

Downconversion mechanoluminescence from lanthanide codoped heterojunctions

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Abstract

During the downconversion process, a high-energy photon undergoes conversion into several low-energy photons, leading to enhanced luminous efficiency in both photoluminescent and electroluminescent devices. This phenomenon has been applied in various fields, including solar cells, plasma display panels, and green lighting technologies such as mercury-free fluorescent lamps. However, the concept of downconversion (quantum cutting) has not been fully explored in the context of mechanoluminescent materials. In this study, we successfully synthesized a heterojunction of $\text{CaF}_2/\text{CaZnOS}$ exhibiting efficient downconversion mechanoluminescence (ML) properties. By controlling the CaF_2 to CaZnOS ratio and incorporating Tb^{3+} doping, we obtained a highly effective heterojunction structure that significantly enhanced ML. Moreover, we extended this material to several commonly utilized downconversion ion-doping combinations, achieving enhanced ML for Tb^{3+} , Pr^{3+} , and Yb^{3+} single ions. For the first time, we demonstrate the downconversion (quantum cutting) ML of $\text{Tb}^{3+}-\text{Yb}^{3+}$ and $\text{Pr}^{3+}-\text{Yb}^{3+}$ pairs within heterojunction microstructures. This study presents the design and synthesis of a novel heterojunction material capable of realizing downconversion ML, which holds promise for future applications in diverse fields.

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1. Introduction

Mechanoluminescence (ML) can emit light directly under an external force and assume various forms, such as sound vibrations, pressing, scratching, skin tension, and stretching. Unlike electroluminescence (EL) and photoluminescence (PL), ML does not require electrical power or illumination. Therefore, devices made from ML materials are passive, representing a smart and energy-saving light emission mode [1–6]. This characteristic offers significant application advantages in many fields, including tactile sensing, electronic skin, human–computer interaction, and intelligent anticounterfeiting [5, 7–9]. Previous ML designs have primarily focused on single-material forms, with notable research conducted on monolithic inorganic ML systems such as oxides [10], sulfides and thio-sulfides [11–15], and fluorides [16–19]. To further enhance the performance of ML, Peng *et al* proposed the concept of ML doping heterojunctions, integrating the synergistic effects of semiconductor heterojunction energy bands, built-in electric fields, and doping luminescent ion energy levels into the design and fabrication of ML materials. To further enhance ML performance, Peng *et al* proposed the concept of ML doping heterojunctions. This approach integrates the synergistic effects of semiconductor heterojunction energy bands, built-in electric fields, and doping luminescent ion energy levels. These elements are introduced into the development and manufacturing of ML materials. In recent years, the construction of heterojunctions has proven to be an efficient method for substantially enhancing ML performance [7, 12, 20–23]. Additionally, the mechanism of ML in heterojunctions was revealed. When two materials with different bandgaps contact the interface, a heterojunction is formed, resulting in an energy-band offset. The interface effect of the heterojunction can reduce the excitation barrier for electrons to reach the conduction band (CB) from the trap energy level, thus increasing the electron-hole complexation between the activators at the interface.

Heterojunctions are contact interfaces between any two solid-state materials and serve as the core structure of various optoelectronic devices, playing a significant role in various applications. Materials that form heterojunctions can include metals, insulators, fast ionic conductors, and crystalline and amorphous structures of semiconductor materials, which can be utilized for the modulation of electrical, optical, magnetic, thermal, and mechanical properties [10, 12, 24–28]. This characteristic provides greater possibilities for constructing heterojunctions by combining various ML materials, presents a strategy for the development of high-performance ML materials that are efficient, energy-saving, environmentally friendly, and have an ultralong lifespan. Therefore, further studies on heterojunctions are required. Currently, most related studies

on ML heterojunctions have focused on combining different materials to construct heterojunctions, primarily exploring single- and multiple-doping strategies to extend the emission spectrum for full-spectrum modulation in terms of luminescence. However, compared to relatively mature research fields such as PL and EL, research on ML heterojunctions still lacks investigations into upconversion and downconversion, which have not yet been integrated into the design and fabrication of ML materials. Upconversion and downconversion are crucial research directions in PL and EL that can effectively achieve energy conversion across different spectral ranges, such as the energy conversion between visible light and near-infrared (NIR) light (e.g., $\text{Tb}^{3+} \leftrightarrow \text{Yb}^{3+}$, $\text{Pr}^{3+} \leftrightarrow \text{Yb}^{3+}$, etc.), the energy conversion between ultraviolet light and visible light (e.g., $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$), and the energy conversion between NIR light and visible light (e.g., $\text{Er}^{3+} \rightarrow \text{Pr}^{3+}$) [29]. Notably, downconversion can absorb one high-energy photon and emit multiple low-energy photons. This process exhibits high luminous efficiency in PL and EL devices. It has several applications across many areas, including solar cells, plasma display panels, and green lighting [30–47]. A unique advantage of ML is its ability to emit light directly under various external forces. Therefore, achieving downconversion in ML is expected to facilitate passive and environmentally friendly applications in these fields. Additionally, the NIR spectrum serves as a dependable non-destructive detection technology employed in food quality assessment, medical diagnostics, and contemporary agriculture. Based on the unique emission form of ML, NIR ML is also anticipated to serve as a new passive light source in these fields. As a result, NIR ML has recently garnered significant attention, leading to the development of an increasing number of ML materials [48–51]. By integrating down-conversion mechanisms, further enhancement of NIR ML is anticipated, paving the way for achieving highly efficient NIR ML emission.

$\text{CaF}_2/\text{CaZnOS}$ (CF/CZOS) heterojunctions were successfully prepared. By controlling the ratio of CaF_2 to CaZnOS and doping with Tb^{3+} , we observed a significant enhancement in the ML of the CF/CZOS heterojunction, a phenomenon that could not be detected in the powdered form of CaF_2 [17, 18]. The integrated ML intensity of the heterojunction was 2.2 times greater than that of CaZnOS . Additionally, doping the heterojunction with a single lanthanide ion (Tb^{3+} , Pr^{3+} , or Yb^{3+}) resulted in enhanced ML. Building on this, we successfully co-doped the heterojunction with $\text{Tb}^{3+}\text{--Yb}^{3+}$ and $\text{Pr}^{3+}\text{--Yb}^{3+}$, thereby demonstrating the downconversion of ML in the heterojunction for the first time. Compared with the samples doped solely with $\text{Tb}^{3+}/\text{Pr}^{3+}$ and Yb^{3+} , the co-doped heterojunction exhibited a reduction in the ML of $\text{Tb}^{3+}/\text{Pr}^{3+}$ ions while significantly enhancing the ML of Yb^{3+} ions. These results are consistent with the proposed mechanism of

heterojunction downconversion of ML, confirming the energy transmission through $\text{Tb}^{3+}/\text{Pr}^{3+}$ to Yb^{3+} in the ML procedure.

2. Experimental section

2.1. Fabrication of heterojunction materials

The raw materials included ZnS (Aladdin, 99.99%), CaCO_3 (Sigma-Aldrich, $\geq 99\%$), CaF_2 (Aladdin, 99.99%), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$. The raw materials for $x\text{CF}/(10-x)\text{CZOS}:\text{Ln}^{3+}$ (Tb^{3+} , Pr^{3+} , Yb^{3+}) were ZnS, CaCO_3 , CaF_2 , and $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$. The weights of the raw components were determined using stoichiometric ratios. They were precisely measured to assure alignment between the sample's true mass and the calculated value. Subsequently, the weighed samples were placed in an agate mortar and dispersed by adding appropriate amount of ethanol. The samples were then milled until the ethanol had primarily vaporized, resulting in a powdery form, and then placed in an oven at $80\text{ }^\circ\text{C}$ – $100\text{ }^\circ\text{C}$ for 10 min to ensure the total evaporation of any remaining ethanol.

Then, the corundum crucible containing the dried sample was positioned in a high-temperature tube furnace with the continuous nitrogen (purity, 99.99%) flow rate of 60 cc. The sample was heated to $1100\text{ }^\circ\text{C}$, where it was maintained for 4 h. Once natural cooling was finished, the sample was removed from the high-temperature tube furnace, pulverized into a fine powder, and subsequently filtered using the stainless steel screen with a mesh size of 150 (0.68 mm aperture distribution). The resulting powder was preserved for further testing and characterization.

2.2. Fabrication of ML test composite films

The ML powder and UV-curable adhesive were first measured in a 5:1 ratio and deposited into a centrifuge tube, with the powder generally weighing 0.3 g. Subsequently, a suitable quantity of anhydrous ethanol was included, and the mixture was thoroughly swirled to disperse. It was promptly put into a hollow mold that is placed over a polyethylene terephthalate (PET) film. The mold was placed in an oven to facilitate the complete evaporation of the ethanol. Subsequent to the removal of the mold, the dimensions of the powder designated for ML testing were $3\text{ cm} \times 3\text{ cm}$. A subsequent PET film was put on top, and the assembly was sealed with a sealing machine. Subsequent to lamination, the composite film underwent exposure to UV radiation for curing.

2.3. Characterization

The samples were systematically analyzed using various characterization techniques. We used x-ray diffraction (XRD, Shimadzu XRD-6100) to obtain the diffraction patterns, while scanning electron microscopy (Thermo APREO S) was utilized to capture surface morphology images. Energy dispersive spectroscopy (EDS) was conducted to provide elemental distribution images of individual particles, and high-resolution

transmission electron microscopy (HRTEM) was also conducted to provide detailed insights into the microstructure of the samples. Traditionally, thin film samples are prepared with focused ion beam (Helios 5 UX). The atomic structure of the interface is revealed at 80 kV by the aberration-corrected transmission electron microscopy (JEM ARM 300 F2). Additionally, the PL characteristics of the sample were systematically characterized using a fluorescence spectrometer (Edinburgh FLS1000), with the aim of evaluating its potential performance in optoelectronic applications.

The ML testing is performed utilizing a bespoke testing apparatus, which mainly comprises a linear motor, a digital push-pull gauge, and a fiber optic spectrometer (Ocean Optics, QE65 pro). The testing procedure involves the following steps: The ML testing composite film is affixed to one side of a clear quartz glass slide. A digital push-pull gauge with a metal head is affixed to the side where the testing film is placed, integrated with a linear motor to regulate the movement of the metal head across the composite film. A fiber optic cable is linked to the fiber optic spectrometer on the opposite side of the quartz glass slide. To guarantee the successful transmission of emitted light signals to the spectrometer, the digital push-pull gauge and the optical fiber are kept in synchronized motion. The force exerted by the metal tip on the ML testing composite film is regulated using the push-pull gauge, while the linear motor enables lateral movement of the metal tip across the film. During the testing procedure, the metal heads glides across the surface of the film, creating light emission, while the fiber optic cable concurrently acquires the ML signals. To guarantee data accuracy, several forces are exerted during testing, and measurements are documented at numerous locations on the film, with each force condition recorded a minimum of five times.

3. Results and discussion

To better characterize and differentiate the mechanisms of ML, we introduce ML energy band models for single-matrix and heterojunction structures, as shown in figure 1(a). First, we describe the ML energy band model for a single matrix. When the matrix undergoes deformation owing to the applied pressure, a piezoelectric field is generated. Under the influence of this piezoelectric field, charge separation occurs and the piezoelectric effect causes the energy bands to tilt, which facilitates the escape of a number of electrons from the shallow trap levels into the CB. Then, these electrons recombine with holes, transferring energy nonradiatively to the luminescent center (electronic transition of Mn^{2+} from $^4\text{T}_1$ to $^6\text{A}_1$), resulting in luminescence.

By contrast, the ML energy-band model for a heterojunction differs from that for a single matrix, as illustrated in figure 1(b). Considering the heterojunction material $3\text{ZnS}/2\text{CaZnOS}:\text{Mn}^{2+}$ as an example [12], when subjected to pressure and deformation, a piezoelectric field is similarly generated, inducing charge separation. However, because of the heterojunction, there is a band offset at the interface between the ZnS and CaZnOS matrices. The interface

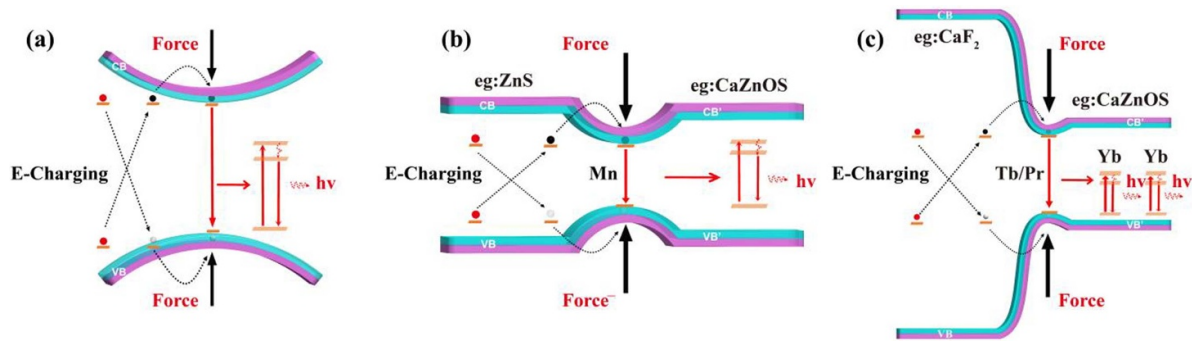


Figure 1. Energy band models of three types of ML: (a) the ML energy band model for a single matrix; (b) the ML energy band model for a heterojunction (e.g., ZnS-CaZnOS) [7, 12, 21, 52–54]. (c) The downconversion ML for a CF/CZOS heterojunction and its energy level model in this study. E-Charging refers to charge separation generated by an electric field; CB denotes the conduction band; VB signifies the valence band; red spheres represent neutral defect centers; white spheres indicate holes; and black spheres symbolize electrons.

effects can reduce the excitation barrier for electrons transitioning from the interlevel energy states to the CB, facilitating the escape of trapped electrons. This increases electron-hole complexation at the interfacial energy level of the activator (such as Mn^{2+}) [12, 20].

Subsequently, we introduce the downconversion ML for a CF/CZOS heterojunction and its energy-level model, as shown in figure 1(c). In this study, wideband CaZnOS and ultrawideband CaF_2 were selected as matrix materials. The reasons for choosing these two materials are threefold. First, CaZnOS can accommodate both Mn^{2+} and lanthanide ion (Ln^{3+}) doping while exhibiting the corresponding ML properties [8], and CaF_2 can also be doped with lanthanide ions to achieve ML [17, 18]. The combination of these two materials in a heterojunction is likely to enhance the ML of rare-earth ions. Second, based on band structure considerations, we selected the ultrawideband material CaF_2 (approximately 12 eV) [55, 56], because its ultrawideband characteristics potentially enhance the downconversion when forming a heterojunction. Third, fluorides can act as fluxes during the reaction process and are expected to improve the stability of the synthesized heterojunction materials. Using the Tb^{3+} – Yb^{3+} downconversion ions as an example, the energy released when electrons and holes combine first excites the Tb^{3+} ion through energy transfer. Some of the energy from excited Tb^{3+} is emitted as visible light in a spontaneous radiative process, whereas some of the energy is further transferred to Yb^{3+} to achieve NIR luminescence. Notably, because the energy transferred by Tb^{3+} can facilitate the transition of Yb^{3+} at twice its energy level. This process results in quantum cutting, where the energy of one high-energy photon is effectively divided into two low-energy (NIR) photons [33, 57].

Figures 2(a)–(c) illustrates the crystal structures of CaZnOS, CaF_2 , and CF/CZOS. Figure 2(a) depicts the crystal structure of CaZnOS, characterized by a non-centrosymmetric arrangement inside the hexagonal system, classified under Space Group $\text{P6}_3\text{mc}$, and exhibiting remarkable piezoelectric capabilities. It can be observed that the ZnS_3O tetrahedra, with Zn atoms at their centers, are aligned in parallel, forming a polar structure. In CaZnOS, the two cation sites, Zn^{2+} and Ca^{2+} , can be respectively substituted by transition metal

ions (such as Mn^{2+}) and lanthanide elements. Figure 2(b) is a schematic diagram of the crystalline structure of CaF_2 , characterized by a face-centered cubic lattice where each Ca^{2+} is encircled by eight fluorine ions (F^-) to create a cube. Each fluorine ion was surrounded by four calcium ions, creating a tetrahedral structure. The fluorine ions occupied the vertices and face-centered positions of the unit cell, whereas the calcium ions were located at the center of each cube. This structure endows CaF_2 with high symmetry and stability. Doping ions (Ln^{3+}) enter the lattice, substituting Ca^{2+} . Figure 2(c) shows the crystalline structure diagram of the CF/CZOS heterojunction.

XRD was performed to further characterize the crystal structures of the CF/CZOS heterojunctions. Figure 2(d) illustrates the XRD patterns of CF/CZOS: ① [1/0]; ② [1/1]; ③ [3/7]; ④ [1/9]; ⑤ [0/1]: 0.5% Tb^{3+} . In comparison with the standard cards for CaZnOS (No. 01-076-3819) and CaF_2 (No. 35-0816), it is evident that the diffraction spectrum of CaZnOS: 0.5% Tb^{3+} aligns with that of the CaZnOS standard card, and the diffraction spectrum of CaF_2 :0.5% Tb^{3+} also matches the corresponding standard card. Most of the diffraction peaks of 1CF/9CZOS: 0.5% Tb^{3+} corresponded well with the characteristic peaks of the CaZnOS standard card. The peaks at 28.2° , 47.0° , 55.7° , 68.7° , 75.8° , and 87.3° associated with CaF_2 correspond to the (111), (220), (311), (400), (331), and (422) crystal planes of cubic CaF_2 [55]. However, the diffraction characteristic peaks for both CaF_2 and CaZnOS approximate each other, such as the proximity of the 28.2° and 55.7° peaks of CaF_2 to the 28.5° and 56° peaks of CaZnOS. As shown in figure S1, as the molar ratio of CaF_2 decreases, the intensities of the respective diffraction peaks of CaF_2 gradually diminish. Notably, beyond the closely situated diffraction peaks, the intensity changes at 47° , 68.7° , 75.8° , and 87.3° , corresponding to the (220), (400), (331), and (422) crystal planes of CaF_2 , respectively, were particularly pronounced, confirming that the material was composed of both CaZnOS and CaF_2 . We further conducted EDS tests for the compositional analysis of the heterojunction materials. As shown in figure 2(e), the elemental mapping of a single particle revealed that the distribution of F was distinctly separated from those of Zn, O, and S, whereas Ca was uniformly distributed

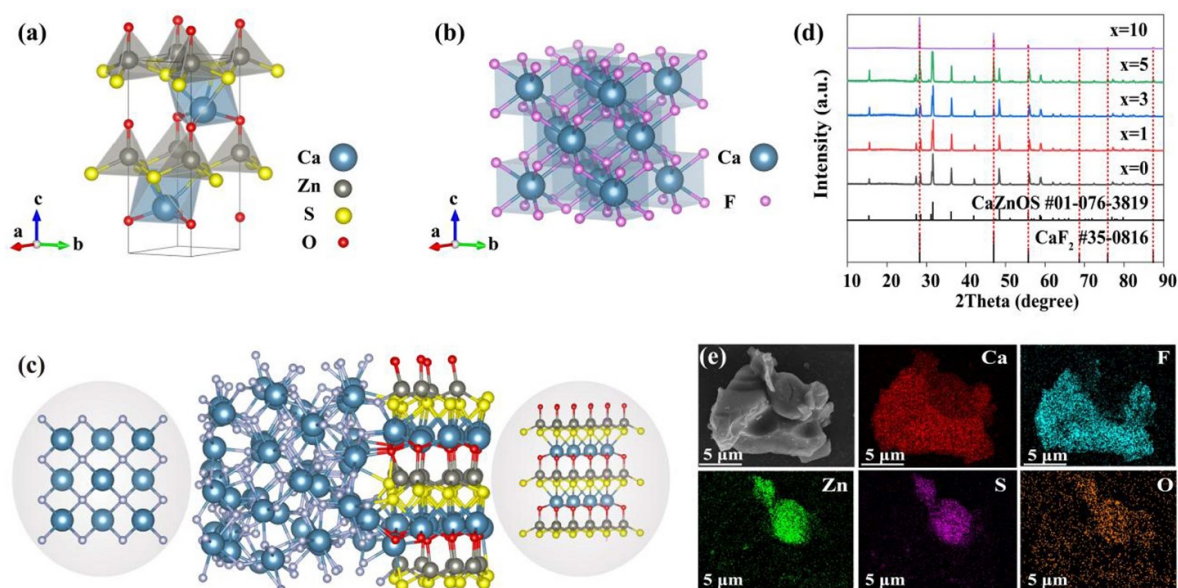


Figure 2. Crystal structures and XRD patterns. (a)–(c) Schematic of the crystal structures of CaZnOS, CaF₂, and CF/CZOS, where different elements are represented by Ca (purple), Zn (brown), O (red), S (yellow), and F (light gray). (d) XRD patterns of $x\text{CF}/(10-x)\text{CZOS}$: ① [10/0]; ② [1/1]; ③ [3/7]; ④ [1/9]; ⑤ [0/10]: 0.5% Tb³⁺; as well as the standard diffraction patterns of CaZnOS (PDF#01-076-3819) and CaF₂ (PDF#35-0816), with the major diffraction peaks of CaF₂ in the heterojunction material aligned using dashed lines corresponding to the CaF₂ standard card. (e) energy dispersive Spectrometer (EDS) of the CF/CZOS heterojunction.

throughout the entire particle. This confirms the presence of both CaZnOS and CaF₂ in the individual powder particles, validating the successful synthesis of this CF/CZOS heterostructured material rather than a simple mixture of CaZnOS and CaF₂. The sample was analyzed utilizing HRTEM, illustrated in figure S11. Figure S11(a) demonstrates the bright-field image of the heterojunction material. Furthermore, by magnifying a selected area, as shown in figure 1(b), the measured interplanar distances were found to be 0.21 nm on the left side and 0.34 nm on the right side. These values were compared with those from standard reference cards, confirming that the left region corresponds to the [104] plane of the CaZnOS crystal, while the right region aligns with the [111] plane direction of the CaF₂ crystal. These results confirm the existence of the CF/CZOS heterojunction.

To characterize the ML performance, the relevant ML tests involved encapsulating the crystals among two layers of PET film and conducting measurements with a custom-designed ML testing apparatus. To investigate the ML performance of the heterojunction samples obtained using different ratios of the two materials, ML tests were performed. Subsequently, we examined the ML characteristics of the CF–CZOS heterojunction under the same pressure (30 N). Figures 3(a)–(c) indicate the ML spectra of $x\text{CF}/(10-x)\text{CZOS}$:0.5% Tb³⁺, a comparison of the integral ML intensities over the 350–700 nm range, and the ML spectra of samples subjected to external forces (5–40 N). The inset illustrates the relationship between the integral ML intensity in the 350–700 nm range and the magnitude of the applied external force. In figure 3(a), aside from the differences in the ML intensity, the characteristic peaks in the 350–700 nm range are ascribed to the emissions

of Tb³⁺ (⁵D₃ → ⁷F_J and ⁵D₄ → ⁷F_J [$J = 2 - 6$]), specifically at wavelengths of ⁵D₃ → ⁷F₆ (382 nm), ⁵D₃ → ⁷F₅ (418 nm), ⁵D₃ → ⁷F₄ (439 nm), ⁵D₄ → ⁷F₆ (487 nm), ⁵D₄ → ⁷F₅ (544 nm), ⁵D₄ → ⁷F₄ (590 nm), ⁵D₄ → ⁷F₃ (624 nm), and ⁵D₄ → ⁷F₂ (659 nm). In order provide a more intuitive evaluation of the ML performance of the heterojunctions at various ratios, we integrated the ML spectra over the 350–700 nm range and compared the integral intensities. As shown in figure 3(b), the ML intensity was strongest at a CF–CZOS ratio of CF/CZOS = 1/9. Figure S2 shows photographs of the ML emissions from the $x = 0$ and $x = 1$ samples under the same conditions using antistatic metal tweezers, along with video recordings of the ML (video S1). By doping Pr³⁺ and Yb³⁺ at the optimal ratio for the heterojunction, we similarly observed an enhancement in ML, as shown in figure S3, which lays the foundation for further exploration of the induced ML downconversion.

The ML intensity of the samples with optimal ML was further investigated subsequently in relation to the external force. ML exhibited a linear increase with increasing external force. The inset demonstrates a strong linear correlation of the integral ML intensity and the external force, as illustrated in figure 3(c). Notably, the CaF₂:0.5% Tb³⁺ sample did not exhibit ML in the powdered state, which is consistent with previous reports on CaF₂:Tb³⁺ [18]. However, in this study, by combining these two materials, we conducted ML testing in the powder state. The ML intensity of 1CF/9CZOS:0.5%Tb was enhanced by 2 times compared to that of CZOS:0.5%Tb, as shown in figure 3(a), achieving a significant improvement in ML intensity. This result demonstrates that CaF₂ is a crucial component of this heterojunction, effectively enhancing

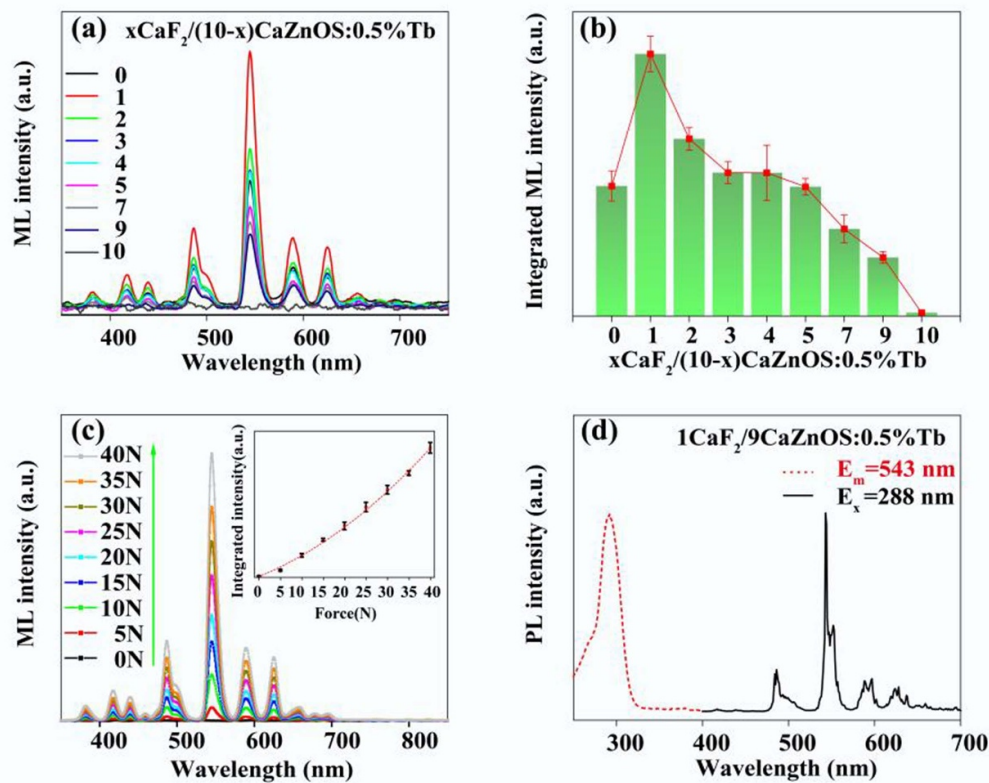


Figure 3. ML and PL characteristics. (a) ML spectrum of $x\text{CF}/(10-x)\text{CZOS:0.5\% Tb}^{3+}$ ($x = 0-10$) under a pressure of 30 N. (b) Comparison of the integral intensities of the ML spectrum from heterojunction samples at varying molar ratios (integrated within its wavelength range of 350–700 nm). (c) ML spectra of $1\text{CF}/9\text{CZOS:0.5\% Tb}^{3+}$ under various external forces ranging from 0 to 40 N. The inset compares and fits the integral intensities of the ML spectra in the range of 350–700 nm. (d) PLE and PL spectra for $1\text{CF}/9\text{CZOS:0.5\% Tb}^{3+}$.

ML in the powder state. This also addresses the issue of pure CaF_2 materials being unable to achieve ML applications in powder form.

Subsequently, we explored other properties of the samples at the optimal ML ratio. First, the recoverability of the ML of the samples was validated by applying a constant load (5 N) to the composite film (powder@PET) during continuous sliding. As shown in figure S4, in the initial stages of sliding cycles, the ML intensity decreased owing to external compression reducing the amount of powder in the tested area, which is an unavoidable consequence of the testing method. After 20 sliding cycles, although the ML intensity fluctuated, no significant decrease in ML intensity was observed. These fluctuations were attributed to the sample exhibiting a relatively weak ML intensity and larger noise signal under a 5 N load. The insets in figures S4(a) and (b) depict the ML spectra for the 5th and 29th sliding cycles, respectively. These results demonstrate that the emission peaks of the emitted spectra remain consistent throughout the sliding process, confirming that the emissions presented in figures S4(a) and (b) originate from Tb^{3+} and Yb^{3+} ions, respectively. Thus, the test results indicated that the sample possessed self-recoverable ML characteristics. Next, we investigated the stability of the powder samples by conducting water-soaking experiments. As demonstrated in

figure S5, We compared the ML of the CZOS and CF/CZOS powders before and after soaking in water for 48 h. The integrated ML intensity of CaZnOS incurred a reduction of approximately 38.6%, whereas the integrated ML intensity of the $1\text{CF}/9\text{CZOS}$ powder diminished by approximately 29.4% after 48 h of soaking. This suggests that the addition of CaF_2 enhances the stability of the heterojunction samples. Fluorides are often used as materials for transparent ceramics, and because their refractive indices are similar to those of high-molecular-weight polymer materials such as PDMS, composites of the two can produce transparent films [16–18, 58, 59]. Therefore, we explored the effects of CaF_2 on the film transparency. As shown in figure S6, by observing the transparency of the PDMS films made from CaZnOS , CaF_2 , and CF/CZOS attached to the Shenzhen University logo, the CaF_2 @PDMS film exhibited nearly complete transparency. Moreover, the CF/CZOS @PDMS film allowed better visibility of the letters and patterns beneath it compared to the pure CaZnOS @PDMS film. This indicates that the incorporation of CaF_2 improves the transparency of the pure CaZnOS @PDMS film, providing the potential for further development of transparent devices using this heterojunction material. Furthermore, we tested the PL of the optimally induced ML heterojunction sample. As shown in figure 3(d), we obtained PLE spectra when the

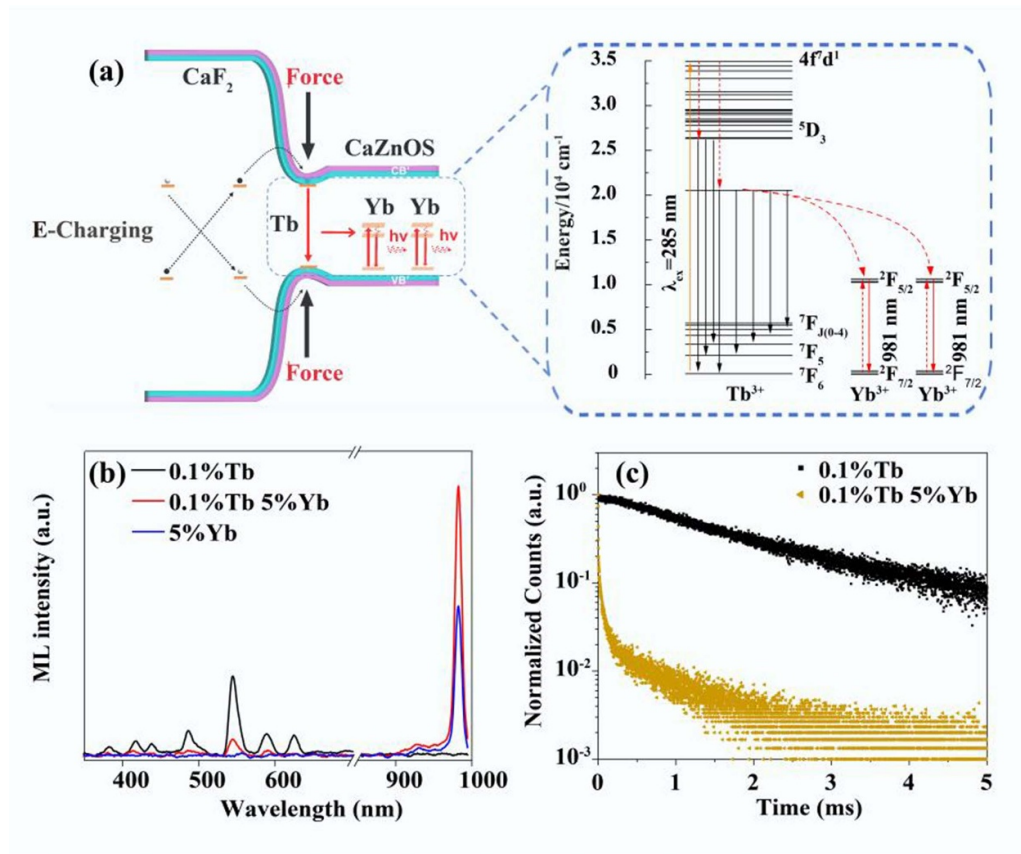


Figure 4. (a) Energy band model of downconversion ML in the CF/CZOS: Tb^{3+} , Yb^{3+} heterojunction, with the enlarged view on the right illustrating the detailed energy level diagram for the energy transfer from Tb^{3+} to Yb^{3+} . (b) ML spectra under 30 N pressure for 1CF/9CZOS:0.1% Tb^{3+} , 0.1% Tb^{3+} 5% Yb^{3+} , and 5% Yb^{3+} . (c) Decay lifetimes of $\text{Tb}^{3+} {}^5D_4 \rightarrow {}^7F_5$ luminescence at 544 nm under 285 nm excitation for 1CF/9CZOS:0.1% Tb^{3+} (black curve) and 1CF/9CZOS:0.1% Tb^{3+} 5% Yb^{3+} (orange curve).

emission wavelength was 544 nm and PL spectra when the excitation wavelength was 288 nm. The emission peaks in the spectra are characteristic of Tb^{3+} and fundamentally consistent with the emission peaks in the ML spectra. We also tested the quantum yield of the $x\text{CF}/(10-x)\text{CZOS}:0.5\% \text{ Tb}^{3+}$ series of samples, as shown in table S1. When $x = 1$, the highest quantum yield of the heterojunction sample is 13.27%.

Building on the previously discussed ML heterojunction energy band model, we introduced the concept of downconversion and explored the downconversion combination of Tb^{3+} – Yb^{3+} , as shown in figure 4(a). In this downconversion ML heterojunction model, the energy produced when electrons and holes combine first excites the Tb^{3+} ion through energy transfer. This energy then relaxes in a nonradiative manner through oscillations to the $^5D_4$ level and subsequently returns to the $^7F_6$ level. The energy from this transition is emitted radiatively as green light with a main wavelength of 544 nm ($^5D_4 \rightarrow {}^7F_5$). Additionally, a portion of the energy is first nonradiatively transferred to Tb^{3+} , exciting it to the $^5D_4$ level, and then transferred to two adjacent Yb^{3+} ions at the $^2F_{5/2}$ energy level, putting them into an excited state. Subsequently, the Yb^{3+} ions return from the $^2F_{5/2}$ level to the $^2F_{7/2}$ level. Because the energy

from a single Tb^{3+} ion transitioning from the $^5D_4$ level back to the $^7F_6$ level is twice that of the Yb^{3+} ions transitioning from the $^2F_{7/2}$ level to the $^2F_{5/2}$ level, this energy allows for the excitation of two Yb^{3+} ions, causing a release of two NIR photons, thereby achieving quantum cutting.

To verify the successful implementation of downconversion in ML, a series of studies were conducted on the downconversion combination (Tb^{3+} – Yb^{3+}) with the optimal ML ratio. First, at a fixed molar ratio of Tb^{3+} doping, we investigated the effect of the Yb^{3+} molar ratio on ML. As demonstrated in figure S7, an enhancement in the Yb^{3+} doping molar ratio resulted in a continuous decline in the visible ML of Tb^{3+} , while the NIR ML of Yb^{3+} showed a preliminary rise followed by a later decline. Second, we compared the ML performances of the codoped samples with those of singly doped samples of Tb^{3+} and Yb^{3+} . As shown in figure 4(b), under a pressure of 30 N, the ML spectra of 1CF/9CZOS:0.1% Tb^{3+} , 0.1% Tb^{3+} 5% Yb^{3+} , and 5% Yb^{3+} show that the ML intensity within the visible light area (350–700 nm) for the Tb^{3+} – Yb^{3+} codoped sample was lower than that of the singly doped Tb^{3+} sample, whereas the ML intensity in the NIR area (900–1000 nm) was higher than that of the singly doped

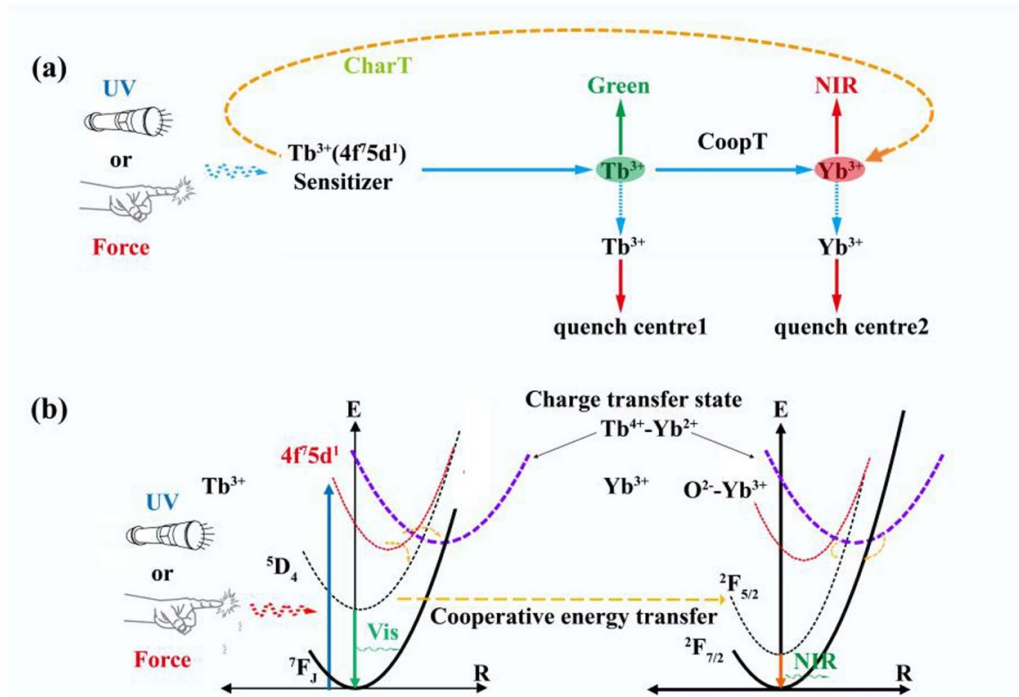


Figure 5. (a) The possibility of energy transfer pathways in the Tb³⁺–Yb³⁺ co-doping system, where CoopT, CharT respectively represent the cooperative transfer process, the charge transfer process. (b) Configurational coordinate plots of Tb³⁺ and Yb³⁺ ions. The black thick solid parabola are the ground state, the dashed black parabolas are the excited state, and the blue dashed parabolas are the charge transfer state Tb⁴⁺–Yb²⁺. The solid vertical arrows indicate the optical leaps, and the green dashed arrows indicate thermal crossings among various states [61]. (a), (b) Reproduced from [63]. © IOP Publishing Ltd. All rights reserved.

Yb³⁺ sample. Moreover, integrating the luminescence in the NIR areas reveals that the integrated intensity of the codoped sample in the NIR area is 1.83 times that of the singly doped Yb³⁺ sample. We also recorded the visible and NIR luminescence of the two samples, so that the ML effects could be clearly compared from a visual perspective (videos S2 and S3). These findings are consistent with the proposed mechanism of ML downconversion in heterojunctions.

We also conducted PL testing on this series of samples with varying Yb³⁺ molar ratios and compared their integrated PL spectra. The variation in the integrated intensity was consistent with the ML behavior, as illustrated in figure S8. In the PL tests of this series of samples, we analyzed their PL and discovered that both Tb³⁺ and Yb³⁺ could be excited by 285 nm ultraviolet light, leading to emission. The emission peaks in the visible area originate from the characteristic luminescence of Tb³⁺, with low concentrations of Tb³⁺ doped providing both ⁵D₃ and ⁵D₄ level transitions, specifically: 380 nm (⁵D₃ → ⁷F₆), 417 nm (⁵D₃ → ⁷F₅), 439 nm (⁵D₃ → ⁷F₄), 486 nm (⁵D₄ → ⁷F₆), 544 nm (⁵D₄ → ⁷F₅), 586 nm (⁵D₄ → ⁷F₄), and 624 nm (⁵D₄ → ⁷F₃), with the emission peak at 544 nm being the strongest [60]. Additionally, the Yb³⁺: ²F₅/₂ → ²F₇/₂ energy level transition produces emission peaks at about 980, 1013, 1028, and 1092 nm within the NIR area.

In the codoped system of Tb³⁺ and Yb³⁺, as shown in figure S8, the PL exhibits a significant reduction in emission

intensity in the visible light area. This phenomenon is related to the potential energy-transfer pathways among Tb³⁺ and Yb³⁺, as shown in figure 5. Under the influence of the PL downconversion mechanism, the radiative intensity in the visible spectrum light area is significantly diminished, which may be attributed to two mechanisms. The first is a cooperative energy transfer mechanism, as mentioned above, where the energy transfer path is characterized by Tb³⁺ (4f⁷5d¹) → Tb³⁺ (⁵D₄) → 2Yb³⁺ (²F₅/₂), which reduces spontaneous radiation from Tb³⁺: ⁵D₄ → ⁷F_J (J = 3 – 6). The second mechanism involved charge transfer [61], as shown in figure 5(b). In the configuration coordinate diagram, the parabolas for Tb⁴⁺–Yb²⁺ intersect with the 4f⁷5d¹ state of Tb³⁺, the ⁷F_J states of Tb³⁺, and the ²F_J (J = 5/2, 7/2) states of Yb³⁺, indicating that it is possible to reach the Tb⁴⁺–Yb²⁺ state from the 4f⁷5d¹ state of Tb³⁺. The formation of the charge transfer state includes the photoionization of Tb³⁺ (Tb⁴⁺ → O²⁻) and the electron capture by Yb³⁺ (O²⁻ → Yb³⁺), resulting in the Tb⁴⁺–Yb²⁺ state reverting to the Yb³⁺ ²F₅/₂ state. Therefore, this mechanism increases the energy loss pathways for the 4f⁷5d¹ state of Tb³⁺ (Tb⁴⁺–Yb²⁺) [62, 63]. The presence of both mechanisms contributes significantly to the reduction in spontaneous radiation from Tb³⁺: ⁵D₃ → ⁷F_J (J = 4 – 6) and ⁵D₄ → ⁷F_J (J = 3 – 6). However, during the charge transfer process from Tb³⁺ (4f⁷5d¹) to Yb³⁺ (²F₅/₂), no quantum cutting occurs, only a portion of the energy from the 4f⁷5d¹ state of Tb³⁺ is released as NIR photons, which does not facilitate

the enhancement of NIR luminescence in Yb^{3+} . Therefore, an analysis combining the results from ML tests was performed. According to figure 4(b), the ML spectrum of the co-doped Tb^{3+} and Yb^{3+} samples demonstrate a significant enhancement of Yb^{3+} NIR emission when compared to the ML spectrum of the singly doped Tb^{3+} and Yb^{3+} samples. This suggests that the cooperative energy transfer process is more probable to be the cause of the significant reduction in the PL of Tb^{3+} .

To demonstrate the existence of a cooperative energy transfer mechanisms of downconversion, a series of samples, including 1CF/9CZOS:0.1% Tb^{3+} y% Yb^{3+} and 1CF/9CZOS:0.1% Tb^{3+} were excited using 285 nm light after determining their excitation spectra (figure S9), while monitoring the emission from Tb^{3+} ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) at 544 nm. Additionally, the fluorescence lifetimes were calculated (table S2). In addition, we used the fluorescence lifetime of the $^5\text{D}_4$ energy level to calculate the energy transfer efficiency and the overall theoretical quantum efficiency, defined as follows:

$$\eta_{\text{ET}} = 1 - \frac{\tau_{\text{Tb}-\text{Yb}}}{\tau_{\text{Tb}}}, \quad (1)$$

$$\eta_{\text{QE}} = \eta_{\text{Tb}} (1 - \eta_{\text{ET}}) + 2\eta_{\text{Yb}}\eta_{\text{ET}}. \quad (2)$$

Let η_{ET} represent the energy transfer efficiency between Tb^{3+} and Yb^{3+} , while η_{QE} is the total theoretical quantum efficiency, $\tau_{\text{Tb}-\text{Yb}}$ and τ_{Tb} refer to the fluorescence lifetimes of Tb^{3+} ions in the presence and absence of Yb^{3+} ions, respectively. In order to calculate the theoretical limit of the downconversion efficiency, focusing only on the energy transfer mechanism rather than material defects or losses, the mathematical model is simplified by setting η_{Tb} and η_{Yb} to represent the quantum efficiencies of Tb^{3+} and Yb^{3+} , both assumed to be 1 [57, 64, 65]. Fluorescence lifetimes were determined by curve fitting. In the case of co-doping with Tb^{3+} and Yb^{3+} , the fluorescence lifetime of Tb^{3+} is significantly shortened, with its average lifetime decreasing from 1.64 ms (when Yb^{3+} ions are absent) to 0.54 ms. This reduction is due to the additional decay pathways introduced by the increased energy migration between Tb^{3+} and Yb^{3+} ions within the aforementioned cooperative energy transfer mechanism. The findings demonstrate that cooperative energy transfer occurs between Tb^{3+} and Yb^{3+} ions in 1CF/9CZOS:0.1% Tb^{3+} 5% Yb^{3+} . Using the aforementioned equations (1) and (2), η_{ET} was calculated to be 66.9%, and η_{QE} was determined to be 166.9%.

Additionally, we expanded our research to another commonly utilized downconversion ion combination, Pr^{3+} – Yb^{3+} . We conducted ML tests under the same external force on three samples, 1CF/9CZOS:0.1% Pr^{3+} , 0.1% Pr^{3+} 5% Yb^{3+} , and 5% Yb^{3+} , and observed effects similar to those of Tb^{3+} – Yb^{3+} downconversion ML, as shown in figure 6(b). 1CF/9CZOS:0.1% Pr^{3+} 5% Yb^{3+} exhibited a reduction in the ML in the visible light region for Pr^{3+} , whereas an enhancement in the ML was observed in the NIR area for Yb^{3+} . The findings are consistent with the cooperative energy-transfer

principle of Pr^{3+} – Yb^{3+} downconversion. Additionally, we recorded the visible light and NIR emissions from these two samples, as shown in Supplementary Videos S4 and S5. We also validated this phenomenon through PL spectrum testing of the three samples, confirming the same trend, as shown in figure S10.

The ML mechanism in the heterojunction doped with Pr^{3+} – Yb^{3+} downconversion is illustrated in figure 6(a). Here, the energy produced when electrons and holes combine excites the Pr^{3+} ion through energy transfer, then generating an excited state. This excitation leads to nonradiative relaxation to the $^3\text{P}_0$ level, with a portion of the energy emitted as spontaneous radiation at a wavelength of 493 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_4$). Meanwhile, another portion of the energy is transferred to the $^2\text{F}_{5/2}$ level of Yb^{3+} , ultimately returning to the ground state through the transition ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$). The energy of one 493 nm photon enables the emission of two 980-nm photons.

To validate the existence of the downconversion energy transfer process and quantitatively calculate the fluorescence lifetime, we further calculated η_{ET} and η_{QE} . As shown in figure 6(c), excitation was performed at 285 nm, monitoring the Pr^{3+} ($^3\text{P}_0 \rightarrow ^3\text{H}_4$) emission from both 1CF/9CZOS:0.1% Pr^{3+} 5% Yb^{3+} and 1CF/9CZOS:0.1% Pr^{3+} . A substantial decrease in the fluorescence lifetime was observed. Based on the fluorescence lifetime spectra, the fluorescence lifetimes for the two samples were found to be 66.8 μs and 9.9 μs , respectively. Subsequently, using the aforementioned equations (1) and (2), η_{ET} was calculated to be 85.1%, and η_{QE} was determined to be 185.1%.

4. Conclusion

In summary, we successfully synthesized CF/CZOS ML heterojunctions for the first time, achieving an enhancement in the ML intensity within the heterojunctions compared to a single matrix. The visible light emission of the codoped Tb^{3+} – Yb^{3+} sample was weaker than that of the Tb^{3+} sample with single doping, whereas the NIR emission was enhanced relative to the Yb^{3+} sample with single doping. As Yb^{3+} concentration increases, the fluorescence lifetime gradually decreases. This behavior is consistent with the influence of cooperative energy transfer on the fluorescence lifetime of Tb^{3+} during the downconversion. The optimal η_{ET} between Tb^{3+} and Yb^{3+} , determined from the fluorescence lifetime, was calculated as 66.9%, resulting in a total theoretical quantum efficiency (η_{QE}) of 166.9%. In addition, we expanded our research to the Pr^{3+} – Yb^{3+} downconversion ion pair, obtaining similar downconversion ML results, η_{ET} was calculated to be 85.1%, and η_{QE} was determined to be 185.1%. The synergistic effects observed in these heterojunctions doped with rare-earth ion pairs can be extended to other systems to achieve further modulation and enhancement of ML, thereby providing alternate materials for diverse applications across many fields.

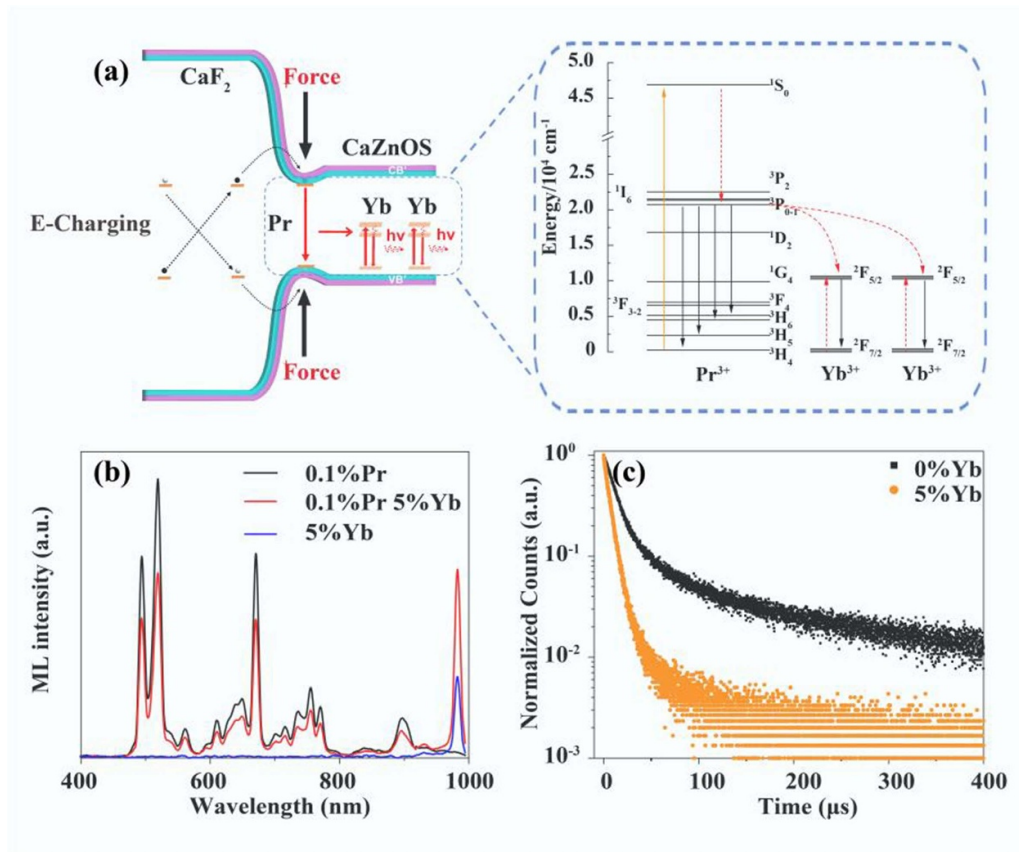


Figure 6. (a) Energy band model of downconversion ML in the CF/CZOS:Pr³⁺, Yb³⁺ heterojunction, with the enlarged view on the right illustrating the detailed energy level diagram for the energy transfer from Pr³⁺ to Yb³⁺; (b) ML Spectra of 1CF/9CZOS:0.1%Pr³⁺, 1CF/9CZnS:0.1%Pr³⁺ 5%Yb³⁺, and 1CF/9CZOS:5%Yb³⁺ under 30 N Pressure; (c) decay lifetimes of Pr³⁺ ³P₀ → ³H₄ luminescence at 493 nm for 1CF/9CZOS:0.1%Pr³⁺ (black curve) and 1CF/9CZOS:0.1%Pr³⁺ 5%Yb³⁺ (orange curve) under 285 nm excitation.

5. Future perspectives

As photoelectric detection and engineering sensing technologies continue to advance, the research and application prospects of ML materials are rapidly expanding, revealing significant potential across various fields. An increasing number of researchers are dedicating themselves to this area, and it is expected that, in the near future, we will integrate AI technology to design superior smart ML structures. These structures will be based on interdisciplinary research that combines semiconductor physics, materials science, chemistry, and information technology. Among these, in terms of the design of high-efficient ML structures, heterojunction thin films can be epitaxially grown using atomic layer deposition or chemical vapor deposition techniques; alternatively, core-shell structured microspheres and other three-dimensional structures can be prepared through soft chemical methods, this enables the synthesis of potentially high-quality epitaxial single-crystal heterojunctions, making it easier to clarify the energy transfer processes and the physical mechanisms of mechano-optical conversion within them. Additionally, one-dimensional whisker/fiber heterojunction structures with mechanical advantages can be fabricated as needed, achieving both ML and composite additive mechanical reinforcement

functions simultaneously. These advanced ML materials and structures will not only emit stable light across a wider range of pressures but will also exhibit enhanced sensitivity and faster response times. Furthermore, the integration of upconversion and downconversion processes in ML will enable efficient conversion of light energy across various wavelengths, resulting in increased luminous efficiency. In addition, future force/pressure sensing systems will have the capability to monitor and analyze the status of various structures in real time, delivering more accurate and reliable feedback. This progress will further promote the use of ML materials in a variety of industries, including smart manufacturing, structural health monitoring, intelligent machines and human-computer interaction, as well as healthcare and sport science. Once the application standard of ML material technology is established, as a new source of light provider, it will play a unique application advantage in many fields and illuminate the path forward for humanity's technological innovation and progress.

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Conflict of interest

The authors declare no conflict of interest.

Authors contribution

Tianlong Liang and Dengfeng Peng conceived this idea. Tianlong Liang conducted the PL and ML experiments, collected and analyzed the data, and wrote the manuscript. Yuntian Zheng, Biyun Ren, Yanze Wang, and Jingnan Zhang provided guidance during the manuscript revision process. Qi'an Zhang, Ziyi Fang, Mingzhi Wu, Yang Liu, Qidong Ma, Jiazhen Zhou, and Maryam Zulfiqar participated in discussions related to the experiments. Dengfeng Peng and Xiaoyu Weng provided guidance and financial support throughout the entire duration of the project. Dengfeng Peng reviewed and corrected the manuscript.

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