

Design and Optimization of $\text{Eu}^{3+}/\text{Tb}^{3+}$ Co-Doped Downconversion Silicate Glasses for UV–Visible Spectral Application in Solar Cells: A Review

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Abstract

Spectral downconversion of ultraviolet (UV) photons into visible photons is a widely investigated strategy for reducing thermalization losses in single-junction silicon solar cells and for pushing device efficiency toward, and potentially beyond, the classical Shockley–Queisser limit. Among the many rare-earth (RE) ion pairs studied for this purpose, the europium(III)–terbium(III) ($\text{Eu}^{3+}/\text{Tb}^{3+}$) couple co-doped into silicate glass hosts has emerged as one of the most extensively characterized systems, owing to the favorable ladder-like energy-level structure of Tb^{3+} , the efficient dipole–dipole energy transfer from the $\text{Tb}^{3+} {}^5\text{D}_4$ level to the $\text{Eu}^{3+} {}^5\text{D}_0/{}^5\text{D}_1$ manifold, and the strong, spectrally narrow ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ red emission of Eu^{3+} that can be tuned toward the spectral response of crystalline silicon. This article synthesizes seventy studies spanning the theoretical foundations of quantum cutting, the mechanistic and spectroscopic behavior of $\text{Eu}^{3+}/\text{Tb}^{3+}$ pairs in silicate and modified-silicate glass hosts, the compositional and fabrication strategies used to optimize such converters, and their integration into working photovoltaic devices. The review is organized to move from fundamental photophysics through materials design to device-level validation, concluding with an assessment of the remaining research gaps — including concentration quenching, scattering losses in glass-ceramic converters, and the largely untapped potential of computational and machine-learning-guided compositional design — that motivate continued investigation of $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped silicate glasses as UV–visible downconversion layers for next-generation solar cells.

Keywords: spectral downconversion; quantum cutting; $\text{Eu}^{3+}/\text{Tb}^{3+}$ energy transfer; silicate glass; rare-earth doping; luminescent solar converter; photovoltaic efficiency

1. Introduction

Single-junction silicon solar cells convert only a fraction of the incident solar spectrum into usable electrical energy. Photons with energy well above the semiconductor bandgap generate charge carriers that rapidly relax to the band edge, dissipating the excess energy as heat, a loss mechanism known as thermalization. Trupke, Green, and Würfel first showed theoretically that splitting a single high-energy UV photon into two or more lower-energy photons, each resonant with the absorber bandgap, could in principle raise the theoretical efficiency limit of a silicon cell to 38–40% under standard illumination, substantially above the classical Shockley–Queisser limit [1]. This process, variously termed spectral downconversion or quantum cutting, has since motivated three decades of materials research aimed at identifying luminescent centers capable of converting one absorbed UV/blue photon into two visible photons with a combined quantum efficiency approaching or exceeding unity.

Rare-earth (RE) ions doped into oxide glass hosts are particularly well suited to this task because their intra-4f transitions are shielded by outer 5s/5p electrons, giving rise to sharp, host-insensitive emission lines and comparatively long excited-state lifetimes. Among the many lanthanide pairs surveyed for spectral conversion, the terbium–europium (Tb^{3+} – Eu^{3+}) couple has attracted sustained attention: Tb^{3+} possesses a ladder of closely spaced excited states that absorb efficiently in the UV, while Eu^{3+} exhibits a strong, narrow, red ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission whose spectral position is well matched to the external quantum efficiency curve of crystalline silicon. Silicate glasses, in turn, remain the most widely used host matrix for such converters because of their low cost, high optical transparency, chemical durability, and mature melt-quenching and sol-gel processing routes.

This article reviews the literature underpinning the design and optimization of $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped silicate glasses as UV–visible downconversion layers for solar cells. The review is organized into four thematic sections that mirror the logical progression of the field: Section 2 summarizes the theoretical and mechanistic basis of downconversion and lanthanide energy transfer; Section 3 reviews the specific experimental literature on $\text{Eu}^{3+}/\text{Tb}^{3+}$ energy transfer within silicate and modified-silicate hosts; Section 4 addresses compositional optimization and fabrication methodology; and Section 5 discusses integration of these converters into photovoltaic devices and recent advances that define the current state of the art. Section 6 discusses open research gaps, and Section 7 concludes.

2. Theoretical Framework of Spectral Downconversion

The concept of spectral downconversion, or “quantum cutting,” emerged as a strategy for addressing thermalization losses in single-junction photovoltaics. Following the initial theoretical proposal of Trupke, Green, and Würfel [1], Righini, Enrichi, and Ferrari reviewed how oxide and oxyfluoride glass matrices doped with lanthanide ions can be engineered as spectrally selective layers, functioning as downshifting, downconversion, or luminescent solar concentrator media, with glass composition, RE concentration, and codoping strategy identified as the principal design levers available to the materials scientist [2]. Huang, Han, Huang, and Liu situated this mechanistic picture within the applied photovoltaic context, surveying luminescent spectral converters (downshifting, downconversion, and upconversion phosphors) and evaluating their integration strategies, efficiency limits, and remaining challenges for practical deployment [3].

Experimental validation of the downconversion principle followed soon after the theoretical proposal. Meijer and co-workers showed that a quantum-cutting phosphor could convert one absorbed UV/blue photon into two visible photons with a combined quantum efficiency exceeding unity, offering the first clear experimental proof that the concept was physically realizable in doped solid-state hosts [4]. The underlying physics and chemistry of luminescent materials — radiative transition probabilities, Judd–Ofelt intensity parameters, non-radiative multiphonon relaxation, and quenching mechanisms — are treated comprehensively in the Phosphor Handbook edited by Shionoya, Yen, and Yamamoto, which remains a standard reference for the theoretical description of luminescence in doped inorganic solids [5].

Richards provided one of the earliest comprehensive treatments of luminescent downshifting and downconversion layers specifically for silicon photovoltaics, distinguishing downshifting (one photon in, one photon out, at lower energy) from true downconversion or quantum cutting (one photon in, two or more photons out), and establishing the design criteria — high quantum efficiency, spectral matching to the cell's external quantum efficiency curve, and minimal reabsorption losses — that continue to guide converter layer design [6]. Van der Ende, Aarts, and Meijerink extended this framework by systematically reviewing lanthanide ion pairs and energy-level schemes best suited to quantum cutting, emphasizing that trivalent lanthanides such as Eu^{3+} , Tb^{3+} , Yb^{3+} , and Gd^{3+} possess ladder-like energy-level structures permitting efficient two-photon emission via cooperative or sequential energy transfer [7].

Zou and co-workers categorized the principal downconversion pathways, quantum cutting via cooperative energy transfer, cross-relaxation, and sequential (cascade) emission, and discussed how host phonon energy, dopant concentration, and ion–ion distance jointly determine which mechanism dominates in a given system [8]. The structural context for these processes in glass hosts was addressed earlier by Jørgensen, who described how incorporation of trivalent lanthanide ions modifies the local glass network, alters the nephelauxetic effect on 4f orbitals, and influences crystal-field splitting of RE energy levels [9]. Auzel's comprehensive review of upconversion and anti-Stokes processes in f–f and d–d ion systems, while primarily concerned with the inverse process, provided essential groundwork for understanding the multiphonon relaxation, excited-state absorption, and energy-transfer pathways that compete with and inform downconversion dynamics [10].

The quantum-mechanical foundation for energy migration between dopant ions was formalized by Dexter, who described how an excited “donor” ion transfers energy non-radiatively to a neighboring “acceptor” ion through short-range exchange interactions or longer-range multipolar coupling, depending on donor–acceptor separation and the degree of spectral overlap between donor emission and acceptor absorption [11]. This Dexter-type formalism remains the standard theoretical tool for interpreting energy migration between sensitizer and activator ions such as Tb^{3+} and Eu^{3+} in codoped glass systems. The experimental breakthrough most frequently cited as the origin of modern quantum-cutting research is Wegh, Donker, Oskam, and Meijerink's demonstration of visible quantum cutting in $\text{LiGdF}_4\text{:Eu}^{3+}$, in which a two-step energy transfer process — first from Gd^{3+} to Eu^{3+} , then a subsequent cross-relaxation step, yielded a quantum efficiency of nearly 200%

for visible emission following VUV excitation, providing unambiguous spectroscopic proof of the two-photon-per-photon downconversion mechanism [12].

To interpret the specific spectroscopic behavior of Eu^{3+} , Binnemans's detailed review offers a systematic treatment of the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-6$) transitions, their hypersensitivity to local symmetry, and the diagnostic use of the $^5\text{D}_0 \rightarrow ^7\text{F}_2/{}^5\text{D}_0 \rightarrow ^7\text{F}_1$ intensity ratio (the asymmetry ratio) as a probe of site symmetry and covalency around the Eu^{3+} ion [13]. Blasse and Grabmaier's classic text complements this by providing the foundational equations — radiative lifetime, branching ratios, and the energy gap law — governing radiative and non-radiative transitions in doped inorganic phosphors [14]. Because the present review is concerned with silicate glass hosts specifically, Soga's foundational study of silicate glass structure established how network-forming SiO_4 tetrahedra, bridging and non-bridging oxygens, and modifier cation content determine the phonon energy, rigidity, and thermal/mechanical stability of the glass matrix — parameters that directly govern non-radiative multiphonon relaxation rates and, consequently, the luminescence quantum efficiency of embedded rare-earth ions [15].

Taken together, these fifteen foundational studies establish three interlocking theoretical pillars: (i) the photon-splitting physics and theoretical efficiency gains of downconversion [1, 4] together with its device-level application to photovoltaics [2, 3, 6, 7]; (ii) the quantum-mechanical energy-transfer formalism [10, 11] and the demonstrated cascade/cooperative mechanisms [8, 12] governing how energy migrates between sensitizer and activator ions such as Tb^{3+} and Eu^{3+} ; and (iii) the structural and spectroscopic framework [5, 9, 13, 14, 15] needed to interpret how the silicate glass host modulates the luminescence efficiency and emission characteristics of the doped rare-earth ions.

3. Eu^{3+} – Tb^{3+} Energy Transfer in Silicate Glass Matrices

Having established the general theoretical basis for downconversion and lanthanide energy transfer, this section reviews the substantial body of experimental work specifically addressing $\text{Eu}^{3+}/\text{Tb}^{3+}$ energy transfer within silicate glass and glass-ceramic hosts, which constitute the direct material precedent for $\text{Eu}^{3+}/\text{Tb}^{3+}$ -based converter design.

3.1 Codoping and cooperative sensitization schemes

Chen, Łukowiak, and co-workers investigated $\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped silicate sol-gel glass-ceramics containing CaF_2 nanocrystals, correlating structural evolution during ceramization with enhanced $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer efficiency and improved red emission intensity as the fluoride nanocrystalline phase precipitated within the glass matrix [2.16]. In a related but distinct pathway, Zhang and Yang examined cooperative energy transfer in Yb^{3+} – Tb^{3+} co-doped silicate glasses, demonstrating that Yb^{3+} , though primarily known as an infrared-active ion, can participate in cooperative sensitization schemes involving Tb^{3+} , broadening the range of possible sensitizer–activator combinations in silicate hosts [17]. Steimacher and co-workers explored Eu^{2+} – Nd^{3+} co-doped glasses designed for near-UV/visible-to-near-infrared downconversion, illustrating that spectral modification strategies extend beyond the $\text{Eu}^{3+}/\text{Tb}^{3+}$ pair to divalent europium sensitizers and providing a comparative efficiency benchmark [18].

3.2 Direct evidence of $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ transfer in silicate hosts

Directly relevant to $\text{Eu}^{3+}/\text{Tb}^{3+}$ converter design, Pan and Liu studied energy transfer from Tb^{3+} to Eu^{3+} in silicate glass for white-LED applications, confirming that $\text{Tb}^{3+} {}^5\text{D}_4$ excited-state energy is efficiently transferred to $\text{Eu}^{3+} {}^5\text{D}_0/{}^5\text{D}_1$ levels via a dipole–dipole mechanism consistent with Dexter-type theory, with transfer efficiency strongly dependent on Eu^{3+} concentration [2.19]. Lyu and co-workers extended this analysis to oxyfluoride silicate glass-ceramics, reporting efficient Tb^{3+} – Eu^{3+} energy transfer accompanied by a marked enhancement in red emission intensity following precipitation of a fluoride nanocrystalline phase, which lowered the local phonon energy around the rare-earth ions and suppressed non-radiative losses [2.20]. Hu and co-workers similarly examined the effect of ceramization on $\text{Tb}^{3+}/\text{Eu}^{3+}$ energy transfer, showing that controlled crystallization of a secondary phase systematically modifies the $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ transfer rate and the corresponding decay lifetime of the donor ion [2.21].

Pisarski, Pisarska, and Ryba-Romanowski investigated Eu^{3+} and Tb^{3+} individually doped into lead-silicate glasses, establishing baseline spectroscopic parameters — Judd–Ofelt intensity parameters, radiative lifetimes, and emission branching ratios — against which co-doped, energy-transfer-enhanced systems can be compared [22]. Ruan and co-workers reported enhanced red emission of Eu^{3+} upon Tb^{3+} co-doping in silicate glass, attributing the intensity increase to efficient

non-radiative energy migration from the $\text{Tb}^{3+} {}^5\text{D}_4$ level to the $\text{Eu}^{3+} {}^5\text{D}_0$ level [23], while Gao and co-workers demonstrated that Tb^{3+} sensitization effectively broadens the excitation spectrum of Eu^{3+} in silicate hosts, allowing the co-doped system to harvest a wider range of UV excitation wavelengths than Eu^{3+} alone — a property of direct relevance to broadband solar spectral conversion [24].

3.3 Quantifying transfer dynamics and compositional influence

Sontakke and Annapurna provided a detailed study of luminescence and energy-transfer dynamics in Tb^{3+} – Eu^{3+} co-doped glasses, using time-resolved photoluminescence decay analysis to extract energy-transfer rates and critical transfer distances, offering a methodological template for quantifying transfer efficiency [25]. Kaur and co-workers examined the structural and optical properties of $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped alkali silicate glasses, linking modifier cation content and network connectivity to variations in energy-transfer efficiency and emission color coordinates [26]. Zheng and co-workers investigated the influence of SiO_2 content on Eu^{3+} luminescence in multi-component glasses, showing that increasing network-former content alters the local ligand field and covalency around the Eu^{3+} ion, directly affecting the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2/{}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ asymmetry ratio [27].

Yu and co-workers demonstrated color-tunable luminescence in Tb^{3+} and Eu^{3+} co-doped silicate phosphors, showing that emission chromaticity can be systematically tuned from green to red by adjusting the relative $\text{Tb}^{3+}:\text{Eu}^{3+}$ doping ratio — a strategy with direct implications for tailoring the downconverted emission spectrum to a target cell's spectral response [2.28]. Wang and co-workers extended this compositional approach to a tri-doped $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ silicate system, elucidating a cascade energy-transfer mechanism ($\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$) in which Ce^{3+} acts as a broadband UV sensitizer feeding energy sequentially through Tb^{3+} to the ultimate Eu^{3+} emitter [2.29].

3.4 Host-network variations and photostability

Lakshminarayana and co-workers reported the luminescence behavior of Tb^{3+} and Eu^{3+} in heavy metal oxide glasses, providing a useful comparative reference for how host network “heaviness” (lower phonon energy, higher polarizability) affects rare-earth emission efficiency relative to conventional silicate hosts [2.30]. Tanabe and co-workers reviewed the spectral properties of rare-earth-doped silicate glasses in the context of fiber amplifiers and spectral converters, contributing foundational spectroscopic data that remains applicable to solar conversion research [2.31]. Lin and co-workers studied the visible luminescence and energy transfer of Eu^{3+} and Tb^{3+} in oxyfluoride silicate glass, again highlighting the beneficial role of a fluoride component in lowering phonon energy and enhancing energy-transfer efficiency [2.32]. Som and Karmakar directly addressed $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped silicate glasses for solar applications, evaluating the spectral overlap between the composite $\text{Tb}^{3+}/\text{Eu}^{3+}$ emission profile and the spectral response of silicon photovoltaic cells, providing one of the most directly comparable prior studies to $\text{Eu}^{3+}/\text{Tb}^{3+}$ silicate converter design [2.33]. Babu and Jayasankar examined the optical properties of Tb^{3+} and Eu^{3+} in oxyfluoride silicate glasses, reporting Judd–Ofelt parameters and radiative properties that further substantiate the beneficial role of fluoride incorporation [2.34]. Finally, Kityk and co-workers investigated photoinduced changes in Eu/Tb -doped silicate glasses, demonstrating that prolonged UV or laser irradiation can induce measurable shifts in the local structural environment and luminescence output of the doped ions — a consideration relevant to the long-term photostability of any proposed downconversion layer under continuous solar illumination [2.35].

Collectively, these twenty studies [2.16–2.35] establish that: (i) $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer in silicate and modified-silicate (oxyfluoride, heavy-metal-oxide, alkali) glass hosts proceeds predominantly via a dipole–dipole non-radiative mechanism whose efficiency is governed by dopant concentration, ion–ion distance, and host phonon energy [2.19, 2.20, 2.23, 2.25]; (ii) compositional strategies — fluoride nanocrystal precipitation, ceramization, network modifier content, and SiO_2 ratio — provide effective levers for tuning transfer efficiency and emission color [2.16, 2.20, 2.21, 2.26, 2.27, 2.32]; (iii) tri-ion and alternative sensitizer schemes ($\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$, Yb^{3+} – Tb^{3+} , Eu^{2+} – Nd^{3+}) extend the achievable excitation bandwidth and spectral conversion range beyond the simple Tb^{3+} – Eu^{3+} pair [2.17, 2.18, 2.29]; and (iv) several studies explicitly evaluate $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped silicate systems for solar spectral conversion, offering direct precedent and comparative benchmarks [2.33].

4. Compositional Design, Optimization, and Fabrication Strategies

Beyond the fundamental spectroscopy reviewed in Section 3, a distinct and equally important body of literature addresses the practical design, compositional optimization, and fabrication methodologies required to translate $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped luminescent glasses into functional photovoltaic device components.

4.1 Device-level structuring and light management

At the device-integration level, Yang, Chen, Zheng, and Chen demonstrated a downshifting Eu^{3+} -doped glass embedded with a concave pyramid microstructure, showing that combining spectral conversion with light-trapping surface texturing produced a measurable improvement in silicon solar cell efficiency beyond what spectral conversion alone could achieve [2.36]. Zur and co-workers examined the visible-to-NIR downconversion process in Tb^{3+} – Yb^{3+} codoped silica-hafnia glass and glass-ceramic sol-gel waveguides, illustrating how sol-gel-derived waveguide geometries can be engineered specifically for solar cell coupling applications [2.37].

4.2 Compositional optimization

Compositional optimization has received particular attention. Dimitriou and co-workers systematically optimized rare-earth doping concentration in silicate glasses for photovoltaic applications, establishing that an optimal dopant concentration exists beyond which concentration quenching offsets any gain in absorption cross-section [2.38]. Reisfeld's authoritative review of rare-earth ions in glasses for solar energy conversion provided a broad synthesis of host selection, dopant concentration, and spectral matching criteria that remains widely cited as a design reference across the field [2.39]. Santos and co-workers investigated the effect of alkali oxide modifiers on the downconversion efficiency of Eu^{3+} in silicate glasses, showing that alkali content systematically alters the non-bridging oxygen ratio and thereby the local crystal field and luminescence yield around the Eu^{3+} ion [2.49]. Li and co-workers similarly pursued luminescence optimization of Eu^{3+} specifically in zinc silicate glasses, reporting compositional windows that maximize red emission intensity [2.48].

4.3 Fabrication methodology

Fabrication methodology is addressed by several comparative studies. Chung and co-workers reported the preparation and optical properties of Eu/Tb silicate glasses synthesized by conventional melt-quenching, establishing baseline processing parameters — melting temperature, quenching rate, annealing schedule — for this synthesis route [2.40]. In contrast, Pawar and co-workers employed sol-gel synthesis for Eu^{3+} and Tb^{3+} co-doped silicate glasses intended for spectral conversion, demonstrating that the lower processing temperatures and finer compositional control afforded by sol-gel chemistry can yield more homogeneous rare-earth dispersion than melt-quenching [2.41]. Valiente and co-workers directly compared glass versus glass-ceramic spectral converters, concluding that partial crystallization to a glass-ceramic state generally improves luminescence efficiency by lowering the effective phonon energy around the rare-earth dopant, at the cost of increased optical scattering losses [2.54]. Chen and Wang extended this comparison by reviewing rare-earth-doped nano-glass-ceramics broadly for photovoltaic applications, emphasizing that nanocrystal size control is critical to balancing luminescence enhancement against parasitic light scattering [2.55].

4.4 Multi-dopant and cascade sensitization strategies

Several studies have pursued multi-dopant and cascade sensitization schemes to broaden spectral coverage. Linghu and co-workers designed high-efficiency downconversion layers using multi-dopant silicate systems, reporting that combining more than two rare-earth species can extend effective absorption bandwidth beyond that achievable with a single sensitizer–activator pair [2.42]. Wang and co-workers demonstrated enhancement of multijunction solar cell efficiency using $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped GeO_2 – PbO – Al_2O_3 glasses as spectral converter cover layers, showing that heavy-metal oxide glass hosts beyond conventional silicates can further improve conversion efficiency when applied as external cover layers rather than embedded layers [2.43]. Zhou and co-workers examined quantum cutting in Pr^{3+} – Yb^{3+} co-doped silicate glasses for photovoltaic application, illustrating an alternative rare-earth pairing capable of near-infrared downconversion relevant to sub-bandgap spectral management [2.47]. Zhang and co-workers reported the synthesis and energy-transfer behavior of Tb^{3+} and Eu^{3+} specifically in magnesium silicate glasses, adding to the compositional design space of alkaline-earth-modified silicate hosts [2.53].

Foundational device-engineering context is provided by two frequently cited early works: Kawano and co-workers demonstrated one of the earliest practical improvements in solar cell efficiency using luminescence downshifting glasses applied as cover layers on silicon cells [2.44], while Strümpel and co-workers authored a comprehensive overview of the available materials and strategies for modifying the solar spectrum to enhance solar cell efficiency, surveying downshifting, downconversion, and upconversion approaches on a common comparative basis [2.45]. Fischer and co-workers later revisited this comparison specifically for upconversion and downconversion mechanisms applied to solar cells, updating the efficiency benchmarks and materials landscape established by earlier reviews [2.51].

Focused specifically on the $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ system, Mazzuca and co-workers examined the optimization of photon management in silicate glasses via the $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy-transfer pathway, directly addressing how compositional and processing parameters can be tuned to maximize the efficiency of this specific transfer route [2.46]. Bhushan and co-workers performed a detailed optical analysis of $\text{Eu}^{3+}:\text{Tb}^{3+}$ -doped silicate systems, contributing spectroscopic data directly comparable to compositional series relevant to $\text{Eu}^{3+}/\text{Tb}^{3+}$ converter design [2.50]. Liu and co-workers addressed the design of UV–visible converters using silicate-based glass-ceramics, providing design guidelines for matching converter absorption/emission bands to the UV–visible spectral region [2.52].

Collectively, these twenty studies [2.36–2.55] establish the practical design and fabrication landscape for $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped silicate converters: (i) dopant concentration and host modifier optimization are essential to avoiding concentration quenching while maximizing energy-transfer efficiency [2.38, 2.39, 2.48, 2.49]; (ii) synthesis route — melt-quenching versus sol-gel versus controlled ceramization to a glass-ceramic state — measurably affects rare-earth ion dispersion, local phonon environment, and resulting luminescence efficiency [2.40, 2.41, 2.54, 2.55]; (iii) multi-dopant and cascade sensitization strategies, alternative host chemistries ($\text{GeO}_2\text{--PbO--Al}_2\text{O}_3$, magnesium silicate, silica-hafnia), and hybrid optical/structural approaches (microtextured surfaces, waveguide geometries) extend the design space beyond simple $\text{Tb}^{3+}\text{--Eu}^{3+}$ silicate systems [2.36, 2.37, 2.42, 2.43, 2.47, 2.53]; and (iv) comparative reviews spanning downshifting, downconversion, and upconversion approaches provide the benchmarking framework against which any new converter design must be evaluated [2.44, 2.45, 2.51].

5. Integration into Photovoltaic Devices and Recent Advances

The final category of literature moves from materials-level spectroscopy and fabrication toward the direct integration of $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped silicate systems into working photovoltaic devices, alongside recent advances that define the current state of the art.

5.1 Device-level validation

Le Donne and co-workers directly evaluated rare-earth-doped silicate glasses for crystalline silicon (c-Si) solar cell efficiency enhancement, reporting measurable short-circuit current gains when the doped glass was applied as a front-surface spectral converter layer on functioning silicon cells [2.56]. Klampaftis, Ross, McIntosh, and Richards authored a widely cited review of luminescent downshifting for solar cell performance enhancement, systematically evaluating the incident-spectrum-modification approach across multiple luminescent material classes and establishing the quantitative framework — external quantum efficiency gain versus wavelength — still used to benchmark new converter layers [2.57]. Goldschmidt and Fischer extended this device-level perspective in their review of advanced photon management strategies in photovoltaics, situating spectral downconversion alongside light trapping, plasmonic scattering, and other photon-management techniques within a unified efficiency-improvement framework [2.58].

Direct experimental validation on industrial-scale devices is provided by Marchionna and co-workers, who tested Eu-doped spectral converters on industrial silicon solar cells, demonstrating that laboratory-scale downconversion gains can be reproduced, albeit with some efficiency loss, under industrial cell processing conditions [2.59]. Pudasaini and co-workers similarly reported efficiency enhancement in c-Si solar cells using Eu^{3+} -doped glass, quantifying the current-density improvement attributable specifically to the Eu^{3+} downshifting contribution [2.60]. Park and co-workers addressed a practical fabrication barrier to such integration, reporting fabrication of high-transmittance Eu-doped silicate glass optimized for photovoltaic application, showing that minimizing parasitic scattering and absorption losses in the host glass itself is essential to realizing net efficiency gains at the device level [2.67]. Kumar and co-workers evaluated Eu/Tb silicate

glasses specifically as cover sheets for photovoltaic modules, providing a module-level (rather than cell-level) integration perspective directly relevant to practical deployment [2.63].

5.2 Synthesizing reviews

Several recent reviews synthesize the rapidly evolving state of the field. Xie and co-workers reviewed recent progress in rare-earth-doped glasses for spectral conversion in photovoltaics, consolidating advances in host chemistry, dopant pairing, and device integration reported over the preceding decade [2.61]. Vetrone and co-workers authored a broader review of next-generation photon management strategies for photovoltaics, situating rare-earth spectral conversion within the wider landscape of emerging photon-management technologies including plasmonics and photonic crystals [2.62]. Ghosh and co-workers specifically reviewed Eu^{3+} - and Tb^{3+} -sensitized solar cell interfaces in silicate hosts, offering a focused synthesis directly relevant to the $\text{Eu}^{3+}/\text{Tb}^{3+}$ pairing [2.65].

5.3 Recent compositional refinements and emerging directions

Compositional and structural refinements specific to the Tb^{3+} – Eu^{3+} system continue to appear in recent literature. Rao and co-workers examined UV-to-visible conversion in Tb/Eu -doped alkali silicate glass, reporting conversion efficiencies and spectral matching data directly comparable to $\text{Eu}^{3+}/\text{Tb}^{3+}$ -based target applications [2.64]. Suresh and co-workers investigated downconversion and energy transfer in Tb^{3+} – Eu^{3+} co-doped oxyfluoride systems, extending the oxyfluoride-silicate design strategy discussed in Section 4 with updated spectroscopic characterization [2.66]. Mukhuti and co-workers explored optimization of solar cell quantum efficiency using rare-earth-doped silicate waveguides, applying an integrated-optics approach to spectral conversion rather than a simple planar cover-layer geometry [2.68]. Zhang and co-workers reported dual-mode spectral conversion in silicate glass for multi-junction photovoltaic applications, demonstrating that a single glass host can be engineered to provide both downshifting and downconversion contributions simultaneously, tailored to the distinct spectral requirements of each sub-cell in a multi-junction stack [2.70].

Notably, Silva and co-workers introduced a machine-learning approach to optimizing rare-earth-doped silicate glass compositions for photovoltaic applications, representing an emerging computational design paradigm that complements the traditional empirical trial-and-error compositional optimization discussed in Section 4, and pointing toward a likely future direction for accelerating converter material discovery [2.69].

Taken together, these fifteen studies [2.56–2.70] demonstrate that: (i) rare-earth-doped silicate spectral converters have progressed from laboratory proof-of-concept to validated efficiency gains on both individual c-Si cells and industrial-scale devices [2.56, 2.59, 2.60]; (ii) authoritative reviews now frame spectral downconversion as one component within a broader, integrated photon-management strategy for photovoltaics [2.57, 2.58, 2.61, 2.62]; (iii) recent work continues to refine the specific Tb^{3+} – Eu^{3+} silicate and oxyfluoride-silicate systems, addressing transmittance, module-level integration, and waveguide geometries [2.63, 2.64, 2.65, 2.66, 2.67, 2.68]; and (iv) emerging directions, including dual-mode conversion for multi-junction cells and machine-learning-guided compositional design, indicate the trajectory along which future $\text{Eu}^{3+}/\text{Tb}^{3+}$ silicate converter research is positioned to contribute [2.69, 2.70].

6. Discussion: Research Gaps and Future Directions

The seventy studies reviewed above collectively establish a mature theoretical and experimental foundation for $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped silicate glasses as UV–visible downconversion layers. Nonetheless, several gaps in the literature remain and define productive directions for continued research.

First, concentration quenching remains an incompletely resolved trade-off. While Dimitriou and co-workers [2.38] and related compositional studies [2.48, 2.49] establish that an optimal dopant concentration exists, the precise interplay between $\text{Tb}^{3+}:\text{Eu}^{3+}$ ratio, total rare-earth loading, and host network structure has been mapped only for a limited subset of silicate compositions; broader, systematic composition–property maps combining Judd–Ofelt analysis [2.13, 2.22] with time-resolved transfer-rate measurements [2.25] would strengthen predictive design capability.

Second, the trade-off between luminescence enhancement and optical scattering in glass-ceramic converters, noted by Valiente and co-workers [2.54] and Chen and Wang [2.55], has not been fully quantified across the range of fluoride- and oxide-nanocrystal systems reported in Section 3 [2.16, 2.20, 2.21, 2.32]. Nanocrystal size control that preserves the phonon-energy benefit of ceramization while minimizing parasitic scattering losses remains an open fabrication challenge.

Third, while several studies validate downconversion gains on individual c-Si cells [2.56, 2.59, 2.60] and at the module cover-sheet level [2.63], long-term photostability under continuous solar illumination — flagged as a concern by Kityk and co-workers [2.35] — has received comparatively little systematic attention in the device-integration literature reviewed in Section 5.

Fourth, the machine-learning-guided compositional design approach introduced by Silva and co-workers [2.69] remains an isolated example within the field. Given the large compositional parameter space spanned by host network formers, modifiers, dopant ratios, and processing routes documented in Section 4, computational and data-driven design methods represent a promising but still underexploited avenue for accelerating the discovery of optimized $\text{Eu}^{3+}/\text{Tb}^{3+}$ silicate converter compositions.

Finally, dual-mode and multi-junction-oriented converter designs [2.70] and cascade tri-ion sensitization schemes [2.29] point toward increasingly sophisticated spectral engineering strategies that extend beyond the simple Tb^{3+} – Eu^{3+} pair; systematic comparison of these emerging multi-ion and multi-mode architectures against the well-characterized binary Tb^{3+} – Eu^{3+} silicate system remains an area for further study.

7. Conclusion

This article has reviewed seventy foundational and recent studies spanning four thematic areas: the theoretical basis of photon downconversion and lanthanide energy transfer; the specific spectroscopic and mechanistic behavior of $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped silicate glasses; the compositional, synthesis, and fabrication strategies used to optimize such glasses; and their integration into, and performance within, functioning photovoltaic devices, together with recent and emerging advances. Across this literature, a consistent picture emerges: $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ dipole–dipole energy transfer in silicate and modified-silicate hosts is a well-characterized, tunable process whose efficiency depends on dopant concentration, host phonon energy, and network modifier content; compositional and fabrication optimization — including fluoride nanocrystal precipitation, sol-gel synthesis, and controlled ceramization — can substantially enhance luminescence efficiency; and device-level studies, from single c-Si cells to industrial modules, have validated measurable efficiency gains from $\text{Eu}^{3+}/\text{Tb}^{3+}$ -doped silicate spectral converters. Together, this body of literature establishes both the scientific rationale and the practical precedent for the continued design and optimization of $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped silicate glasses as UV–visible downconversion layers for solar cell efficiency enhancement, while also identifying concentration quenching, scattering losses, photostability, and computational compositional design as priority areas for future investigation.

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