

Review

Sodium-Based Germanate Garnet Phosphors: Fundamentals, Luminescence Regulation and Applications

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Abstract

Garnet-structured compounds have long been recognized as versatile host platforms for luminescent phosphors, owing to their robust chemical stability and highly tunable cationic sublattices. Conventional aluminate and gallate garnets, however, generally face intrinsic limitations, including severe concentration quenching at high dopant levels, relatively high phonon energy, and unsatisfactory efficiency for long-wavelength near-infrared (NIR) emission. In recent years, sodium-based germanate garnets, constructed by introducing aliovalent Na⁺ into dodecahedral sites combined with Ge⁴⁺ substitution in tetrahedral frameworks, have emerged as a promising branch of garnet phosphors. The aliovalent Na⁺ incorporation brings unique structural effects, including energy migration blocking, coordination environment distortion, and defect level modulation, which endow the materials with advantages in mitigating concentration quenching, boosting energy transfer efficiency, and enhancing thermal stability. This review systematically summarizes the crystal structure classification and luminescence fundamentals of sodium-based germanate garnet systems, and introduces mainstream synthesis techniques represented by the high-temperature solid-state method. Focusing on representative host systems, the luminescence characteristics and energy transfer mechanisms of both rare earth- and transition metal-doped systems are elaborated in detail, followed by a summary of four representative performance regulation strategies: cationic disorder engineering, crystal field engineering, defect engineering and dual-site cooperative regulation. The multifunctional applications of these materials in white light-emitting diodes, plant growth lighting, fluorescence temperature sensing, NIR imaging, and information encryption are also presented. Finally, existing challenges and future research perspectives are proposed to provide guidance for the development of high-performance garnet phosphors.

Keywords: sodium-based germanate garnet; phosphor; luminescence regulation; energy transfer; Na⁺ blocking effect

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1. Introduction

Garnet-structured compounds, with the general formula A₃B₂(XO₄)₃ and cubic *Ia $\bar{3}$ d* space group, represent one of the most versatile functional material families. Owing to their flexible cationic accommodation capability and robust structural stability, garnets

have found wide applications in solid-state lighting, laser gain media, microwave dielectrics, and scintillators [1–6]. For luminescent phosphor applications, the polyhedral coordination environments of different crystallographic sites provide tunable crystal fields for various activator ions, enabling precise modulation of luminescence properties across the ultraviolet to infrared spectral range [7]. Early mineralogical studies have documented the widespread occurrence of trace elements, including Na, Y, Sc, and Ge in natural garnets, laying the foundation for artificial composition design of synthetic garnet phosphors [8–11].

For decades, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) has dominated both academic research and industrial production of garnet phosphors, benefiting from their mature synthesis process and good chemical durability. Nevertheless, the relatively high phonon energy ($\sim 800\text{ cm}^{-1}$) of aluminate lattices leads to pronounced non-radiative relaxation losses, especially for NIR emissions with small energy level spacing [2,12]. In addition, the uniform trivalent cation occupation at dodecahedral A-sites facilitates long-range energy migration among activators, causing severe concentration quenching at high dopant concentrations and limiting the achievable luminescence efficiency and color purity of red emissions [13,14].

To address these issues, germanate garnets have attracted growing attention as an alternative host system. The replacement of Al^{3+} by Ge^{4+} in tetrahedral sites reduces the maximum phonon energy to below 700 cm^{-1} , which fundamentally suppresses multiphonon relaxation and benefits efficient NIR luminescence [15–17]. Early studies on germanate garnet phosphors mainly focused on A-site divalent cation systems, including $\text{Ca}_3\text{B}_2\text{Ge}_3\text{O}_{12}$, $\text{Mg}_3\text{B}_2\text{Ge}_3\text{O}_{12}$, and $\text{Sr}_3\text{B}_2\text{Ge}_3\text{O}_{12}$ ($\text{B} = \text{Sc}, \text{Y}, \text{Al}, \text{etc.}$), and have demonstrated promising luminescence performance for both visible and NIR applications [18–21]. For instance, Cr^{3+} -doped $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ and $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$ phosphors exhibit broadband NIR emission with favorable thermal stability, and have been explored for phosphor-converted LED (pc-LED)-based NIR light sources [19,21]. $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$ phosphors deliver tunable warm white emission with ultrahigh thermal stability, showing potential for single-phase white LEDs [22]. Beyond luminescence, calcium and strontium germanate garnets have also been investigated as microwave dielectric ceramics, owing to their low sintering temperature and tunable dielectric properties [23–30].

On the basis of divalent A-site germanate garnets, researchers further proposed an aliovalent substitution design strategy by introducing monovalent Na^+ into the dodecahedral sublattice, giving rise to a series of novel sodium-based germanate garnet systems. Different from isovalent substitution, the incorporation of aliovalent Na^+ not only modifies the lattice parameters and crystal field strength, but also introduces unique structural effects that cannot be achieved in conventional garnets. Specifically, the non-luminescent Na^+ ions periodically distributed at A-sites can interrupt long-range energy migration among activators, enabling high-concentration doping with mitigated concentration quenching [13,31–35]. The valence mismatch between Na^+ and trivalent rare earths also induces local lattice distortion and controllable defect levels, which contribute to enhanced transition probability and regulable persistent luminescence [14,36].

Over the past few years, sodium-based germanate garnet phosphors have undergone rapid development. The host systems have expanded from indium-containing high-performance compositions such as $\text{NaY}_2\text{Ga}_2\text{InGe}_2\text{O}_{12}$ (NYGIG) and $\text{NaGd}_2\text{Ga}_2\text{InGe}_2\text{O}_{12}$ (NGGIG) to indium-free low-cost alternatives represented by $\text{NaGd}_2\text{Ga}_3\text{Ge}_2\text{O}_{12}$ (NGGGO) [13,31,37]. Activator ions cover rare earth elements, main-group metals, and transition metals, enabling luminescence tuning from visible cyan to long-wavelength NIR [14,38–43]. Meanwhile, diverse performance regulation strategies, including cationic disorder engineering and solid solution crystal field engineering, have been established, further enriching the material design toolbox [44–52]. Corresponding applications have extended

from conventional white lighting to fluorescence thermometry, NIR imaging, and information encryption [36,49,53–60].

Despite these fruitful achievements, a systematic review focusing on sodium-based germanate garnet phosphors is still lacking. Previous comprehensive reviews on garnet luminescent materials only briefly mention sodium-containing systems without in-depth elaboration of the unique structural effects and design principles behind this family [7,61–69]. To fill this gap, this work provides a thorough overview of recent advances in sodium-based germanate garnet phosphors. The crystal structure features, core Na⁺-induced effects, and luminescence fundamentals are first introduced. Representative synthesis methods are then summarized, followed by detailed discussion on the luminescence properties of rare earth- and transition metal-doped systems. Four typical performance regulation strategies are generalized, and the multifunctional applications of these materials are presented. Finally, current challenges and future research directions are outlined, aiming to offer insights for the development of next-generation high-performance garnet phosphors.

2. Crystal Structure and Luminescence Fundamentals

All sodium-based germanate garnets crystallize in the cubic $Ia\bar{3}d$ space group, retaining the classic $A_3B_2(XO_4)_3$ garnet framework with three distinct cation sites: eight-coordinated dodecahedral A-site, six-coordinated octahedral B-site, and four-coordinated tetrahedral X-site [70]. The defining feature of this family is the presence of monovalent Na⁺ at the dodecahedral A-sites. According to the cationic composition and occupation mode, sodium-based germanate garnets can be categorized into three main types, as schematically illustrated in Figure 1.

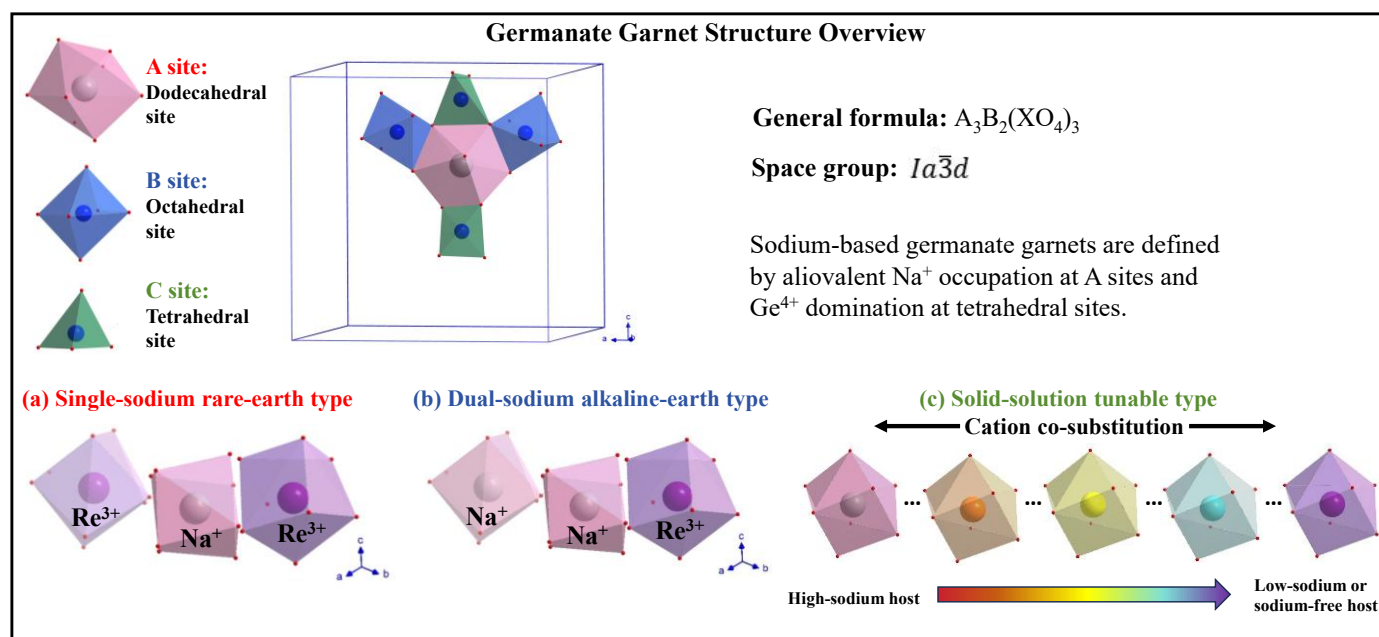


Figure 1. Schematic illustration of three types of sodium-based germanate garnet crystal structures: (a) single-sodium rare earth-type, (b) dual-sodium alkaline earth-type, and (c) solid-solution tunable type.

2.1. Structural Classification

2.1.1. Single-Sodium Rare Earth-Type

This is the most extensively studied category, with the general formula $NaRE_2B_2(XO_4)_3$, where the A-sites are jointly occupied by 1/3 Na⁺ and 2/3 trivalent rare earth RE³⁺ (Y³⁺, Gd³⁺, Lu³⁺, etc.). Typical representatives include the indium-containing

NYGIG and NGGIG systems, where octahedral sites are occupied by mixed Ga^{3+} and In^{3+} , and tetrahedral sites by mixed Ge^{4+} and Ga^{3+} [13,31]. To reduce material cost, indium-free systems such as NGGGO and $\text{NaLu}_2\text{Ga}_3\text{Ge}_2\text{O}_{12}$ (NLGO) have also been developed, with Ga^{3+} fully occupying the octahedral sites while maintaining the core A-site Na^+ occupation feature [36,37].

In this structure type, $[\text{NaO}_8]$ and $[\text{REO}_8]$ dodecahedral units exhibit short-range ordering with long-range disorder in the A-site sublattice, where Na^+ acts as non-luminescent energy barriers to interrupt long-range energy migration between rare earth activators. This intrinsic A-site compositional disorder is consistent with the widely reported cation disorder behavior in Ga/Al and Ga/In mixed garnets, as verified in previous structural studies [31,44]. This structural characteristic is the physical origin of the unique energy blocking effect. The flexible cation substitution at octahedral and tetrahedral sites also provides multiple degrees of freedom for luminescence performance tuning [3,14].

2.1.2. Dual-Sodium Alkaline Earth-Type

With the general formula $\text{Na}_2\text{MB}_2\text{Ge}_3\text{O}_{12}$ ($\text{M} = \text{Ca}, \text{Sr}; \text{B} = \text{Zr}, \text{Ti}, \text{Hf}, \text{Sn}, \text{etc.}$), this type features A-sites fully occupied by a mixture of Na^+ and divalent alkaline earth ions, while tetrahedral sites are completely occupied by Ge^{4+} , and octahedral sites accommodate tetravalent cations such as Zr^{4+} and Ti^{4+} . Representative systems include $\text{Na}_2\text{CaZr}_2\text{Ge}_3\text{O}_{12}$, $\text{Na}_2\text{CaTi}_2\text{Ge}_3\text{O}_{12}$, $\text{Na}_2\text{CaHf}_2\text{Ge}_3\text{O}_{12}$, and $\text{Na}_2\text{CaSn}_2\text{Ge}_3\text{O}_{12}$ [38,53,71,72].

Compared with the single-sodium rare earth-type, dual-sodium alkaline earth garnets generally have higher lattice distortion and weaker crystal field strength at octahedral sites, making them particularly suitable for Cr^{3+} doping to achieve long-wavelength NIR emission. For example, $\text{Na}_2\text{CaZr}_2\text{Ge}_3\text{O}_{12}:\text{Cr}^{3+}$ delivers an internal quantum efficiency (IQE) as high as 98% with an emission peak at 832 nm, representing one of the most efficient NIR garnet phosphors reported to date [53]. In addition to luminescence applications, $\text{Na}_2\text{CaTi}_2\text{Ge}_3\text{O}_{12}$ has also been investigated as a low-temperature co-fired ceramic (LTCC) material due to its anti-reductive property and good chemical compatibility with Ag/Cu electrodes, demonstrating the multifunctional potential of this structure family [23].

2.1.3. Solid-Solution Tunable Type

Based on the above two structure types, continuously tunable solid solution systems are constructed through cationic co-substitution strategies, which enable precise regulation of lattice parameters and crystal field strength. Typical examples include $\text{Na}_x\text{Ca}_{3-2x}\text{Gd}_x\text{In}_2\text{Ge}_3\text{O}_{12}$ and $\text{Na}_x\text{Lu}_{3-x}\text{Ga}_{5-2x}\text{Ge}_2\text{O}_{12}$, where the substitution ratio x can be continuously adjusted within a certain range [44,45].

By varying the composition, the emission peak can be continuously tuned from a sharp line to a broad band and from a short to a long wavelength. For instance, in the $\text{Na}_x\text{Lu}_{3-x}\text{Ga}_{5-2x}\text{Ge}_2\text{O}_{12}:\text{Cr}^{3+}$ system, increasing x leads to gradual lattice expansion and weakened crystal field at octahedral B-sites, red-shifting the Cr^{3+} emission peak from 708 to 812 nm [45]. Such a solid solution design provides a powerful approach for customizing spectral profiles to meet specific application requirements.

Besides the above three mainstream types, special sodium germanate garnets with hydroxyl groups, such as $\text{Na}_3\text{Hf}_{1.7}\text{Ge}_3\text{O}_{10}(\text{OH})_{1.8}$ and sodium zirconium germanate, have been synthesized via mild hydrothermal methods [73,74]. These materials feature unique hydroxyl inclusion mechanisms caused by octahedral site vacancies, enriching the structural diversity of the sodium-based germanate garnet family. It is worth noting that garnet structures with various A-site cations (Ca^{2+} , Mg^{2+} , Sr^{2+} , Li^+ , etc.) have been widely reported, but the aliovalent Na^+ substitution brings unique structural and luminescent characteristics that distinguish sodium-based systems from conventional isovalent garnets [18,24,75]. First-principles calculations on calcium germanate garnets have provided deep insights

into their structural, elastic, and lattice dynamical properties under pressure, which can also serve as theoretical guidance for the study of sodium-based systems [76].

2.2. Core Structural Effects of Aliovalent Na^+ Substitution

The aliovalent incorporation of Na^+ at dodecahedral sites is the defining feature that distinguishes sodium-based germanate garnets from traditional garnet systems. Its regulation on luminescence performance is mainly reflected in three aspects.

2.2.1. Energy Migration Blocking Effect

Na^+ itself is optically inert and acts as a non-luminescent center in the lattice. When periodically occupying A-sites, it divides the originally continuous rare earth ion sublattice into multiple isolated ion clusters, interrupting the long-range migration path of excitation energy and localizing the energy within a limited range [13,31]. This effect fundamentally mitigates concentration quenching at high dopant concentrations. For example, in NYGIG:Eu³⁺, the optimal Eu³⁺ doping concentration can reach 60 mol% relative to the Y³⁺ dodecahedral sites. It is several times higher than that in traditional YAG:Eu³⁺, and the corresponding photoluminescence quantum yield (QY) reaches 95.6% [31]. Statistical analysis of Tb³⁺-Eu³⁺ co-doped NYGIG shows that Na^+ increases the formation probability of Tb³⁺-Eu³⁺ pairs to 7%, while effectively suppressing the formation of long energy migration chains, leading to more targeted and efficient energy transfer [13].

A similar blocking effect of Na^+ has also been observed in sodium-modified laser garnets, where Na^+ incorporation increases the optical bandwidth of Yb³⁺ by introducing diverse electric charge distributions over the dodecahedral sublattice, further confirming the universality of Na^+ -induced structural modulation in garnet systems [77].

2.2.2. Coordination Environment Distortion Effect

The significant differences in ionic radius and valence state between Na^+ and RE³⁺ induce local lattice distortion upon aliovalent substitution, reducing the site symmetry at A-sites. The broken symmetry relaxes the parity-forbidden rule of f-f transitions for rare earth ions, enhancing the electric dipole transition probability and improving both luminescence intensity and color purity [3,14].

In NGGIG:Sm³⁺, a statistical probability model confirms that approximately 97% of Sm³⁺ ions reside in highly distorted coordination environments due to the combined effect of A-site Na/Gd mixing and octahedral/tetrahedral cation disorder. The enhanced electric dipole transition leads to a high red-to-orange (R/O) intensity ratio of 2.97, and the CIE chromaticity coordinate shifts significantly to the red region [3]. A similar symmetry-lowering effect is also observed in Bi³⁺-doped sodium garnets, where the distorted coordination environment promotes the metal-to-metal charge transfer (MMCT) transition of Bi³⁺, giving rise to broadband cyan emission [38].

2.2.3. Defect and Carrier Regulation Effect

The substitution of trivalent rare earths by monovalent Na^+ is inevitably accompanied by charge compensation processes, which introduce controllable defect energy levels in the lattice. By adjusting the Na^+ content and charge compensation mode, the depth and concentration of trap levels can be precisely tuned to realize special functions such as long-persistent luminescence and enhanced thermal stability [14,36].

In NLGO:Tb³⁺ long-persistent phosphor, the charge imbalance induced by Na^+ creates a trap level with a depth of 0.367 eV, which matches the optimal range for room temperature persistent luminescence, enabling an ultra-long afterglow of over 1200 s [36]. In NGGGO:Tb³⁺,Eu³⁺, high-concentration Tb³⁺ doping induces oxygen vacancy defects that act as local energy reservoirs to compensate for non-radiative losses at elevated

temperatures. As a result, the Eu^{3+} emission intensity at 450 K even exceeds that at room temperature, demonstrating an effective defect engineering approach to improve thermal stability [14].

2.3. Luminescence Physical Fundamentals

The excellent luminescence performance of sodium-based germanate garnets also benefits from the intrinsic low phonon energy of germanate lattices. Compared with aluminate garnets, the Ge-O bond in germanate systems has a lower vibration frequency, with a maximum phonon energy around 700 cm^{-1} . The introduction of heavy atoms such as Ga^{3+} and In^{3+} can further reduce the phonon energy of the system [2,12]. Low phonon energy greatly reduces the probability of non-radiative transitions via multiphonon relaxation, and the improvement in quantum efficiency is particularly significant for NIR emission levels with small energy level spacing.

In addition, the synergistic effect of low phonon energy and structural confinement endows these materials with generally good thermal stability. Most sodium-based germanate garnet phosphors retain more than 80% of their room temperature luminescence intensity above 425 K, and some indium-free systems can even exceed 96%, which is superior to commercial YAG phosphors [37]. Early thermal expansion studies on various garnet compositions, including $\text{Na}_2\text{CaZr}_2\text{Ge}_3\text{O}_{12}$ have provided basic thermophysical data, which support the reliability of these materials under high-temperature operating conditions [78]. As a classic oxide structure type, garnet lattices are well known for good intrinsic chemical and thermal stability. Early thermal expansion studies on sodium-containing germanate garnets confirmed that the cubic garnet framework remains structurally stable without decomposition up to 1223 K, demonstrating good high-temperature stability of this structure family. For the representative NGGIG system, aging tests verified good photostability: after 7 days of continuous 365 nm UV irradiation or direct sunlight exposure, only a negligible decrease in XRD diffraction intensity was observed, with no impurity phase formation, indicating good resistance to photodegradation [79]. It should be noted that long-term water immersion (7 days) leads to partial surface hydrolysis and formation of a small amount of amorphous phase, suggesting that proper encapsulation is required for practical application in high-humidity environments [79]. For solid-state synthesis of sodium-based germanate garnets, secondary phases (e.g., Na_2GeO_3 , RE_2O_3 , REGaO_3) are commonly observed when calcination temperature is insufficient ($<1100\text{ }^\circ\text{C}$) or Na source is deficient due to high-temperature volatilization. Appropriate 5–10% excess Na_2CO_3 and two-step calcination can effectively inhibit impurity formation and yield single-phase products [13,31,37].

3. Synthesis Methods

The preparation process directly affects the crystallinity, grain morphology, defect concentration, and final luminescence performance of phosphors. At present, high-temperature solid-state reaction is the dominant synthesis method for sodium-based germanate garnet phosphors, while wet chemical methods and novel auxiliary sintering techniques have also been reported.

3.1. High-Temperature Solid-State Reaction Method

The high-temperature solid-state method is the most mature and widely used technique for preparing sodium-based germanate garnet phosphors, and most high-performance samples reported to date are synthesized via this route [13,31,37]. Typically, corresponding oxides (Y_2O_3 , Gd_2O_3 , Ga_2O_3 , In_2O_3 , GeO_2 , etc.) and carbonates (Na_2CO_3 , CaCO_3 , etc.) are used as raw materials. After accurate weighing according to stoichiometric ratio, the raw materials are ball-milled with anhydrous ethanol or acetone as the mixing

medium. The dried mixture is then placed in an alumina crucible and calcined at 1200–1500 °C for 2–6 h in an air atmosphere. The final product is obtained after crushing, grinding, and sieving.

Notably, the introduction of Na⁺ can effectively reduce the synthesis temperature. Taking the NGGGO:Eu³⁺ system as an example, the reconstruction of traditional garnet into a sodium-rich matrix significantly lowers the required calcination temperature without compromising luminescence performance. A quantum yield of up to 96.78% is achieved under 394 nm excitation, indicating that sodium introduction not only reduces energy consumption during synthesis but also minimizes excitation energy loss during the light conversion process [37].

To further lower the calcination temperature and promote grain growth and crystallization perfection, 1–5 wt% fluxes are usually added, with common systems including H₃BO₃, NaF, and BaF₂. Appropriate fluxes can reduce the phase formation temperature by 100–200 °C, optimize grain morphology, reduce lattice defects, and improve luminescence intensity. To address the issues of large particle size and defect introduction during ball milling in conventional solid-state synthesis, a two-step calcination process is widely adopted: pre-calcination at 800–1000 °C to decompose raw materials, followed by high-temperature calcination to complete crystallization, which effectively improves product uniformity. Similar to aluminate garnets, phase purity is highly temperature-dependent. Insufficient calcination temperature usually leads to rare earth germanate secondary phases, while excessive temperature causes severe Na volatilization and formation of rare earth-rich impurity phases that reduce luminescence performance. Appropriate flux addition and two-step calcination (pre-calcination followed by high-temperature crystallization) effectively inhibit these impurities by promoting liquid-phase mass transfer and compensating Na loss during high-temperature treatment [13,31,37].

The high-temperature solid-state method features a simple process, good repeatability, and suitability for large-scale production, and the prepared samples have high crystallinity and stable luminescence properties. A number of invention patents on preparation methods and material formulas have been filed by research groups around core material systems, forming technical protection from formula to process.

3.2. Wet Chemical Methods

Aiming at the shortcomings of high calcination temperature and limited component uniformity of the solid-state method, wet chemical methods such as sol-gel, co-precipitation, and hydrothermal methods have also been applied to the preparation of sodium-based germanate garnet phosphors. These methods can achieve uniform mixing of components at the molecular level, with calcination temperatures usually 200–300 °C lower than the solid-state method, and the products have small particle size and narrow distribution, making them suitable for preparing nano-scale phosphors and long-persistent materials [73,74].

Among them, the mild hydrothermal method enables the synthesis of special systems that are difficult to obtain via high-temperature solid-state reaction. For example, the first garnet-structured sodium hafnium germanate Na₃Hf_{1.7}Ge₃O₁₀(OH)_{1.8} was synthesized as single-phase nanoparticles under mild hydrothermal conditions at 230 °C and autogenous pressure. Its special hydroxyl inclusion mechanism caused by octahedral site vacancies enriches the structural diversity of sodium-based germanate garnets [73]. Similarly, sodium zirconium germanate garnet was first synthesized via the same hydrothermal route, showing the feasibility of low-temperature synthesis for this material family [74]. In general, wet chemical methods are still mainly used for fundamental laboratory research at present, and high-temperature solid-state reactions remain the first choice for large-scale preparation. Phase purity is highly sensitive to reaction parameters. Improper

control of precursor pH, calcination temperature, mineralizer concentration and hydro-thermal conditions easily leads to secondary phases or unreacted precursors, so strict parameter control is essential to obtain single-phase products via wet chemical routes [73,74]. Careful control of these parameters is essential to obtain single-phase products via wet chemical routes.

3.3. Novel Preparation Techniques

Novel processes such as combustion synthesis and microwave-assisted sintering have also been gradually applied to this system. Combustion synthesis uses the heat released by redox reactions to achieve rapid crystallization, with short reaction time and loose products that are easy to grind, making it suitable for rapid screening of new systems. Microwave-assisted sintering improves heating uniformity through the volume heating effect, shortens the reaction time, inhibits abnormal grain growth, and improves luminescence uniformity.

For single crystal growth required for fundamental optical research, the optical floating zone method has been successfully applied to manganese aluminum germanate garnets for magnetic property studies, and this technique may also be extended to grow sodium-based garnet single crystals in future work [80]. In addition, spray pyrolysis and electrospinning can be used to prepare phosphors and thin film materials with special morphologies, providing material support for emerging applications such as flexible optoelectronics and 3D printed light-emitting devices.

4. Luminescent Properties of Doped Systems

Benefiting from the structural advantages of sodium-based germanate garnets, a rich variety of doped systems have been developed, covering the visible to NIR spectral range. Rare earth-doped systems are mainly used for lighting and sensing applications, while transition metal-doped systems represent an important branch for high-performance NIR luminescence. The typical luminescence properties of several representative doped germanate garnet systems are summarized in Figure 2.

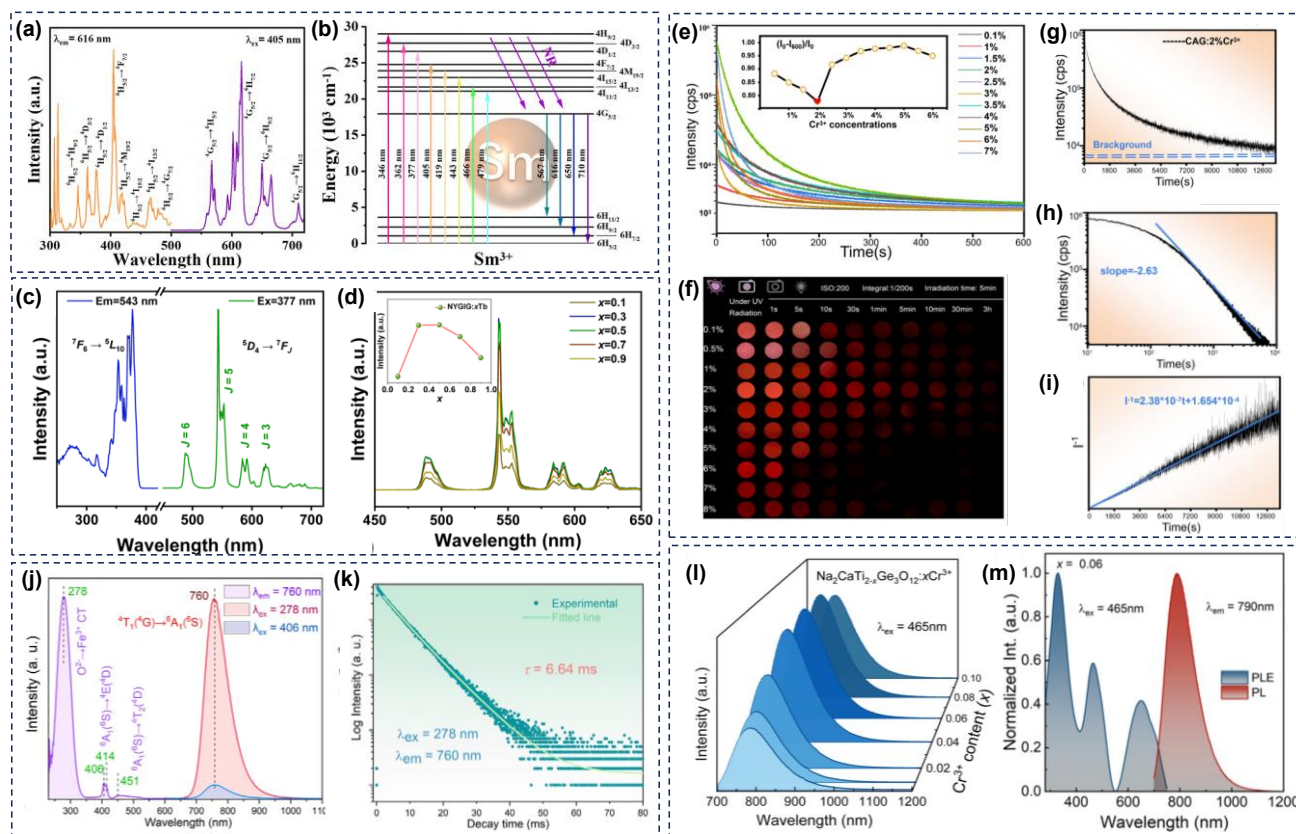


Figure 2. Luminescent properties of doped germanate garnet systems. (a) PLE and PL spectra of NGGIG:Sm³⁺ and (b) energy level scheme of Sm³⁺ ion [3]. (c) PLE and PL spectra of the NYGIG:0.5Tb³⁺ phosphor. (d) PL spectra of NYGIG:xTb³⁺ [13]. (e–i) Concentration-dependent persistent luminescence and decay kinetics of Cr³⁺-doped CAG phosphors [81]. (j) PL and PLE spectra of CSGG:Fe³⁺ sample at room temperature. (k) Decay curve and the corresponding fitted line of CSGG:Fe³⁺ [82]. (l) PL spectra with excitation at 465 nm of Na₂CaTi_{2-x}Ge₃O₁₂:xCr³⁺ ($x = 0.005$ – 0.10). (m) Normalized excitation and emission spectra of the Na₂CaTi_{1.94}Ge₃O₁₂:0.06Cr³⁺ [71]. Different colors in figures 2f and 2l correspond to different doping concentrations as indicated by the respective legends.

4.1. Rare Earth-Doped Luminescent Systems

4.1.1. Single-Doped Emission Phosphors

Eu³⁺ is the most representative red activator ion, and its luminescence performance fully reflects the structural advantages of sodium-based systems. In NYGIG:Eu³⁺, the energy blocking effect of [NaO₆] units enables ultra-high concentration doping, and anomalous thermal quenching and temperature-dependent spectral red shift are observed under charge transfer band excitation, revealing the regulation effect of Na⁺ introduction on excited state relaxation pathways [31]. Xie et al. further improved the efficiency record with the NGGGO:Eu³⁺ system. The white LED fabricated by combining this red phosphor with commercial green and blue phosphors delivers a color rendering index (CRI) of up to 90 and a correlated color temperature (CCT) as low as 3986 K, showing great potential for high-quality lighting [37].

Besides efficient red emission, Eu³⁺-doped NGGIG also exhibits unique far-red emission centered at 704 nm, corresponding to the ⁵D₀ → ⁷F₄ transition. This emission band matches well with the absorption of phytochrome's far-red form (Pfr), and the phosphor retains 80.6% of its room temperature emission intensity at 398 K. The fabricated far-red LED prototype shows stable color performance with increasing driving current, making it suitable for plant cultivation lighting [83].

In addition to rare earth activators, Pr^{3+} -doped $\text{Na}_2\text{CaTi}_2\text{Ge}_3\text{O}_{12}$ also delivers good red emission performance. Under 451 nm excitation, it emits intense red light at 609 nm with CIE coordinates of (0.6524, 0.3457), and its color gamut is wider than that of commercial nitride red phosphors, showing potential value in display applications [84]. Bi^{3+} -doped NGGIG exhibits broadband cyan emission covering 350–550 nm originating from MMCT transition, with CIE coordinates of (0.1814, 0.1937). This phosphor can fill the cyan gap in full-spectrum lighting and improve the visual health of illumination sources [38].

For comparison, Eu^{3+} -doped calcium germanate garnets such as $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$ also show high quantum efficiency for deep-red emission, but their thermal stability is generally inferior to sodium-based systems, limiting high-power applications [85]. Systematic studies on the correlation between garnet host composition and Eu^{3+} luminescence properties have confirmed that aliovalent cation substitution is an effective way to modulate the local coordination environment and optimize red emission performance [86].

4.1.2. Co-Doped Energy Transfer Systems

Co-doping is commonly used to broaden excitation spectra, tune emission color, and enable multifunctional luminescence in phosphor materials. Thanks to the structural confinement effect of Na^+ incorporation, sodium-based germanate garnets typically support more efficient and targeted energy transfer than conventional garnet hosts.

The Tb^{3+} - Eu^{3+} energy transfer pair has been studied in both the indium-containing NYGIG and indium-free NGGGO hosts. Both systems deliver good luminescence performance with efficient energy transfer, consistent with the expected effects of Na^+ site engineering. In the NGGGO system in particular, high-concentration Tb^{3+} doping introduces oxygen vacancy defects that lead to anomalous thermal stability, adding to the practical appeal of these low-cost compositions [13,14]. In Gd-containing sodium-based germanate garnets, the Gd^{3+} sublattice can act as an energy sensitizer for activators, a widely used mechanism in aluminum-gallium garnets that broadens UV excitation bands and improves absorption efficiency. This sensitization mechanism is fundamentally different from the structural regulation effect of aliovalent Na^+ incorporation: Gd^{3+} contributes to excitation energy harvesting, while Na^+ mainly acts as an energy migration barrier to mitigate concentration quenching. These two mechanisms are fully compatible and can be combined to achieve improved luminescence performance [3,31].

Unlike most co-doped systems optimized for efficient energy transfer, Dy^{3+} and Sm^{3+} co-doped into NGGIG show negligible interionic energy transfer and behave as largely independent luminescent centers. Their temperature-dependent emission intensities are determined primarily by their own thermal relaxation processes, which avoids measurement uncertainty introduced by energy transfer variations. A fluorescence intensity ratio (FIR) thermometer based on this system reaches a maximum relative sensitivity of 0.63% K^{-1} at 325 K, offering a useful route toward reliable luminescence thermometry [79].

For solid-state lighting, NGGGO: Dy^{3+} , Tm^{3+} has been developed as a single-phase white-emitting phosphor. Under 353 nm excitation, the yellow emission of Dy^{3+} and blue emission of Tm^{3+} complement each other to produce white light with CIE coordinates of (0.329, 0.329). Benefiting from the rigid garnet framework and tailored defect structure, the phosphor maintains 96.21% of its room-temperature emission intensity at 475 K, which is among the highest thermal stability values reported for single-phase white garnet phosphors [37].

4.1.3. Long-Persistent and Multimode Luminescent Systems

Through defect engineering regulation, sodium-based germanate garnets can realize long-persistent luminescence and multimode luminescence functions, expanding application scenarios in information security and detection fields.

The NLGO:Tb³⁺ phosphor prepared by solid-state reaction exhibits strong green emission at 543 nm under 272 nm UV excitation. Thermoluminescence curves confirm the existence of a trap level with a depth of 0.367 eV, which plays a key role in carrier storage and release. This green phosphor can realize Level I–III latent fingerprints on various substrates with high contrast and resolution. When mixed with commercial Y₂O₃:Eu³⁺ red phosphor, it enables information encryption with different fluorescent information under sunlight, UV light, and darkness, showing application prospects in latent fingerprint detection and information encryption [36].

In addition, Mn²⁺-doped Na₂CaSn₂Ge₃O₁₂ garnet can realize multimode luminescence, including persistent luminescence, X-ray storage, and mechanoluminescence via ion substitution strategies such as Na⁺/Sr²⁺/Ba²⁺ substitution on Ca²⁺ sites and anti-site occupation of Sn⁴⁺/Ge⁴⁺. It shows application value in X-ray luminescence extension imaging and stress sensing, further enriching the functional diversity of sodium-based germanate garnet systems [49]. Cr³⁺-doped Na₂CaSn₂Ge₃O₁₂ and Na₂CaTi₂Ge₃O₁₂ also exhibit NIR long-persistent luminescence, providing non-gallate alternatives for NIR long-persistent phosphors [72].

For comparison, Mg₃Y₂Ge₃O₁₂:Tb³⁺ garnet with divalent A-site cations also delivers tunable persistent luminescence with afterglow lasting more than ten hours, but its regulation mechanism mainly relies on intrinsic defects rather than aliovalent Na⁺ induced traps [18]. Calcium germanate garnets have also been developed for dynamic anti-counterfeiting applications based on Cr³⁺ long-persistent luminescence, yet the multimode capability of sodium-based systems offers higher security level for encryption designs [81].

4.2. Transition Metal-Doped Near-Infrared Luminescent Systems

Sodium-based germanate garnets also show good structural compatibility for transition metal activators, making them an important system for high-performance NIR phosphors and fully verifying the universality of the sodium-based structural design strategy.

4.2.1. Cr³⁺-Doped Broadband NIR Phosphors

Intrinsic cationic disorder is a natural advantage of sodium-based germanate garnets for broadband NIR emission. Taking NaGd₂Ga₃Ge₂O₁₂:Cr³⁺ as an example, the intrinsic Na/Gd disorder at A-sites and Ga/Ge occupation disorder at tetrahedral sites in the second coordination shell of Cr³⁺ create multiple distinct crystal field sites, enabling inhomogeneous emission from 600 to 1300 nm with a maximum at 820 nm. After Sc³⁺ co-doping, the full width at half maximum (FWHM) is widened to 183 nm while maintaining an IQE of 85% and thermal stability of 71% at 423 K, which is comparable to the best-performing Cr³⁺-doped intrinsic disordered garnet phosphors with $\lambda_{\max} > 800$ nm reported previously [44].

Introducing additional disorder via solid solution substitution can further expand the spectral tuning range. In the Na_xCa_{3-2x}Gd_xIn₂Ge₃O₁₂:Cr³⁺ system, the introduction of cationic disorder at dodecahedral sites leaves the excitation peak in the blue region nearly unchanged, while the emission wavelength is continuously tunable from 800 to 905 nm, with a maximum FWHM of 205 nm, realizing ultra-broadband NIR emission under blue light excitation [38].

For dual-sodium alkaline earth systems, Na₂CaZr₂Ge₃O₁₂ stands out for its near-unity IQE of 98% and long-wavelength emission at 832 nm. The high efficiency is attributed to the reconstructed crystal environment with structural distortion coupled with a weak crystal field, which is uncommon for most rigid garnet phosphors. The fabricated NIR pc-LED device outperforms devices using well-known efficient NIR phosphors in the same emission range, and has been applied in night vision, bioimaging, and nondestructive analysis [53]. Na₂CaTi₂Ge₃O₁₂:Cr³⁺ achieves a photoluminescence quantum yield (PLQY)

of 75% with an emission peak at 790 nm, and the fabricated pc-LED delivers an output power of 18.24 mW and a photoelectric conversion efficiency of 6.49% at 100 mA driving current, showing good performance in biological tissue imaging and nondestructive testing [71]. $\text{Na}_{1.5}\text{Gd}_{1.5}\text{Sc}_2\text{Ge}_3\text{O}_{12}:\text{Cr}^{3+}$ pushes the emission peak to a longer wavelength of 882 nm, with a maximum IQE of 84.6% and EQE of 20.6%, representing an efficient long-wavelength NIR phosphor with great prospects in spectroscopy applications [49]. $\text{Na}_2\text{CaHf}_2\text{Ge}_3\text{O}_{12}:\text{Cr}^{3+}$ exhibits an IQE of 79.2% at 830 nm, and the emission peak can be gradually tuned to 903 nm via chemical unit co-substitution with the emission intensity maintained above 60%, combining high efficiency with wide-range spectral tunability [87].

It is worth noting that Cr^{3+} -doped calcium germanate garnets such as $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ and $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$ also deliver good NIR performance, but their emission wavelengths are generally shorter than 800 nm, and the spectral bandwidth is relatively narrower compared with sodium-based systems [19,21]. Other germanate garnets like $\text{Ca}_3\text{MgHfGe}_3\text{O}_{12}:\text{Cr}^{3+}$ and $\text{Ca}_3\text{GdZnScGe}_3\text{O}_{12}:\text{Cr}^{3+}$ have also been reported with high IQE above 90%, but they still cannot match the long-wavelength and ultra-broadband advantages of sodium-based disordered systems [88,89]. Strategies including octahedral distortion induction, valence conversion, and excitation transition regulation have been developed for calcium garnets to improve NIR performance, which can also provide reference for the optimization of sodium-based systems [21,90,91].

4.2.2. Fe^{3+} -Doped NIR Phosphors

As an emerging NIR activator, Fe^{3+} has shown great potential in germanate garnet hosts, but systematic studies on sodium-based germanate systems are still rarely reported. Wang et al. reported Fe^{3+} -activated $\text{Ca}_3\text{Sn}_2\text{Ga}_2\text{GeO}_{12}$ (CSGG) garnet, a calcium-based germanate system, which produces robust NIR emission peaking at 760 nm, covering 600–1100 nm, with an IQE of 54.1%, EQE of 40%, and thermal stability of 72% at 423 K, superior to most previously reported Fe^{3+} -activated systems. First-principles calculations reveal that the efficient NIR luminescence from tetrahedral Fe^{3+} is attributed to the lower iron occupation at octahedral sites and the luminescence quenching of octahedral Fe^{3+} by the ${}^2\text{T}_2$ intermediate energy level. This finding deepens the understanding of Fe^{3+} photophysics in germanate lattices and provides a valuable reference for the future development of Fe^{3+} -doped sodium-based germanate garnet NIR phosphors [82].

In addition to Cr^{3+} and Fe^{3+} , Yb^{3+} and Nd^{3+} have been extensively investigated in calcium-based germanate garnet crystals for laser and NIR luminescence applications. Site-selective spectroscopy studies on Yb^{3+} -doped $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ and Judd–Ofelt analysis on Nd^{3+} -doped $\text{CaY}_2\text{Mg}_2\text{Ge}_3\text{O}_{12}$ have provided fundamental photophysical data, which can guide the exploration of ytterbium- and neodymium-doped sodium-based germanate garnet phosphors in future work [92,93].

5. Performance Regulation Strategies

The performance regulation of sodium-based germanate garnet phosphors follows the overall idea of multi-site cooperative tailoring. At present, four mature regulation strategies have been formed, providing systematic guidance for material design.

5.1. Cationic Disorder Engineering

Compositional disorder engineering is a long-developed material design strategy rather than a recent invention. As early as the 1960s–1980s, researchers utilized cation/anion mixing in alkali halide scintillators to trap charge carriers and improve scintillation light yield. In the 1990s, compositional disorder in $(\text{Y,Gd})_3(\text{Al,Ga})_5\text{O}_{12}$ mixed garnets was widely applied to adjust band structure and improve the performance of laser gain media and scintillators, where disorder-induced inhomogeneous broadening of emission spectra

was used to generate ultrashort laser pulses [9]. In the field of luminescent phosphors, cation disorder was initially used to broaden emission spectra in the early 2000s, and this strategy has been widely developed in various garnet phosphor systems [2]. Recent work on sodium-based germanate garnets extends this strategy to intentionally introduce energy barriers in the activator sublattice via $[\text{NaO}_8]$ units, achieving high quenching concentration and ultra-broadband NIR emission for spectroscopy and bioimaging applications [38,44]. Cationic disorder is one of the most effective strategies to broaden the emission spectrum and realize ultra-broadband luminescence. By introducing random occupation of different cations at the same crystallographic site, multiple crystal field environments are formed around activator ions, resulting in inhomogeneous broadening of the emission spectrum [44,46].

Intrinsic cationic disorder is a natural advantage of sodium-based germanate garnets, as the mixed occupation at A-sites and tetrahedral sites inherently creates diverse local environments. As mentioned above, the intrinsic disorder in $\text{NaGd}_2\text{Ga}_3\text{Ge}_2\text{O}_{12}:\text{Cr}^{3+}$ directly leads to ultra-broadband NIR emission covering 600–1300 nm [44]. Introducing extra disorder through solid solution substitution can further expand the regulation range, as demonstrated by the 205 nm FWHM achieved in $\text{Na}_x\text{Ca}_{3-2x}\text{Gd}_x\text{In}_2\text{Ge}_3\text{O}_{12}:\text{Cr}^{3+}$ [38]. This strategy is particularly useful for developing ultra-broadband NIR light sources for spectroscopy applications, as shown in Figure 3.

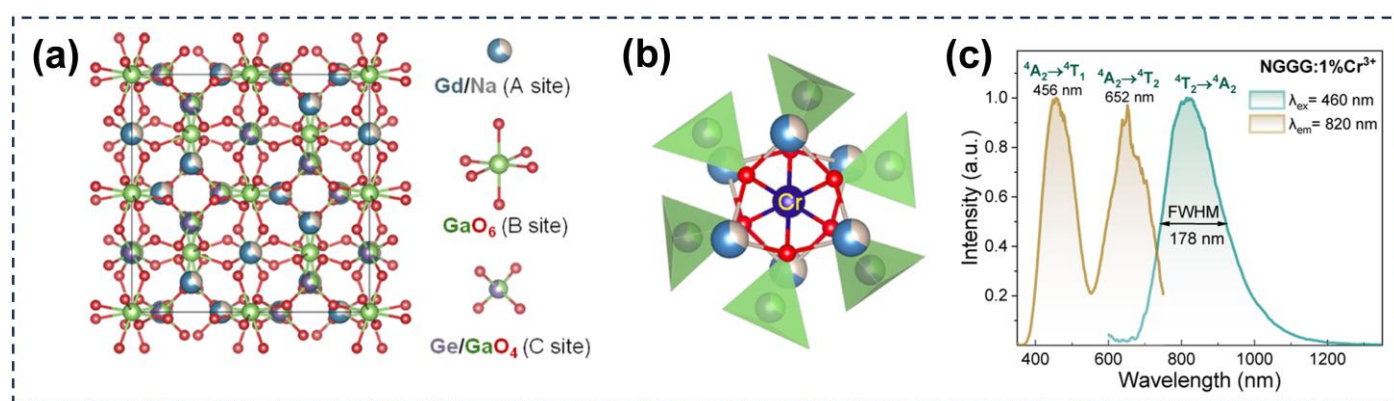


Figure 3. Cationic disorder engineering in sodium-based germanate garnets. (a–c) Crystal structure, local Cr^{3+} coordination environment and luminescence spectra of disordered NGGG: Cr^{3+} phosphor, showing inhomogeneous emission broadening induced by A-site cation disorder [44].

5.2. Crystal Field Engineering via Solid Solution

Through continuous composition adjustment of solid solutions, the crystal field strength at activator sites can be continuously regulated, realizing precise tuning of emission peak shape and wavelength.

In the $\text{Na}_x\text{Lu}_{3-x}\text{Ga}_{5-2x}\text{Ge}_2\text{O}_{12}:\text{Cr}^{3+}$ garnet solid solution system, the co-substitution strategy of “ $\text{Lu}^{3+} + 2\text{Ga}^{3+} = \text{Na}^+ + 2\text{Ge}^{4+}$ ” leads to gradual lattice expansion and weakened crystal field strength at octahedral B-sites, successfully tuning Cr^{3+} emission from sharp peak to broad band with the peak wavelength red-shifted from 708 to 812 nm. For the sample with $x = 0.1$, the FIR thermometer based on the ${}^2\text{E}$ and ${}^4\text{T}_2$ transitions of Cr^{3+} exhibits a highly linear Arrhenius response and achieves a relative sensitivity of $1.17\% \text{ K}^{-1}$ at 183 K. The prototype pc-LED fabricated with $x = 1.0$ phosphor shows a high output power of 44.68 mW and a photoelectric conversion efficiency of 14.89% at 100 mA driving current, providing new design principles for high-performance tunable NIR phosphors [45].

Similar crystal field engineering has been widely applied in calcium germanate garnets, such as $\text{Ca}_3\text{Al}_{2-y}\text{Sc}_y\text{Ge}_3\text{O}_{12}:\text{Cr}^{3+}$, where octahedral distortion induced by Sc^{3+} substitution effectively enhances NIR luminescence efficiency (Figure 4) [21]. The consistency of

this strategy across different garnet families confirms its general applicability. Inverse garnet systems such as $\text{Mg}_3\text{Yb}_2\text{Ge}_3\text{O}_{12}$ further expand the composition space for crystal field engineering, and the normal-inverse structural transformation strategy enables a near-zero temperature coefficient of resonant frequency for microwave dielectric garnets, which may also inspire new luminescence regulation designs [94].

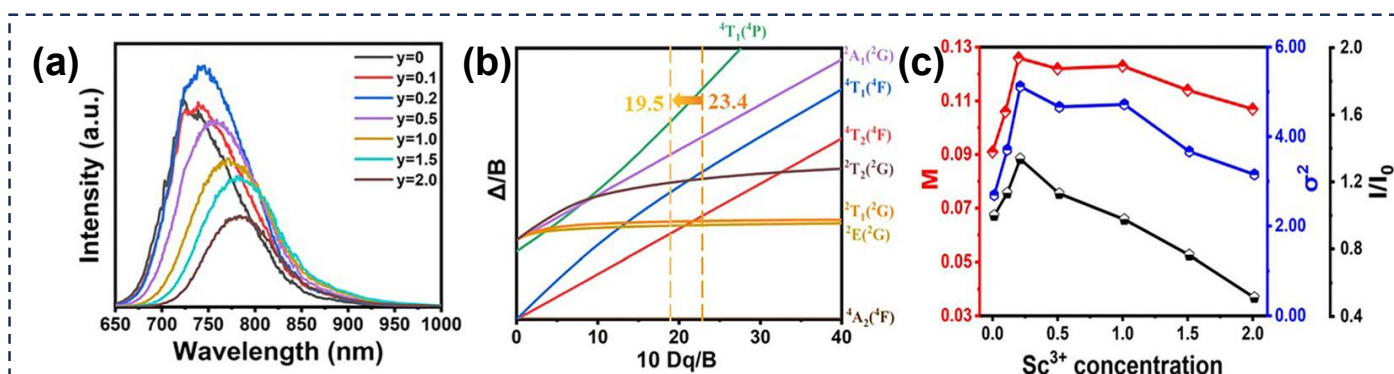


Figure 4. B-site crystal field engineering via solid solution design. (a–c) Spectral evolution with solid solution composition, Tanabe–Sugano diagram for Cr^{3+} energy levels, and correlation between octahedral distortion and luminescence intensity in Sc-substituted calcium germanate garnets [21].

5.3. Defect Engineering

By adjusting the Na^+ doping ratio and introducing charge compensation ions, the depth and concentration of trap energy levels in the lattice can be precisely regulated to achieve different functional goals, including enhanced thermal stability and long-persistent luminescence. For thermal stability regulation, oxygen vacancy defects induced by high-concentration Tb^{3+} doping in the NGGGO system can act as local energy reservoirs to compensate for non-radiative losses at high temperatures, making Eu^{3+} luminescence intensity at 450 K even higher than at room temperature, providing a new way to improve phosphor thermal stability via defect engineering, as illustrated in Figure 5 [14]. For long-persistent luminescence, the aliovalent Na^+ substitution in NLGO creates shallow trap levels suitable for room-temperature carrier release, enabling an ultra-long afterglow duration of over 1200 s, which verifies the feasibility of defect regulation in sodium-based garnet systems [36].

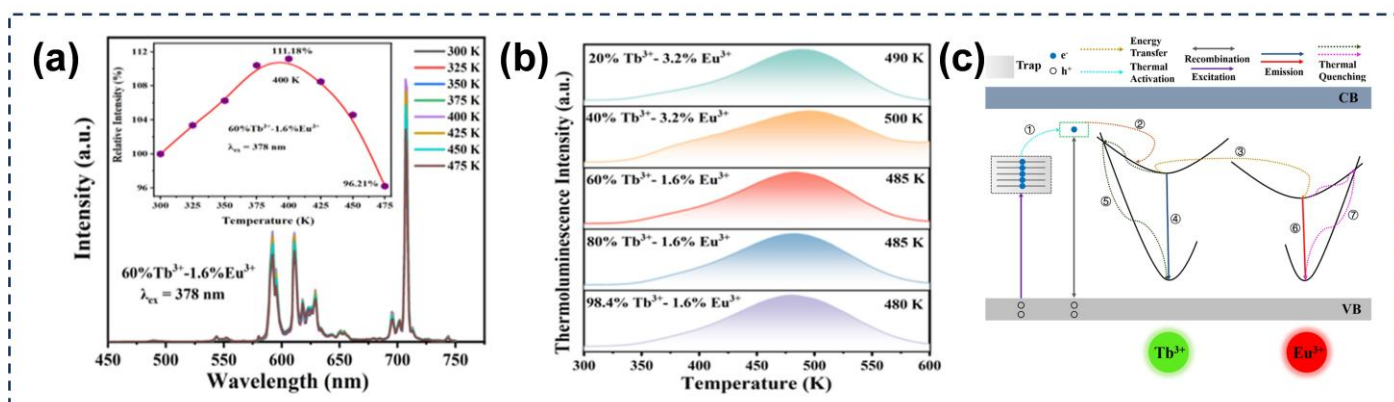


Figure 5. Defect engineering for luminescence performance optimization. (a–c) Temperature-dependent PL spectra, thermoluminescence curves, and schematic of oxygen vacancy-mediated thermal quenching compensation mechanism in Tb^{3+} -co-doped NGGGO:Eu³⁺ [14].

5.4. Dual-Site Cooperative Regulation

Simultaneous cooperative substitution at A-sites and tetrahedral C-sites can realize multi-dimensional regulation of luminescence performance, achieving simultaneous optimization of emission wavelength, FWHM, luminescence intensity, and thermal stability.

Taking the $[\text{Ca}_{2+y}\text{Gd}_{1-y}]\text{Zr}_2[\text{Al}_{3-y}\text{Ge}_y]\text{O}_{12}:\text{Cr}^{3+}$ system as an example, cooperative substitution at A-site ($\text{Ca}^{2+}/\text{Gd}^{3+}$) and C-site ($\text{Al}^{3+}/\text{Ge}^{4+}$) induces multi-dimensional effects: 35 nm FWHM broadening, a 47 nm emission peak redshift, and a 2.58-fold luminescence enhancement. The $[\text{CrO}_6]$ octahedral distortion caused by dodecahedral expansion and tetrahedral contraction, together with the change in electron paramagnetic resonance, elucidates the intrinsic mechanism of FWHM broadening and emission redshift. The dual-site cooperative regulation effectively widens the material bandgap while significantly enhancing structural rigidity, thereby achieving excellent thermal stability (93.8% retention at 423 K). Based on the differential response of this phosphor to acidic environments, a Morse code-based encryption system was developed, and the fabricated pc-LED realizes nondestructive testing, NIR imaging, night vision, and stable wireless optical communication, providing an innovative design strategy for the development of high-performance NIR phosphors (Figure 6) [95].

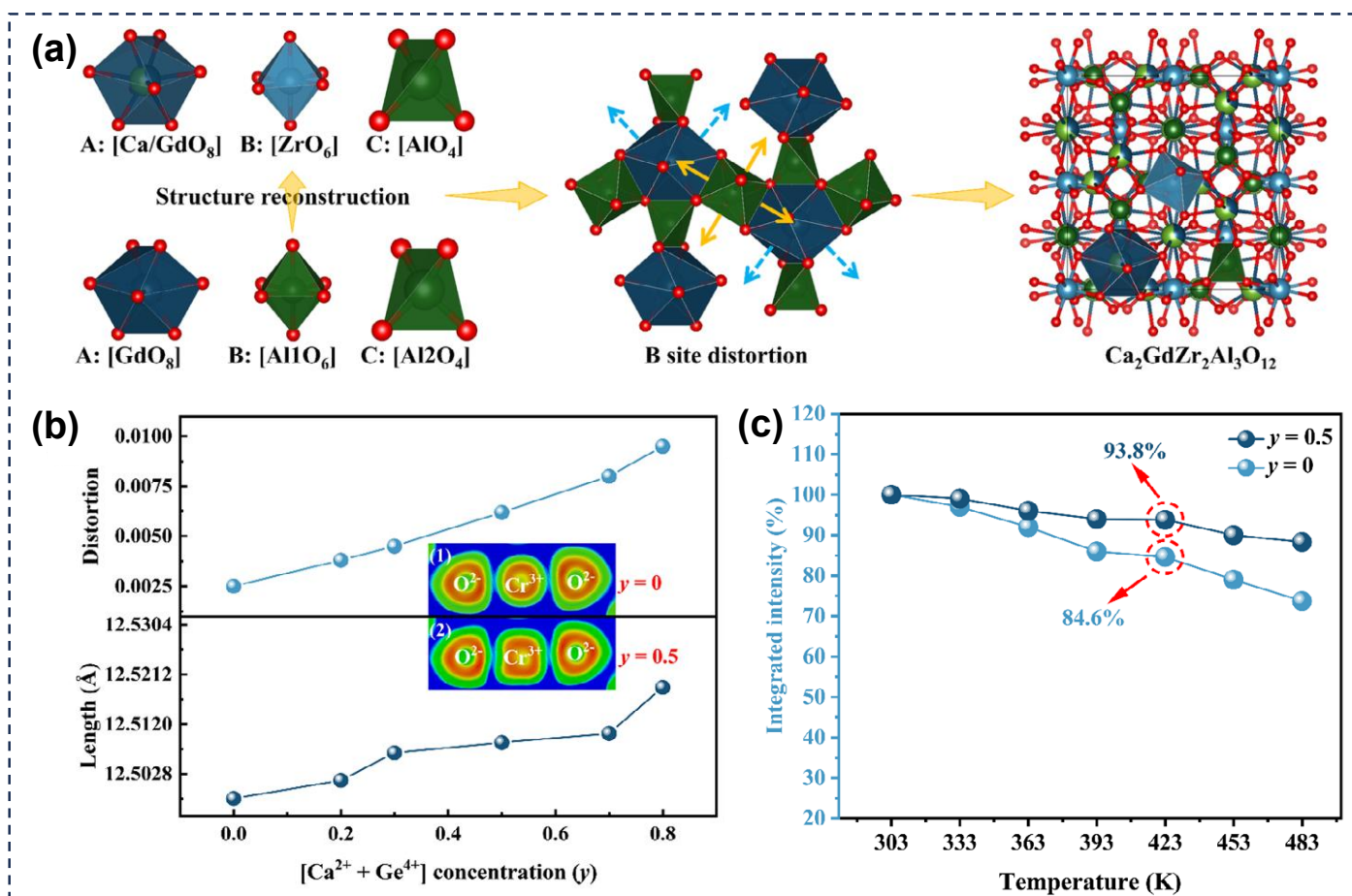


Figure 6. Dual-site cooperative regulation strategy. (a–c) Schematic of A/C-site co-substitution structure reconstruction, octahedral distortion evolution with composition, and thermal stability comparison of optimized phosphors (the insets labeled (1) and (2) in (b) show electron density difference maps at $y = 0$ and $y = 0.5$, respectively, illustrating the local structural evolution induced by A/C-site co-substitution). [95].

6. Applications

With the continuous optimization of material properties, the application scenarios of sodium-based germanate garnet phosphors continue to expand, with basic research and application transformation advancing simultaneously. Related material formulas and device packaging technologies have formed a series of invention patents, providing intellectual property support for industrial transformation.

6.1. White Light-Emitting Diodes

Lighting is the most mature application direction of sodium-based germanate garnets. Eu^{3+} and Sm^{3+} red phosphors with high quantum yield and good color purity can be matched with commercial $\text{YAG}:\text{Ce}^{3+}$ yellow phosphors to supplement the red component of white LEDs and significantly improve the color rendering index and warm light quality. Tb^{3+} - Eu^{3+} co-doped systems can be used as single-matrix warm white phosphors to simplify the device packaging process (figure 7) [13]. Dy^{3+} - Tm^{3+} single-phase white phosphors with ultra-high thermal stability are suitable for high-power driving scenarios [37]. Bi^{3+} cyan phosphors can fill the cyan gap in full-spectrum lighting, making the spectrum closer to natural light and improving visual health [38].

At present, warm white light devices based on such materials can achieve a CRI above 87, with CCT covering the warm light range of 3000–4000 K, suitable for indoor home and office scenarios. Supporting patent layouts have been formed around full-spectrum lighting modules and device packaging, promoting the transformation of material achievements into lighting products.

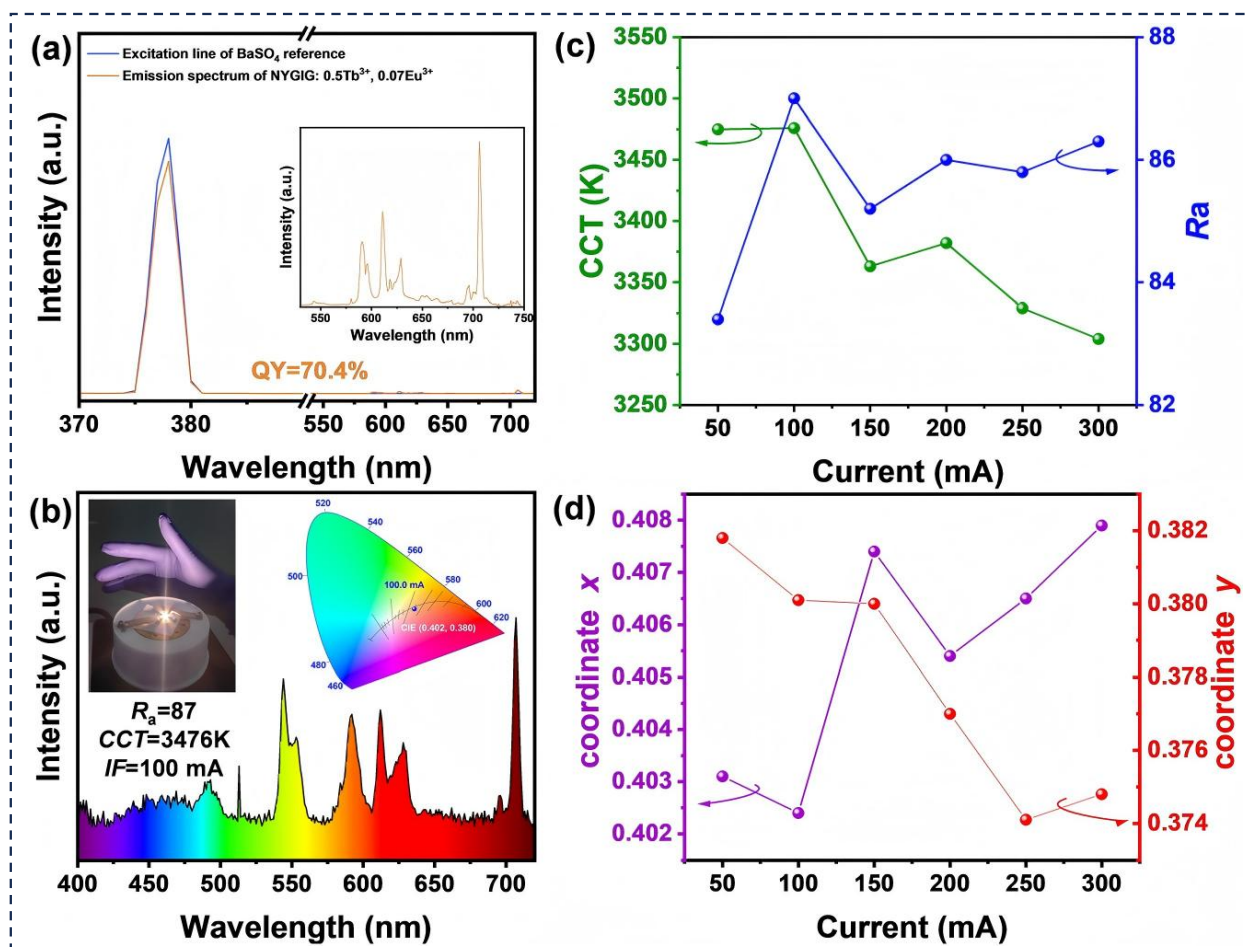


Figure 7. Visible light applications of sodium-based germanate garnet phosphors. (a–d) WLED device performance of NYGIG: Tb^{3+} , Eu^{3+} phosphor, including internal quantum yield,

electroluminescence spectrum, color rendering parameters and CIE chromaticity coordinates (arrows in (c) and (d) indicate the corresponding y -axis) [13].

6.2. Plant Growth Lighting

The far-red emission of Eu^{3+} -doped NGGIG matches the absorption band of plant phytochromes and can effectively regulate plant photomorphogenesis. The fabricated far-red LED prototype has stable color performance with increasing current, and its emission spectrum has high overlap with the absorption bands of phytochrome Pr and Pfr. It can be used for artificial lighting in plant factories to regulate plant growth, flowering, and fruiting, expanding the application boundary of sodium-based germanate garnets in agricultural lighting [82]. For comparison, $\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}:\text{Eu}^{3+}$ deep-red phosphor also shows positive effects on plant growth, but its thermal stability is inferior to sodium-based systems, limiting its application in high-power plant lighting fixtures [85].

6.3. Fluorescence Temperature Sensing

FIR-based fluorescence temperature sensors have the advantages of non-contact, anti-electromagnetic interference, and fast response, which are irreplaceable in scenarios such as high-voltage power, extreme environments, and biomedicine. The $\text{Dy}^{3+}\text{-Sm}^{3+}$ co-doped sodium-based germanate garnet system has outstanding performance in temperature measurement reliability and sensitivity due to its independent excitation and no energy transfer interference [79]. Cr^{3+} -doped systems can also achieve high-sensitivity temperature measurement based on the thermal coupling characteristics of ${}^2\text{E}$ and ${}^4\text{T}_2$ energy levels, with a relative sensitivity up to $1.17\% \text{ K}^{-1}$ [45]. Combined with the high thermal stability of the matrix, such materials can realize wide-temperature-range and high-precision temperature sensing. Comprehensive reviews on rare earth luminescence thermometry have summarized the development status of this field, and sodium-based garnet systems represent an important emerging branch with great application potential in industrial detection and intelligent perception [96].

6.4. Near-Infrared Imaging and Nondestructive Testing

Cr^{3+} -doped sodium-based broadband NIR phosphors can be integrated with blue LED chips to construct miniaturized, low-power phosphor-converted NIR light sources with emission bands spanning 700–900 nm and beyond, enabling versatile applications, including venous imaging, nondestructive food inspection, and night-vision surveillance. Compared with conventional tungsten halogen lamps, NIR pc-LEDs offer distinct advantages of prolonged operational lifetime, reduced energy consumption, and compact form factor. The growing prevalence of portable spectrometers and intelligent detection instrumentation has further stimulated market demand for such devices. To date, device-level demonstrations of high-performance sodium-based NIR phosphors have yielded promising results, with output power and photoelectric conversion efficiency approaching practical application thresholds. Meanwhile, the industrial validation of other mature NIR pc-LED systems provides a valuable benchmark for the future development of sodium-based garnet phosphors [53,97–100]. As presented in Figure 8, the fabricated NIR pc-LED based on sodium germanate garnet phosphor exhibits favorable optoelectronic performance, with the NIR output power reaching 18.24 mW at 100 mA driving current. Benefiting from the strong penetration capability of NIR light, clear venous imaging of human palm and nondestructive detection of internal cable damage have been successfully demonstrated, verifying the practical application potential in biomedical imaging and industrial inspection.

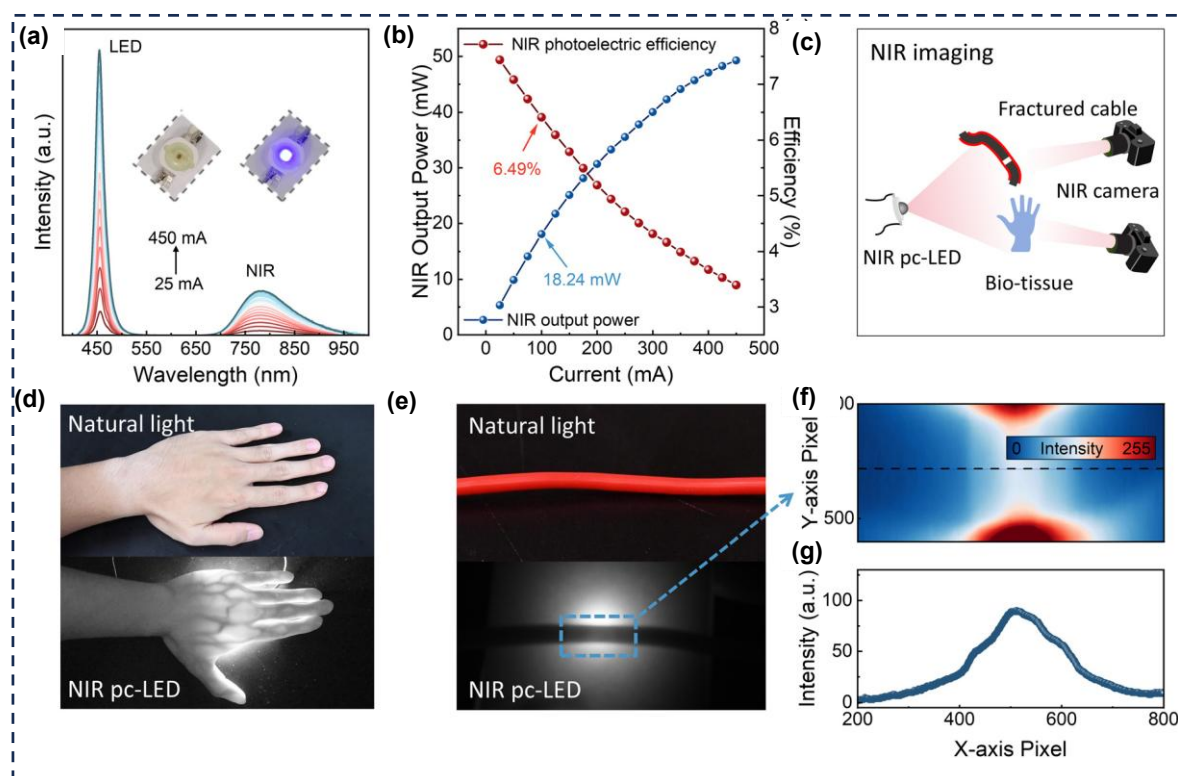


Figure 8. Broadband NIR pc-LED performance and nondestructive imaging applications. (a–g) Device performance of the fabricated NIR pc-LED based on sodium germanate garnet phosphor, including electroluminescence spectrum, output power, biological tissue penetration imaging results and nondestructive testing of internal cable damage [71].

The long-term operation stability and practical night-vision imaging performance of the fabricated device are further evaluated in Figure 9. The device exhibits stable output under different driving currents and maintains good performance after multiple thermal cycles between 303 K and 373 K, demonstrating excellent reliability for practical applications.

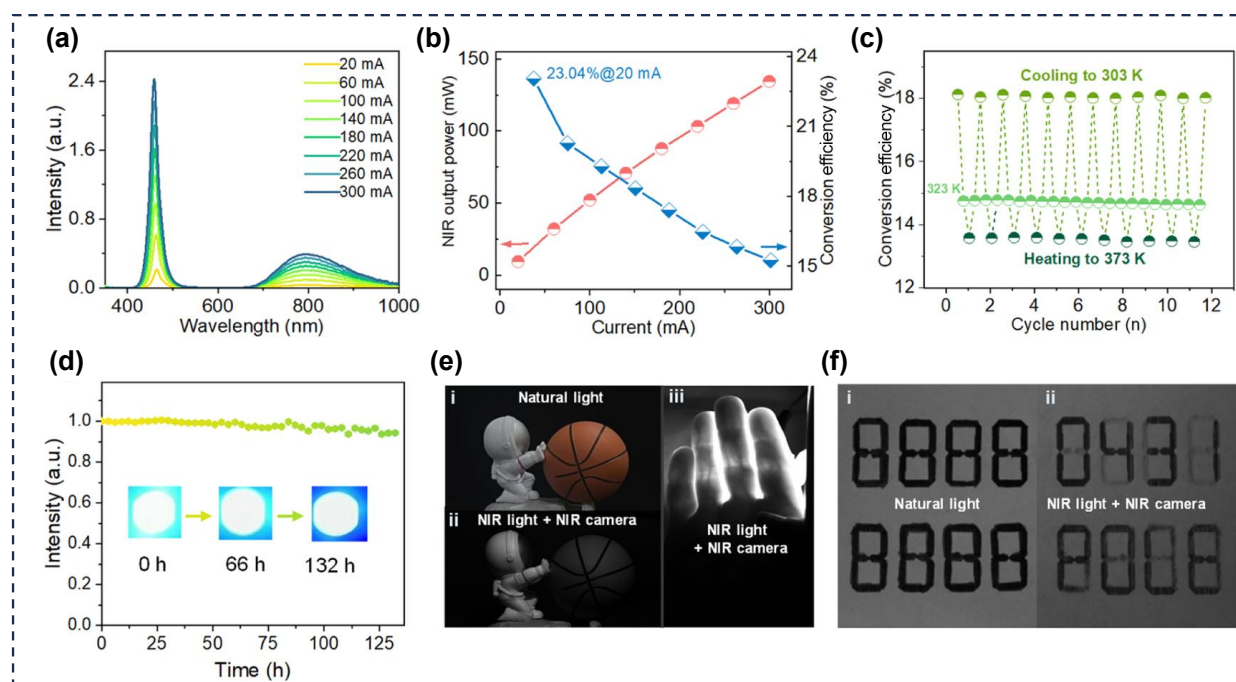


Figure 9. Operation stability and application demonstration of NIR pc-LED devices. (a–f) Long-term photoelectric stability under different driving currents, thermal cycling performance, and practical night-vision imaging results of NGGG:Cr³⁺,Sc³⁺-based NIR pc-LED under different working conditions [44].

6.5. Information Encryption and Anti-Counterfeiting

Tb³⁺-doped sodium-based germanate garnet long-persistent phosphors combine efficient fluorescence emission with ultra-long afterglow characteristics, and can be used for latent fingerprint identification, information encryption, and anti-counterfeiting marks. Such materials can achieve high-contrast fingerprint imaging on various substrates. After mixing phosphors with different emission colors, anti-counterfeiting inks and marks that show different display effects under natural light, ultraviolet light, and dark environments can be prepared, which have application value in certificate anti-counterfeiting and high-end commodity traceability [36]. Multimode luminescent materials with X-ray storage and mechanoluminescence properties further enrich the anti-counterfeiting modes and improve the security level. Furthermore, the NIR through-barrier optical communication capability demonstrated in Figure 10 also enables covert information transmission, as the invisible near-infrared signal can penetrate opaque media, which provides a new dimension for secure optical communication and information encryption applications [49].

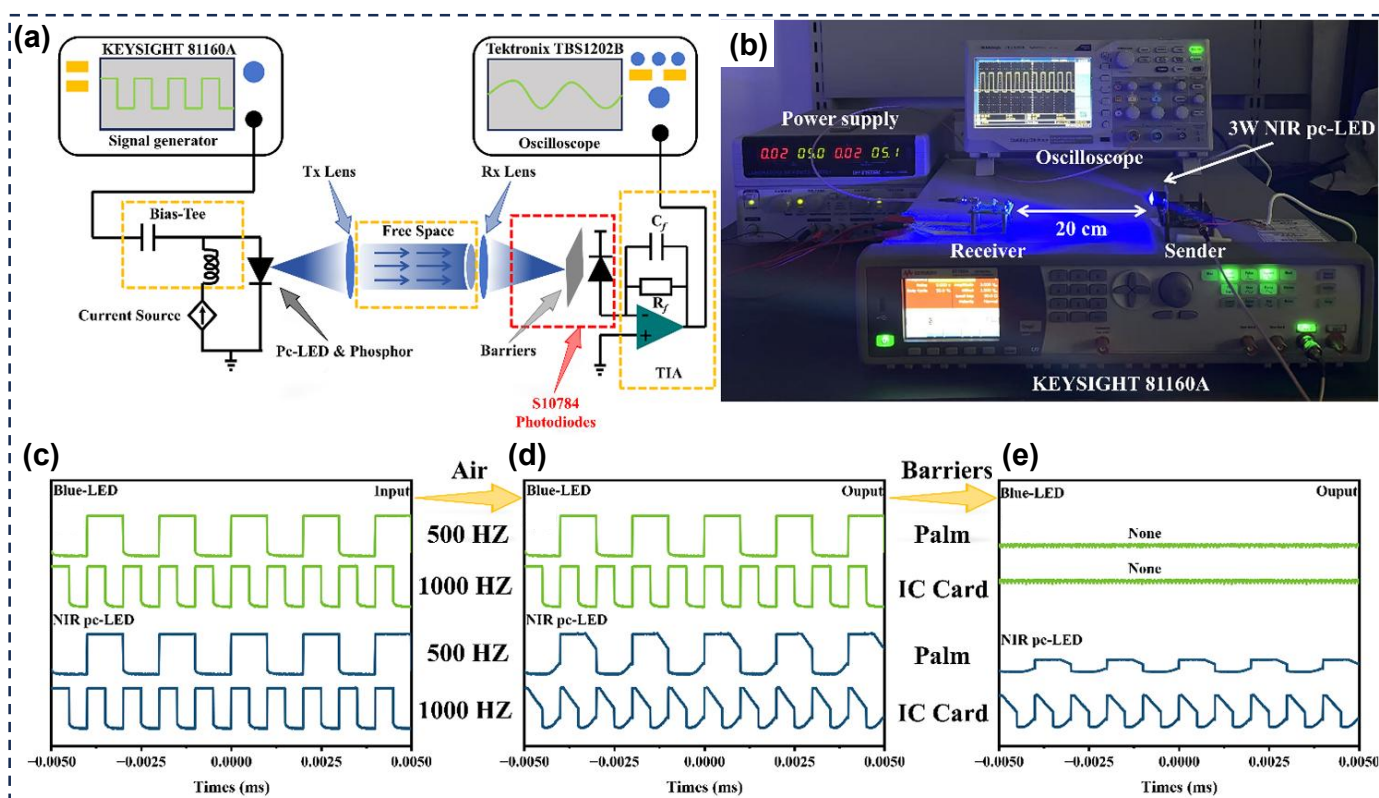


Figure 10. Wireless optical communication demonstration based on NIR pc-LED. (a) Schematic diagram of the wireless optical communication system. (b) Photograph of the experimental setup with a free-space transmission distance of 20 cm. (c) Input and (d) output signals of blue LED and NIR pc-LED at modulation frequencies of 500 Hz and 1000 Hz under air transmission. (e) Comparison of output signals when using palm and IC card as obstacles, demonstrating that NIR emission can penetrate biological tissues while visible blue light is completely blocked [49].

6.6. Other Potential Applications

Besides the above mainstream applications, sodium-based germanate garnets also show potential in other fields. $\text{Na}_2\text{CaTi}_2\text{Ge}_3\text{O}_{12}$ ceramics have excellent microwave dielectric properties and anti-reduction characteristics, with good chemical compatibility with Ag and Cu electrodes, showing application prospects in LTCC [23]. Garnet structure materials also have good chemical stability, endowing them with great potential for optoelectronic applications in harsh service environments. In addition, sodium-modified garnet single crystals have been investigated as laser gain media, indicating the broad application prospect of this structural family beyond phosphors [77]. Lithium-containing germanate garnets are widely studied as solid electrolytes for all-solid-state lithium batteries, further demonstrating the versatile functional value of garnet-type germanate materials [101].

7. Conclusions and Perspectives

Sodium-based germanate garnet phosphors exhibit remarkable material characteristics in high-concentration luminescence efficiency, energy transfer efficiency, thermal stability, and spectral tunability, relying on the energy blocking, site distortion, and defect regulation effects brought by aliovalent Na^+ substitution, combined with the low phonon energy advantage of Ge^{4+} . In recent years, the field has developed abundant host systems and doping types, with application scenarios expanding from white light lighting to fluorescence temperature sensing, NIR imaging, and information anti-counterfeiting, forming clear structural design methods and performance regulation paths.

Despite the remarkable progress, several issues still need to be addressed for further development. First, current research mainly focuses on visible and short-wave NIR systems, while studies on long-wave NIR above 1000 nm and upconversion luminescence are relatively scarce, and the host and activator systems still need to be expanded. Second, there is a lack of systematic evaluation data on long-term aging performance, thermal reliability under high-power driving, and environmental tolerance, leaving a gap from large-scale commercial application. Third, the luminescence efficiency of low-cost indium-free systems still has room for improvement, and the controllable preparation technology for nano-scale and morphology-controlled phosphors needs to be broken through. Fourth, device-level integration research is relatively weak, and the conversion efficiency of material properties to actual products still needs to be improved.

Future research can focus on the following directions. First, combining first-principles calculations and high-throughput screening, carry out reverse design of novel sodium-based germanate garnet systems to accelerate the development of new functional materials such as long-wave NIR and scintillators. Second, deeply study the energy transfer kinetics, non-radiative relaxation mechanism, and defect evolution law of multi-ion co-doped systems to provide more accurate theoretical guidance for performance optimization. Third, develop low-cost and large-scale preparation processes, optimize the luminescence performance of indium-free systems, and promote the industrial implementation of materials. Fourth, strengthen the whole-chain research and development of materials–devices–applications, and promote the practical application of sodium-based phosphors in full-spectrum lighting, intelligent sensing, NIR detection and other fields to fully release the technical value of such materials.

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review and editing; X.L., funding acquisition, conceptualization, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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