

Phosphors For Dye Sensitized Solar Cell

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ABSTRACT

Dye sensitized solar cell (DSSC) are considered as economically viable, alternative to costly Silicon solar cell. Typically used dye molecules generally have poorer absorption in the red part of the spectrum compared to silicon, also IPCE value in UV part is not good enough, which limits the current generated by a DSSC. Moreover, dyes and hence DSSC performance degrade when exposed to ultraviolet radiation. Use of phosphors which will absorb near UV/ blue light (300-450 nm) and convert it to green (510 nm) light where the typical DSSC dyes like N3 are most effective will improve the DSSC performance in two ways. Degradation due to UV exposure will be eliminated and availability of more photons in the most sensitive spectral region will increase the efficiency.

Synthesis and characterization of some such phosphors is described here.

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1. Introduction

Electric power generation via the dye sensitization solar cell (DSSC) principle was demonstrated and discussed in 1972 [1]. In the dye-sensitized solar cell, the bulk of the semiconductor is used solely for charge transport, the photoelectrons are provided from a separate photosensitive dye. A modern DSSC, the Graetzel cell, is composed of a porous layer of titanium dioxide nanoparticles, covered with a molecular dye that absorbs sunlight which excites electrons that then flow into the titanium dioxide. The dye molecules are quite small (nanometer sized), so in order to capture a reasonable amount of the incoming light the layer of dye molecules needs to be made fairly thick, much thicker than the molecules themselves. To address this problem, a nanomaterial is used as a scaffold to hold large numbers of the dye molecules in a 3-D matrix, increasing the number of molecules for any given surface area of cell.

Although the dye is highly efficient at converting absorbed photons into free electrons in the TiO_2 , only photons absorbed by the dye ultimately produce current. The rate of photon absorption depends upon the absorption spectrum of the sensitized TiO_2 layer and upon the solar flux spectrum. The overlap between these two spectra determines the maximum possible photocurrent. Typically used dye molecules generally have poorer absorption in the red part of the spectrum compared to silicon, which means that fewer of the photons in sunlight are usable for current generation. These factors limit the current generated by a DSSC, for comparison, a traditional silicon-based solar cell offers about 35 mA/cm², whereas current DSSCs offer about 20 mA/cm². Moreover, dyes and hence DSSC performance degrade when exposed to ultraviolet radiation. Also IPCE value in UV part is not good enough. Though several dyes have been suggested for DSSC, most of them suffer from these drawbacks [2]. It will thus prove fruitful to use nanophosphors which will absorb near UV/ blue light (300-450 nm) and convert it to green (510 nm) light where the typical DSSC dyes like N3 are most effective. This will improve the DSSC performance in two ways. Degradation due to UV exposure will be eliminated and availability of more photons in the most sensitive spectral region will increase the efficiency.

In this paper we describe synthesis and characterization of some such phosphors.

2. Experimental:-

Polycrystalline Calcium Zinc Chlorosilicate was prepared by a solid-state reaction, following recipe given by Lu et al [3] using analytical reagent grade CaCO_3 , ZnO , SiO_2 and CaCl_2 . For doping, corresponding salts of the activators in the desired quantities were added. Following Lu et al the reagents were taken in molar ratio $\text{CaCO}_3:\text{ZnO}:\text{SiO}_2:\text{CaCl}_2$ as 1:1:1:1.2 and ground in an agate mortar. The homogenized powder was heated at 950 C for 2 hours in a reducing atmosphere provided by burning charcoal. After cooling, the powder was repeatedly washed with distilled water and dried. Details are described elsewhere [4].

Polycrystalline BAM and SAM phosphors were prepared by solution combustion method [5, 6]. Activation of Eu and Mn were also achieved through combustion synthesis at 500 C furnace temperature. All metal nitrates of barium, samarium, magnesium, aluminium, europium and manganese were mixed with urea and crushed in agate mortar pestle for half hour. The mixture was dried to form a thick solution by keeping on hot plate at 35 C. The china dish containing the mixture was kept in pre heated furnace at 500 C temperatures, within minute the solution starts burning and a foamy structure is left out. The prepared sample is crushed and taken for measurement.

3. Results and Discussions

Fig.1 shows PL spectra for $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:0.05 \text{Eu}^{2+}$. Strong emission (Fig.1, curve a) is observed for Eu^{2+} in green region with maximum around 505 nm. Excitation spectrum (Fig.1, curve b) is very broad, stretching from 250 to 500 nm with broad maxima around 320 and 375 nm with prominent shoulders at about 450 and 280 nm. These are typical of transitions between lowest band of $4f^65d^1$ configuration to $^8\text{S}_{7/2}$ state of $4f^7$ configuration. These results are in excellent agreement with the literature results. PL spectra for $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:0.05 \text{Eu}^{2+}$ were first reported by Liu and Xu⁷. Emission spectra were reported on the basis of 3 types of cation sites in $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2$ structure. Green emission was attributed to eight- and six- coordinated sites. Hai et al⁸ reported PL of both Ce^{3+} and Eu^{2+} , and also energy transfer from the former to latter.

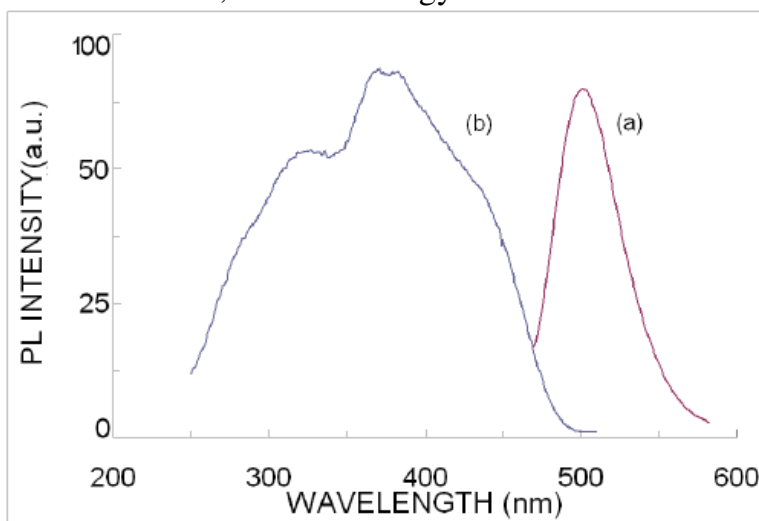


Figure 1 PL spectra of $\text{Ca}_8\text{Zn}(\text{SiO}_4)_4\text{Cl}_2:0.05 \text{Eu}^{2+}$ (a) Emission for 365 nm excitation (b) Excitation for 510 nm emission

Fig.2 shows PL spectra for $\text{SAM}:\text{Eu}^{2+}$ and $\text{SAM}:\text{Mn}^{2+}$. Upon excitation of Eu^{2+} band (360nm), the PL spectrum consists of a blue emission band. The emission spectrum covers 400–550 nm region. Excitation spectrum

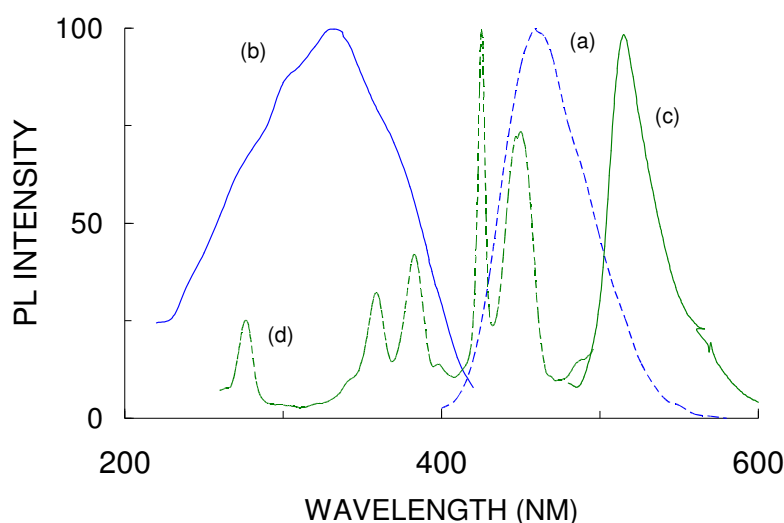


Figure 2 PL spectra of SAM: Eu²⁺ (a and b) and SAM: Mn²⁺ (c and d) (a) Emission for 327 nm excitation, (b) Excitation for 460 nm emission, (c) Emission for 327 nm excitation (d) Excitation for 510 nm emission

contains a prominent band around 327 nm and several unresolved, overlapping bands. The PLE spectrum monitored for the Mn²⁺ emission (515 nm) includes several excitation bands including one around 450 nm. Overlap between Eu²⁺ emission and Mn²⁺ excitation imply an efficient ET from Eu²⁺ and Mn²⁺ in SAM. Therefore, the relative intensities of these two emissions (i.e., the emission color) can be varied by adjusting the concentrations of the two activators through the principle of ET. In order to tune the emission color of the phosphors, a series of samples with compositions of SAM:0.1Eu²⁺,yMn²⁺ (y=0.36) were synthesized and their PL spectra are depicted in Fig. 3.

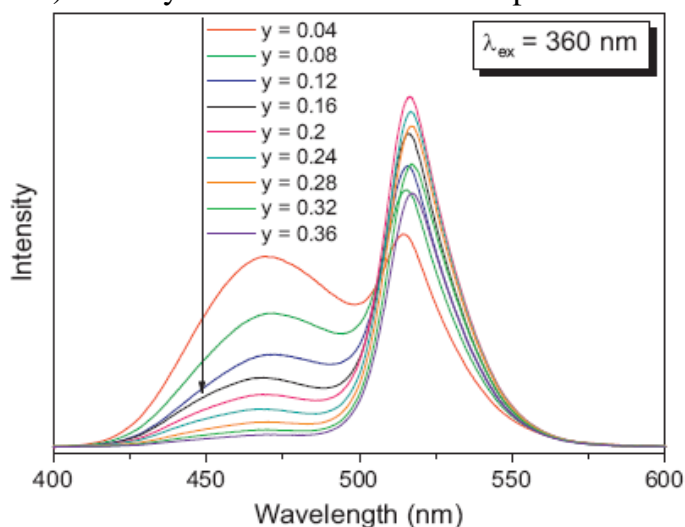


Figure 3: Effect of Mn²⁺ concentration on PL emission in SAM:Eu,Mn

The intensity of the Eu²⁺ emission was found to decrease monotonically with increasing Mn²⁺ dopant content, whereas the emission intensity of the Mn²⁺ reaches a maximum at y=0.2 and then begins to decrease as a result of concentration quenching effect of the Mn²⁺ ions (Fig. 3).

Similar results were obtained for BAM:Eu²⁺,Mn²⁺ phosphor also.

4 Conclusions

Ca₈Zn(SiO₄)₄Cl₂:Eu²⁺, SAM:Eu²⁺,Mn²⁺ and BAM:Eu²⁺,Mn²⁺ phosphors which efficiently absorb UV light and emit around 510 nm have been synthesized. These will prove useful in improving performance of TiO₂ based dye sensitized solar cells.

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