12_1/n_1$) space group.

Fig. 1a shows the double perovskite structure of $\text{Sr}_2\text{ScSbO}_6$ and the coordination polyhedra of Sr^{2+} , Sb^{5+} , and Sc^{3+} . Sc^{3+} and Sb^{5+} are both six-coordinated with oxygen anions. $[\text{ScO}_6]$ and $[\text{SbO}_6]$ octahedra are alternatively arranged to form a double perovskite skeleton with Sr^{2+} ions occupying the center of octahedral cavities. Fig. 1b–g demonstrate the particle morphology and element distribution mapping, demonstrating that the size of crystal grain prepared in this study is $\sim 10 \mu\text{m}$ with uniform elemental distribution.

Fig. S1 shows the Rietveld refinement result of $\text{Sr}_2\text{ScSbO}_6$ with 2θ ranging from 5° to 120° . The result demonstrates that only a single monoclinic phase of $\text{Sr}_2\text{ScSbO}_6$ was observed with the $P12_1/n_1$ space group. At room temperature, the lattice parameters of $\text{Sr}_2\text{ScSbO}_6$ are $a = 5.685(7) \text{ \AA}$, $b = 5.671(1) \text{ \AA}$, $c = 8.013(5) \text{ \AA}$, $\beta = 90.05(7)^\circ$, $V = 259.31(1) \text{ \AA}^3$, $Z = 2$, and the average bond lengths of Sc–O and Sb–O are 2.06 and 1.98 Å, respectively. Note that Table S1 shows additional details of the atomic parameters of the $\text{Sr}_2\text{ScSbO}_6$ sample. Fig. 2 compares the

Figure 1 (a) Crystal structure of $\text{Sr}_2\text{ScSbO}_6$ and coordination diagram of Sr^{2+} , Sc^{3+} and Sb^{5+} sites. (b) Grain size of $\text{Sr}_2\text{ScSbO}_6$:3% Cr^{3+} detected by SEM. (c–g) Element distribution of Sr, Sc, Sb and Cr for the selected $\text{Sr}_2\text{ScSbO}_6$:3% Cr^{3+} particle.

Figure 2 (a) XRD patterns of Sr₂ScSbO₆:x% Cr³⁺ ($x = 1, 3, 5, 7, 10, 15, 20$) and standard pattern of Sr₂ScSbO₆ (262994-ICSD). (b) Partially enlarged patterns at $\sim 56^\circ$. (c) Dependence of cell volumes and lattice parameter a on the Cr³⁺ content obtained from Le-Bail fitting.

XRD patterns of experimental samples doped with different concentrations of Cr³⁺. All diffraction peaks agree with the standard pattern (262994-ICSD), indicating that only a single phase Sr₂ScSbO₆ exists. The partially magnified patterns at $\sim 56^\circ$ show that the diffraction peak (204) slightly shifts to a higher angle when the doped Cr³⁺ concentration gradually increases because of the replacement of larger Sc³⁺ (0.745 Å, coordination number (CN) = 6) ions by smaller Cr³⁺ (0.615 Å, CN = 6) ions. As shown in Fig. 2c, the Le-Bail fitting results demonstrate that the lattice parameter a and unit cell volume V gradually reduced with an increase in Cr³⁺ concentration. Because of the volatilization of the raw material Sb₂O₃ at high temperatures, the lattice parameter a and unit cell volume V are non-linearly related to Cr³⁺ concentration. As shown in Fig. S2a, an excess of 5% Sb₂O₃ was added to balance the Sb volatilization, producing improved luminescence intensity without generating new impurities. To eliminate the influence of trace impurities on luminescence performance, we obtained the PL spectra of Cr₂O₃, Sc₂O₃, and Sb₂O₃ doped with Cr³⁺. All raw materials have no luminescence detected at ~ 890 nm (Fig. S2b).

Fig. 3a shows the DR spectra of Sr₂ScSbO₆:x% Cr³⁺, and the absorption coefficient increases with higher Cr³⁺ concentration. Both Cr³⁺-doped and undoped samples exhibit prominent absorption peaks at 260 and 310 nm, indicating that the band at 260 nm arises because of interband absorption caused by the electronic transition of Sr₂ScSbO₆ host, whereas the band at 310 nm arises because of host defects. The absorption bands at 350, 550, and 780 nm are attributed to $^4A_2(^4F) \rightarrow ^4T_1(^4P)$, $^4A_2(^4F) \rightarrow ^4T_1(^4F)$, and $^4A_2(^4F) \rightarrow ^4T_2(^4F)$ transitions of Cr³⁺, confirmed in the following PL excitation (PLE) spectral analysis. The interband absorptions exhibit gradual redshift with an

increase in Cr³⁺ concentration, and the Tauc relation can be used to calculate the optical band gap E_g , as shown in Equation (1) [29]:

$$[F(R_\infty)h\nu]^n = A(h\nu - E_g), \quad (1)$$

where $h\nu$ represents the energy of interaction between lattice vibration and electronic transition; A is a constant; for $n = 2$, the calculated result represents the direct transition of Sr₂ScSbO₆; $F(R_\infty)$ is defined using the Kubelka-Munk function, as shown in Equation (2):

$$F(R_\infty) = \frac{(1-R)^2}{2R}, \quad (2)$$

where R is the reflectance coefficient. Fig. 3c shows that the calculated optical band gap of Sr₂ScSbO₆ is 4.25 eV. With the increase in Cr³⁺ concentration in Sr₂ScSbO₆, the optical band gaps decreased from 4.25 to 3.69 eV (Fig. 3b).

Fig. 4a shows the PLE spectra of Sr₂ScSbO₆:x% Cr³⁺ phosphors. The undoped Cr³⁺ sample exhibits only one excitation peak at 310 nm, whereas the Cr³⁺-doped samples show five excitation peaks at 260, 310, 350, 550, and 780 nm. In the undoped Cr³⁺ sample, host defects cause the excitation peak at 310 nm, whereas interband absorption causes the absorption peak at 260 nm. This agrees with the previous DR spectra. Moreover, these four extra excitation peaks for Cr³⁺-doped samples can be considered as the characteristic excitations of Cr³⁺ embedded in the octahedral coordination, i.e., the excitation peaks at 350, 550, and 780 nm are attributed to $^4A_2(^4F) \rightarrow ^4T_1(^4P)$, $^4A_2(^4F) \rightarrow ^4T_1(^4F)$ and $^4A_2(^4F) \rightarrow ^4T_2(^4F)$ inter-configurational transitions of Cr³⁺. Note that the intensity of excitation peak at 310 nm decreases with an increase in Cr³⁺ concentration;

Figure 3 (a) DR spectra of $\text{Sr}_2\text{ScSbO}_6:x\% \text{Cr}^{3+}$ at different Cr^{3+} concentrations. (b) Relationship between the optical band gap of $\text{Sr}_2\text{ScSbO}_6:x\text{Cr}^{3+}$ and the Cr^{3+} content calculated according to the Kubelka-Munk formula. (c) $[F(R) \cdot hv]^2$ as a function of the $h\nu$ photon energy of $\text{Sr}_2\text{ScSbO}_6$ host.

Figure 4 PLE and PL spectra of $\text{Sr}_2\text{ScSbO}_6:x\% \text{Cr}^{3+}$ at different Cr^{3+} doping concentrations ($x = 0, 1, 3, 5, 7, 10, 15, 20$): (a) excitation spectra monitoring at an emission wavelength of 890 nm at room temperature; (b) emission spectra excited by 310 and 550 nm; (c) emission spectra excited by 310 nm; (d) the peak intensities of given excitation wavelengths (310 and 550 nm) versus Cr^{3+} concentration.

the intensities of four excitation peaks of Cr^{3+} first increase and then decrease, supporting two different emission centers in

$\text{Sr}_2\text{ScSbO}_6:x\% \text{Cr}^{3+}$. Therefore, for the Cr^{3+} -doped samples, the host defects and Cr^{3+} absorption synergistically contribute to the

NIR emission.

Fig. 4b, c show the PL spectra excited by 310 and 550 nm at room temperature. All samples show broadband NIR emission covering 800–1100 nm with a peak at 890 nm. As the Cr^{3+} concentration changes, the intensity changes of PL and PLE spectra follow the same pattern. Fig. 4d shows our conclusions more intuitively to compare their luminescence properties. With the increase in Cr^{3+} concentration, the NIR emission intensity at 310 nm continuously decreases, indicating that adding Cr^{3+} ions affects the luminescence of host defects. Under the excitation of 550 nm, the NIR emission intensity first increases and then decreases because the spin-allowed ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transition of Cr^{3+} enhances octahedra with weak crystal fields. With the increase in Cr^{3+} concentration, the concentration quenching phenomenon becomes increasingly obvious; furthermore, the optimal doping concentration is 3%. By comparison, the defect-related emission intensity excited at 310 nm is somewhat higher than that at 550 nm; however, the excitation peak at 310 nm is not conducive for our subsequent applications. The excitation peak at 550 nm can combine with other commercial phosphors to simulate sunlight using a 465-nm-sized blue-light chip. In the application section, additional detailed content will be discussed later.

The energy-level splitting of Cr^{3+} in $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ could be characterized using the Tanabe-Sugano diagram of $3d^3$ electrons embedded in a six-coordinated octahedron. The red lines in Fig. S3 represent the four energy levels ${}^2\text{A}_1$, ${}^2\text{T}_2$, ${}^2\text{T}_1$, and ${}^2\text{E}$ that split out of the ${}^2\text{G}$ state as the crystal field magnitude changes. The blue lines depict the three energy levels ${}^4\text{A}_2$, ${}^4\text{T}_1$, and ${}^4\text{T}_2$ that split from the ${}^4\text{F}$ state. Because $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$ has broadband NIR emission and no characteristic R-line is reported, Cr^{3+} is located in an environment of a weak crystal field. The local crystal field parameter $10Dq/B$ can be obtained by the formula shown in Equations (3–5) [30–32]:

$$10Dq = E({}^4\text{T}_2) = E({}^4\text{A}_2 \rightarrow {}^4\text{T}_2) - \Delta S / 2, \quad (3)$$

$$\frac{B}{Dq} = \frac{\left(\frac{\Delta E_{4T}}{Dq}\right)^2 - 10\left(\frac{\Delta E_{4T}}{Dq}\right)}{15\left(\frac{\Delta E_{4T}}{Dq} - 8\right)}, \quad (4)$$

$$\Delta E_{4T} = E({}^4\text{T}_1) - E({}^4\text{T}_2), \quad (5)$$

where Dq is the crystal field strength; B is the Racah parameter; ΔE_{4T} can be obtained from the energy difference between the peak positions of ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ in PLE spectra. Because of the effect of electron-phonon interaction and Stokes shift (ΔS) in the lattice host, the $E({}^4\text{T}_2)$ used in Tanabe-Sugano diagram is not exactly equal to the excitation peak energy $E({}^4\text{A}_2 \rightarrow {}^4\text{T}_2)$ but to zero-phonon line energy. The energy level of $E({}^4\text{T}_2)$ can be estimated using Equation (3), where $E({}^4\text{A}_2 \rightarrow {}^4\text{T}_2)$ represents the excitation peak energy of ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition, and ΔS can be estimated by calculating the energy difference between the excitation (${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$) and emission (${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$) peaks. Subsequently, the obtained zero-phonon line energy of $E({}^4\text{T}_2)$ and $10Dq/B$ values are $11,928\text{ cm}^{-1}$ and 20.3 , respectively, indicating a weak crystal field strength in $\text{Sr}_2\text{ScSbO}_6\text{:Cr}^{3+}$, consistent with the observed broadband ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ emissions.

As shown in Fig. 5, the luminescence decay curves of $\text{Sr}_2\text{ScSbO}_6\text{:x}\% \text{Cr}^{3+}$ phosphors were measured at room tem-

perature. The data agree with the double exponential equation, as shown in Equation (6) [33]:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right), \quad (6)$$

where A_1 and A_2 are constant; I is the emission intensity, and τ_1 and τ_2 are the decay lifetimes under the exponential component. The total lifetime of $\text{Sr}_2\text{ScSbO}_6\text{:x}\% \text{Cr}^{3+}$ can be calculated using Equation (7) [34]:

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}. \quad (7)$$

The results demonstrate that as Cr^{3+} doping concentration increases, the decay lifetime of $\text{Sr}_2\text{ScSbO}_6\text{:x}\% \text{Cr}^{3+}$ ($x = 1\text{--}15$) decreases from 149 to 68 μs . Compared with previous literature, the decay lifetime of several hundred microseconds is a typical magnitude for the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transition of Cr^{3+} shown in Table S2. The distance between the activated ions gradually decreases as doping concentration increases; thus, the interaction of $\text{Cr}^{3+}\text{--Cr}^{3+}$ and the possibility of energy transfer to the luminescence center are enhanced, leading to a shorter decay lifetime. The lifetime of undoped $\text{Sr}_2\text{ScSbO}_6$ is $\sim 8.7\text{ ms}$, which is about two orders of magnitude longer than that of Cr^{3+} -doped $\text{Sr}_2\text{ScSbO}_6$. This difference can be hardly attributed to the same luminescence center. The considerable difference in lifetime magnitude confirms two different luminescence processes in this material. When Cr^{3+} acts as the luminescence center, the lifetime decay is fast, $\sim 100\text{ }\mu\text{s}$. The luminescence with a lifetime of $\sim 8.7\text{ ms}$ is caused by host defects.

Fig. 6 shows the characterization of luminescent thermal stability, which is important for application, and the integrated intensities of the temperature-dependent PL spectra. The PL intensity of $\text{Sr}_2\text{ScSbO}_6\text{:3}\% \text{Cr}^{3+}$ gradually decreases with an increase in temperature. The luminous intensity of $\text{Sr}_2\text{ScSbO}_6\text{:3}\% \text{Cr}^{3+}$ at 380 K remains 86% that at 80 K. And the value is 66% at 430 K. The working temperature of phosphor layers is $\sim 400\text{ K}$ in pc-LEDs; thus, $\text{Sr}_2\text{ScSbO}_6\text{:x}\% \text{Cr}^{3+}$ phosphors can maintain stable efficiency under general operating conditions. Fig. S4 shows the details of emission spectrum changes. The FWHM broadens from 93 to 147 nm as the temperature increases, which can be explained by the enhanced electron-

Figure 5 Luminescence decay curves of undoped $\text{Sr}_2\text{ScSbO}_6$ and $\text{Sr}_2\text{ScSbO}_6\text{:x}\% \text{Cr}^{3+}$ ($x = 1, 3, 5, 7, 10, 15$) monitored at the optimal emission peak.

Figure 6 (a) PL spectra of $\text{Sr}_2\text{ScSbO}_6:3\% \text{Cr}^{3+}$ varying with temperature under excitation at 550 nm. (b) FWHM and PL intensity of $\text{Sr}_2\text{ScSbO}_6:x\% \text{Cr}^{3+}$ dependence on the temperature. (c) Configuration coordinate diagram of $\text{Sr}_2\text{ScSbO}_6:x\% \text{Cr}^{3+}$ for band broadening and thermal quenching process. (d) PL spectra with BaSO_4 as a reference under 550 nm excitation for quantum efficiency measurement of $\text{Sr}_2\text{ScSbO}_6:3\% \text{Cr}^{3+}$. The inset shows the integrated intensity ratio of the test part S_1 and the missing part S_2 .

phonon interaction [23]. Moreover, as shown in Fig. 6c, a decrease in luminescence intensity can be explained by thermal quenching in the process of non-radiative transition. When electrons are excited to the $^4\text{T}_2$ energy state at low temperatures, most of them return to their ground state by radiative transition and emit NIR light. However, with an increase in temperature, additional electrons in the $^4\text{T}_2(4\text{F})$ state are thermally stimulated to the intersecting state between the $^4\text{A}_2(4\text{F})$ ground state and $^4\text{T}_2(4\text{F})$ excited state because of the greater electron-phonon interaction. Then, electrons can non-radiatively be transferred to the ground state by releasing phonons. Therefore, the higher the temperature, the greater the energy loss of the non-radiation transition, resulting in a decrease in PL intensity. To characterize the properties of phosphors, we measured the quantum efficiency of $\text{Sr}_2\text{ScSbO}_6:3\% \text{Cr}^{3+}$, as shown in Fig. 6d. Because the upper limit of the QE instrument is 950 nm, we integrated the intensity against the emission spectrum for data beyond the wavelength range to obtain the complete quantum efficiency [24]. The IQE is 64.10%, and the EQE is 27.5%. However, when S_2 is considered, the internal and EQEs are 82.0% and 35.7%, respectively.

For comparison, we listed certain reported Cr^{3+} -doped NIR phosphors with a wavelength of 800 nm in Table 1. We used the unified data process method for crystal field strength, as shown in Equations (3–5). The data of crystal field strength ($10Dq/B$) of Cr^{3+} are listed in Column 3 (Table 1). There is no obvious

correlation between $10Dq/B$ and the emission wavelength. The excitation band of $^4\text{A}_2 \rightarrow ^4\text{T}_2$ is usually broad, e.g., the broadband excitation is superimposed via two Cr^{3+} emitting centers in the $\text{La}_2\text{MgZrO}_6$ host [22], making it difficult to determine the accurate zero-phonon line, which causes calculation errors. However, Tanabe-Sugano diagram describes the function of E/B versus $10Dq/B$, and Racah parameter B is closely related to excitation/emission energy E , e.g., although $10Dq/B$ of halogen perovskite $\text{Cs}_2\text{AgInCl}_6:\text{Cr}^{3+}$ is estimated to be 20.3 [23], the calculated Racah parameter B is only 552.7 cm^{-1} , smaller than that of $\text{Sr}_2\text{ScSbO}_6:\text{Cr}^{3+}$ (586.0 cm^{-1}). This leads to more redshift broadband NIR emissions. Generally, for the efficiency part, the quantum efficiency of phosphor in this emission interval is not high, while $\text{Sr}_2\text{ScSbO}_6:\text{Cr}^{3+}$ belongs to a relatively high level. Along with emission peak position and other factors, the NIR phosphors emitted at 900 nm are relatively rare; the longer emission wavelength indicates that Cr^{3+} ions are in a weaker crystal field environment. The decrease in the $^4\text{T}_2(4\text{F})$ energy level increases the possibility of electron non-radiative transition, which makes it difficult for phosphors to obtain the same efficiency as other low-wavelength emission materials. Compared with reported NIR phosphors whose emission wavelength is $\sim 900 \text{ nm}$, $\text{Sr}_2\text{ScSbO}_6:3\% \text{Cr}^{3+}$ phosphors have the highest IQE/EQE. We believe that the luminescence efficiency of this material can be improved via additional optimization in the future.

Finally, we encapsulated $\text{Sr}_2\text{ScSbO}_6:3\% \text{Cr}^{3+}$ phosphor with

Table 1 Important photoluminescence data of certain Cr³⁺-doped NIR phosphors with a peak wavelength of >800 nm

NIR Phosphor	$\lambda_{\max}$ (nm)	10Dq/B	IQE/EQE (%)	$I_{430\text{ K}}$ (%)	Refs
Sr ₂ ScSbO ₆ :Cr ³⁺	890	20.3	82.0/35.7	66	This work
La ₂ MgZrO ₆ :Cr ³⁺	825	~20.5*	56/17.9	<30	[22]
LiInSi ₂ O ₆ :Cr ³⁺	840	17.5	75/–	~77	[19]
Sr ₉ Cr(PO ₄) ₇ :Cr ³⁺	850	~19.5*	63.6/28.1	<10	[12]
LiScP ₂ O ₇ :Cr ³⁺	880	18.5	38/20	~20	[35]
LaSc ₃ (BO ₃) ₄ :Cr ³⁺	871	~20.4*	23.2/–	~56	[36]
NaScGe ₂ O ₆ :Cr ³⁺	895	~16.9*	40.2/–	~20	[18]
Cs ₂ AgInCl ₆ :Cr ³⁺	1010	~20.3*	22/–	<5	[23]
LiInGe ₂ O ₆ :Cr ³⁺	880	16.56	81.2/39.8	~20	[17]
Mg ₂ GeO ₄ :Cr ³⁺	940	~17.0*	48.1/16.3	<10	[16]

* Data are calculated by re-considering the zero-phonon line as the $E(^4T_2)$.

Figure 7 (a) Electroluminescence spectrum of the LED device made with Sr₂ScSbO₆:3% Cr³⁺ phosphor, LaMgGa₁₁O₁₉:Cr³⁺, commercially available yellow phosphor YAG:Ce³⁺, and red phosphor CaAlSiN₃:Eu²⁺ on the blue chip. The small picture is a packaged model at the inset. (b) The spectrum of the LED device compared with the standard solar spectral data (AM 1.5).

blue-light chip and other commercial phosphors to develop a high-efficiency pc-LED device. Fig. 7 shows the broadband emission spectrum compared with the entire solar spectrum (AM 1.5). Among the commercial powders that were selected, commercial phosphor YAG:Ce³⁺ can be excited by a blue-light chip with a wavelength coverage range of 500–700 nm. Its optimal emission is at 550 nm, which exactly matches the excitation peak of Sr₂ScSbO₆:3% Cr³⁺. The emission ranges of CaAlSiN₃:Eu²⁺ and LaMgGa₁₁O₁₉:Cr³⁺ are 630–680 and 670–810 nm, respectively. These four phosphors are all efficient and can be packaged together with a blue-light chip, successfully simulating the solar-like light source. We believe that this pc-LED device with NIR light can play an important role in multiple fields, including plant lighting, infrared detection generators for mobile phones, simulated sunlight, and healthy lighting.

CONCLUSIONS

In this study, we successfully developed a Cr³⁺-doped double perovskite-type oxide Sr₂ScSbO₆ phosphor with efficient broadband NIR emission. The material exhibits broadband NIR emission ranging from 800 to 1100 nm under UV light and visible light excitation with a peak at 890 nm and an FWHM of

~130 nm. The broadband NIR emission is attributed to the $^4T_2(^4F) \rightarrow ^4A_2(^4F)$ spin-allowed transition of Cr³⁺ in octahedral coordination. The excitation band peaks at 260, 310, 350, 550, and 780 nm correspond to the interband absorption, host defects absorption, $^4A_2(^4F) \rightarrow ^4T_1(^4P)$, $^4A_2(^4F) \rightarrow ^4T_1(^4F)$, and $^4A_2(^4F) \rightarrow ^4T_2(^4F)$ spin-allowed transitions of Cr³⁺, respectively. Under 550-nm excitation, this material shows 82.0%/35.7% PL internal/external efficiency, respectively. Furthermore, it shows excellent luminescent thermal stability, i.e., the integrated luminescence intensity at ($I_{430\text{ K}}$) remains ~66.4% of the initial intensity. We successfully fabricated pc-LEDs combining with 465-nm blue chip and other commercial phosphors, thus presenting a relatively complete solar-like spectrum from blue to NIR light. This is expected to be used in daily health lighting, plant lighting, sunlight simulation, and other applications.

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Author contributions Liu Q and Zhao M conceived the idea; Liu Q supervised the project; Zhao M carried out materials synthesis, device fabrication, and most of the measurements. Cai H and Zhao F participated in part of the experiments; Zhao M analyzed the data and charted the figures and table. Liu Q, Song Z, and Liu S revised the paper. All authors discussed the results and revised the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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高效宽带近红外发光材料 $\text{Sr}_2\text{ScSbO}_6:\text{Cr}^{3+}$ 及其在类太阳光源中的应用

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摘要 类太阳光光源包含可见光和近红外(NIR)光, 在健康照明等领域具有重要的应用。然而众多应用却由于目前缺乏具有高效率和高发光热稳定的900 nm附近的NIR发光材料而受到限制。在此, 我们报道了一种具有双钙钛矿型结构的宽带NIR荧光粉 $\text{Sr}_2\text{ScSbO}_6:\text{Cr}^{3+}$, 其具有高发光效率和良好的发光热稳定性。在550 nm光激发下, 该材料具有以~890 nm为中心的宽带NIR发射, 发光内/外量子效率分别为82.0%/35.7%。此外, 材料显示出优良的发光热稳定性, 在430 K下的发光积分强度保持初始强度的66.4%。结合465 nm蓝光芯片和其他商用荧光粉, 我们成功制作了荧光粉转换发光二极管器件, 呈现出从蓝色到近红外光的相对完整的类太阳光谱, 有望用于日常照明和类太阳光谱发光器件。