Li/Na substitution and Yb$^{3+}$ co-doping enabling tunable near-infrared emission in LiIn$_2$SbO$_6$:Cr$^{3+}$ phosphors for light-emitting diodes

Gaochao Liu, Tao Hu, Maxim S. Molokeev, Zhiguo Xia

HIGHLIGHTS
- LiIn$_2$SbO$_6$:Cr$^{3+}$ exhibits near-infrared emission in the range 780-1400 nm
- Li$^+$/Na$^+$ substitution in LiIn$_2$SbO$_6$:Cr$^{3+}$ enables peak shift from 970 nm to 1020 nm
- Efficient energy transfer process from Cr$^{3+}$ to Yb$^{3+}$ is reported
- The application of LiIn$_2$SbO$_6$:Cr$^{3+}$,Yb$^{3+}$ phosphor in non-invasive detection is demonstrated
Li/Na substitution and Yb$^{3+}$ co-doping enabling tunable near-infrared emission in LiIn$_2$SbO$_6$:Cr$^{3+}$ phosphors for light-emitting diodes

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SUMMARY
Near-infrared (NIR) phosphor-converted light-emitting diode (pc-LED) has great potential in non-invasive detection, while the discovery of tunable broadband NIR phosphor still remains a challenge. Here, we report that Cr$^{3+}$-activated LiIn$_2$SbO$_6$ exhibits a broad emission band ranging from 780 to 1400 nm with a full width at half maximum (FWHM) of 225 nm upon 492 nm excitation. The emission peaks are tuned from 970 to 1020 nm together with considerable broadening of FWHM (285 nm) via Li/Na substitution. Depending on Yb$^{3+}$ co-doping, a stronger NIR fluorescence peak of Yb$^{3+}$ appears with improved thermal resistance, which is ascribed to efficient energy transfer from Cr$^{3+}$ to Yb$^{3+}$. A NIR pc-LED package has been finally designed and demonstrated a remarkable ability to penetrate pork tissues (2 cm) so that the insertion depth of a needle can be observed, indicating that the phosphor can be applied in non-destructive monitoring.

INTRODUCTION
Near-infrared (NIR) luminescence materials have been extensively investigated over the past decades for their flexible applications, ranging from night vision, remote control, security system, and other traditional directions to emerging areas such as bioimaging, food component identification, iris recognition, optical communication, targeted therapy, and tumor tissue diagnosis. In particular, the popularization and multifunctional trend of smart devices have stimulated researchers to design a lightweight broadband NIR light source that can be integrated with a real-time analysis component. Although traditional halogen tungsten lamps show an ultra-broadband emission cover from near-violet to middle-infrared region, they are suspended by large sizes, poor efficiency, short lifetime, high spherical temperature, and long response time. NIR light-emitting diodes (LEDs) also fail to meet the requirements of spectroscopy analysis technology due to their narrow full width at half maximum (FWHM) and disappointing luminous efficiency. Therefore, numerous investigations on exploring new broadband NIR luminescent materials have been done, which involves quantum dots, fluorescent glasses, phosphors, polymer nanocrystals, organic metal halides, organic LEDs, and so forth. Recently, NIR phosphor-converted LEDs (pc-LEDs) have become the subject of focused interests owing to their tunable broadband emission, high radiant power, good durability, and simple preparation method by coating the NIR phosphor on a commercial InGaN blue chip.

Since the optical performance of NIR pc-LEDs mainly depends on the phosphors used, intensive efforts have been made to exploit broadband NIR phosphors via rare-earth ions, transition metal ions, or Bi ions (Br$^{3+}$)-activated inorganic matrices. Unfortunately, single invisible fluorescence emissions of Eu$^{2+}$, Mn$^{2+}$, and Fe$^{3+}$ ions are hard to acquire, and their emissions FWHM are insufficient. Although Ni$^{2+}$ and Bi ion-activated crystal or glass materials usually exhibit an ultra-broadband emission in the second NIR window (NIR-II, 1000-1700 nm), their luminous efficiency is disappointed. On the contrary, Cr$^{3+}$ ion has been considered as an ideal NIR luminescence center in view of its high quantum efficiency and tunable emission spectrum in 650-1600 nm which strongly depends on the crystal field strength. For
example, the luminous efficiency of Ca3Sc2Si3O12:Cr3+ under the excitation of 460 nm blue light can reach 92.3% with an exceptional thermal stability (Jia et al., 2020). The increase of lattice parameters in Cr3+-doped X3Sc2Ga3O12 (X = Lu, Y, Gd, La) can give rise to a red shift of emission band from 722 nm to 818 nm (Malysa et al., 2018). Furthermore, Rajendran et al. reported the ultra-broadband emission of La3Ga5GeO14:Cr3+ phosphor with a FWHM of 330 nm (Rajendran et al., 2018; Zhao et al., 2020), and He et al. and Yao et al. improved the luminous efficiency, thermal resistance, and FWHM of Ca2LuZr2Al3O12:Cr3+ and LiScP2O7:Cr3+ phosphors by Yb3+ co-doping, respectively (He et al., 2020; Yao et al., 2020). However, the emission spectra of most NIR phosphors activated by Cr3+ ions have a considerable part in the visible light range (650-780 nm), which has inferior permeability to biotissues compared with long-wavelength NIR light and will cause irritation to naked eyes. As we know, only LiNbO3:Cr3+ and Cs2AgInCl6:Cr3+ can achieve completely invisible fluorescence but cannot be pumped efficiently by the blue LED chips (Torchia et al., 2001; Zhao et al., 2019). Therefore, the development of long-wavelength ultra-broadband NIR phosphors that can be excited by blue LEDs is a challenging and far-reaching task. For example, we developed MgTa2O6:Cr3+ phosphor with an asymmetrical emission band ranging from 700 nm to 1150 nm and a large FWHM of 140 nm upon 460 nm blue light excitation, which matched LED applications (Liu et al., 2020a, 2020b).

In the present study, Cr3+-doped LiIn2SbO6 phosphors are firstly designed and synthesized. Under 492-nm irradiation, LiIn1.97SbO6:0.03Cr3+ shows a broader emission band covering from 780 nm to 1400 nm with a FWHM of 225 nm. The introduction of Na+ on Li+ sites induced a tunable emission spectrum and corresponding mechanism is discussed. After Yb3+ was co-doped with Cr3+ ions, an efficient NIR radiation of Yb3+ emitters with great thermal stability occurs upon 492-nm excitation and attributed to the energy transfer from Cr3+ to Yb3+ ions. The feasibility of LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ phosphor for non-destructive biological monitoring and safety inspection applications is also investigated.

RESULTS AND DISCUSSION
Crystal structure and optical properties of LiIn2−xSbO6:xCr3+ (x = 0 - 0.12)
The X-ray diffraction (XRD) patterns of as-prepared LiIn2−xSbO6:xCr3+ (x = 0 - 0.12) samples are shown in Figure 1A and the corresponding reference data are taken from the Crystallography Open Database (COD No 4003560). Obviously, all diffraction peaks can be assigned to the standard data of the LiIn2SbO6 phase, indicating the successful phase formation and Cr3+ doping. To obtain detailed

Figure 1. Crystal phase and structural characterization of LiIn2SbO6:Cr3+
(A) XRD patterns of LiIn2−xSbO6:xCr3+ (x = 0 - 0.12) and the standard data of LiIn2SbO6 phase (COD No. 4003560).
(B) Variation of cell volume, In-O, Sb-O, and Li-O bond lengths with the increase of Cr3+ concentration, respectively.
(C) Rietveld refinement XRD pattern of LiIn1.97SbO6:0.03Cr3+. The inset illustrates the substitute model of Cr3+ in LiIn2SbO6 host.
crystallographic information, Rietveld refinement was performed by TOPAS 4.2 software, and the results are displayed in Figures 1B and 1C (Bruker and Topas, 2008). It is notable that both the cell volume $V$ and the average In-O bond length $d$(In-O) decrease linearly but the average Sb-O bond length $d$(Sb-O) increases with increasing Cr$^{3+}$ concentration, which is in good agreement with the fact that the effective ion radius of Cr$^{3+}$ (0.62 Å when CN = 6) is much smaller than that of In$^{3+}$ (0.80 Å when CN = 6) but slightly bigger than that of Sb$^{5+}$ (0.60 Å when CN = 6) (Shannon, 1976). Therefore, it is reasonable to conclude that Cr$^{3+}$ replaces In$^{3+}$ and Sb$^{5+}$ simultaneously in LiIn$_2$SbO$_6$ host. However, Cr$^{3+}$ ions occupying In$^{3+}$ sites should be the main mechanism in view of the charge balance and the absence of impure phase, as well as the lattice totally shrinks after Cr$^{3+}$ was doped. Furthermore, the increase of $d$(Sb-O) may also be caused by the typical adjacent polyhedron substitution effect, which means that the doping of Cr$^{3+}$ at In$^{3+}$ sites will increase the strain of In-O bonds so that the O-Sb distance will increase to release this strain (Li et al., 2014). Nevertheless, this effect has minor influence on LiO$_4$ coordination polyhedron with smaller volume because the average bond length $d$(Li-O) remains almost unchanged with x increases.

Figure 1C shows the Rietveld refinement result of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ with satisfactory residual factors $R_{wp}$ = 6.66%, $R_p$ = 5.08%, $R_B$ = 1.05%, and $\chi^2$ = 3.73%. The detailed parameters are listed in Tables S1 and S2, which emphasizes the purity of target phase and the rutile-related lattice structure with a space group of $Pnmm$ (Flynn et al., 2020). The inset in Figure 1C shows the substitute model of Cr$^{3+}$ in octahedral coordination. The point of M (10 $D_q/B = 23$) means the intersection of $^2E$ and $^4T_2$ ($^4F$) energy levels and the division of weak and strong crystal field.
The fundamental luminescence properties of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ were investigated using the photoluminescence (PL) and PL excitation (PLE) spectra as shown in Figure 2A. Under 492-nm irradiation, the sample exhibits an ultra-broad NIR emission band peaking at 790 nm and extending from 780 nm to 1400 nm with a satisfactory FWHM of 225 nm. Furthermore, a continuous PLE spectrum composed of four peaks can be acquired when monitoring at the emission maximum. The first band centered at 294 nm may originate from the charge transfer (CT) from O ligands to central Sb atoms in the SbO$_6$ octahedral groups, and the others peaking at 360, 492, and 700 nm should be assigned to the $^4A_2 \rightarrow ^4T_1$ ($^4F$), $^4A_2 \rightarrow ^4T_1$ ($^4F$), and $^4A_2 \rightarrow ^4T_2$ ($^4F$) energy level transitions of Cr$^{3+}$ ions, respectively (Li et al., 2015; Mao et al., 2020). Clearly, LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ phosphor can be pumped by the most efficient InGaN blue light chips (460 nm), as verified from the emission spectrum monitored by the 492-nm excitation. It is worth noting that the phosphor also exhibits the similar NIR spectrum under 294-nm excitation (Figure S1), which may be attributed to the energy transfer process (ET1) from the CT band (CTB) to the excited energy level of Cr$^{3+}$ as confirmed by the PLE spectra of LiIn$_{2-x}$SbO$_6$:xCr$^{3+}$ ($x = 0 - 0.12$) as shown in Figure 2B. It is obvious that the LiIn$_{2-x}$SbO$_6$ host shows no fluorescence but a strong CT absorption peaked at 294 nm in its ultraviolet-visible-near infrared (UV-VIS-NIR) diffuse reflectance spectrum (Figure S2). After 0.01 Cr$^{3+}$ was doped, the 294-nm excitation band appeared along with the three energy level transitions of Cr$^{3+}$ ions when monitoring at 970 nm, indicating that the energy absorbed by LiIn$_{2-x}$SbO$_6$:xCr$^{3+}$ was transferred to Cr$^{3+}$ emitters. With the further increase of Cr$^{3+}$ content, the intensity of CT excitation band in Figure 2B began to decrease which was mainly caused by the cross-relaxation process between Cr$^{3+}$ ions so that certain excitation energy is consumed. The influence of Cr$^{3+}$ concentration on the emission properties of LiIn$_{2-x}$SbO$_6$:xCr$^{3+}$ ($x = 0 - 0.12$) is presented in Figure 2C. Obviously, the PL intensity reaches its maximum when $x = 0.03$, and then, the concentration quenching effect occurs (Yu et al., 2019). Therefore, LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ is selected as the optimum composition for further characterizations.

As is known that the valence electrons of Cr$^{3+}$ ions are not shielded by outer shells, there are strong interactions with the crystal field and lattice vibrations due to the spatial extension of the d electron wavefunctions in crystals, and thus it enables tunable optical properties of Cr$^{3+}$ doped phosphors (Malysa et al., 2018). When considering Cr$^{3+}$ ions in the center of coordinated octahedrons (O$_6$ symmetry), the influence of the host lattice on luminescence properties can be expressed by the spectroscopic parameters of $D_q$, $B$, and $\beta$, which can be roughly estimated by the following equations (Tanabe and Sugano, 1954):

$$10D_q = E(^4T_2) - E(^4A_2 \rightarrow ^4T_2) \quad \text{(Equation 1)}$$

$$B = D_q \frac{x^2 - 10x}{15(x - \beta)} \quad \text{(Equation 2)}$$

where parameter $x$ is defined as follows:

$$x = \frac{E(^4T_1) - E(^4T_2)}{D_q} = \frac{E(^4A_2 \rightarrow ^4T_1) - E(^4A_2 \rightarrow ^4T_2)}{D_q} \quad \text{(Equation 3)}$$

$$\beta = \frac{B}{B_0} \quad \text{(Equation 4)}$$

In the above equations, $D_q$ is the crystal field strength and closely related to the metal-ligand distance, $E(^4T_2)$ and $E(^4A_2)$ are the equilibrium positions of the $^4T_2$ and $^4A_2$ levels, and $E(^4A_2 \rightarrow ^4T_2)$ and $E(^4A_2 \rightarrow ^4T_2)$ represent the corresponding transition energies which can be obtained from the PLE spectrum of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ (Figure 2A). The Racah parameter $B$ represents the repulsive force between electrons in the 3d orbital. The value for free Cr$^{3+}$ ions ($B_0 = 918$ cm$^{-1}$) is much higher than that of Cr$^{3+}$ in crystals, and their ratio $\beta$ is often used to evaluate the covalency of host which varies in a more complex manner on interionic distances and the chemical nature of the ions (Malysa et al., 2018). The value of $x$ is calculated from the energy differences between $^4A_2 \rightarrow ^4T_2$ (4F) and $^4A_2 \rightarrow ^4T_2$ (4F) transitions. The crystal field parameter $D_q/B$ and is finally determined to be $2.32$ for LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ (Figure 2D) and slightly bigger than Cr$^{3+}$ in weak crystal field ($D_q/B < 2.3$) in which a broad emission band appears (De Guzman et al., 2020). This inconsistency is not uncommon in certain oxide materials as shown in Table S3, which may be ascribed to the distortion of coordinate polyhedron (Figure S3) since the classical Tanabe-Sugano diagram is based on Cr$^{3+}$ in a nearly perfect octahedral site (Mao et al., 2020; Henderson and Imbusch, 1989).

To investigate the detailed luminescence mechanism of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$, temperature-dependent PL spectra and fluorescence decay curves were recorded in Figures 3A and 3B, respectively. Apparently,
the PL intensity gradually declines (Figure S4) but is broadened significantly (~50 nm, Figure 3A) as the temperature increases, which should be ascribed to the temperature-induced enhancement of electron-phonon interactions (Zhao et al., 2019). Furthermore, the fluorescence decay curve of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ is close to mono-exponential at 15 K but bi-exponential at 300 K (Figure 3B), which may be caused by the introduction of additional energy decay paths at high temperature like cross-relaxation, energy migration, or the defect-induced non-radiative relaxation process (Yu et al., 2019; Bachmann et al., 2009). The shortening of lifetime with the increase of temperature and Cr$^{3+}$ content (Figure 3C) could be the evidence of temperature quenching and concentration quenching effect, respectively. The bi-exponential fitting of room temperature fluorescence decay curves for LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ is shown in Figure 3D. The average lifetime was calculated to be 4.54 μs based on the following relationships:

$$I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$  \hspace{1cm} (Equation 5)

$$\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$  \hspace{1cm} (Equation 6)

where $I$ represents the emission intensity, $A_1$ and $A_2$ are constants, $\tau_1$ and $\tau_2$ are the decay time for the exponential components, and $\tau_{ave}$ is the average decay time. The fitting results ($\tau_1 = 3.86 \mu$s and $\tau_2 = 21.65 \mu$s) are in line with the typical Cr$^{3+}$-doped compounds, and the shorter one is regarded as intrinsic ionic luminescence when the influence of temperature is taken into consideration (Gao et al., 2020).

**Figure 3.** Temperature-dependent PL spectra and fluorescence decay curves of LiIn$_{2-x}$SbO$_6$:xCr$^{3+}$ ($x = 0.01 - 0.12$) (A and B) Normalized temperature-dependent PL spectra and fluorescence decay curves of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ under 492-nm excitation between 15 and 300 K, respectively. (C) Room temperature fluorescence decay curves of LiIn$_{2-x}$SbO$_6$:xCr$^{3+}$ ($x = 0.01-0.12$) monitored at 970 nm upon excitation at 492 nm. (D) Bi-exponential fitting of room temperature fluorescence decay curves for LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$.
PL broadening by local structure regulation

According to the Tanabe-Sugano diagram shown in Figure 2D, the emission spectrum of Cr\(^{3+}\) ions in the center of coordinated octahedrons is closely related to surrounding crystal field. Generally, the ion substitution strategy is considered as an effective way to regulate the local structure and crystal field distortion so that a great change in the emission spectrum will take place (Chen et al., 2017). In addition, the Li\(^+\) ions in LiIn\(_2\)SbO\(_6\) (0.59 Å when CN = 4) are located at unique channels and play a role in charge balance, which determine that it can be replaced by equivalent ions conveniently. Therefore, Na\(^+\) ions with larger effective radius (0.99 Å when CN = 4) were introduced into this host with a certain stoichiometric Li\(_{1-x}\)Na\(_x\)In\(_{1.97}\)SbO\(_6\) : 0.03Cr\(^{3+}\) (x = 0 - 0.9), and their XRD patterns are shown in Figure 4A. No impurity patterns have been detected even in the case of x = 0.7, and it reveals that the regulated phosphors keep the same crystal structure as LiIn\(_2\)SbO\(_6\). The inset demonstrates the shift of the strongest diffraction peak toward lower angle side, suggesting that the crystal lattice expands gradually with the increase of Na\(^+\) content, which is further verified by the variations of cell volume and average Li/Na-O bond length obtained by Rietveld refinement (Figure 4B). After Na\(^+\) was introduced, both of them increase linearly, and the PL spectrum of Cr\(^{3+}\) can be tuned from 970 nm to 1020 nm with considerable broadening of FWHM (Δx/Δy 60 nm) (Figures 4C and 5). According to the calculated crystal field strength D\(_q\) almost unchanged which is in line with their average Li/Na-O bond length (Figure 4B), while Racah parameter B increase significantly from 616 cm\(^{-1}\) to 854 cm\(^{-1}\) means a reduction of host covalency and consists with the change of average Li/Na-O bond length (Malysa et al., 2018; Malysa et al., 2017). Finally, the crystal field parameter D\(_q\)/B is decreased from 2.32 to 1.67 as displayed in Figure 4B and Table S4. This tunable long-wavelength NIR fluorescence is closely associated with the crystallographic parameters of the host that are governed by alkali metal ions in this open 3D tunnel framework and will take an avenue to broaden the research direction and application prospects of NIR fluorescence materials.

Yb\(^{3+}\) co-doping enabling increased PL intensities and enhanced thermal stability

Yb\(^{3+}\) ions are considered as ideal spectral converters, especially coupling with other lanthanide ions, for their NIR emission and efficient pumping by 980-nm laser. Inspired by the possible energy transfer between Cr\(^{3+}\) and Yb\(^{3+}\) ions, as well as the closed effective ion radius of Yb\(^{3+}\) (0.87 Å when CN = 6) to In\(^{3+}\) (0.80 Å when CN = 6), Cr\(^{3+}\) and Yb\(^{3+}\) co-doped phosphors were developed to further improve its application potential. It can be seen in Figure 5A that after Yb\(^{3+}\) was doped singly, the sample can still exhibit strong NIR fluorescence under excitation at 294 nm, indicating that there is another ET process (ET\(_2\)) between CTB and the Yb\(^{3+}\) excited state energy level in the phosphor. When Yb\(^{3+}\) was co-doped with Cr\(^{3+}\), the emission spectrum changes from the broadband emission of Cr\(^{3+}\) to the sharp line emission of Yb\(^{3+}\), while the shape and position of the excitation spectrum of LiIn\(_{1.82}\)SbO\(_6\) : 0.03Cr\(^{3+}\), 0.15Yb\(^{3+}\) remains

![Figure 4. Rietveld refinement and fluorescence spectra of (Li\(_{1-x}\)Na\(_x\))In\(_{1.97}\)SbO\(_6\) : 0.03Cr\(^{3+}\) (x = 0 - 0.9)](image-url)
basically unchanged compared with LiIn1.97SbO6:0.03Cr3+ except that the 294-nm excitation band was further enhanced due to the additional ET2 process, indicating that there is the third ET process (ET3) from Cr3+ to Yb3+ ions. This process was confirmed by the emission spectra of LiIn1.97-ySbO6:0.03Cr3+, yYb3+ (y = 0 - 0.18) as shown in Figure 5B. The emission intensity of Cr3+ located at 900 nm and 1150 nm decreases monotonously while the luminescence of Yb3+ at 998 nm increases rapidly with the increase of Yb3+ content, which should be attributed to the enhancement of ET3. The emission of Yb3+ upon 492-nm excitation starts to decrease when y > 0.15 due to the shortening of the distance among Yb3+ ions so that the concentration quenching effect occurs. In this process, the relative and integrated emission intensity of co-doped sample can be improved up to 13.83 times and 3.27 times, respectively, even if the emission bandwidth is narrowed significantly compared with LiIn1.97SbO6:0.03Cr3+, as indicated in Figure 5C. This remarkable enhancement of PL intensity should be attributed to the efficient ET3 and Yb3+ emitters in the co-doped samples, which was characterized through the change of fluorescence lifetime of Cr3+ and Yb3+ as shown in Figures 6A and 6B. Upon 492-nm excitation, both of Cr3+ and Yb3+ show emission at ~1000 nm so that the decay curves of LiIn1.97-ySbO6:0.03Cr3+, yYb3+ (y = 0 - 0.18) actually stem from the joint contributions of their luminescence. Through the bi-exponential fitting for the fluorescence decay curves of co-doped samples (Figure S6), the specific lifetime values of Cr3+ in each sample was obtained and depicted in Figure 6B (black line), and then, the ET efficiency (\(\eta_{ET}\)) from Cr3+ to Yb3+ can be calculated based on Equation 7:

\[
\eta_{ET} = 1 - \frac{\tau}{\tau_0}
\]  

(Equation 7)

where \(\tau\) and \(\tau_0\) are the corresponding decay times of Cr3+ in the presence and absence of Yb3+, respectively. According to the above fitted lifetimes, the ET efficiency in LiIn1.92SbO6:0.03Cr3+, 0.13Yb3+ reached above 80% and will be further enhanced for higher Yb3+ concentration samples. This efficient ET3 process may be ascribed to two main reasons: on the one hand, Cr3+ and Yb3+ ions both occupy the In3+ sites in...
LiIn2SbO6 host, and the shorter distance between activators and sensizers is conducive to the occurrence of ET3 process. On the other hand, the maximum emission wavelength of Cr3+ ions is quite close to the absorption of Yb3+ ions in LiIn2SbO6, indicating that there is a tiny energy difference between Cr3+ and Yb3+ excited state energy level and a slight relaxation will facilitate the transfer of energy. The schematic diagram of three ET processes in LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ phosphor is demonstrated in Figure 6C, and the specific positions of each energy level were calculated through the corresponding transition energy in Figure 5A. The three basic energy transfer processes ET1, ET2 and ET3 originate from the CTB to Cr3+, the CTB to Yb3+ and Cr3+ to Yb3+ excited state energy level, respectively. It is clear that the energy difference of ET3 is so inappreciable that this process will happen significantly and may improve luminescence intensity by over an order of magnitude.

In order to evaluate the thermal stability and temperature-quenching mechanisms of LiIn1.97SbO6:0.03Cr3+ and LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+, PL/temperature correlation maps of the two phosphors upon 492-nm excitation were measured as shown in Figures 7A and 7B, respectively. Apparently, the thermal resistance of LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ (31% @ 95°C) is much better than that of LiIn1.97SbO6:0.03Cr3+ (10% @ 95°C) upon 492-nm excitation but worse than that of LiIn1.97SbO6:0.03Yb3+ (95% @ 95°C) upon 980-nm laser excitation (Figure 7C), which can be explained by the typical configuration coordinate diagram in Figure 7D. Normally, the large stokes shift (3976 cm⁻¹) and low radiant energy (1.28 eV) are accompanied by a smaller activation energy $E_a$ for Cr3+ ions in LiIn2SbO6 so that the non-radiative transition is quite serious (Yao et al., 2020). However, the temperature-quenching effect of Yb3+ mainly governed by the multi-phonon emission is smaller than the 5-fold vibration energy of the surrounding environment. Therefore, one can think that the Yb3+ in LiIn2SbO6 exhibits a satisfactory thermal resistance. Moreover, the reduced thermal quenching effect can be found in LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ in view of the efficient ET3 from Cr3+ to thermally more stable Yb3+ ions other than non-radiative process.

Quantum efficiency and non-invasive detection application

The quantum efficiency (QE) of LiIn1.97SbO6:0.03Cr3+ and LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ phosphors is measured to evaluate their luminescence properties as shown in Figure S7. The relatively low internal (7%) and external (3.44%) QEs of LiIn1.97SbO6:0.03Cr3+ are attributed to the serious non-radiation relaxation process and parity-forbidden transition of Cr3+ ions, respectively. Given that the LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ phosphor shows a stronger NIR fluorescence than LiIn1.97SbO6:0.03Cr3+ under 492-nm excitation, an NIR pc-LED was fabricated by coating the LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ phosphor on a commercial blue light-emitting InGaN chip (460 nm) to evaluate the potential practical application of the NIR luminescence material. Figure 8 demonstrates the schematic diagram of NIR pc-LED imaging device showing the application principle. Some details are shown in this figure. Firstly, one can fabricate the NIR pc-LED based on LiIn1.82SbO6:0.03Cr3+, 0.15Yb3+ phosphor, and the driven current-dependent emission spectra and operating temperature of the fabricated NIR pc-LED are shown in Figure S3. Under the optimal driven current of 40 mA, the NIR fluorescence of the light source can penetrate ~2 cm pork tissue so that a nail behind this tissue and the insertion depth of a needle can be observed through smart networking devices such as mobile phones and computers with the assistance of an NIR camera, as given in the inset of Figure 8. These
images with a fundamental model indicate that the phosphor will be potentially applied in accurate measurements of non-destructive examination.

Conclusion
In summary, we have developed a broadband NIR phosphor by introducing Cr$^{3+}$ ions in LiIn$_2$SbO$_6$ host, and the LiIn$_2$SbO$_6$:Cr$^{3+}$ phosphors exhibit NIR emissions in the range 780-1400 nm with an FWHM of $\approx$225 nm. The open 3D tunnel framework of LiIn$_2$SbO$_6$ allows a good flexibility in composition so that the emission maximum can be tuned from 970 nm to 1020 nm together with broadened FWHM of $\approx$285 nm by substituting Li$^+$ with Na$^+$ gradually, which mainly attributed to the weakening of crystal field from $D_q/B = 2.32$ to 1.67. When Yb$^{3+}$ ions were co-doped with Cr$^{3+}$ in LiIn$_2$SbO$_6$, the PL intensity of Cr$^{3+}$ was suppressed but a stronger narrow-band NIR peak of Yb$^{3+}$ (more over 13 times of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$) appeared under 492 nm excitation. Spectroscopic and lifetime analysis shows that this enhancement is mainly due to efficient energy transfer from Cr$^{3+}$ to more efficient and thermally stable Yb$^{3+}$ emitters. Finally, an NIR pc-LED is fabricated by LiIn$_{1.82}$SbO$_6$:0.03Cr$^{3+}$, 0.15Yb$^{3+}$ phosphor and an InGaN blue chip peaking at 460 nm. The result demonstrates that a nail inside pork tissues ($\approx$2 cm) and the insertion depth of a needle can be observed, indicating that the as-fabricated NIR pc-LED based on NIR phosphor can be applied in the field of non-destructive detection and also provide new insights for the design of new NIR materials for LED applications.

Limitations of the study
The thermal stabilities and quantum efficiency of the Cr$^{3+}$-activated or Cr$^{3+}$-Yb$^{3+}$-doped LiIn$_2$SbO$_6$ NIR phosphors should be especially followed with interests and improved for the practical applications.

A commercial InGaN blue chip with the peak at 460 nm was used to fabricate the NIR pc-LED for the lack of 492-nm chip.
METHODS
All methods can be found in the accompanying transparent methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2021.102250.

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AUTHOR CONTRIBUTIONS
Z.X. conceived the project, revised the paper, and was primarily responsible for the experiment. G.L. synthesized the materials, performed experimental characterization, and wrote the paper. T.H. contributed the luminescence mechanism analysis. M.M performed the structure refinement. All authors contributed to the general discussion.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental information

Li/Na substitution and Yb$^{3+}$ co-doping enabling tunable near-infrared emission in LiIn$_2$SbO$_6$:Cr$^{3+}$ phosphors for light-emitting diodes

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Supplemental Figures

Figure S1. Normalized PL spectra of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ under 294 nm, 460 nm and 492 nm excitation, related to Figure 2A.
Figure S2. UV-VIS-NIR diffuse reflectance spectra of LiIn$_{2-x}$SbO$_6$:xCr$^{3+}$ ($x = 0 - 0.12$) phosphors, related to Figure 2B.
Figure S3. Distorted coordinate octahedron of Cr$^{3+}$ in LiIn$_2$SbO$_6$ host, related to Figure 2D.
Figure S4. Temperature-dependent PL spectra of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$ upon 492-nm excitation, related to Figure 3A.
Figure S5. (A-B) Room-temperature PLE and PL Spectra of \((\text{Li}_{1-z}\text{Na}_z)\text{In}_{1.97}\text{SbO}_6:0.03\text{Cr}^{3+} (z = 0 - 0.7)\) phosphors, related to Figure 4C.
Figure S6. (A-B) Bi-exponential fitting of room-temperature fluorescence decay curve for LiIn$_{1.967}$SbO$_6$: 0.03Cr$^{3+}$, 0.003Yb$^{3+}$ and LiIn$_{1.88}$SbO$_6$:0.03Cr$^{3+}$, 0.09Yb$^{3+}$, respectively, related to Figure 6B.
Figure S7. Integrated intensity of LiIn_{1.97}SbO_6:0.03Cr^{3+} and LiIn_{1.82}SbO_6:0.03Cr^{3+}, 0.15Yb^{3+} for quantum yields measurements, related to Figure 8.
Figure S8. Luminous intensity and operating temperature of fabricated NIR pc-LED under variable current, related to Figure 8.

(A) Driven current dependent emission spectra of fabricated NIR pc-LED. The abnormal decrease at 973 nm may be caused by the absorption of curable adhesives.

(B) Thermographs at different driven currents from 20 mA to 100 mA.
Table S1. Main refined structural parameters of the LiIn$_2$SbO$_6$:0.03Cr$^{3+}$ sample, related to Figure 1.

| Compound          | LiIn$_2$SbO$_6$:0.03Cr$^{3+}$ |
|-------------------|--------------------------------|
| Symmetry          | Orthorhombic                   |
| Space group       | $P_{nnm}$                      |
| $a$, Å            | 5.10471 (3)                    |
| $b$, Å            | 5.33298 (3)                    |
| $c$, Å            | 8.86988 (5)                    |
| $V$, Å$^3$        | 241.467 (2)                    |
| $Z$               | 2                              |
| 2θ-interval, °    | 5-120                          |
| $R_{wp}$, %       | 6.66                           |
| $R_p$, %          | 5.08                           |
| $R_B$, %          | 1.05                           |
| $\chi^2$         | 3.73                           |
Table S2. Fractional atomic coordinates and isotropic displacement parameters (Å$^2$) of LiIn$_{1.97}$SbO$_6$:0.03Cr$^{3+}$, related to Figure 1.

| Atom | $x$     | $y$     | $z$     | $B_{iso}$ | Occ. |
|------|---------|---------|---------|-----------|------|
| Sb   | 0.5     | 0.5     | 0.5     | 0.7 (2)   | 1    |
| In   | 0.5     | 0       | 0.30068 (8) | 0.6 (2) | 0.97 |
| Cr   | 0.5     | 0       | 0.30068 (8) | 0.6 (2) | 0.03 |
| Li   | 0.036 (16) | 0.110 (6) | 0.5     | 2.0 (12) | 0.5  |
| O1   | 0.2808 (16) | 0.3343 (9) | 0.3429 (9) | 0.7 (3) | 1    |
| O2   | 0.698 (2)  | 0.1814 (16) | 0.5     | 0.9 (3)  | 1    |
Table S3. Crystal field parameters of different Cr$^{3+}$-doped broadband NIR phosphors, related to Figure 2D and Figure S3.

| Host                        | $D_q$ (cm⁻¹) | $B$ (cm⁻¹) | $\beta = B / B_0$ | $D_q / B$ | PL maximum | Reference         |
|-----------------------------|--------------|------------|-------------------|-----------|-------------|-------------------|
| Y$_3$Sc$_2$Ga$_3$O$_{12}$   | 1587         | 635        | 0.69              | 2.50      | 740 nm      | (Malysa, et al., 2018) |
| Y$_2$CaAl$_4$SiO$_{12}$     | 1647         | 678        | 0.74              | 2.43      | 744 nm      | (Mao, et al., 2020)  |
| La$_2$MgZrO$_6$              | 1589         | 628        | 0.68              | 2.53      | 825 nm      | (Zeng, et al., 2019) |
| Cs$_2$AgInCl$_6$             | 1250         | 527        | 0.57              | 2.37      | 1010 nm     | (Zhao, et al., 2019) |
| Mg$_6$Ga$_4$Ge$_3$O$_{16}$   | 1695         | 712        | 0.78              | 2.38      | 750 nm      | (Zhan, et al., 2019) |
| MgTa$_2$O$_6$                | 1471         | 588        | 0.64              | 2.50      | 834 nm      | (Liu, et al., 2020)  |
| LiIn$_2$SbO$_6$              | 1428         | 616        | 0.67              | 2.32      | 970 nm      | This work          |
Table S4. Spectroscopy and crystal field parameters of Li_{1-z}Na_{z}In_{1.97}SbO_{6}:0.03Cr^{3+} (z = 0 - 0.7) phosphors, related to Figure 4B.

| Host  | $D_q$ (cm$^{-1}$) | $[E(4T_1)-E(4T_2)]$ (cm$^{-1}$) | $B$ (cm$^{-1}$) | $\beta = B / B_0$ | $D_q / B$ |
|-------|------------------|-------------------------------|----------------|-----------------|-----------|
| Z = 0 | 1428             | 6039.49                       | 616.10         | 0.67            | 2.32      |
| Z = 0.1 | 1435          | 6122.45                       | 627.94         | 0.68            | 2.28      |
| Z = 0.3 | 1432          | 6375.44                       | 665.35         | 0.72            | 2.15      |
| Z = 0.5 | 1436          | 6634.79                       | 705.95         | 0.77            | 2.02      |
| Z = 0.7 | 1440          | 7453.42                       | 854.04         | 0.93            | 1.67      |
Transparent Methods

Synthesis of materials: Powder samples with compositions of Li\textsubscript{1+2x}In\textsubscript{2-x}Sb\textsubscript{2}O\textsubscript{6}:xCr\textsuperscript{3+}, Li\textsubscript{1+2z}Na\textsubscript{1-z}In\textsubscript{1.97}Sb\textsubscript{0.03}O\textsubscript{6}:0.03Cr\textsuperscript{3+} and Li\textsubscript{1+2y}In\textsubscript{1.97-y}Sb\textsubscript{0.03}O\textsubscript{6}:0.03Cr\textsuperscript{3+},Yb\textsuperscript{3+} (0 ≤ x ≤ 0.12, 0 ≤ z ≤ 0.9 and 0 ≤ y ≤ 0.18) phosphors were prepared through high temperature solid-state reaction method. The analytical reagents of LiCO\textsubscript{3} (99%, Aladdin), NaCO\textsubscript{3} (99.9%, Aladdin), In\textsubscript{2}O\textsubscript{3} (99.9%, Aladdin), Sb\textsubscript{2}O\textsubscript{3} (99.99%, Aladdin), Cr\textsubscript{2}O\textsubscript{3} (99%, Aladdin) and Yb\textsubscript{2}O\textsubscript{3} (99.99%, Aladdin) were used as raw materials. Typically, stoichiometric amounts of raw materials were weighted and put in an agate mortar. The mixtures were ground thoroughly for 15 minutes and then transferred into a corundum crucible and put into a muffle furnace to sinter at 1250°C for 6 h in air. Finally, after the samples were naturally cooled down to room temperature, they were crushed to fine powders and stored in a chamber at the constant temperature and humidity for further measurements.

Sample characterization: The phase and purity of the as-prepared powder samples were examined by X-ray diffraction (XRD) analysis using a Bruker D8 ADVANCE power diffractometer with CuK\textsubscript{α} radiation source (\(\lambda = 0.15406\) nm) and a linear VANTEC detector. The operation voltage and current were set as 40 kV and 15 mA, respectively. The data were collected in the range of 5°-120° with a step size of 0.0217 nm (2\(\theta\)) and a count time of 5 s per step. Structural characterization and Rietveld refinement were conducted using TOPAS 4.2 software. Room-temperature photoluminescence (PL) spectra and PL excitation (PLE) spectra were recorded using a FLS920 fluorescence spectrophotometer equipped with a continuous xenon lamp (450 W) as an excitation source and a liquid-nitrogen cooled NIR photomultiplier tube as a detector (Hamamatsu, R5509, InP/InGaAsP). The PL decay curve was also measured by the same FLS920 instrument using a microsecond flash lamp (\(\mu\)F900) as the excitation source, and the statistical photons are 5000. The luminescence thermal quenching behavior of the samples was measured by the same spectrophotometer, which was equipped with a TAP-02 high-temperature fluorescence instrument (Tian Jin Orient - KOJI instrument Co., Ltd.). Photographs for the application of NIR pc-LEDs were taken by an industrial night-vision camera (MV-CA050-20GN, HIKVISION, China). The diffuse reflection (DR) spectra of the samples were recorded using an UV-Vis-NIR spectrophotometer (Hitachi High-Tech Science Corporation, UH4150) with BaSO\textsubscript{4} as a standard. The quantum efficiency at room temperature was measured by an absolute PL quantum yield spectrometer (Quantaurus - QY Plus C13534-12, Hamamatsu Photonics).

LEDs fabrication: The NIR LED was fabricated based on the as-synthesized NIR emitting phosphor and the chip-on-board (COB) blue LED (X1901, 5 W, Guangzhou LEDteen Optoelectronics Co., Ltd., China), and the mass ratio of the epoxy resin to NIR phosphor is fixed at 1:1. The blue InGaN chips in the COB LEDs are (S-35EBMUD-A, 450-452.5 nm, 2.9-3.1V/150 mA, San'an Optoelectronics co., LTD., China). The demonstration images were collected by an industrial night-vision camera (MV-CA050-20GN, HIKVISION, China). Meanwhile, the temperatures of the fabricated working NIR LEDs were recorded by a thermal infrared camera (Fotric 225S).
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