NaYS₂:Er³⁺ - a highly efficient NIR II response multi-photon up-conversion phosphor

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Article

Keywords: NIR II response, UC materials, β -NaYS₂:Er³⁺

Posted Date: July 9th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-506182/v1>

Abstract

The second near-infrared (NIR II) response photon up-conversion (UC) materials show great application prospects in the fields of biology and optical communication. However, it is still an enormous challenge to obtain efficient NIR II response materials. Herein, we developed a series of Er³⁺ doping ternary sulfides phosphors with highly efficient UC emissions under 1532 nm irradiation. Excitingly, β -NaYS₂:Er³⁺ achieves a breakthrough visible UC efficiency as high as 6.13%, along with outstanding brightness, spectral stability of lights illumination and temperature. Such efficient UC dominates by excited state absorption process accompanied by the advantage of super long lifetimes of excited state levels of Er³⁺, instead of the well-recognized energy transfer UC between sensitizer and activator. NaYS₂:Er³⁺ phosphors are further developed for high-performance underwater communication and a narrowband NIR photodetectors. Our findings breakthrough the traditional thinking of realizing efficient UC, and open up a novel frontier for developing NIR II response UC materials.

Main Text

Lanthanide doped photon up-conversion (UC) materials can absorb two or more low-energy photons, and emit high-energy photons, which have attracted extensive attention due to the superior optical performance, such as large anti-Stokes shift, excellent stability against photo-bleaching, and no auto-fluorescence¹⁻⁵. The first discovery of an effective UC host material was NaYF₄ by Pierce in 1972. Until 2004, the hexagonal phase NaYF₄ (β -NaYF₄) with high UC efficiency was demonstrated⁶. With the development of nanotechnology, lanthanide doped UC materials experienced the explosive growth, especially in biological applications⁷⁻⁹, photon-conversion devices^{10,11}, super-resolution nanoscopy¹²⁻¹⁴, and information storage and security etc¹⁵⁻¹⁷. Much efforts have been devoted to manipulate UC, and Yb³⁺, Nd³⁺-sensitized energy transfer (ET) and interfacial energy transfer (IET) are recognized as the promising ways to achieve efficient UC luminescence¹⁸⁻²³.

Recently, the near-infrared second (NIR II) spectral region, especially for 1530 nm, shows great potential in the large penetration depth for tissue, and high-resolution imaging etc²⁴⁻²⁷. Particularly, 1530 nm is also the wavelength of optical communication, exhibits a low loss in transmission, and is widely used in metro, long-distance, ultra-long-distance and submarine optical cable systems²⁸⁻³¹. However, the development of the highly efficient NIR II 1530 nm response photon UC materials still faces great challenges. Up to date, the recognized efficient UC materials (eg., NaYF₄:Yb,Er/Tm) are based on the sensitized ET, owing to the efficient ET process from sensitizers (eg., Yb³⁺, Nd³⁺) to activators (eg., Er³⁺, Tm³⁺, Ho³⁺). Despite the great progress made in UC, the existing UC materials strongly depend on the excitation of short near-infrared wavelengths (as 808 and 980 nm). Er³⁺ has a well spectral response around 1530 nm with a relative large absorption cross-section, but it is not suitable for sensitizer owing to the lacking of the matchable activator. Actually, a number of the literatures has announced Er³⁺ doped UC materials pumping around 1530 nm realized via the excited state absorption process of Er³⁺ ions

themselves³²⁻⁴⁰. Disappointedly, their up-conversion quantum yields (UCQY) are extremely low, less than 0.5%, limited by the deleterious quenching interactions, and strong electron-phonon coupling etc. To date, because of lacking of appropriate host materials, it still remains a challenge to achieve efficient NIR II 1530 nm response UC materials.

In this work, we fabricated a series of efficient NIR II 1532 nm response UC materials: Er^{3+} sensitized MLnS_2 ($\text{M}=\text{Li}, \text{Na}, \text{K}$; $\text{Ln}=\text{Y}, \text{Lu}, \text{La}, \text{Gd}$) materials. They exhibit cubic (α -) and hexagonal (β -) phase depending on the radius ratios between the trivalent lanthanide metal ions and the monovalent alkali metal ions ($\text{RLn}^{3+}/\text{RM}^+$). It should be highlighted that $\beta\text{-NaYS}_2$ presents the most efficient UC emissions with the UCQY as high as 6.13% under 1532 nm excitation ($\sim 4.8 \text{ W/cm}^2$), originating from the super long lifetimes of excited state levels of Er^{3+} . Compared to the commercial $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ phosphors, the $\text{NaYS}_2:\text{Er}^{3+}$ owns much higher UCQY, brightness, and spectral stability of lights illumination and temperature at the same conditions. Finally, the $\text{NaYS}_2:\text{Er}^{3+}$ phosphors were employed to obtain a sensitive narrowband responsive NIR photodetectors (800 nm, 980 nm, and 1532 nm), and green light underwater communication.

A series of Er^{3+} -doped MLnS_2 UC phosphors were synthesized by the high temperature solid reaction method, in which the IA alkali metal elements ($\text{M}=\text{Li}, \text{Na}, \text{or K}$) and trivalent rare earth elements ($\text{Ln}=\text{Y}, \text{Lu}, \text{La}, \text{or Gd}$) were selected to occupy the M and Ln sites, respectively (See the experimental methods). Fig. 1a and 1b display the X-ray diffraction (XRD) patterns of MYS_2 and NaLnS_2 prepared at 1173 K, which coincide well with the corresponding standard cards. The synthesis temperature dependent XRD patterns and UC luminescence spectra further reveal that the optimized temperature is 1173 K, otherwise the impurity phase of $\text{Y}_2\text{O}_2\text{S}$ is formed at 1273 and 1373 K (Fig. S1, 2), which leads to the decrease of UC luminescence. Interestingly, MLnS_2 phosphors have two structural types: NaLaS_2 and LiYS_2 present a cubic structure (α -), while KYS_2 , NaGdS_2 , NaLuS_2 , and NaYS_2 are indexed as hexagonal phase (β -) under the same conditions (Fig. 1a, b). As represented in Fig. 1c, the phase structure of MLnS_2 phosphors mainly depends on the radius ratios between the trivalent lanthanide metal ions and the monovalent alkali metal ions ($\text{RLn}^{3+}/\text{RM}^+$)⁴¹. When the $\text{RLn}^{3+}/\text{RM}^+$ ratio is larger than 1.0, MLnS_2 tends to form cubic phase (NaCl or Th_3P_4 type). Conversely, the hexagonal phase structure is dominant. The $\alpha\text{-NaLaS}_2$ and $\beta\text{-NaYS}_2$ were taken as examples to illustrate the representative structure of MLnS_2 family (Fig. 1d, e). In $\alpha\text{-NaLaS}_2$ with cubic structure, Na and La are randomly disordered on an identical lattice site and are coordinated with six S atoms to form $(\text{NaLa-S})_6$ octahedrons. In hexagonal $\beta\text{-NaYS}_2$, Na and Y ions are orderly situated in alternating NaS_6 and YS_6 octahedral layers.

In addition, the XRD patterns of NaYS_2 with various doping concentration Er^{3+} are recorded in Fig. 1f. $\beta\text{-NaYS}_2$ is obtained according to the standard cards (PDF No. 46-1051), and two characteristic peaks located at 26.34° and 31.64° correspond to the (101) and (104) crystal planes, respectively. Meanwhile, the diffraction peaks of $\text{NaYS}_2:\text{Er}^{3+}$ shift to large angle with increasing the doping concentration of Er^{3+} .

owing to the replacement of Y^{3+} (89.3 pm) by Er^{3+} (88.1 pm) with a smaller radius. The similar morphologies of $MLnS_2:Er^{3+}$ are obtained as displayed in Fig. S3. The transmission electron microscopic (TEM) and high resolution TEM (HRTEM) images of the as-prepared $NaLaS_2$ and $NaYS_2$ phosphors are presented in Fig. 1g, h and Fig. 1j, k. The lattice fringes of 0.34 nm and 0.28 nm are associated with (111) and (104) planes of $NaLaS_2$ (d-spacing of 0.339 nm; JCPDS No. 38-1391) and $NaYS_2$ (d-spacing of 0.282 nm; JCPDS No. 46-1051), respectively. The selected area electron diffraction (SAED) patterns (Fig. 1i, l) further demonstrate the good crystallinity of samples. All of the above results indicate that the Er^{3+} -doped $MLnS_2$ phosphors with two phases are successfully fabricated.

The NIR II response UC luminescence characteristics of $MLnS_2:Er^{3+}$ under 1532 nm excitation are systematically evaluated. As presented in Fig. 2a, b, two emission bands in green and red luminescence region are identified in the normalized visible UC spectra of $MLnS_2:Er^{3+}$, assigned to the $^4S_{3/2}/^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} . Note that, β - $MLnS_2:Er^{3+}$ shows clearer and sharper splitting of emission lines than those of α - $MLnS_2:Er^{3+}$, implying the better optical performance of β -phosphors. As expected in Fig. 2c, d, the emission intensities of β - $MYS_2:Er^{3+}$ and β - $NaLnS_2:Er^{3+}$ are significantly higher than those of α -phase phosphors, and $NaYS_2:Er^{3+}$ is found to be the most efficient UC phosphors in $MLnS_2:Er^{3+}$ excited by 1532 nm. Meanwhile, the UC intensity ratios of green to red emissions in β - $MLnS_2:Er^{3+}$ are larger compared to the cubic phase ones. These suggest that the β - $MLnS_2:Er^{3+}$ phosphors are benefit to the UC emissions. Such phenomenon can be explained by the following reason: the Er^{3+} in β - $MLnS_2$ are ordered separated by NaS_6 octahedral layers along the c axis direction, which blocks the energy transfer and/or cross relaxation between each other to a certain extent. However, the Er^{3+} in α - $MLnS_2$ are randomly disordered on an identical lattice site, inevitably leading to the intensified negative energy exchange^{42,43}. Furthermore, the distance of the nearest Y^{3+} ions (d_{Y-Y}) in $NaYS_2$ is determined to be 3.9808 Å. Since the probability of energy transfer between luminous centers (concentration quenching) is proportional to $1/d^6$, therefore, the large adjacent distance d often causes high doping level and intense luminescence.

The visible-NIR UC luminescence spectra of $NaYS_2:Er^{3+}$ illuminated by 1532 nm are further performed to clarify the UC populating process. Five UC emission bands spanning from 400-1100 nm are recorded in Fig. 2e. There are two additional NIR emission bands in the range of 790~840 nm and 950~1050 nm expect the visible ones, attributed to the $^4I_{9/2}, ^4I_{11/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} , respectively. A schematic illustration of UC populating mechanism for $NaYS_2:Er^{3+}$ pumping under 1532 nm is provided in Fig. 2f, originating from the multi-photon excited state absorption (ESA) process. Firstly, the electrons on the ground state ($^4I_{15/2}$) of Er^{3+} ions are pumped to $^4I_{13/2}$, and further excited to $^4I_{9/2}$ via resonantly illumination, producing the $^4I_{9/2} \rightarrow ^4I_{15/2}$ transition. The electrons on $^4I_{9/2}$ jump to the higher excited levels ($^4S_{3/2}/^2H_{11/2}$) through continuous three-photon absorption processes, realizing the green emissions. Moreover, a part of electrons on $^4I_{9/2}$ is non-radiative to $^4I_{11/2}$, then populates to $^4F_{9/2}$,

generating $^4I_{11/2} \rightarrow ^4I_{15/2}$ and red ($^4F_{9/2} \rightarrow ^4I_{15/2}$) emissions, respectively. ET- sensitized UC is always being considered as the most efficient strategy to achieve UC emissions, while the excited state absorption is basically denied limited by the weak absorption. However, the efficient UC emissions in $MLnS_2:Er^{3+}$ are realized through ESA process, where Er^{3+} presents both sensitizer and activator in such system. It is different from the UC from typical energy transfer (eg., Yb^{3+} , Er^{3+} system: Yb^{3+} serves as sensitizer and Er^{3+} ions are as activators.). Thus, the visible and NIR emissions are ascribed to the three and two photons UC, as evidenced by the power dependence of the integrated UC emission intensity of $NaYS_2:Er^{3+}$ (Fig. S4).

As displayed in Fig. 2g, the visible UC luminescence intensity of $NaYS_2:Er^{3+}$ initially increases, then decreases with increasing the Er^{3+} doping concentration due to the concentration quenching, in which the optimal doping concentration of Er^{3+} ion is 5 mol%. Similarly, the corresponding decay time curves and constants of Er^{3+} in Fig. S5-S9 and Table S1 present that the lifetime first increases, and then decreases as the Er^{3+} concentration continuously increases to 15%. Such increase of decay time constants may be attributed to the re-absorbed process induced by high doping concentration of Er^{3+} ions, and further decrease comes from the concentration quenching. It should be highlighted that the decay profiles of $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition (green emissions) change from single exponential to double exponential, suggesting that the energy transfer UC mechanism among Er^{3+} ions involve into the UC populating process (Fig. 2f).

As revealed in Fig. 2g, the energy levels of $^4I_{13/2}$ and $^4I_{9/2}$ play a crucial in UC emissions for $MLnS_2:Er^{3+}$. To deeply understand the essence of highly efficient UC emissions for $NaYS_2:Er^{3+}$, the decay time curves of $MLnS_2:Er^{3+}$ were measured (Fig. S10,11) and the lifetimes histogram of $^4I_{13/2}$ and $^4I_{9/2}$ are performed as Fig. 2h,i, the corresponding lifetimes constants were listed in Table S2. It is very interesting to observe that the decay time constants for α - $MLnS_2:Er^{3+}$ (2.4-2.8 ms for $^4I_{9/2}$; 4.9-8.0 ms for $^4I_{13/2}$) is significantly shorter than that of β - $MLnS_2:Er^{3+}$ (7.4-9.2 ms for $^4I_{9/2}$; 13.1-30.2 ms for $^4I_{13/2}$). Excitingly, the $NaYS_2:Er^{3+}$ phosphors have super long and the longest lifetimes in all the samples, reaching 30.27 ms and 9.24 ms for $^4I_{13/2} \rightarrow ^4I_{15/2}$ and $^4I_{9/2} \rightarrow ^4I_{15/2}$ transitions, respectively. Such ultralong decay time constants could be stemmed from the low non-radiative transition and weak electron-phonon coupling in $NaYS_2$ host. As mentioned in Fig. 2f, the UC emissions origins in the electrons populating process via ESA from low to high energy levels step by step. Significantly, the delayed lifetimes in $NaYS_2:Er^{3+}$ mean that the electrons on $^4I_{13/2}$ and $^4I_{9/2}$ levels stay longer, which is in favor of being re-simulated to higher green energy levels ($^4S_{3/2}/^2H_{11/2}$), bringing about efficient green UC emissions. It is in line with the results in Fig. 2c,d, where the stronger of UC emissions, the longer lifetimes of $^4I_{13/2} \rightarrow ^4I_{15/2}$ and $^4I_{9/2} \rightarrow ^4I_{15/2}$ transitions in $MLnS_2:Er^{3+}$ phosphors.

In order to understand qualitatively the UC luminescence mechanism in Er^{3+} , a set of rate equations were established based on the well-known UC process in $\text{MLnS}_2:\text{Er}^{3+}$ phosphors (See Supplementary Note 1):

$$I_{\text{green}} = \frac{\sigma_{12}^2 \sigma_{35} \rho^3}{W_1(R_3 + R'_{32} + \sigma_{35} \rho)}, \quad (1)$$

where R_3 presents the radiative rates of $^4\text{I}_{9/2}$ level of Er^{3+} , and R'_{ij} is non-radiative rate from level i to level j . W is the rate of the energy transfer process between Er^{3+} ions. ρ is the laser photon number density. σ_{ij} denotes the absorption cross-section between level i and j of Er^{3+} . It can be found from Equation (1) that the I_{green} value shows a cubic dependence on the laser photon number density, which means the green emission is a three-photon process, coinciding with the results in Fig. S6. The green emission intensity is proportional to σ_{12}^2 and σ_{35} , and the larger absorption cross-section of $^4\text{I}_{9/2}$ level, especially for $^4\text{I}_{11/2}$ level can lead to the strong green emission. The I_{green} is inversely proportional to the R_3 and R'_{32} , that is, it is inversely proportional to the radiative lifetime (τ) of $^4\text{I}_{9/2}$ level. The ultralong lifetime of $^4\text{I}_{9/2}$ level for 9.24 ms in $\text{NaYS}_2:\text{Er}^{3+}$ should generate the strong green UC luminescence. Meanwhile, because of small nonradiative rate (R'_{32}), it leads to weak red UC emission.

Table 1 Comparison of reported visible UCQYs with $\text{NaYS}_2:\text{Er}^{3+}$ by using 980 or 1500 nm as the excitation source.

Sample	UCQY	λ_{ex}	Power density	Ref.
$\text{LiLuF}_4:20\%\text{Yb}^{3+},1\%\text{Er}^{3+}$	5.00 %	980 nm	127 W/cm ²	44
$\text{NaYF}_4:20\%\text{Yb}^{3+},2\%\text{Er}^{3+}$	1.66 %	980 nm	22 W/cm ²	45
$\text{Gd}_2\text{O}_3\text{S}:3\%\text{Yb}^{3+},7\%\text{Er}^{3+}$	0.46 %	980 nm	3.8W/cm ²	45
$\text{NaYF}_4:20\%\text{Yb}^{3+},2\%\text{Er}^{3+}$	3.00 %	980 nm	150 W/cm ²	46
$\text{SrF}_2:5\%\text{Yb}^{3+},1\%\text{Er}^{3+}$	0.20 %	1532 nm	850 W/cm ²	47
$\text{LiYF}_4:10\%\text{Er}^{3+}$	0.20 %	1490 nm	150 W/cm ²	48
$\text{NaYS}_2:5\%\text{Er}^{3+}$	6.13 %	1532 nm	4.8 W/cm ²	This work

As is well known, the rare earth doped $\beta\text{-NaYF}_4$ (eg., $\beta\text{-NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$) has been recognized as the most efficient UC luminescent materials. Therefore, the commercial $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ phosphor is selected as a comparison with the as-prepared $\text{NaYS}_2:\text{Er}^{3+}$ phosphors. Fig. 3a shows the normalized UC luminescence spectra of $\text{NaYS}_2:\text{Er}^{3+}$ excited by 1532 nm and $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ pumped by 980 nm with the same power density (0.57 W/cm²). It is amazing to observe that the green emission intensity of $\text{NaYS}_2:\text{Er}^{3+}$ is 3.4 times stronger than that of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ (Fig. 3a). The ratio of green to red emissions is much higher in $\text{NaYS}_2:\text{Er}^{3+}$, suggesting the much weaker non-radiative transition from $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{11/2}$, further confirming

the weak electron-phonon coupling. Fig. S12 demonstrates that $\text{NaYS}_2:\text{Er}^{3+}$ has higher UC emission intensity than $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ as increasing the illuminating power density. The luminescence brightness of $\text{NaYS}_2:\text{Er}^{3+}$ and $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ at different power densities are measured, as displayed in Fig. 3b. The brightness of $\text{NaYS}_2:\text{Er}^{3+}$ is as high as 8224 cd/m^3 , while 3985 cd/m^3 for $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ at the excitation power density of 1532 and 980 nm of 1.42 W/cm^3 . Up-conversion quantum yield (UCQY) of the $\text{NaYS}_2:\text{Er}^{3+}$ sample is estimated to be 6.13% for the green and red emissions under 1532 nm excitation of 4.8 W/cm^2 (See Supplementary Note 2-3 and Fig. S13,14 in supporting information). At the same excitation power density, the UCQY of commercial $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ excited by 980 nm is measured to be 2.61%. Compared to the other representative UC materials (Table 1), the UCQY of $\text{NaYS}_2:\text{Er}^{3+}$ improves 30 folds than others under around 1532 nm excitation, and is also much higher than that of 980 nm excitation, whereas the excitation power density in our system is much smaller than that of the literatures⁴⁴⁻⁴⁸. For example, the reported UCQYs of $\text{LiYF}_4:\text{Er}^{3+}$ and $\text{NaLuF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ are 0.2% and 5.0% with the power density of 127-150 W/cm^2 at 1532 nm and 980 nm, respectively, which are markedly higher than that of 4.8 W/cm^2 . It should be noted that the $\text{NaYS}_2:\text{Er}^{3+}$ based ESA process not only obtains the more efficient UC emissions, but also expands its pumping wavelength to NIR II region. Such efficient UC emissions induced ESA may be ascribed to the significantly longer lifetimes of $^4\text{I}_{9/2}$ and $^4\text{I}_{13/2}$ levels of Er^{3+} ions in $\text{NaYS}_2:\text{Er}^{3+}$, which are 9.4 folds and 3.05 folds longer than that of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ (0.98 ms and 9.92 ms for $^4\text{I}_{9/2}$ and $^4\text{I}_{13/2}$ levels, as shown in Fig. 3c and Table S2).

More importantly, the UC spectra of $\text{NaYS}_2:\text{Er}^{3+}$ remains unchanged with varying the excitation power density under 1532 nm excitation, nevertheless, the red emission ratio obviously enhances in $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ illuminated by 980 nm (Fig. 3d). The CIE chromaticity coordinates and digital camera images in Fig. 3e demonstrate that the emission color of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ gradually shifts from green (0.3671, 0.6057) to red (0.4290, 0.5596) region, while $\text{NaYS}_2:\text{Er}^{3+}$ shows higher brightness and excellent color stability with concentrating in the green emission region (0.3131, 0.6737) by varying the pumping power. In addition, the UC luminescence ratio of red to green emissions in $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ significantly increases, whereas it changes little for $\text{NaYS}_2:\text{Er}^{3+}$ (Fig. 3f). These advantages can be attributed to the lower non-radiation in $\text{NaYS}_2:\text{Er}^{3+}$. These indicate that $\text{NaYS}_2:\text{Er}^{3+}$ phosphors have outstanding lighting and temperature spectral stability.

Narrowband NIR photodetection has been attracting substantial attention in diverse areas, including biological analysis, bio-imaging/sensing, and encrypted communications etc^{49,50}. As a proof of concept, we designed and fabricated narrowband responsive NIR photodetectors (PDs) using a simple $\text{NaYS}_2:\text{Er}^{3+}/\text{MAPbI}_3$ hybrids. As illustrated in Fig. 4a, a high quality MAPbI_3 film acting as the photon-to-current material was spin-coated on the top of $\text{NaYS}_2:\text{Er}^{3+}$ film (the top view SEM image of the $\text{NaYS}_2:\text{Er}^{3+}/\text{MAPbI}_3$ hybrids was shown in Fig. S15), then the silver electrodes were deposited on the

MAPbI₃ film. The working mechanism of the NaYS₂:Er³⁺/MAPbI₃ PD can be explained in Fig. S16. Briefly, the NaYS₂:Er³⁺ phosphor can absorb the incident NIR photons peaking around 808, 980, and 1532 nm, respectively, and convert them to visible lights in the spectral range of 400-700 nm through photon UC processes. The up-converted light can be efficiently absorbed by the perovskite MAPbI₃ with a narrow band gap (~800 nm), thereby producing photocurrents. Fig. 4b displays the typical on-off photocurrent-time (*I-t*) response curves of the NaYS₂:Er³⁺/MAPbI₃ device separately under 808, 980, and 1532 nm illumination with an incident light intensity of 5 mW/cm² at the bias voltage of 1V. The photocurrents are 1.26 μA, 2.19 μA, and 3.78 μA in NaYS₂:Er³⁺/MAPbI₃ PDs for 808, 980, and 1532 nm, while it is in well agreement with the UC luminescence intensities for the NaYS₂:Er³⁺ phosphor under corresponding excitations, respectively, and shown in Fig. S16. Importantly, three representative parameters (See Supplementary Note 4) to characterize the performance of the PDs including photo-responsivity (*R*), detectivity (*D*^{*}) and external quantum efficiency (*EQE*). As exhibited in the inset of the Fig. 4b and Fig. S17, *R*, *D*^{*} and *EQE* of the NaYS₂:Er³⁺/MAPbI₃ PDs are determined to be 0.26 A/W, 0.44 A/W, and 0.73 A/W; 0.4610¹⁰ Jones, 0.5610¹⁰ Jones, and 0.8410¹⁰ Jones; 39%, 55%, and 59% for the 808, 980, and 1532 nm light, respectively. The device at 1532 nm shows the best performance owing to the most effective UC at this excitation wavelength. The Fig. 4c shows that the photon-response times, which were extracted from the dynamic response curves of photocurrents of the device under 808, 980, or 1532 nm light illumination. The NaYS₂:Er³⁺/MAPbI₃ PD exhibits response times in the range of 310-570 ms. As shown in Fig. S18, the photodetection thresholds for the NaYS₂:Er³⁺/MAPbI₃ PDs reached below 2 mW/cm² for 808 nm and 980 nm light, particularly below 1 mW/cm² for 1532 nm light. Compared to other representative NIR PDs, our PDs based on NaYS₂:Er³⁺ phosphors demonstrate the excellent ability to multi wavelength detection and good performance (Table S3).

The development and collection of marine resources are closely related to underwater optical communication. Because 1532 nm is an optical communication wavelength, which can be easily coupled into optical fiber with low coupling and transmission losses. As a proof of concept demonstration, the NIR II responsive NaYS₂:Er³⁺ phosphors are used to construct the UC underwater information transmission system, as illustrated in Fig. 4d. The system is composed of three parts: transmitter, channel, and receiver. Firstly, the NaYS₂:Er³⁺ phosphors mixed with epoxy resin were packaged on the optical fiber, and 1532 LDs was coupled into the optical fiber which further simulated the NaYS₂:Er³⁺ phosphors, then generating UC green emission lights. The input signal of 1532 nm with different frequencies was adjusted by the signal generator, Then, the emitted UC lights carrying information passed through the seawater, and collected by receivers. As shown in Fig. 4e, the input signals are the pulsed 1532 nm lights at different working frequency, and the output signals present the 564 nm green emissions of NaYS₂:Er³⁺ excited by the 1532 nm. The green UC emission lights remain the frequency after passing through 0.6 m seawater (See the video in supporting information). In addition, the received signal strengths of UC green emissions are compared in air and seawater medium at the fixed distance of 1 m. It is clearly observed from Fig. 4f that the reduced rates of green emission of

NaYS₂:Er³⁺ are basically the same in these two mediums. These suggest that such NIR II responsive NaYS₂:Er³⁺ phosphors can effectively convert 1532 nm into green light signals to realize underwater optical communication.

In summary, the Er³⁺ doped MLnS₂ (M=Li, Na, K; Ln=La, Y, Gd, Lu; phases: cubic, or hexagonal) phosphors were successfully prepared through the high temperature solid reaction method. All of them demonstrate the efficient UC emissions under the illumination of NIR II 1532 nm based on the ESA process. By comparison, β-NaYS₂ phosphors are recognized as the most UC materials in MLnS₂:Er³⁺ under 1532 nm excitation. It can be explained by ordered layer structure of β phase instead of disordered structure of α phase, as well as super long lifetimes of excited state levels of NaYS₂:Er³⁺. More encouragingly, β-NaYS₂:Er³⁺ displays remarkably higher UCQY and brightness, and much better spectral stability of lights illumination and temperature than those of commercial NaYF₄:Yb³⁺, Er³⁺ phosphors. β-NaYS₂:Er³⁺ realizes a breakthrough UC efficiency as high as 6.13% under 1532 nm excitation, and the brightness of NaYS₂:Er³⁺ is 8224 cd/m³ under 1532 nm irradiation. Such high optical performances can be assigned to low non-radiative transition and electron-phonon coupling in NaYS₂:Er³⁺ phosphors. Furthermore, we designed and fabricated the sensitive narrowband responsive NIR PDs at wavelength of 808, 980, and 1532 nm, and the UC green light underwater communication application. Our work provides a new strategy for constructing NIR II responsive UC materials and expanding the scope of applications.

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Methods

All experimental details including samples synthesis, characterization and optical measurements are provided in the Supplementary Information.

Declarations

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Grant No. 11974069), Liao Ning Revitalization Talents Program (XLYC1902113), Science and Technology Project of Liaoning Province (2020JH2/10100012).

Author contributions

B.D., X.L., W.X. and L.G. conceived and supervised the project. X.Y. designed the experiment. X.Y. synthesized the samples with the help of Q.X., X.D, and N.Z. G.Z. Y.J., M.H., B.C., Q.X. and M.Y. performed the characterization and optical measurements. W.X., M. Y. and B.D. wrote the manuscript, with input from all authors.

Competing interests

The authors declare no competing interests.

Figures

Figure 1

Structure and morphology characterizations of $MLnS_2:Er^{3+}$. a-b, XRD patterns of $MYS_2:Er^{3+}$ ($M=Li, Na, K$) and $NaLnS_2:Er^{3+}$ ($Ln=La, Y, Lu, Gd$) prepared at 1173 K. c, Radius ratios between the trivalent lanthanide metal ion and the monovalent alkali metal ion (RLn^{3+}/RM^{+}) of $MLnS_2$. d-e, Crystal structure models of cubic $NaLaS_2$ ($\alpha-NaLaS_2$) and hexagonal $NaYS_2$ ($\beta-NaYS_2$). f, XRD patterns of $\beta-NaYS_2$ doped with 2, 5, 10, 15 mol% Er^{3+} . TEM, HRTEM images, and corresponding SAED of g-i $\alpha-NaLaS_2$ and j-l $\beta-NaYS_2$ crystals.

Figure 2

UC luminescence characterization of $MLnS_2:Er^{3+}$. a-b, Normalized visible UC luminescence spectra of Er^{3+} doped MYS_2 ($M=Li, Na, K$) and $NaLnS_2$ ($Ln=La, Y, Lu, Gd$) under 1532 nm excitation. c-d, Integral luminescence intensity and green to red emission ratio (I_g/I_r) of $MYS_2:Er^{3+}$ and $NaLnS_2$. e, UC luminescence spectrum of $NaYS_2:Er^{3+}$ in visible and NIR regions. f, UC luminescence populating mechanism of $NaYS_2:Er^{3+}$ under 1532 nm excitation. g, UC luminescence spectra of $NaYS_2$ doped with 2, 5, 10, 15 mol% Er^{3+} (inset: integral intensity varies with concentration of Er^{3+}). h-i, Lifetimes of $^4I_{9/2}$ and $^4I_{13/2}$ levels to $^4I_{15/2}$ transitions of $MLnS_2:Er^{3+}$.

Figure 3

Luminescence properties comparison of NaYS₂:Er³⁺ (1532 nm) and commercial NaYF₄:Yb³⁺,Er³⁺ (980 nm). a, Normalized UC luminescence spectra of NaYS₂:Er³⁺ excited by 1532 nm and NaYF₄:Yb³⁺,Er³⁺ excited by 980 nm with the same power density (0.57 W/cm²). b, Brightness of NaYS₂:Er³⁺ and NaYF₄:Yb³⁺,Er³⁺ varying with power density (W/cm²) of 1532 and 980 nm lasers. c, Decays curves of ⁴I_{9/2} and ⁴I_{13/2} levels to ⁴I_{15/2} transitions of Er³⁺ in NaYF₄:Yb³⁺,Er³⁺ and NaYS₂:Er³⁺. d, Normalized UC luminescence spectra of NaYS₂:Er³⁺ (1532 nm) and NaYF₄:Yb³⁺,Er³⁺ (980 nm) at 0.45 and 1.05 W/cm². e, CIE chromaticity coordinates and luminescence detail images of NaYS₂:Er³⁺ excited by 1532 nm and NaYF₄:Yb³⁺,Er³⁺ excited by 980 nm with the power density increase from 0.41 to 1.05 W/cm². f, Temperature dependence of UC luminescence ratios between red and green emissions.

Figure 4

Multispectral narrowband NIR photodetection and underwater information transmission of NaYS2:Er3+ phosphor. a, Schematic illustration of structure and working mechanism in the NaYS2:Er3+/MAPbI3 PDs. b, Photocurrent response of NaYS2:Er3+/MAPbI3 PDs under 808, 980, and 1532 nm excitation at power density of 5 mW/cm², respectively (inset: the responsivity and detectivity of NaYS2:Er3+/MAPbI3 device under separately 808, 980, and 1532 nm light excitation). c, On-off switching currents at lowest detectable excitation power density of NaYS2:Er3+/MAPbI3 device under 808, 980, and 1532 nm, respectively. d, Schematic illustration of the NaYS2:Er3+ underwater information transmission in seawater. e, Input and output signal information of transmitter and receiver at different frequencies (Hz) with the seawater depth of 0.6 m. f, Received signal strength of NaYS2:Er3+ in air and water at different distance between transmitter and receiver.

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