

# *Introduction of Photoconversion Rare Earth Phosphors Fabrication*

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**Abstract:** Heterojunction photovoltaic cells exhibit two types of parasitic absorption, namely band edge absorption of ITO thin film and light absorption by doped amorphous silicon layer. These two types of parasitic absorption result in a decrease in EQE or IQE of heterojunction photovoltaic cells in the short wavelength region. Rare earth elements are widely used in optical functional materials due to their unique electronic configuration, which is attributed to the 4f electronic properties. The photoconversion phosphors composed of different rare earth elements are sorted with up/down conversion rare earth luminescent materials. The results of spectral allocation can make up for the shortcomings of the low absorption efficiency of the short wavelength of heterojunction photovoltaic cell. The preparation processes of rare earth phosphors generally include high-temperature solid-state method, precipitation method, sol-gel method, hydrothermal method, combustion method, etc. In this paper, the main preparation methods of rare earth phosphors are presented, and some typical cases are listed.

## 1. Introduction

Crystalline silicon cells have evolved into their third generation<sup>[1]</sup>. Currently, amorphous-silicon-based heterojunction with intrinsic thin-film (HIT/HJT), composed of two distinct semiconductor materials, has a robust competitive advantage in the N-type cell market. The factors affecting the photoelectric conversion efficiency of crystalline silicon cells encompass both optical and electrical losses. Specifically, the optical loss is partially attributed to the low absorption efficiency of HJT cell for short-wavelength sunlight, a characteristic significantly inferior to other cell types such as PERC and TOPCon. The aforementioned reasons can be attributed to the band-edge absorption of ITO thin films and the light absorption of doped amorphous silicon layers<sup>[2,3]</sup>. Given its unique electronic configuration, photoconversion rare earth phosphors can absorb short wavelengths (ultraviolet wavelengths) and emit long wavelengths (visible and near-infrared wavelengths), thus matching the optimal band gap width of crystalline silicon. Therefore, auxiliary materials like films and glass incorporating photoconversion rare earth phosphors have emerged as the preferred choice for HJT photovoltaic modules.

This paper reviews recently reported methods for preparing photoconversion phosphors, including the high-temperature solid-state method, precipitation method, sol-gel method, hydrothermal method, and combustion method. Notably, the high-temperature solid-state method is the most employed one.

## 2. Preparation methods of photoconversion rare earth phosphors

### 2.1 High-temperature solid-state reaction method

The high-temperature solid-state method is suitable for preparing various inorganic materials, such as metal oxides, silicates, and sulfides. It offers the advantage of a relatively straightforward preparation process, yielding materials with excellent crystallization and thermal stability. However, this method also has some limitations, notably its requirement for high temperatures and prolonged reaction periods, signifying its characteristic of a slow reaction rate.

The preparation process starts with preparing different pure oxides and weighing them according to the chemical ratio (mole ratio). Then, these oxides are sequentially placed in an agate mortar for mixing and grinding. After the particles are uniformly fine, they are transferred to a corundum crucible. The crucible is then put into a high-temperature furnace, typically a muffle furnace, where the temperature is set to 1000°C or above, and a nitrogen or argon atmosphere is introduced for sintering. Finally, these oxides are taken out from the furnace for crushing and re-grinding. The introduction of inert gases is essential to prevent some oxides from oxidizing into other valence states in the presence of oxygen, ensuring the acquisition of the target valence state.

The process flow of the high-temperature solid-state reaction method is shown in Figure 1.

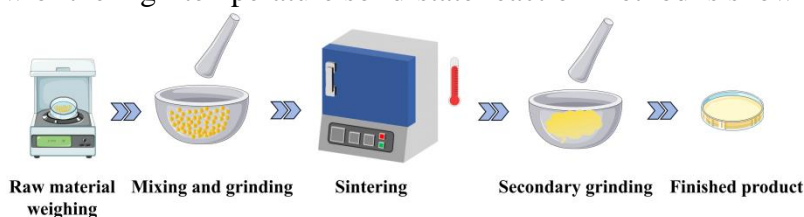


Figure 1: Schematic diagram of the high-temperature solid-state reaction method

The widely studied matrix material for photoconversion materials is yttrium aluminum garnet (YAG), to which rare earth substances, such as  $\text{Ce}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Tb}^{3+}$ , or their combinations, are added. Through the high-temperature solid-state method, down-conversion rare earth phosphors of yellow powder series can be prepared, which can improve the photoelectric conversion efficiency of photovoltaic modules to varying degrees. Other researched rare earth materials include red powder series, such as  $\text{CaAlSiN}_3: \text{Eu}^{2+}$ .

In a typical case<sup>[4]</sup>, the target products encompassed single-doped ( $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ ), double-doped ( $\text{Ce}^{3+}\text{-Tb}^{3+}$ ,  $\text{Ce}^{3+}\text{-Yb}^{3+}$ ,  $\text{Tb}^{3+}\text{-Yb}^{3+}$ ), and triple-doped ( $\text{Ce}^{3+}\text{-Tb}^{3+}\text{-Yb}^{3+}$ )  $\text{Y}_3\text{Al}_5\text{O}_{12}$  powders. First,  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{Al}_2\text{O}_3$  (99.99%),  $\text{CeO}_2$  (99.99%),  $\text{Tb}_4\text{O}_7$  (99.99%), and  $\text{Yb}_2\text{O}_3$  (99.99%) were weighed according to the stoichiometric ratio, uniformly ground in an agate mortar, and then mixed for 30 minutes. The resulting mixture was transferred to an alumina crucible and sintered at 1600°C in a high-temperature furnace for 6 hours under an  $\text{N}_2+\text{H}_2$  atmosphere. After the sintering process, the sample was slowly cooled to room temperature in the furnace and then taken out for secondary grinding.

### 2.2 Chemical co-precipitation method

The chemical coprecipitation method involves adding a precipitant into solutions containing two

or more cations, generating precursor precipitates through stirring. These obtained precipitates are then filtered, washed, dried, and calcined to yield the required phosphor powder. Despite its lengthy production process, complex influencing factors, and inconsistent repeatability, this method can produce high-performance products.

The process flow of the co-precipitation method is shown in Figure 2.

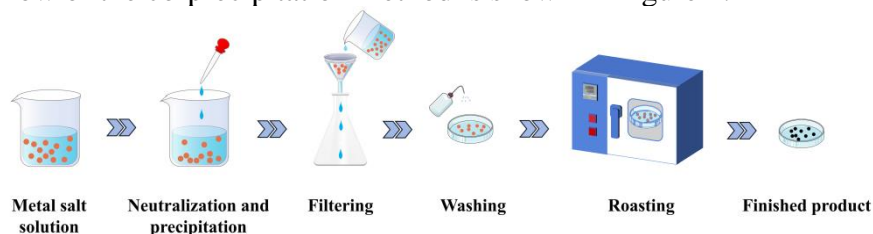


Figure 2: Schematic diagram of the co-precipitation method

In a typical case<sup>[5]</sup>, raw materials  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrCO}_3$ ,  $\text{NH}_4\text{HCO}_3$ , and  $\text{H}_3\text{BO}_3$  of the analytical reagent grade, along with an aqueous solution of  $\text{EuCl}_3$  with a concentration of 66.8 g/L, were prepared first. Based on the mole number of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrCO}_3$  was weighed to achieve the composition  $(\text{Sr}_{0.96}\text{Eu}_{0.04})_3\text{Al}_2\text{O}_6$ , with the addition of 3% (mass fraction)  $\text{H}_3\text{BO}_3$  as a fluxing agent and 0.04 mol  $\text{EuCl}_3$  as an activator.  $\text{SrCO}_3$  was dissolved in an  $\text{HCl}$  solution (0.06 mol/L), and a homogeneous solution was formed by adding  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{EuCl}_3$ , and a suitable amount of distilled water. Subsequently,  $\text{NH}_4\text{HCO}_3$  was added dropwise into the solution under magnetic stirring to ensure homogeneity, during which the system PH was maintained between 7 and 7.5. Afterward, the resulting solution was stirred for 1 hour, aged for another hour, and then filtered and rinsed with distilled water. After being dried at 80°C for 12 hours, the obtained material underwent uniform grinding. It was then calcined at 300°C for 1 hour, followed by successive calcination at 800°C, 900°C, 1000°C, 1100°C, 1150°C, and 1200°C to determine the optimal calcination temperature. Finally, the material was maintained at the optimal temperature for 1 hour, 2 hours, 4 hours, and 5 hours to identify the optimal holding time.

### 2.3 Sol-gel method

The basic principle of the sol-gel method is to dissolve metal alkoxide or metal inorganic salts in water or organic solvents, leading to hydrolysis and alcoholysis reactions in the solution to produce particles that agglomerate to form sols. The sol is then transformed into a gel through drying, and the required target powder is obtained through subsequent heat treatment. This method has the advantages of high reactant purity, excellent chemical homogeneity, fine particle size, low sintering temperature, and energy saving, while its drawbacks include a lengthy reaction time, low yields, high costs, and the need for further performance improvement.

The process flow of the sol-gel method is shown in Figure 3.

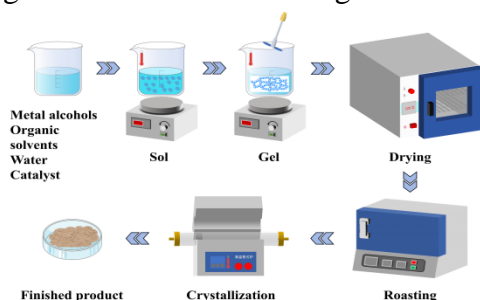


Figure 3: Schematic diagram of the sol-gel method

A typical instance<sup>[6]</sup> employed the sol-gel method to prepare  $\text{Gd}_2\text{O}_3:\text{Bi}^{3+}$ ,  $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$ , and  $\text{Gd}_2\text{O}_3:\text{Bi}^{3+}, \text{Yb}^{3+}$  down-conversion rare earth phosphors. A suitable amount of citric acid (twice the amount of metal cations) was dissolved for later use. According to the specified ratios,  $\text{Gd}_2\text{O}_3(4\text{N})$ ,  $\text{Yb}_2\text{O}_3(4\text{N})$ , and  $\text{Bi}_2\text{O}_3(4\text{N})$  were weighed properly and dissolved in hot concentrated nitric acid. The solution was then added to the citric acid solution for complete dissolution, followed by slow stirring at a constant temperature of  $80^\circ\text{C}$  in a water bath to form a sol, eventually transforming into a gel. The gel was then dried at  $120^\circ\text{C}$  for 4 hours in a blast drying oven to obtain xerogel. After being ground, the xerogel was subjected to muffle furnace calcination at  $600^\circ\text{C}$  and further crystallization in a tube furnace at a specified temperature in an air atmosphere, thus yielding the samples. The optimal crystallization temperature for  $\text{Gd}_2\text{O}_3:\text{Bi}^{3+}$  was determined to be  $1000^\circ\text{C}$ , with a crystallization time of 3 hours, during which the excitation and emission fluorescence spectra reached their maximum values.

## 2.4 Hydrothermal synthesis method

Hydrothermal synthesis refers to the process of preparing raw materials into a solution according to a certain ratio at a temperature of  $100\sim 1000^\circ\text{C}$  and a pressure of  $1\text{ MPa}\sim 1\text{ GPa}$  and then pouring it into a sealed reactor (usually a reaction kettle) for reaction. As a chemical component, water also participates in the reaction, while the reactor serves as the core equipment in a hydrothermal synthesis plant. However, this method has several disadvantages, including low luminescence efficiency and unstable fluorescence performance of the resulting phosphors, the need for process improvement, high equipment requirements, challenging process control, and substantial difficulties in industrialization.

The process flow of the hydrothermal synthesis method is shown in Figure 4.

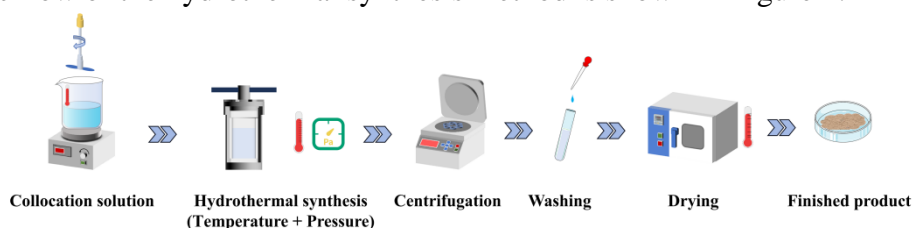


Figure 4: Schematic diagram of the hydrothermal synthesis method

In a typical case<sup>[7]</sup>,  $\text{CeF}_3: 0.2\text{ mol}\% \text{Tm}^{3+}, 2.8\text{ mol}\% \text{Tb}^{3+}, 4\text{ mol}\% \text{Eu}^{3+}$  synthetic phosphors were prepared by the hydrothermal method. During the synthesis, stoichiometric  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 10 ml of deionized water. Subsequently,  $\text{NH}_4\text{F}$  dissolved in 5 ml of deionized water was slowly dripped into the rare earth ion solution with continuous stirring. The mixed solution was stirred with a magnetic stirrer for 1 hour and then put into a sealed Teflon high-pressure tank. After being heated at  $120^\circ\text{C}$  for 12 hours, it was cooled to room temperature, centrifuged at 10000 r/min for 5 minutes, and washed with deionized water and ethanol in turn. Finally, the obtained product is dried at  $60^\circ\text{C}$  for 2 hours.

## 2.5 Combustion synthesis method

The combustion synthesis method achieves its target products by burning precursor materials. This method employs soluble metal salts (mainly nitrates) and organic fuels (such as urea, citric acid, and amino acetic acid) as reactants. While the former acts as the oxidant, the latter serves as the reducing agent. The precursor is ignited in a certain way and then experiences an oxidation-reduction reaction. Sustained by the released heat, the combustion process concludes within minutes. The resulting combustion product is the required target material. This method offers

notable advantages in terms of safety, time efficiency, and energy saving, marking it as an innovative method.

The process flow of the combustion synthesis method is shown in Figure 5.

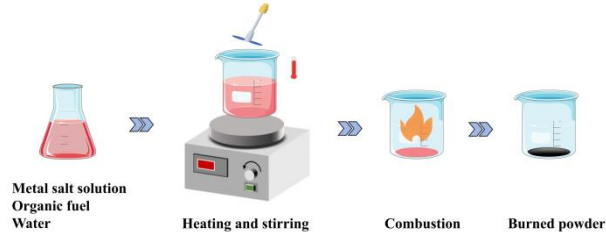


Figure 5: Schematic diagram of the combustion synthesis method

In a typical case<sup>[8]</sup>, YAG doped with 0.3 mol%  $\text{Ce}^{3+}$  was synthesized through microwave solution combustion (MSC) at various microwave periods. The precursor materials included  $\text{Y}(\text{NO}_3)_3$  (99.8%),  $\text{Al}(\text{NO}_3)_3$  (98.5%),  $\text{Ce}(\text{NO}_3)_3$  (99.99%),  $\text{CO}(\text{NH}_2)_2$ , and  $\text{C}_2\text{H}_5\text{NO}_2$ . With the atomic ratio of Y:Al set as 3:5, the metal nitrate and fuel were weighed and dissolved in deionized distilled water. The mixture was heated and stirred at 70 °C for 30 minutes. Afterward, the solution was heated in a microwave oven for 5, 10, and 15 minutes, during which ignition and flame were observed, and the solution evaporated instantaneously. This combustion process arises from the dehydration and decomposition of nitrates and fuels, emitting a substantial amount of gas. After combustion was completed, the powder was extracted, finely ground with a mortar and pestle, then annealed at 1050 °C for 5 hours, and finally cooled to room temperature.

### 3. Conclusions

With the rapid industrialization of HJT cell modules, photoconversion rare earth phosphors will play a pivotal role in the coming years. Consequently, the preparation methods and performance optimization of these phosphors have become research hot-spots, which include developing new preparation methods, optimizing current techniques, understanding the influence mechanism of phosphor particle morphology/size on fluorescence, and determining how to match fluorescence characteristics with diverse cell.

### References

- [1] Lin H, Yang M, Ru X N, et al. Silicon heterojunction solar cells with up to 26.81% efficiency achieved by electrically optimized nanocrystalline-silicon hole contact layers[J]. *Nature Energy*, 2023, 8: 789-799.
- [2] Zhang D, Deligiannis D, Papakonstantinou G, et al. Optical enhancement of silicon heterojunction solar cells with hydrogenated amorphous silicon carbide emitter[J]. *IEEE Journal of Photovoltaics*, 2014, 4(6): 1326-1330.
- [3] Holman Z C, Descoedres A, Barraud L, et al. Current losses at the front of silicon heterojunction solar cells[J]. *IEEE Journal of Photovoltaics*, 2011, 2(1): 7-15.
- [4] Kumar K S, Lou C G, Xie Y F, et al. Energy transfer in co- and tri-doped  $\text{Y}_3\text{Al}_5\text{O}_{12}$  phosphors[J]. *Journal of Rare Earths*, 2017, 8(35): 775-782.
- [5] Yan F Y, Gao H M, Liu L, et al. Preparation of  $\text{Sr}_3\text{Al}_2\text{O}_6$ :  $\text{Eu}^{3+}$  red phosphors by co-precipitation method[J]. *Bulletin of the Chinese Ceramic Society*, 2015, 34(9): 2487-2490.
- [6] Xiao L J, Yan F Q, Xie Y, et al. Preparation and fluorescent properties of  $\text{Bi}^{3+}$  doped,  $\text{Yb}^{3+}$  doped and  $\text{Bi}^{3+}$ ,  $\text{Yb}^{3+}$  codoped  $\text{Gd}_2\text{O}_3$  phosphors [J]. *Chinese Journal of Luminescence*, 2012, 33(4): 383-388.
- [7] Li Y, Cai Y X, Ming C G, et al. Simple synthesis, adjusting luminescence colour and white light emission of  $\text{Ln}^{3+}$ :  $\text{CeF}_3$  ( $\text{Ln} = \text{Tm}, \text{Tb}, \text{Eu}$ ) phosphors[J]. *Bulletin of Materials Science*, 2023, 46(2): 113.
- [8] Lau K S, Hassan Z, Lim W F, et al. Effect of microwave time on the structural and luminescence properties of YAG:Ce prepared by microwave solution combustion (MSC) synthesis[J]. *Optik*. 2020, 212: 164437.