Highly transmissive luminescent down-shifting layers filled with phosphor particles for photovoltaics

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Abstract: We study the optical properties of polymer layers filled with phosphor particles in two aspects. First, we used two different polymer binders with refractive indices \( n = 1.46 \) and \( n = 1.61 \) (\( \lambda = 600 \text{ nm} \)) to study the influence of \( \Delta n \) with the phosphor particles (\( n = 1.81 \)). Second, we prepared two particle size distributions \( D_{50} = 12 \) µm and \( D_{50} = 19 \) µm. The particles were dispersed in both polymer binders in several volume concentrations and coated with thicknesses of 150-600 µm onto glass substrates. Experimental results and numerical simulations show that the layers of the higher refractive index binder with larger particles result in the highest optical transmittance in the visible light spectrum. Finally, we used numerical simulations to determine optimal layer composition for application in realistic photovoltaic devices.

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References and links


1. Introduction

Photovoltaics is one of the most promising solutions to the world’s energy demand problem. By the year 2050, it is expected to provide about 16% of the entire global electricity [1]. The increase in efficiency and the drop in the production costs of solar modules are, therefore, of great importance.

Modern solar cell devices cannot use the entire incident solar spectrum [2]. This is due to the fact that the optimum efficiency requires a certain band gap. This leads to thermalization losses in the UV- and near-UV spectral region.

Luminescent down-shifting (LDS) is known for decades as an approach to improve the conversion efficiency of various devices in the short-wavelength spectral region [3, 4]. Separate layers or blocks of polymer filled with photoluminescent materials are put in front of the device to modify the incident spectrum. The layer converts the UV and near-UV photons into photons in the visible spectrum via photoluminescence process, thus, increasing the amount of incident “useful” photons.

Recently developed materials allow this method to be applied to photovoltaics. Klampapitis et al. achieved increased efficiency of multi-crystalline silicon and CIGS (Cu(In,Ga)Se2) solar cells [5, 6]. They used EVA (ethylene vinyl acetate copolymer) encapsulation layers doped with organic dyes. Semiconductor quantum dots have been also used for LDS purposes in photovoltaics [7, 8]. Their small sizes and sensitivity to surrounding medium enable the
production of transparent layers with tunable absorption and emission bands [9, 10]. Such layers can be adjusted to specific photovoltaic devices and raise their overall efficiency. However, both material types share such disadvantages as high re-absorption, followed by luminescence efficiency drop, and unknown long-term stability. Producers of modern solar modules guarantee stable efficiency for 20 years. Therefore, LDS films have to remain stable and efficient for the same period of time to become a real market technology.

Phosphors form the third group of possible luminescent materials for LDS layers [11]. Typically, they have large Stokes shift, high photoluminescent quantum yield (PLQY), and long-term stability. Phosphors have a high refractive index \( n \) from 1.6 to 2.6 depending on the crystal lattice. This is why their usual particle sizes of several \( \mu m \) represent the main drawback for photovoltaic application: adding phosphors to transparent polymer binder results in strong light scattering and, therefore, reflection losses.

Scattering by phosphor particles embedded in transparent silicones has been studied in depth within the field of solid-state lighting [12–20]. There are two main approaches to reduce the scattering in the layers: matching the refractive indices of the particles and the binder and using particles of large sizes. Park et al. proved experimentally that large phosphor particles produce less scattering and lead to higher light outputs [12, 17]. This is especially true for phosphors with spherical shapes [19]. Lipnitskaya et al. simulated light losses for binder materials with \( n = 1.4-1.8 \) and YAG (\( Y_3\text{Al}_5\text{O}_{12}, n = 1.83 \)) particles with sizes up to 50 \( \mu m \) [16]. They found that losses increased with increasing \( n \) of the binder due to total internal reflection on the air-binder interface. They also predicted that particles of 50 \( \mu m \) would cause the least light scattering.

All these studies concentrate on optical transmittance and reflectance of layers for blue and yellow light that are used for white light creation in LEDs. Luminescent down-shifting for photovoltaics requires a detailed study of the optical properties of such layers under solar irradiation. There are, furthermore, only a few experimental studies on systems with varied particle size distributions [13], binders [21], and their resultant scattering properties. To the best of our knowledge, no extensive studies on the scattering of phosphors under the solar spectrum have been carried out.

We examined the optical properties of phosphor-filled polymer layers on glass. We varied such parameters as the refractive index of the binder, particle size distribution and particle volume concentration (PVC) in the layers. We estimated how these parameters influence optical transmittance of the layers and confirmed the experimental results with simulations using our computational model CROWM [22, 23]. Our aim was to achieve the highest possible transmittance of visible light with the exception of the phosphor absorption region. Finally we calculated the optical transmittance through such phosphor-filled layers with silicon wafers as a substrate. Our results show that scattering by phosphors particles can enhance the light-coupling into the silicon and prove that our concept has promise.

2. Experimental

2.1 Materials

Phosphor powder GAL 545L (Intematix Corp., USA) was used for this study. It belongs to the garnet family with a modified structure of \( \text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+} \). The refractive index of the bulk material is \( n \approx 1.86-1.81 \) for visible wavelengths \( \lambda = 400-800 \text{ nm} \) [24].

To prepare different particle size distributions, we used a wet-sieving process with nylon grid mesh size 15 \( \mu m \) (Linker Industrie-Technik).

Binder materials are described in Table 1. LIM (“low-index” matrix), and HIM (“high-index” matrix) are both solution-processable and form stable, smooth layers.
### Table 1. Properties of the chosen matrix materials LIM (low-index) and HIM (high-index)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Binder Name</th>
<th>Supplier</th>
<th>Type</th>
<th>Mixing Ratio</th>
<th>Viscosity&lt;sup&gt;a&lt;/sup&gt;, Pa·s</th>
<th>n&lt;sup&gt;b&lt;/sup&gt; (λ=600 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIM low-index matrix</td>
<td>QSil 218 (A+B)</td>
<td>ACC Silcones Ltd., UK</td>
<td>Addition cure silicone elastomer</td>
<td>10:1</td>
<td>2.2</td>
<td>1.46</td>
</tr>
<tr>
<td>HIM high-index matrix</td>
<td>SA-251P</td>
<td>Nagase ChemteX Corp., Japan</td>
<td>Acrylic oligomer and acrylic monomer with (1-hydroxycyclohexyl)-phenylketone 99% (Sigma Aldrich)</td>
<td>97:3</td>
<td>2.1</td>
<td>1.61</td>
</tr>
</tbody>
</table>

<sup>a</sup>From product datasheets.

<sup>b</sup>Calculated. See sections 2.4 and 3.1 for detail.

2.2 Layer preparation

To prepare the solutions, we slowly added phosphor powder to the liquid binders while stirring continuously. The films were then coated by doctor blade onto glass substrates (float glass, 25 × 25 × 1 mm) and dried. LIM layers were dried at 100°C for 60 min. Layers of HIM were first pre-dried at 140°C for 30 min, then cooled in the refrigerator at 7°C for 10 min, and additionally hardened upside down for 10 min under UV illumination (UV-Belichtungsgerät 1, isel AG) to avoid particle sedimentation. The chosen binders showed different shrinkage ratios. To achieve the same particle volume concentrations in different layers we adjusted weight concentrations of the particles in the initial dispersions. The thicknesses of the layers were in the range 150-600 µm. Phosphor particles were homogeneously dispersed.

2.3 Characterization methods

To characterize phosphor powder we used field-emission scanning electron microscope (FE-SEM Carl-Zeiss ULTRA plus, Oberkochen, Germany).

To determine photoluminescent excitation and emission spectra we used the fluorescence spectrometer Jasco FP-8200 with a 450 W Xenon lamp.

To measure particle size distributions, we used a particle analyzer LS-100Q (Beckman-Coulter, Krefeld, Germany).

To measure spectroscopic data of pure binder layers and of the phosphor-filled layers we used a Perkin Elmer Lambda 950 high performance double beam spectrometer including a 150 mm integrating sphere with a photomultiplier and a InGaAs detector. Samples were placed in transmission and reflection ports of the sphere (glass substrate before the layer with respect to illumination) to measure the total and diffused transmittance and reflectance respectively. Due to the side losses caused by scattering, the sum of total transmittance, total reflectance and absorbance was only 94 ± 2% for all characterized layers.

To estimate the thickness of the dried layers, we used a Nikon Eclipse L150 confocal microscope.

2.4 Computational model

To determine refractive indices and absorption coefficients of the binders, we used the home-built software NIKA [25]. The software employs an algorithm based on the one-dimensional transfer matrix method to find the solution for the complex refractive index throughout the spectral range without knowing the dielectric dispersion functions of the material. The input data are: the measured thickness, illumination incident angle and, the reflectance and transmittance spectra of binder layers deposited on the glass substrate.
To perform optical simulations of the luminescent down-shifting layers, we used the optical simulator CROWM (Combined Ray Optics / Wave Optics Model), developed by Lipovšek et al. [22]. The optical simulator is based on the combination of three-dimensional ray tracing and one-dimensional transfer matrix methods. They are used together to analyze light propagation through thick and thin layers, respectively. Volumetric scattering at the phosphor particles is modeled in CROWM by employing the Mie scattering theory and the so-called effective scattering approach. Further details of the optical model can be found in [23].

3. Results and Discussion

3.1 Materials

The calculated optical constants of the two binders LIM and HIM are given in Fig. 1(a). The measured transmittance, reflectance, and absorbance of neat LIM and HIM layers deposited on glass are shown in Fig. 1(b). The reflectance of the HIM ("high-index" matrix) on glass is higher because of the higher refractive index. Note that both materials do not absorb in the visible light region.

Fig. 1. (a) Calculated with NIKA index of refraction and extinction coefficient dispersions of the chosen matrix materials LIM (low-index) and HIM (high-index); (b) Transmittance (T), reflectance (R), and absorbance (A) of the coatings on glass (layer thicknesses between 290 and 370 µm).

Figure 2 shows the morphology and the photoluminescent excitation and emission spectra of the phosphor particles. For the simulations, we assumed particles to be spherical, which is well justified, as can be seen in Fig. 2(a).

Fig. 2. Properties of the phosphor particles GAL 545L (modification of Lu₃Al₅O₁₂:Ce³⁺): (a) SEM image of the powder; (b) photoluminescence excitation (PLE) and emission (PL) spectra.
3.2 Influence of matrix refractive index on layer transmittance

We show the optical properties of layers with varied matrices in Fig. 3 for the case of two binders (LIM and HIM), two values of particle volume concentration (PVC = 6%, 18%), different layer thicknesses (200 – 650 μm), and the initial particle size distribution (see further). A wavelength of $\lambda = 600$ nm was chosen to analyze the optical properties of the layers in the visible light outside of the PLE spectrum of the phosphor. Thus, the photoluminescence effect is not present in the measurements at this stage. Results indicate that the transmittance of LDS layers based on the high-index (HIM) binder is 5-7% higher compared with LIM-based layers. There are two major reasons for that. Firstly, the decrease in the difference between the refractive indices of the binder and the particles leads to decreased reflection at the particle interfaces. And secondly, according to the Mie scattering theory [26], the angular distribution of the scattered light becomes narrower with a smaller difference in the refractive indices of the phosphor and the binder. This means that a higher portion of light propagates in the near-specular forward direction. Thus, the optical transmittance increases for HIM-based LDS layers.

Our optical model was calibrated for the given phosphor particles in a given layer. Using the calibrated model, we simulated the layers of both binders and with all of the experimental concentrations [23]. Good agreement between the experiment and the simulations can be observed. We think that the discrepancies are mainly caused by experimental errors, such as: possible inhomogeneities in the coating thickness, possible slight sedimentation of particles during the curing process and, most of all, the side losses in the layers. Total internal reflection on the interfaces of HIM layers as well as significant light scattering contributed to the increased side losses and measurement errors.

3.3 Influence of particle size distributions on layer transmittance

Particles of different sizes have different light scattering capabilities that are mainly characterized by the extinction efficiency and the angular distribution of the scattered light [26]. These capabilities primarily depend on the electromagnetic properties of the surrounding medium and the particle diameter. Broad particle size distributions contain particles with different light scattering properties. To verify the influence of the phosphor size distributions on the transmittance and reflectance of the LDS layers, we divided the particles into “small” (mean 18.8 μm) and “large” (mean 11.3 μm) fractions via sieving the initial particles provided by the producer. Figure 4 shows the calculated extinction efficiencies in LIM and HIM for the experimentally produced particle size distributions. Note, that smaller particles have larger extinction efficiencies.
Fig. 4. Calculated extinction efficiency ($Q_{ext}$) as a function of phosphor particle diameter in LIM ($n = 1.45$) and HIM ($n = 1.61$). Also shown are different particle diameter distributions (right axis), where “Initial” – initial powder size distribution (mean 12.2 µm), and the two sieved distributions: “Large” (mean 18.8 µm) and “Small” (mean 11.3 µm). Simulations were done for the wavelength $\lambda = 600$ nm, where the particle refractive index is $n = 1.81$.

Based on these simulation results, we then produced layers in two binders, LIM and HIM, with the “small” fraction and “large” fraction size distributions. Particle volume concentrations (PVC) were kept constant again. Figure 5 shows the values of the total transmittance of these layers with the PVC’s 6% and 13% for the wavelength $\lambda = 600$ nm deposited onto glass. The transmittance increases by 9-11% in both binder systems when “large” fraction particles are used instead of “small” fraction particles. Also as expected the transmittance drops with increasing particle concentration.

Two major effects influence the increase of the optical transmittance in the layers when we use the “large” fraction distribution of the phosphor particles. First, particles in the “large” fraction scatter light less efficiently compared with the particles in the “small” fraction (see Fig. 4). This means that light is more likely to propagate in the forward direction in the layer with larger particles. Second, particle number density changes as a function of particle radius $\sim r^3$ when we change particle size distribution. We kept the particle volume concentration constant, and thus, put fewer particles of larger sizes into the coatings with the “large” fraction phosphor. Therefore, light ray “meets” fewer particles as it propagates through the layer and the scattering becomes less pronounced.

To ensure that the change of the particles size distribution caused the increase in transmittance, we simulated the layers with CROWM. We used the model, calibrated for the initial particle size distribution layers. Again, good agreement between the simulation and experimental results was achieved. The discrepancies are attributed mainly to the experimental errors, as explained before.
3.4 Optical transmittance of phosphor-filled matrices depending on substrate

So far the characterization of the luminescent down-shifting layers was performed for layers deposited onto glass. All the measurements were performed in air. However, in a realistic photovoltaic application, the layers are laminated directly onto the top of a solar cell. Therefore, it is not enough to optimize phosphor-filled layers only on glass substrates. One must keep in mind that the optical transmittance of the LDS layers is different depending on the substrate, i.e. solar cell device. In this case the reflectance at the interfaces depends also on the refractive index of the upper layer of the solar cell, the surface texture commonly used for light-trapping, the angle of incidence, etc.

CROWM allows us to simulate the changes that can be expected in case if a phosphor-filled layer is laminated onto a solar cell. Figure 6 shows the simulated transmittance in the substrate, or the amount of light that is coupled into the substrate, for the structures on glass and on a silicon wafer. Flat interfaces were assumed in all the simulations for simplicity, although realistic pyramidal textures (in the case of silicon) could also be included in the model. The results for the structure “air / LDS layer / glass” are in agreement with the results from above, where the transmittance of the samples was shown (actual structure “air / LDS layer / glass / air”). As the refractive index of the binder comes closer to the refractive index of the particles, scattering is reduced, and transmittance increases. However, simulations reveal that the maximum transmission occurs for a refractive index slightly lower than the exact value of the refractive index of the phosphor. We think that for this refractive index, scattering is already mostly suppressed. At the same time the somewhat lower refractive index of the binder material results in a lower reflectance at the air / LDS layer interface, and thus, higher overall transmittance.

Note that the maximum achievable transmittance value for HIM layers with the phosphor particles is about 92% (see Fig. 6). 4% of light gets additionally lost at the interface “glass / air” during the experimental measurements. Taking into account the unavoidable measurement error in the integrating sphere, we can, therefore, assume that the layers with “large” fraction phosphor particles in HIM (see Fig. 5) are fully optimized and highly transmissive.

As a rule, the use of phosphor particles in polymer coatings on glass leads to a pronounced drop in the optical transmittance. This is, however, not necessarily true for the layers on silicon wafer (or in fact, on any other substrate with a higher index of refraction than the binder). In fact, our simulations resulted in an unexpected and interesting finding: they show that in such a case particles can actually increase the amount of light transmitted to the wafer! Compare the structures “air / LDS layer / silicon” and “air / binder / silicon”. We
have two regions where the transmittance of the particle-filled layer is higher than that of the neat binder layer. This phenomenon is due to the particle scattering and can be explained as follows: At the left peak there is already significant back-reflection present at the front internal interface (LDS layer / air) due to the total internal reflection of scattered light, which propagated outside the escape cone defined by the critical angle. So the back-scattered light from particles cannot fully escape at the front side, yet there is still good transmission into the silicon below, as here no total reflection can occur. So the back-scattered light from particles cannot fully escape at the front side, yet there is still good transmission into the silicon below. The right peak matches the optimal refractive index grading condition, which additionally increases (specular) transmission through the structure. Therefore, phosphor-filled LDS layers can increase light-coupling into silicon and could possibly complement other light-coupling techniques in photovoltaics.

![Graph showing simulation results](image_url)

**Fig. 6.** Simulation results of the total transmittance of the LDS layers at $\lambda = 600$ nm with ("LDS layer") and without ("binder") phosphor particles coated on glass and on silicon wafer ($n = 3.933$, no absorption in silicon is assumed) depending on binder’s refractive index $n_b$. (Layer thickness 230µm, particle volume concentration 13%).

4. **Summary**

In conclusion, we have demonstrated experimentally and numerically ways to increase optical transmittance of the phosphor-filled polymer layers in the visible light spectral region. Our results prove that two separate approaches combined lead to the highly transmissive LDS layers with decreased back-scattering. The following conclusions can be drawn:

1. Polymer binders with high refractive indices (close to the $n$ of particles) are desired for luminescent down-shifting (LDS) layers with phosphor particles. Particles embedded in these binders produce less scattering, thus, the layers become nearly transparent. Although high refractive index silicones cause total internal reflection at the internal silicone/air interfaces, and thus, high losses in LEDs, this can be beneficially used for efficient light confinement in photovoltaic devices. Silicon wafers have refractive index $n = 3.9$, so no total internal reflection effect can occur on the interface LDS layer / silicon. The measured optical transmittance of the layers in HIM binder ($n = 1.61$) with phosphor particles is close to the theoretical maximum.
2. Particle size distribution should be narrow and contain large phosphor particles. Small particles of a few microns in size should be screened out, since such particles cause strong light scattering. Scattering becomes less pronounced for larger particles and virtually constant for the particles larger than 20-30 µm (Fig. 4). Therefore, we do not see a need to further increase the size of the phosphor particles in the LDS layers.

3. Scattering of the phosphor particles in the LDS layers may increase the overall light harvesting in the solar cell. Optical simulations should be used to determine the desired properties of the LDS layers and to tailor them specifically for the chosen PV application. Our model reproduces experimental results fairly well and can be used efficiently to this end.

As the next step towards, we are currently working on light-conversion processes in the phosphor-filled LDS layers. Due to their complexity, they are regarded as a separate research topic.

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