

Rare earth oxychalcogenide nanophosphors: novel optoelectronic materials for next-generation photovoltaics

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The escalating global energy demand, in conjunction with an impending and looming danger posed by climate change, has necessitated the relentless pursuit of viable and long-lasting sources of energy that are both sustainable and renewable in nature [1]. Amongst the myriad of available alternatives, solar energy has emerged as a leading contender due to its vast availability and the environmentally friendly byproducts it generates. The process of harnessing solar energy revolves around the utilization of photovoltaic (PV) devices, which can directly convert sunlight into electrical energy. These devices play a pivotal role in the efficient extraction and utilization of solar energy, serving as the primary means through which this renewable resource can be effectively harnessed for various applications [2]. The efficiency of some of the conventional PV materials currently in use, for example, silicon, is sniffing to the threshold of its theoretical limits, thereby necessitating the pursuit of novel materials possessing enhanced material properties [3]. Amongst new materials explored for PV applications are kesterite (limited by high open-circuit voltage (Voc) deficient), perovskite (limited by instability of the organic component), and quantum dots (limited by poor efficiency), to name a few [3]. Due to the remarkable and unparalleled stability of their chemical composition as well as their ability to withstand high temperatures, rare earth metal oxychalcogenides (ROC), specifically their oxysulfides, have garnered considerable attention and interest from the scientific community. ROCs are chemical compounds characterized by the presence of a rare-earth (RE) metal in its trivalent oxidation state, combined with oxygen and one of the chalcogens (sulfur, selenium, or tellurium) in their -2 oxidation states. In the chemical structure of these compounds, the negative oxidation states of oxygen and chalcogens do not engage in any bonding interactions. Instead, the oxygen atoms and chalcogen atoms exclusively form bonds with the trivalent RE metals. The interest in ROCs lies in their remarkable phosphor properties, which refer to their ability to emit photons with significantly enhanced luminescence efficiency [4]. These properties make ROCs a subject of great interest and investigation, as they hold potential for various applications in the field of materials science and optoelectronics. The study of ROCs aims to unravel their structural and electronic characteristics, as well as their applications in areas such as solid-state lighting, display technologies, and energy conversion devices. The intricate interplay between the RE metal, oxygen, and chalcogens in these compounds provides a rich avenue for exploring novel materials with tailored luminescent and optoelectronic properties. Hence, understanding the fundamental aspects of ROCs opens new

avenues for the design and development of advanced materials for a wide range of technological applications [4,5]. The exceptional nature of this class of compounds lies in the modifications made to their properties through the process of doping the parent ROCs with minute quantities of other rare earth (RE) metals, thus initiating the activation of phosphor properties. The parent ROCs can undergo the process of doping to achieve either up-conversion (UC) or down-conversion (DC) luminescence. DC luminescence entails the conversion of light with low wavelengths, such as X-rays and ultraviolet (UV) light, into light within the visible spectrum. For DC luminescence, elements such as terbium (Tb) and europium (Eu) are frequently doped into the parent ROCs to enable green and red phosphor emissions, respectively. On the other hand, UC luminescence involves the conversion of light with high wavelengths, such as infrared and microwave, into visible light. For UC luminescence, elements such as erbium (Er), thulium (Tm), and holmium (Ho) are doped into the parent ROCs [5,6]. These compounds have witnessed extensive utilization in various fields, such as catalysts, medical diagnostic imaging, and luminescence hosts, owing to their expansive array of advantageous characteristics that contribute to their versatility and applicability in numerous contexts.

Recently, ROCs have become a great source of interest for the development of future-generation solar cells [7]. These materials possess some unique properties that are very promising for photovoltaic applications and include [4,8]:

Broad light absorption: Unlike many conventional semiconductors that are commonly used in solar cells, ROCs possess bandgaps that span across a large region of the solar spectrum, covering both the visible and near-infrared (NIR) wavelengths. This remarkable characteristic confers upon them some advantage, which enables them to capture a significantly larger portion of the incident solar energy in comparison to other materials. The broader range of light absorption exhibited by ROCs can be attributed to the diverse electronic structures due to the incorporation of rare earth elements within these materials [9]. These unique elements possess multiple energy levels, thus ensuring numerous transitions that can be excited by different wavelengths of light within the solar spectrum. The efficient capture of the NIR portion of the solar spectrum is important as it constitutes a significant fraction of the total solar energy available. Conventional solar cell materials, unfortunately, often encounter problems in effectively using NIR light due to their bandgaps. Therefore, the emergence of ROCs as

promising optical materials to substantially enhance the overall efficiency of solar cells by harnessing a larger fraction of the abundant solar energy that is readily accessible shows great promise for increased exploration.

High carrier mobility: The transfer of charge carriers, specifically electrons and holes, which are produced when light is absorbed, is necessary for the effective conversion of solar energy into electrical energy within a solar cell. High carrier mobility for both electrons and holes is a unique property of ROCs, which makes it easier for these charges to move quickly and effectively throughout the solar cell. The distinct crystal structures of ROCs and the type of chemical bonds present in these materials are responsible for their remarkable carrier mobility. These properties enable the charge carriers to flow through the material with the least amount of energy loss and resistance [9-11].

Tunable optical and electronic properties: The optical and electrical properties of ROCs can be tuned, which is one of their appealing characteristics for solar cell applications. This remarkable characteristic enables researchers to alter the material's properties to meet distinct specifications and maximize its performance for various solar cell designs. The great variety of potential combinations of rare earth metal ratios with the oxychalcogenide counterparts accounts for the tunability of ROCs. Researchers can effectively control the bandgap, carrier mobility, and other significant variables by changing the composition to get the optimal properties for solar cell applications. Due to their tunability, ROC-based solar cells may be designed and optimized with great flexibility [9,11,12].

Thermal stability: For any viable solar cell material, long-term stability and dependable performance are essential. Because of their remarkable thermal stability, ROCs can withstand the operating temperatures found in solar cells without experiencing any performance loss or deterioration [4,5,13,14]. Strong chemical bonds and stable crystal structures are the factors driving ROCs' excellent thermal stability. At extremely high temperatures, these properties preserve the material from deteriorating dramatically or breaking down. Since ROC-based solar cells have such remarkable thermal stability, they can withstand lengthy exposure to heat and sunshine as well as a variety of other environmental challenges. This makes them perfect for solar energy applications for reliable, long-term operations.

ROC's exceptional properties have positioned them as highly promising contenders for a range of photovoltaic applications, including but not limited to [15,16]:

Thin-film solar cells: ROCs can be deposited as thin films onto various substrates, such as polymers, glass, and metal foils. This unique feature allows for the fabrication of lightweight and flexible PV devices, making them ideal for applications where weight and flexibility are critical, such as building-integrated photovoltaics (BIPV), wearable electronics, and portable power sources. Compared to traditional bulk materials, thin-film solar cells require less material, leading to potentially lower production costs. Additionally, the ability to deposit ROCs onto various substrates enables the use of cheaper and more readily available materials, further reducing the overall cost of PV devices. The thin-film deposition process also allows for large-scale production of ROC-based solar cells, making them a viable option for meeting the growing demand for renewable energy [4].

Perovskite solar cells: The incorporation of ROCs into perovskite solar cells can enhance their stability and efficiency, unlocking new frontiers in PV technology. Perovskite solar cells have attracted tremendous interest due to their remarkable light-absorbing properties and low production costs. However, their long-term stability remains a major challenge. ROCs, with their inherent stability and tunable properties, can address this issue, leading to improved long-term performance. ROCs can enhance the stability of perovskite solar cells by preventing degradation from moisture, heat, and UV radiation. This results in longer lifespans and higher energy output over time, increasing the economic viability of perovskite solar technology. The tunable bandgap of ROCs allows for precise control of the perovskite solar cell's spectral response. This enables optimized light absorption, leading to increased efficiency and improved power conversion [12,13].

Tandem solar cells: ROCs can serve as good absorber layers in tandem solar cells, paving the way for achieving record-breaking power conversion efficiencies. Tandem solar cells combine multiple absorber layers with different bandgaps to capture a wider portion of the solar spectrum, leading to significantly higher efficiencies than single-junction cells. ROCs, with their tunable bandgaps and excellent light-absorbing properties, are ideal candidates for such applications reaching beyond the single-junction limit. The efficiency of single-junction solar cells is limited by the Shockley-Queisser limit, around 33%. By employing tandem structures with ROCs as absorber layers, this limit can be surpassed, leading to power conversion efficiencies exceeding 40%. The diverse range of bandgaps available in ROCs allows for the efficient absorption of a broader range of sunlight wavelengths. This minimizes energy losses and maximizes the overall power output of the tandem solar cell. Tandem solar cells with ROCs offer the potential for reaching grid parity, making solar energy even more competitive with fossil fuels. This paves the way for a future powered by clean and renewable energy sources [6,17,18].

Notwithstanding their optimistic potential, ROCs encounter certain obstacles that necessitate resolution before their widespread adoption in photovoltaic technology. These challenges include:

Synthesis complexity: The synthesis of ROCs involves intricate and multi-step procedures often essential for achieving the desired chemical structure and properties. Consequently, these complex procedures impose significant challenges in terms of both cost and scalability of material production, as they often require the utilization of expensive reagents, sophisticated equipment, and skilled personnel. As a result, the synthesis of ROCs becomes a labor-intensive and resource-consuming task, ultimately leading to higher production costs and limited opportunities for large-scale production [19].

Interfacial compatibility: Ensuring compatibility between the ROCs and other essential components of the PV devices, such as the electrodes responsible for conducting electricity and the charge transport layers that facilitate the movement of charge carriers, is a necessity to optimize the overall performance and efficiency of these devices [6,13,20].

Device optimization: The maximization of the performance of ROC-based photovoltaic devices relies on the imperative

task of optimizing both the device architecture and the fabrication processes, as they play a crucial role in determining the overall efficiency and performance of these devices. Therefore, it becomes essential to carefully and meticulously refine and enhance the design and construction of these devices in order to achieve the highest possible level of performance and output [12,15,21].

In summary, it is imperative to address and surmount these obstacles. This endeavor requires a collective and cooperative effort from experts and researchers in the fields of materials science, chemistry, and device engineering. By boldly confronting these challenges and exploring the extensive range of opportunities presented by ROCs, we have the potential to usher in a novel epoch of photovoltaic technologies that exhibit exceptional efficiency, stability, and economic feasibility.

Disclosure Statement

No potential conflict of interest was reported by the author.

References

- Abolhosseini S, Heshmati A, Altmann J. A review of renewable energy supply and energy efficiency technologies. IZA Discussion Paper No. 8145. 2014;1-35. <http://dx.doi.org/10.2139/ssrn.2432429>
- Aryal D. Solar energy: a potential source of renewable and clean energy. Int J Res Granthaalayah. 2018;6:214-217. <http://dx.doi.org/10.29121/granthaalayah.v6.i8.2018.1452>
- Nwambaeke KC, John-Denk VS, Douman SF, Mathumba P, Yussuf ST, Uhuo OV, et al. Crystal engineering and thin-film deposition strategies towards improving the performance of kesterite photovoltaic cell. J Mater Res Technol. 2021;12:1252-1287. <https://doi.org/10.1016/j.jmrt.2021.03.047>
- Nwambaeke KC, Ramoroka ME, Yussuf ST, Morudu TC, Ndipungwi MM, Iwuoha EI. Tb- and Eu-doped yttrium oxyselenides as novel absorber layers for superstrate thin-film photovoltaics: improved spectral optical absorption and green-red phosphor activation. Nanoscale. 2023;15(42):17147-17172. <https://doi.org/10.1039/d3nr01162c>
- Larquet C, Carencio S. Metal oxysulfides: from bulk compounds to nanomaterials. Front Chem. 2020;8:179. <https://doi.org/10.3389/fchem.2020.00179>
- Kataria V, Mehta DS. Multispectral harvesting rare-earth oxysulphide based highly efficient transparent luminescent solar concentrator. J Rare Earths. 2022;40(1):41-48. <https://doi.org/10.1016/j.jre.2020.09.021>
- Meng F, Dehouche Z, Ireland TG, Fern GR. Improved photovoltaic performance of monocrystalline silicon solar cell through luminescent down-converting Gd₂O₂S: Tb³⁺ phosphor. Prog Photovolt. 2019;27(7):640-651. <https://doi.org/10.1002/pip.3139>
- Ortega-Berlanga B, Betancourt-Mendiola L, del Angel-Olarte C, Hernández-Adame L, Rosales-Mendoza S, Palestino G. An overview of gadolinium-based oxide and oxysulfide particles: synthesis, properties, and biomedical applications. Crystals. 2021;11(9):1094. <https://doi.org/10.3390/cryst11091094>
- Admane S, Chopde D. Performance Enhancement of polycrystalline silicon based solar cell using Ba₂SiO₄: Eu²⁺, Nd³⁺ phosphor. Helix. 2018;8(6):4498-4503. <https://doi.org/10.29042/2018-4498-4503>
- Martinez-Gomez NC, Vu HN, Skovran E. Lanthanide chemistry: from coordination in chemical complexes shaping our technology to coordination in enzymes shaping bacterial metabolism. Inorg Chem. 2016;55(20):10083-10089. <https://doi.org/10.1021/acs.inorgchem.6b00919>
- Kurzen H, Bovigny L, Bulloni C, Daul C. Electronic structure and magnetic properties of lanthanide 3+ cations. Chem Phys Lett. 2013;574:129-132. <https://doi.org/10.1016/j.cplett.2013.04.070>
- Datt R, Bishnoi S, Hughes D, Mahajan P, Singh A, Gupta R, et al. Downconversion materials for perovskite solar cells. Solar RRL. 2022;6(8):2200266. <https://doi.org/10.1002/solr.202200266>
- Li B, Tian F, Cui X, Xiang B, Zhao H, Zhang H, et al. Review for rare-earth-modified perovskite materials and optoelectronic applications. Nanomaterials. 2022;12(10):1773. <https://doi.org/10.3390/NANO12101773>
- Orr M, Heberd GR, McCabe EE, Macaluso RT. Structural diversity of rare-earth oxysulfides. ACS Omega. 2022;7(10):8209-8218. <https://doi.org/10.1021/acsomega.2c00186>
- Tahhan A, Dehouche Z, Fern GR, Haverkamp E. Photovoltaic cells energy performance enhancement with down-converting photoluminescence phosphors. Int J Energy Res. 2015;39(12):1616-1622. <https://doi.org/10.1002/er.3358>
- Meng F, Dehouche Z, Ireland TG, Fern GR. Improved photovoltaic performance of monocrystalline silicon solar cell through luminescent down-converting Gd₂O₂S: Tb³⁺ phosphor. Prog Photovolt. 2019;27(7):640-651. <https://doi.org/10.1002/pip.3139>
- Kumar P, Singh S, Lahon R, Gundimeda A, Gupta G, Gupta BK. A strategy to design lanthanide doped dual-mode phosphor mediated spectral converter for solar cell applications. J Lumin. 2018;196:207-213. <https://doi.org/10.1016/j.jlumin.2017.12.035>
- Logothetidis S, editor. Nanostructured materials and their applications. Springer Science & Business Media; 2012;213. Available from: https://books.google.co.in/books?hl=en&lr=&id=zpZcYfzAgv8C&oi=fnd&pg=PR3&dq=18.%09Logothetidis+S,+editor.+Nanostructured+materials+and+their+applications.+Springer+Science+%26+Business+Media%3B+2012%3B213p.&ots=g1lEwqEbvE&sig=yIvSVzJKCFXQ6JvJDbZCJ9Ic0uI&redir_esc=y#v=onepage&q&f=false
- Xu GX, Sang XT, Lian JB, Wu NC, Zhang X. Solvothermal Synthesis and Luminescence Properties of Gd₂O₂S: RE³⁺ (RE³⁺=Eu³⁺/Tb³⁺) Hollow Sphere. Key Eng Mater. 2019;807:1-10. <https://doi.org/10.4028/www.scientific.net/KEM.807.1>
- Ho WJ, Chen JC, Liu JJ, Ho CH. Enhancing luminescent down-shifting of Eu-doped phosphors by incorporating plasmonic silver nanoparticles for silicon solar cells. Appl Surf Sci. 2020;532:147434. <https://doi.org/10.1016/j.apsusc.2020.147434>
- Richards BS. Luminescent layers for enhanced silicon solar cell performance: Down-conversion. Sol Energy Mater Sol Cells. 2006;90(9):1189-1207. <https://doi.org/10.1016/j.solmat.2005.07.001>