Title: NON-SELF ABSORBING LUMINESCENT SOLAR CONCENTRATOR

Abstract: A luminescent solar concentrator (LSC) is provided, which is capable of absorbing solar energy in the UV and visible regions of the spectrum, the LSC incorporating a luminescent system comprising at least two rare earth materials.
NON-SELFABSORBING LUMINESCENT SOLAR CONCENTRATOR

FIELD OF THE INVENTION

This invention generally relates to luminescent systems.

BACKGROUND

Luminescent solar concentrators (LSC) generate electricity from solar energy, and are based on the entrance of solar radiation into a homogeneous medium collector containing a fluorescent species in which the emission bands have little or no overlap with the absorption bands.

This emission is trapped by total internal reflection and concentrated at the edge of the collector by the geometrical shape which is typically a thin plate. Thus, the concentration of light trapped in the plate is proportional to the ratio of the surface area to the edges. The advantages of LSC over conventional solar concentrators are the following:

a) High collection efficiency of both direct and diffuse solar light,

b) Good heat dissipation from the large area of the collector plate in contact with air, so that the light remains essentially "cold light", which is significant in converter devices such as silicon cells, whose efficiency is reduced at high temperatures;

c) Tracking of the sun is unnecessary; and

d) The choice of the luminescent species allows optimal spectral matching of the concentrated light to the maximum sensitivity of the photovoltaic (PV) process, minimizing undesirable side reactions in the PV cells.

The performance of an LSC is given by the effective concentration ratio which is the product of the geometrical factor and the optical conversion efficiency of the collector. The geometrical factor is the ratio of the surface area $A_s$ to the area of the plate edges $A$. The optical conversion efficiency $\eta_{opt}$ of the collector plate may be defined as:

$\eta_{opt} = \frac{P_{out}}{P_{in}}$

where $P_{in}$ is the total solar power in watts incident on the collector and $P_{out}$ is the total power delivered from the edges.
The optical efficiency of the plate, which is the energy coming out of the edges of the plate divided by the energy falling on the plate, taking into account reflectance, is given by:

$$\eta_{\text{opt}} = (1 - R) \eta_{\text{abs}} \eta_{t} \eta_{f} \eta_{\text{self}}$$  \hspace{1cm} (1)

where $R$ is the reflectance.

The parameters determining the optical plate efficiency depend on the following factors:

a) The fraction $\eta_{\text{abs}}$, which is the ratio of the number of photons absorbed by the plate to the number of photons falling on the plate;

b) The quantum efficiency of fluorescence $\eta_{t}$, which is the ratio of the number of photons emitted to the number of photons absorbed;

c) The Stokes efficiency $\eta_{S}$ which is the ratio of the average energy of emitted photons to the average energy of the absorbed photons, which is given by

$$\eta_{S} = \frac{\langle \epsilon_{\text{em}} \rangle}{\langle \epsilon_{\text{abs}} \rangle}$$  \hspace{1cm} (2)

d) The trapping efficiency $\eta_{t}$ of the light trapped in the collector, which is given by

$$\eta_{t} = \left(1 - \frac{1}{n} \right)^{1/2}$$  \hspace{1cm} (3)

where $n$ is the refractive index of the light-emitting medium;

If the surrounding medium does not have a refractive index $n_0$ very close to 1 (such as air), the quantity $(1/n)$ is everywhere replaced by the ratio $(n_0/n)$. The trapping efficiency $\eta_{t}$ is shown below for four different values of the refractive index $n$:

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\eta_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.414</td>
<td>0.7071</td>
</tr>
<tr>
<td>1.556</td>
<td>0.7660</td>
</tr>
<tr>
<td>1.743</td>
<td>0.8191</td>
</tr>
<tr>
<td>2.000</td>
<td>0.8660</td>
</tr>
</tbody>
</table>

e) The transport efficiency $\eta_{t}$ which takes into account transport losses due to matrix absorption and scattering;

f) The efficiency $\eta_{\text{self}}$ due to losses arising from self-absorption of the colorants.

The overall power efficiency obtained from a fluorescent plate connected to photovoltaic cells is the product of plate efficiency and the efficiency of the solar cells.

It has been shown that the trapping efficiency $\eta_{\text{trap}}$ can be increased by applying photonic crystals. A photonic structure which serves as a band-stop reflection filter for
the light-emitted from the dye increases the trapping efficiency of a collector preventing
the escape from the system (as shown below).

REFERENCES


SUMMARY OF THE INVENTION

Existing luminescent solar concentrators (LSC) are known to suffer from a variety of intrinsic deficiencies which greatly reduce the amount of fluorescence reaching the solar cells. As known, a small fraction of the incident sunlight is reflected from the front surface of the concentrator sheet. A single fluorophore has a limited absorption range, some sunlight can pass through the sheet unabsorbed. Fluorescence emission is only trapped inside the sheet if the angle of incidence with the surface is greater than the critical angle.
Fluorescence emission can also be re-absorbed by the fluorophore molecules if their absorption spectrum overlaps the emission; thus only a small portion of the created fluorescence reaches the collector edges in large plates. Re-absorption results in a loss because fluorescence which was originally trapped within the sheet may be directed out of the sheet and lost.

As a result of these intrinsic deficiencies, optical efficiencies have so far been too low for practical use. The technology disclosed herein provides a development for achieving increased efficiencies.

Thus, in one aspect of the present invention, there is provided a luminescent solar concentrator (LSC) capable of totally absorbing solar energy in the UV and visible regions of the spectrum. A total separation between absorption and fluorescence achieved by a two-rare earth ions or complexes thereof (herein referred to as the "luminescent system") utilized in accordance with the invention, prevents the self-absorption (which causes efficiency lose in large plates) of luminescence. There is no energy transfer between the donor and the acceptor entities in the luminescent system and each of them contributes totally to the fluorescence.

The LSC of the invention is capable of absorbing solar energy in the UV and visible regions of the spectrum; it incorporates a luminescent system comprising at least two rare-earth (RE) materials in a form selected from rare-earth ions and rare-earth complexes, the LSC being in the form of stacked sheets, each sheet in said stack being separated from the other by an air-gap.

In some embodiments, the rare-earth materials being based on rare-earth (RE) elements selected from elements of the periodic table having a Z value of 21, 39 or any one value from 57 and 71. In some embodiments, the RE elements are lanthanides.

In some embodiments, the at least two RE materials may be based (ions or complexes) on the same RE element, or on two or more elements, each of which being an ion or a RE element or a complex of a RE element or mixtures of ions and complexes of RE elements.

In accordance with the present invention, the luminescent system is incorporated in the LSC sheets (glass sheets, plates) either by employing a sol-gel film in which the luminescent system is distributed or by incorporating the luminescent system in a plurality of pores in the sheet material (porous glass plates).
In some embodiments, the luminescent system is incorporated in a sol-gel coating on the surface of the glass plate.

In other embodiments, the luminescent system is incorporated in a plurality of pores in the glass plate.

As stated above, the luminescent system utilized in accordance with the invention, may be one or more of the following:

(1) an ion such as Ce$^{3+}$, Pb$^{2+}$, Bi$^{3+}$ in combination with a lanthanide salt;
(2) a lanthanide complex with an organic ligand, wherein the ligand acts as the solar absorbent;
(3) a lanthanide-ligand complex together with a metal plasmon selected from silver plasmon, gold plasmon, copper plasmon, platinum plasmon, palladium plasmon, ruthenium plasmon, rhodium plasmon, osmium plasmon, iridium plasmon and alloys thereof;

Thus, the luminescent solar concentrator (LSC) of the invention comprises a luminescent system selected from:

(1) ions selected from Ce$^{3+}$, Pb$^{2+}$, Bi$^{3+}$ in combination with at least one lanthanide salt;
(2) at least one lanthanide complex with at least one organic ligand, wherein the ligand acts as the solar absorbent;
(3) a lanthanide-ligand complex together with a metal plasmon selected from silver plasmon, gold plasmon, copper plasmon, platinum plasmon, palladium plasmon, ruthenium plasmon, rhodium plasmon, osmium plasmon, iridium plasmon and alloys thereof;

In some embodiments, the luminescent system comprises a lanthanide material.

In some embodiments, the lanthanide material comprises a lanthanide ion such as Ce or Pr or Gd or Eu or Tb or Dy or Er or Tm or Nd or Yb or any combination thereof or a complex of these ions. The lanthanide material may be combined with at least one of:

(1) ions selected from Ce$^{3+}$, Pb$^{2+}$, Bi$^{3+}$;
(2) silver plasmons;
(3) gold plasmons; and
(4) copper plasmons.
In some embodiments, the lanthanide is employed as a lanthanide chelate. In other words, the lanthanide complex is presented in the form of a molecular entity containing a central lanthanide ion, associated with at least one bidentate ligand and one or more monodentate ligands; or with a multidentate ligand. The bonds between the lanthanide atom and the ligand(s) may be selected from covalent bonds, ionic bonds, and coordinative bonds.

The term "ligand", as used herein, generally refers to a molecular group that is associated with the lanthanide atom. The ligand may be selected amongst ligands which are capable of forming a chelate with the lanthanide.

In some embodiments, the ligand may be selected from monodentate, bidentate, tridentate, tetradeinate and multidentate ligands.

In some embodiments, the ligand is an organic ligand. In some embodiments, the organic ligand is selected amongst monodentate, bidentate, tridentate, tetradeinate and multidentate organic ligands.

In some embodiments, the organic ligand has a conjugated electronic structure. In some embodiments, the organic ligand is a polynuclear heterocyclic aromatic compound, which may optionally have two or more fused ring structures. In some embodiments, the aromatic organic ligands are selected from rhodamine, fluorescein, fluorescein, 2-quinolone, 4-quinolone, 4-trifluoromethylcoumarin (TFC), 7-diethylamino-coumarin-3-carbohydrazide, 7-amino-4-methyl-2-coumarin, 7-amino-4-methyl-2-coumarin, 7-amino-4-trifluoromethyl-2-coumarin, and aminomethyltrimethylpsoralen.

In some embodiments, the organic ligands may be prepared according to procedures detailed inter alia in US Patent Nos.: 5,639,615; 5,656,433; 5,622,821; 5,571,897; 5,534,622; 5,220,012; 5,162,508 and 4,927,923, each of which being incorporated herein in its entirety.

In some embodiments, the organic ligand may be selected amongst cryptands, podands, calixarenes, macrocyclic ligands, 1,3-diketones, hetero-biaryl ligands, carboxylic acid derivatives, terphenyl ligands, and proteins.

In some embodiments, the lanthanide complex is a complex with a cryptand.

As used herein, a "cryptand" is a bi- or a polycyclic multidentate ligand. The cryptand is selected amongst such having a cyclic or polycyclic assembly of binding
sites. In some embodiments, the number of binding sites through which association with a lanthanide ion may occur is at least three.

In some embodiments, the cryptand ligand is selected to contain conjugated organic moieties. In some embodiments, the cryptand ligands are selected from tribipyridine pentacarboxylates such as trisbipyridine (TBP, e.g., TBP pentacarboxylate), and pyridine bipyridine (e.g., pyridine bipyridine tetracarboxylate). In some embodiments, the cryptand ligands are prepared according to methodologies known inter alia from US Patent Nos. 5,639,615; 5,656,433; 5,622,821; 5,571,897; 5,534,622; 5,220,012; 5,162,508 and 4,927,923, each of which being incorporated herein in its entirety.

In some embodiments, the lanthanide material is combined with metal plasmons selected as above.

The term "metal plasmon" according to the present invention has the standard meaning known in the art. The metal plasmons are provided in combination with the lanthanide material, e.g., lanthanide complex, as metal nanoparticles of silver, gold, platinum, palladium, ruthenium, rhodium, osmium, or iridium, and alloys thereof. In some embodiments, the metal plasmons are selected from gold, silver and copper plasmons.

The metal nanoparticles may have any one dimension in the nanoscale. In some embodiments, the plasmon metal nanoparticles are less than about 500 nm in diameter. In some embodiments, the nanoparticles are less than about 200 nm in diameter. In some embodiments, the nanoparticles are less than about 100 nm in diameter, less than about 50 nm in diameter, less than about 25 nm in diameter or less than about 10 nm in diameter.

The sheets, plates or generally the substrate constructing the LSC may be made from glass, porous glass, quartz, indium tin oxide (ITO), fluorinated tin oxide (FTO) or mica. In some embodiments, the acceptor-donor system may be incorporated either in a transparent ornoncer matrix or in porous glasses deposited on transparent glass sheet. The coating thickness may be between 1 μm and 10 μm or between 100 nm and 100 μm.

The LSC of the present invention utilizes three plates each plate consists of two rare earth ions or their complexes. Each pair absorbs solar energy and emits it at longer wavelengths. No overlap between exists between absorption and emission.
Thus the invention also provides a stack of several LSC sheets (2 or three), each sheet being incorporated by two fluorescent species with no overlapping of their absorption or emission spectra. The sheets are stacked to ensure that sunlight strikes sheets containing the luminescent system with higher quantum yields and shorter emission wavelengths first. In such a construction, electrical output is taken separately from each sheet and combined externally. This has the advantage that the systems do not affect the photon transport inside the sheets with high-quantum yield systems.

Stacked sheets can also result in lower fluorescent losses, as the losses from one sheet can be re-absorbed by an adjacent sheet if the luminescent system in the adjacent sheet has a suitable absorption range. An additional advantage of a multi-sheet system is the possibility of matching the edge emission wavelength of each sheet to a different type of solar cells.

Thus in another aspect there is provided a luminescent solar concentrator comprising of three plates (porous glasses or thin films on transparent glasses) incorporated by fluorescence species that absorb the entire solar light in UV and visible part of the spectrum with no overlapping of absorption and emission circumventing reabsorption losses. The fluorescence is strongly enhanced by surface plasmons created by excitation of silver, gold and copper nanoparticles.

In some embodiments, the LSC of the invention comprises at least three transparent substrates (glass plates), each of said substrates comprising same or different acceptor-donor pair system. In some embodiments, each of substrates in a three-substrate LSC may be colored, and different layers may have a different color.

In some embodiments, in the LSC stack the upper sheet may be colored with a fluorescent violet/blue fluorescent species, the middle sheet may be colored with a fluorescent green fluorescent species, and the bottom sheet may be colored with a fluorescent red fluorescent species.

The LSC may further comprise any one or more solar cells, an anti-reflective coating on a top surface and a reflecting coating on a bottom surface.

In some embodiments, each of the plates making up the LCS stack may be separated by an air-gap having a thickness of between 1 and 20 nm.

The invention also provides a unit for use in the LCS according to the invention, the unit comprising one or more transparent substrate utilizing a pair of not reabsorbing fluorescent species that are selected in such way that each of them absorbs a part of
solar spectrum and emits fluorescence at longer wavelengths without overlap of absorption with the emission.

The invention thus provides a luminescent solar concentrator (LSC) capable of absorbing solar energy in the UV and visible regions of the spectrum, the LSC incorporating a luminescent system comprising at least two rare earth materials in a form selected from rare-earth ions and rare-earth complexes, the LSC being in the form of stacked sheets, each sheet in said stack being separated from the other by an air-gap.

In some embodiments, the luminescent system is incorporated in a plurality of LSC sheets by employing a sol-gel film in which the luminescent system is distributed or by incorporating the luminescent system in a plurality of pores in the sheet material.

In some embodiments, the luminescent system is incorporated in a sol-gel coating on the surface of the glass plate.

In some embodiments, the luminescent system is incorporated in a plurality of pores in the glass plate.

In some embodiments, said rare-earth material is a lanthanide material selected from:

1. a lanthanide salt in combination with an ion selected from Ce, Pb and Bi;
2. a lanthanide complex with an organic ligand; and
3. a lanthanide-ligand complex in combination with a metal plasmon.

In some embodiments, the lanthanide material comprises a lanthanide selected from La, Ce, Pr, Gd, Eu, Tb, Dy, Er, Tm, Nd, Yb or any combination thereof or a complex of these ions.

In some embodiments, the LSC sheet is selected from glass, porous glass, quartz, indium tin oxide (ITO), fluorinated tin oxide (FTO) or mica.

In some embodiments, the LSC sheet is ormocer matrix or a porous glass.

In some embodiments, the coating thickness is between 1 µm and 10 µm or between 100 nm and 100 µm.

In some embodiments, the metal plasmon is selected from silver plasmon, gold plasmon, copper plasmon, platinum plasmon, palladium plasmon, ruthenium plasmon, rhodium plasmon, osmium plasmon, iridium plasmon and alloys thereof.

In some embodiments, the metal plasmon is selected from silver, gold and copper.

In some embodiments, said metal plasmons are in the form of nanoparticles.
In some embodiments, the lanthanide material comprises a lanthanide ion selected from Ce, Pr, Gd, Eu, Tb, Dy, Er, Tm, Nd, Yb and any combination thereof or a complex of these ions, in combination with at least one of ions selected from Ce$^{3+}$, Pb$^{2+}$ and Bi$^{3+}$, silver plasmons, gold plasmons and copper plasmons.

In some embodiments, the lanthanide is in the form of a molecular entity containing a central lanthanide ion, associated with at least one bidentate ligand and one or more mono- or multi-dentate organic ligands.

In some embodiments, the ligand is selected amongst monodentate, bidentate, tridentate, tetradentate and multidentate organic ligands.

In some embodiments, the organic ligand is a polynuclear heterocyclic aromatic compound, optionally having two or more fused ring structures.

In some embodiments, the aromatic organic ligands are selected from rhodamine, fluorescein, fluorescein, 2-quinolone, 4-quinolone, 4-trifluoromethylcoumarin (TFC), 7-diethyl-amino-coumarin-3-carbohydrazide, 7-amino-4-methyl-2-coumarin, 7-amino-4-methyl-2-coumarin, 7-amino-4-trifluoromethyl-2-coumarin, and aminomethyltrimethylpsoralen.

In some embodiments, the organic ligand is selected amongst cryptands, podands, calixarenes, macrocyclic ligands, 1,3-diketones, heterobiaryl ligands, carboxylic acid derivatives, terphenyl ligands, and proteins.

In some embodiments, said ligand is a cryptand.

In some embodiments, said cryptand is selected from bi- and polycyclic multidentate ligand.

In some embodiments, said cryptand is selected amongst cryptands having a cyclic or polycyclic assembly of binding sites.

In some embodiments, the cryptand ligand is selected from tribipyridine pentacarboxylates.

In some embodiments, said ligand is selected from trisbipyridine and pyridine bipyridine.

In some embodiments, the LSC is constructed of three plates; each plate consisting two rare earth ions or their complexes.

In some embodiments, the LSC is the form of a stack of several LSC sheets, each sheet being incorporated by two fluorescent species with no overlapping of their absorption or emission spectra.
In some embodiments, the LSC comprises three plates, each being incorporated by fluorescence species that absorb the entire solar light in UV and visible part of the spectrum with no overlapping of absorption and emission spectra, thereby circumventing re-absorption losses. In some embodiments, each of said plates comprises same or different luminescent species.

In some embodiments, in the LSC stack the upper sheet may be colored with a fluorescent violet/blue fluorescent species, the middle sheet may be colored with a fluorescent green fluorescent species, and the bottom sheet may be colored with a fluorescent red fluorescent species.

In some embodiments, the LSC further comprises any one or more solar cells, an anti-reflective coating on a top surface and a reflecting coating on a bottom surface.

In some embodiments, the LSC is a solar cell. In some embodiments, the LSC is incorporated in a solar cell.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In order to understand the invention and to see how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

**Fig. 1** depicts loss mechanisms in LSCs: 1-reflection from the surface; 2-light not absorbed by the fluorescent species; 3-quantum efficiency of the colorant less than one; 4-light emitted outside the capture cone; 5-re-absorption of emitted light by another dye molecule; 6-internal matrix scattering and absorption; 7-solar cell losses, and 8-internal waveguide scattering;

**Fig. 2** shows increase of the fluorescence of the compound 6,60-diheptyl (2,20-bipyridyl)- 3,30-diol in presence of silver nanoparticles: 1-excitation and emission spectra of the compound without silver nanoparticles; 2-excitation and emission spectra of the compound with silver nanoparticles; 3-extinction spectrum of the silver nanoparticle in film of polyvinyl butyral;

**Fig. 3** shows the energy diagram of trivalent RE relevant transitions for LSCs;

**Fig. 4** depicts optical excitation and emission of 2 wt.% Ce(¾-doped LSCAS glass, monitoring the emission at 410 and 550 nm. The dark lines are the emission
obtained under 320-nm excitation and the lighter lines represent the emission under 405-nm excitation;

Fig. 5 shows a profile of the optimize luminescent solar concentrator;
Fig. 6 shows the excitation and emission spectra of Ce³⁺-doped glass;
Fig. 7 shows the excitation and emission spectra of divalent Europium in borosilicate glasses;
Fig. 8 shows the emission spectra of Tb³⁺-codoped glass;
Fig. 9 shows the absorption spectra of silver spheroid nanoparticles obtained in an ormosils composite matrix;
Fig. 10 shows polyurethane silica obtained by a sol-gel polycondensation reaction of diurethane-siloxane;
Fig. 11 shows the chemical structure of the Europium complex;
Fig. 12 shows the structure of **Eu-RR-2-4** complex tris-[2-(N-diphenylphosphin oxycarbamoyl)aminoethyl]-amine;
Fig. 13 shows the emission spectra of the complexes incorporated in silica-polyurethane films in the presence of silver nanoparticles for the Europium **Eu-RR-2-4** complex;
Fig. 14 shows the tetrapodal octadentate chelating agent TsoxMe in which the chromophoric moieties are connected to a N,N,N°,N°-tetra-aminopropyl-2-ethylenediamine framework proved to generate a good antenna effect for Yb³⁺;
Fig. 15 shows the low-resolution emission spectra of YbTsoxMe at 295 K;
Fig. 16 shows UV-vis absorption spectra of copper colloids prepared in aqueous acetonitrile solution by borohydride reduction under an argon purge;
Fig. 17 shows the excitation spectrum of Nd³⁺ and Nd³⁺ + U0 ²⁺;
Fig. 18 shows the emission spectrum of Nd³⁺;
Fig. 19 shows the solar spectrum (1), the spectrum of the sensitivity of a silicon photovoltaic ceil, (3) and the spectrum of the sensitivity of an AlGaAs photovoltaic cell;
Fig. 20 shows the quantum efficiency for solar cells: AlGaAs (1), CdS/CdTe (2), monocrystalline silicon (3), amorphous silicon (4) and the solar spectrum (5).

**DETAILED DESCRIPTION OF EMBODIMENTS**

The sol-gel method is a low-temperature technique for creating solid glass bulks or thin-films. Using this method, coatings on glass, ceramic, metal or other solid
substrates may be easily fabricated. In addition, the relatively gentle synthetic conditions allow for the addition of various dopands such as organic dyes or inorganic ions, which convert the resulting glass/dopant combination into an active material which may be used in accordance with the invention, e.g., in various optical or sensing applications. The incorporation of organic materials into glasses prepared using sol-gel methods permits the formation of unique thin-film sol-gel coatings required for the applications of the present invention.

The precursor solution for sol-gels consists of various alkoxydes or inorganic sols. This solution was applied by dip coating, spin coating or laminar coating. The most common precursors are utilized for obtaining a variety of silicates, titania, germanate, alumina, zirconia, tungstate, vanadates and ormosils.

The sol-gel process is based on hydrolysis and polycondensation reactions of metalorganic compounds such as silicon alkoxide compounds. As an example for a silicon alkoxide is the family of tetra alkoxy silanes which have the general form Si(OR)₄, where R is an alkyl group and therefore OR is an alkoxy group, mostly, ethoxy or methoxy; these being tetraethoxy-silane (TEOS) and tetramethoxy-silane (TMOS). TEOS or TMOS were used as a component in a starting mixture which contains also water, as the second reactant.

Basically, the sol-gel process can be realized without using any solvent, but in most cases, a solvent (alcohol for example) may be used in the starting mixture in order to control the reaction rate of the process. The molar ratio between the different components of the starting mixture has a great influence on the final product.

In the starting mixture which includes tetra alkoxy silane and water, hydrolysis reactions of the form \(=\text{Si-OR}+\text{H}_2\text{O} \rightarrow =\text{Si-OH}+\text{ROH} \) occur. This is the first stage of the sol-gel process. A complete hydrolysis of a tetra alkoxy silane molecule: \(\text{Si(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{ROH} \) and a solution of silanol groups, \(\text{Si(OH)}_4\), in alcohol is obtained. The hydrolysis can be catalyzed by acidic catalysts in electrophilic mechanism. The reaction rate of the hydrolysis is increased with the strength of the acid; therefore, \(\text{HCL}\) and \(\text{HNO}_3\) are common catalysts. On the other hand, base can also catalyze the reaction, by a nucleophilic mechanism. The reaction rate of the hydrolysis is also influenced by steric considerations and is decreased with the size of the alkoxy group. For this reason, TMOS hydrolysis is faster than TEOS hydrolysis.
The second stage of the process includes polycondensation interactions of the hydrolysis products. Each condensation reaction of two hydrolysis products has the form: \( \equiv\text{Si} -\text{OH}+\text{HO-Si} \equiv \leftrightarrow \equiv\text{Si} -\text{O-Si} \equiv +\text{H}_2\text{O} \). If one considers, for simplicity, an ideal model in which condensation reactions take place only after a complete hydrolysis, one may assume that the reactants are silanols and a general form which describes the polycondensation stage is: \( n\text{Si(OH)}_4 \rightarrow (\text{SiC}_2)_n + 2n\text{H}_2\text{O} \). The result of the polycondensation reactions is the creation of inorganic three dimensional crosslinked polymer, leading to formation of sol particles. Further condensation reactions link between the sol particles forming wet gel. Evaporation of the liquids leads to dry gel (xerogel).

The glass obtained by the sol-gel process is porous. The polycondensation can be catalyzed by hydrofluoric acid (HF), since F- ions can replace hydroxyl ion in the hydrolysis product Si(OH)4 and being more electronegative than the hydroxyl, they increase the attraction to other silanols, leading to Si-O-Si bonds. In a similar way, the polycondensation can be catalyzed by a base. The rate of the condensation reaction influences glass porosity. Higher condensation reaction rates result in higher porosity. Therefore, the choice of catalyst (acid or alkaline) allows a degree of control of the porosity of the glass. For example, when HF is used as a catalyst the porosity increases with increasing concentration of HF. Heating the glass to high temperatures evaporates the water leading to dehydroxylation and complete condensation, which stabilizes the glass.

The mechanical and optical properties of glasses prepared by the sol-gel process can be improved by modifying the sol process by using a variety of organo-functional silicone alkoxides. Modified alkoxide precursors RSi(OEt)3 where R is a nonhydrolizable group such as methyl, vinyl or amyltriethoxysilane (denoted as MTEOS, VTEOS and ATEOS, respectively) lead to organic-inorganic hybrid matrices. The covalently bonded organic groups decrease the mechanical tensions during the drying process. Functionalized alkoxides F-R'Si(OEt)3, where F is a chemical function such as an amino or isocyanate group and R' is an alkyl spacer, allow to covalently graft onto the xerogel matrix to avoid phase separation and consequently to increase the concentration of the guest molecules.

The various characteristics of the sol-gel process (metallo-organic precursors, organic solvents, low processing temperatures, processing versatility of the colloidal
state, etc.) allow the introduction of "sensitive" organic molecules inside the inorganic network. The inorganic and organic components, such as those utilized in accordance with the invention, may be mixed at the nanometer scale, in virtually any ratio, leading to the formation of the so-called hybrids organic/inorganic nanocomposites. These hybrids are extremely versatile in their composition, processing and optical and mechanical properties. The properties of hybrid materials do not depend only of interface between both phases, which can be used to tune many properties. The general tendency is to increase the interfacial interactions by creating intimate mixing and/or interpenetration at the nanometer scale between both components.

The nature of the interface between the organic and inorganic components has used to classify these hybrid nanocomposites into two classes. Class I corresponds to all those systems where organic and inorganic components only exchange weak interactions such as van der Waals, hydrogen bonds or electrostatic forces. On the contrary in class II materials, at least a part of the organic and inorganic components are linked through strong chemical bonds (covalent or ionic-covalent).

Among hybrid compounds, siloxane-based materials present several advantages for the design of materials for photonics: firstly, many precursors are commercially available or can be easily modified or synthesized; secondly, the control of precursor reactivity can be achieved by using acid, basic or nucleophilic catalysts; thirdly, transparent films or monoliths having a good mechanical integrity can be easily processed; and fourthly, the resulting materials are generally not toxic. The precursors of siloxane-based hybrids are organo-substituted silicic acid esters of general formula R'nSi(OR)4-n' where R' can be any organo-functional group and R is an alkyl group. If R' is a simple non-hydrolyzable group bonded to silicon through a Si—C bond, it will have a network modifying effect (e.g. SiCH3). On the other hand, if R' can react with itself (R' contains a methacrylate group for example) or additional components, it will behave as a network former. Network modifiers and network former functionalities can also be used to target many other specific properties (e.g., photochemical, electrochemical, optical).

Therefore, numerous siloxane-based hybrid organic/inorganic materials have been developed in the past few years. This development yields many interesting new materials, with improved mechanical properties, tunable between those of glasses and those of polymers.
The mechanical and optical properties of glasses, prepared by the sol-gel, may be further improved by modifying the sol process using a variety of organofunctional silicon alkoxides. Modified alkoxide precursors, RSi(OEt)₃ or RSi(OMe)₃ (where R is a non-hydrophobic group), such as methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), amyltriethoxysilane (ATEOS), 3-(trimethoxysilyl)propylmethacrylate (TMSPMA), methyltriethoxysilane (MTEOS), 3-glycidoxypropyltrimethoxysilane (GLYMO) or methyltrimethoxysilane (MTMOS) lead to organic-inorganic hybrid matrices. The permanent organic group decreases the mechanical tensions during the drying process. Functionalized alkoxides F-R’—Si(OEt)₃, where F is a chemical function such as an amino or isocyanate group and R’ is an alkyl spacer, allow to covalently graft onto the xerogel matrix to avoid phase separation and consequently to increase the concentration of the guest molecules. After drying, optically clear and dense inorganic/organic hybrid xerogels (30 mm diameter and 15 mm thick) were obtained.

The matrix of zirconia-silica-polyurethane (ZSUR) may also be used. This matrix allows incorporation of a wide range of photonic molecules and possesses the high mechanical and thermal stability and high refractive index. The matrix of polyethylene urethane silica possesses the high mechanical and thermal stability and high refractive index of zirconium oxide. By combining the strength and hardness of sol-gel matrices with the processability and ductility of polymers, novel transparent hybrid material can be obtained.

Diurethane siloxane (DURS) was synthesized from 3-isocyanatopropyl triethoxysilane (ICTEOS) and polyethylene glycol (PEG), chloro benzene was used as a solvent. The epoxy-silica-ormosil (ESOR) precursor was obtained from tetramethoxysilane (TMOS) and 3-glycid oxypropyl trimethoxysilane (GLYMO). These two types of ormols were combined with zirconium oxide matrix which was used as an inorganic hetero network and as an efficient catalyst for the epoxy polymerization.

Due to strong chemical bonding between organic and inorganic parts, the hybrid materials offer superior mechanical properties (elasticity, flexibility) and are suitable for incorporation of organic dyes. The hybrid materials were obtained by using three precursor composites: (a) poly(ethylene)glycol chain covalently linked by urethane bridges with thriethoxysilane groups synthesized separately, (b) epoxy-silica ormosil precursor and (c) a zirconium oxide precursor. The solubility of most laser dyes is
limited in pure hydrophobic or hydrophilic matrices, which can cause migration and aggregation of the dyes, resulting in decreased efficiency when used in a laser. The novel organic-inorganic ORMOCER matrix can efficiently solubilize many laser dyes. The combination of two types of clusters creates two sub-phases with different degrees hydrophilicity/hydrophobicity, and results in an active interface. Polymethylmetacrylate (PMMA), polyethylene glycol dimethacrylate (PEGDM), polyurethane (PU) and various epoxides have also been used as polymer hosts for solid state dye lasers.

Common precursor list for preparation of laser matrices

Silica precursor list:
Tetraalkoxysilanes, general form: Si(OR)₄
TEOS—trimethoxysilylen, Si(OCH₃)₄
TMOS—trimethoxysilylene, Si(OCH₃)₄
Organoalkoxysilanes, general form: G-Si(OR)₃
TMSPMA-3-(trimethoxysilyl)propylmethacrylate, C₇H₁₈O₂-Si-(OCH₃)₃
GLYMO-3-glycidoxypropylmethacrylate, C₆H₁₀O₂-Si-(OCH₃)₃
MTMOS—methyltrimethoxysilane, CH₃-Si-(OCH₃)₃

Zirconia precursor list.
Zirconium-n-propoxide, Zr(OCH₃)₄

Organic monomers for polymerization:
MMA—methyl methacrylate, CH₂C(CH₃)COOCH₃
EGDM—ethylene glycol dimethacrylate,
CH₂C(CH₃)COO-CH₂-CH₂-OOC(CH₃)CH₂.

Composite glass/polymer hosts:
First, a standard sol-gel glass using acidic catalysis was prepared. Then, MMA with 1.5 x 10⁻⁴ M dye laser dye was allowed to diffuse into the porous glass. The monomers were polymerized by drying for a few weeks at 40°C, after which the impregnated samples were polished to obtain high optical quality.
Organically modified silicates:
ORMOSIL: TMOS, MTMOS and GLYMO commonly used as precursors to create a sol-gel glass in which dye are incorporated in a one step process.

Luminescent solar concentrators based on the sol-gel method
LSCs operate on the principle of collecting solar radiation over a large area, converting it to luminescence (commonly expressed as fluorescence) and directing the generated radiation into a relatively small output target. The concentration of the absorbed solar light is proportional to the ratio of the plate surface to its edges. Efficient LSCs are based on the entrance of solar radiation into a homogeneous medium of collector containing a fluorescent species in which the emission bands have little or preferable overlap with the absorption bands.

This emission is trapped by total internal reflection and concentrated at the edge of the collector by the geometrical shape which is usually a thin plate. Thus, the concentration of light trapped in the plate is proportional to the ratio of the surface area to the edges. The advantages of LSC over conventional solar concentrators are the following:

(a) High collection efficiency of solar light direct and diffuse;
(b) Good heat dissipation from the large area of the collector plate in contact with air, so that essentially "cold light" is used for converter devices such as silicon cells, whose efficiency is reduced by high temperatures;
(c) Tracking of the sun unnecessary; and
(d) Choice of the luminescent species allows optimal spectral matching of the concentrated light to the maximum sensitivity of the photovoltaic (PV) process, minimizing undesirable side reactions in the PV cells;
(e) Shift of the light by the solar cell to longer wavelength where the sensitivity of the solar cell is higher;
(f) Possibility of incorporating the LSCs as a part of existing buildings;
(g) Possibility of guiding the solar light to dark areas (day lightning).

Fig. 1 demonstrates the loss mechanism in LSC.

The performance of LSC is given by the effective concentration ratio which is the product of the geometrical factor and the optical conversion efficiency of the
collector. The optical efficiency of the plate, which is the energy coming out of the edges of the plate divided by the energy falling on the plate, including reflection.

The parameters determining the optical plate efficiency depend on the following factors:

a) The fraction which is the ratio of photons absorbed by the plate to the number of photons falling on the plate;

b) The quantum efficiency of fluorescence which is the ratio of the number of photons emitted to the number of photons absorbed;

c) The Stokes efficiency which is the ratio of the average energy of emitted photons to the average energy of the absorbed photons;

d) The trapping efficiency of the light trapped in the collector. The trapping efficiency can be increased by applying photonic crystals. A photonic structure which serves as a band-stop reflection filter for the light-emitted from the dye increases the trapping efficiency of a collector preventing the escape from the system (as shown below);

e) The transport efficiency which takes into account the transport losses due to matrix absorption and scattering;

f) The efficiency due to losses arising from self-absorption of the colorants.

The overall power efficiency obtained from a fluorescent plate connected to photovoltaic cells is the product of plate efficiency to that of the solar cells.

**Non-self-absorbing systems based on proton transfer**

A system undergoing excited state intramolecular proton transfer was suggested as a solar energy collector. Moreover, since such systems reveal a very large Stokes shift due to the excited state intramolecular proton transfer (ESIPT) reactions, resulting in the photo-tautomeric fluorescence with a relatively high quantum yield (about 30%), they are recommended as potential solar energy concentrators. In many cases the reaction is so fast in comparison to the primary luminescence emission that the latter is not observed. In consequence, the only fluorescence observed is the band emitted by the excited product of such reaction. The resulting emission is energetically largely separated from the absorption, sometimes by $10^4$ cm$^{-1}$. This phenomenon is called the anomalous Stokes shift. The best known group of such luminophors is represented by the systems undergoing the Excited State Intramolecular Proton Transfer (ESIPT)
reactions. In majority of these systems the reaction is 'prepared' by the intramolecular hydrogen bond. As an example can serve 6,60-diheptyl-bipyridyl-diol (DH-BP(OH)2). This compound is proposed as a model luminescent molecule exhibiting the above described property of separation from absorption spectrum.

**Fig. 2** presents an example of the absorption and emissions spectra of the molecule and in addition the intensity of fluorescence increase as result of silver nanoparticles co-existing with the colorant by 34%. The enhancement of fluorescence by the plasmons of silver NPs is elaborated hereinbelow and will play an important role in increasing efficiency of LSCs. **Fig. 2** shows the enhancement of fluorescence of the compound 6,60-diheptyl (2,20-bipyridyl)-3,30-diol by influence of plasmons of silver NPs. The efficiency of the system can be increased additionally by silver plasmons. While the phenomenon of increase of fluorescence in the presence of silver plasmons has an effect, the separation of absorption from emission prevents self-absorption when the fluorescent light travels along way. It should be stated that the lifetimes of the fluorescent molecules in presence of silver nanoparticles decreased as a result of the increase of transition probabilities. In the case of DH-BP(OH)2 in polyvinyl-butyral (PVB) lifetime of the DH-BP(OH)2 fluorescence in the PVB films appeared nearly the same in absence and in presence of silver nanoparticles. This important observation indicates that the increased fluorescence efficiency does not result from increasing emission rate, kf, but rather from increasing efficiency of excitation in the neighborhood of the Ag NPs.

An interaction of the fluorophore molecule, with the scattered light from silver surface plasmons in the neighborhood of the Ag NPs enhances the excitation of the fluorophore. This can be understood since absorption and emission originate from different electronic levels. It should be noted that DH-BP(OH)2 is a new compound belonging to the family of molecules widely studied and described in the literature as strongly fluorescent systems with large Stokes shift.

**Lanthanide complexes as a way to prevent self absorption**

Another possibility to overcome the self absorption is to separate the emission from absorption by using RE complexes which can be excited in their charge transfer state or using the f-d transitions.
Recent developments in the field of supramolecular chemistry have allowed the design of ligands capable of encapsulating lanthanide ions, thus forming kinetically inert complexes. By introduction of chromophoric groups in these ligands, an intense luminescence of the ion can be obtained via the "antenna effect", defined as a light conversion process involving distinct absorbing (ligand) and emitting (metal ion) components. In such a process, the quantities that contribute to the luminescence intensity are the efficiency of the absorption, the efficiency of the ligand-to-metal energy transfer, and the efficiency of the metal luminescence. Encapsulation of lanthanide ions with suitable ligands may therefore give rise to "molecular devices" capable of emitting strong, long-lived luminescence.

In conclusion, the inventor of the invention disclosed herein, presents the possibility to strongly increase the emission intensity of RE by incorporating their macrocyclic complexes in stable glasses. In order to use the model for exchange interaction, which arise from the overlap of the ligands function with the excited state of the RE, the geometry of the complex and the distances between the RE and the ligand atoms should be determined. The efficiency of luminescence of RE complexes depends on several processes, among others light absorption by the complex, energy transfer from the ligand to the Ln(III) ion, multiphoton relaxation and energy-back transfer. The charge-transfer states can also play an important role. The studies of the decay times and the respective rate constants of these processes in many systems can finally lead to finding new materials with highly efficient emission at room temperature.

As mentioned above the weak luminescence of RE arising from Laporte forbidden f-f transition can be strongly enhanced by preparing a complex with strong light absorbing ligands followed by energy transfer from the ligands to the RE ion. Such complexes may be seen as light conversion molecular devices (LCMDs), coining the term "antenna effect" to donate the absorption, energy-transfer, emission sequence involving distinct absorbing (the ligand) and emitting (the RE ion) components, thus overcoming the very small absorption coefficients of the lanthanide ions. The design of efficient lanthanide complexes has become an important research goal.

Silicon inorganic and organic-inorganic hybrids, synthesized through sol-gel process may be used to produce silica glasses with trapped Tb\(^{3+}\) and Eu\(^{3+}\) fluorescent compounds. Silicon hybrids have, as advantage, their very low solubility in water and in many polar and non-polar solvents, as well as their high thermal stability.
Other important matrices for incorporation of the complexes are zirconia glasses. Organic complexes of rare earths doped in zirconia and zirconia-GLYMO have much higher fluorescence then in pure inorganic matrices. Zirconia glasses were chosen because of their photo- and mechanical stability. The excitation and emission spectra of the glasses incorporated by the complexes were compared to Eu and Tb oxides in the identical glasses. The ratio of the intensities of the complexed species to that of uncomplexed oxides was about 30 times.

**Fig. 3** shows the energy diagram of trivalent RE relevant transitions for LSCs. An example of Ce³⁺ in glasses can be found in **Fig. 4**. Ce is important in absorbing light in UV and blue part of the solar spectrum and transferring it to the number of RE complexes. In these studies it was noted that the self-absorption is low in the inorganic material, especially when the absorption and emission arises from different electronic levels in the same ion or the absorption and emission originate from different species which transfer energy between them. It may be quite appreciable in organic dyes which have overlapping absorption and emission spectra when the dyes are homogeneously dispersed in a plastic or liquid solvent. This may decrease significantly the optical plate efficiency of the collector based on organic dyestuffs in homogeneous media. The self-absorption is reduced in the thin film configuration where the emitted luminescence travels in an optically transparent medium. Self-absorption can also be diminished to some extend by utilizing energy transfer from an acceptor molecule to the donor molecule, thus separating the absorption and emission bands.

A dramatic increase of luminescence may be observed by using diheptyl-bipyridyl-diol, organic dyes and other species in the presence of silver, gold and copper NPs (plasmons) as compared to the luminescence of the same complex without plasmons. Since the absorption coefficient of the NPs is higher by six orders of magnitude than that of organic molecules. The finding that Ag, Au and Cu NPs increase the laser dye fluorescence in glassy medium leads to important consequences in designing new active fluorescent materials.

The sol-gel procedure was used for Ag crystals growth process; reduction of silver NPs was performed in situ in hybrid composite ormosil sol-gel solution using silver nitrate and dimethylformamide (DMF); the hybrid composite matrix involves diurethane terminated silica network which acts as a stabilizing and coupling agent.
The interaction of RE with silver NPs was also used for increased of upconversion of infrared energy which cannot be used for solar cells, to visible light where the solar cells are sensitive. Energy transfer enhanced by silver plasmons allowed a strong upconversion from infrared light absorbed by Yb to visible photoluminescence of Er.

The optical absorption and emission of Rh B with CuNPs incorporated into glass films formed by sol-gel method were studied by steady state and picosecond spectroscopy. The observed increased luminescence is the result of interaction of the excited state of the dye with scattered light created by copper plasmons and possible energy transfer from the excited Cu NPs which occur at femtosecond time range. The steady state absorption, excitation, fluorescence and lifetimes excited by picosecond pulses were measured. The quantum efficiencies of the films were obtained by comparative method.

In an LCS according to the invention, the optimal plates may be used for providing electricity or as active waveguides transporting light to dark areas during the day. Fig. 5 presents a picture of optimized LSC which absorbs in the total spectral range and emits at longer wavelengths (without overlapping of absorption with emission) of available solar energy being the band gap of solar cell the plates are separated by energy gap in order to prevent leakage of fluorescence from one layer to another.

Thus, it may be concluded that the LSCs of the invention, having high efficiency and stability, may be used in a broad spectrum of applications, e.g., in populated areas in part of existing buildings, in dark mines, etc. The development of increasing efficiencies of LSCs from late 1970s up to the present resembles the development of silicon solar cells from starting 1-2% to about 20% efficiency.

The design presented herein also affords efficient luminescent concentrators having highly luminescent complexes of RE ions with nanosized noble metal and copper particles may be incorporated in thin glass films covering highly transparent glasses or stable polymers. Antireflecting coating can be such as photonic crystals or cholesteric materials. In order to cover the maximum absorption in the white solar spectrum two or three plates incorporated by the appropriate luminescent species must be used. The only loss mechanism which cannot be circumvented is the Stock shift which is necessary to avoid the overlapping of the absorption and emission.
As a non-limiting embodiment of the invention, provided in Fig. 5 is a schematic profile of an LCS 2 in accordance with embodiments of the invention. The LCS comprises a top plate 4, a middle plate 6, and a bottom plate 8. A blue film 10 is applied onto the top plate 4, and an anti-reflective coating 12 is applied to the blue film 10. Between the top plate 4 and the middle plate 6 is a green film 14, and between the middle plate 6 and the bottom plate 8 is a red film 16. Below the bottom plate 8 is a white reflecting coating 20. The LCS 2 further comprises a first solar cell 22 and a second solar cell 24. The dimensions of the LSC 2 are provided in Table 1. The optimum efficiency of the LCS 2 is about 40%.

<table>
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<tr>
<th>LSC layer</th>
<th>Thickness</th>
</tr>
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<tbody>
<tr>
<td>Anti reflecting coating</td>
<td>1.0 – 3.0 μm</td>
</tr>
<tr>
<td>Blue thin film</td>
<td>20 – 50 μm</td>
</tr>
<tr>
<td>Transparent glass plate</td>
<td>3.0 – 5.0 mm</td>
</tr>
<tr>
<td>Green thin film</td>
<td>20 – 50 μm</td>
</tr>
<tr>
<td>Transparent glass plate</td>
<td>3.0 – 5.0 mm</td>
</tr>
<tr>
<td>Red thin film</td>
<td>20 – 50 μm</td>
</tr>
<tr>
<td>Transparent glass plate</td>
<td>3.0 – 5.0 mm</td>
</tr>
</tbody>
</table>

Table 1

Top plate 4 is made from a borosilicate glass incorporated by Ce³⁺ or Eu²⁺. The excitation and emission spectra of Ce³⁺-doped glass and Eu³⁺-doped glass is shown in Fig. 6 and Fig. 7, respectively. The glass can be a conventional glass or a porous glass obtained by leaching out boron oxide. The density of the pores and their dimensions can be controlled.

The glass layer 2 is covered by a thin blue film of a sol-gel based on silica with the addition of polyurethane with a high concentration of Tb³⁺ complex and nanoparticles of silver having extinction between 400-450 nm. The emission spectra of Tb³⁺-codoped glass and the absorption spectra of silver spheroid nanoparticles obtained in ormosils composite matrix are presented in Fig. 8 and Fig. 9, respectively.
The middle plate 6 is made from transparent glass covered by thin green sol-gel layer 14 containing silica-polyurethane film containing a highly luminescent Europium complex (with phenanthroline or polypiridine) doped with silver nanoparticles.

The polyurethane silica obtained by a sol-gel polycondensation reaction of diurethane-siloxane is presented in Fig. 10.

The chemical structures of the Europium complex, and Eu-RR-2-4 complex tris-[2-(N-diphenylphosphinoxy carbamoyl)aminoethyl]-amine is presented in Fig. 11 and Fig. 12, respectively. The Emission spectra of the complexes incorporated in Silica-polyurethane films in the presence of silver nanoparticles in the Europium Eu-RR-2-4 complex is presented in Fig. 13.

The bottom plate 8 is a transparent glass plate coated with a red film 16 containing Nd\(^{3+}\) and Yb\(^{3+}\) complexes in a silica-polyurethane matrix doped with copper nanoparticles.

The ligand TsoxMe (in particular, the tetrapodal octadentate chelating agent TsoxMe, shown in Fig. 14, in which the chromophoric moieties are connected to aN,N,No,No-tetra-aminopropyl-1,2-ethylenediamine framework) proved to provide a good antenna effect for the Yb\(^{3+}\).

The spectral data of the various complexes and species are presented in Figs. 15 to 18. The low-resolution emission spectra of the YbTsoxMe at 295 K is presented in Fig. 15. The UV-vis absorption spectra of copper colloids prepared in aqueous acetonitriie solution by borohydride reduction under the argon purge is presented in Fig. 16. The excitation of Nd\(^{3+}\) and Nd\(^{3+}\) + UO\(_2\)^{2+} are presented in Fig. 17. The emission spectrum of Nd\(^{3+}\) is presented in Fig. 18.

Referring to Fig. 19, curve 1 shows the spectrum of solar radiation. Curve 2 shows the spectrum of the sensitivity of a silicon photovoltaic cell. Curve 3 shows the spectrum of the sensitivity of an AlGaAs photovoltaic cell. The spectrum of the quantum efficiency for the solar cells: AlGaAs (1), CdS/CdTe (2), Monocrystalline silicon (3), Amorphous silicon (4) and Solar spectrum (5) are presented in Fig. 20.
CLAIMS:

1. A luminescent solar concentrator (LSC) capable of absorbing solar energy in the UV and visible regions of the spectrum, the LSC incorporating a luminescent system comprising at least two rare earth materials in a form selected from rare-earth ions and rare-earth complexes, the LSC being in the form of stacked sheets, each sheet in said stack being separated from the other by an air-gap.

2. The LSC of claim 1, wherein the luminescent system is incorporated in a plurality of LSC sheets by employing a sol-gel film in which the luminescent system is distributed or by incorporating the luminescent system in a plurality of pores in the sheet material.

3. The LSC according to claim 2, wherein the luminescent system is incorporated in a sol-gel coating on the surface of the glass plate.

4. The LSC according to claim 2, wherein the luminescent system is incorporated in a plurality of pores in the glass plate.

5. The LSC according to claim 1, wherein said rare-earth material being a lanthanide material selected from:

   (1) a lanthanide salt in combination with an ion selected from Ce, Pb and Bi;
   (2) a lanthanide complex with an organic ligand; and
   (3) a lanthanide-ligand complex in combination with a metal plasmon.

6. The LSC according to claim 5, wherein the lanthanide material comprises a lanthanide selected from La, Ce, Pr, Gd, Eu, Tb, Dy, Er, Tm, Nd, Yb or any combination thereof or a complex of these ions.

7. The LSC according to claim 1, wherein the LSC sheet is selected from glass, porous glass, quartz, indium tin oxide (ITO), fluorinated tin oxide (FTO) or mica.

8. The LSC according to claim 7, wherein LSC sheet is ormocer matrix or a porous glass.

9. The LSC according to claim 2, wherein coating thickness being between 1 µm and 10 µm or between 10 µm and 100 µm.

10. The LSC according to claim 5, wherein the metal plasmon being selected from silver plasmon, gold plasmon, copper plasmon, platinum plasmon, palladium plasmon, ruthenium plasmon, rhodium plasmon, osmium plasmon, iridium plasmon and alloys thereof.
11. The LSC according to claim 10, wherein the metal plasmon being selected from silver, gold and copper.
12. The LSC according to any one of claims 5, 10 and 11, wherein said metal plasmons being in the form of nanoparticles.
13. The LSC according to claim 5, wherein the lanthanide material comprises a lanthanide ion selected from Ce, Pr, Gd, Eu, Tb, Dy, Er, Tm, Nd, Yb and any combination thereof or a complex of these ions, in combination with at least one of ions selected from Ce$^{3+}$, Pb$^{2+}$ and Bi$^{3+}$, silver plasmons, gold plasmons and copper plasmons.
14. The LSC according to claim 5, wherein the lanthanide being in the form of a molecular entity containing a central lanthanide ion, associated with at least one bidentate ligand and one or more mono- or multi-dentate organic ligands.
15. The LSC according to claim 14, wherein the ligand being selected amongst monodentate, bidentate, tridentate, tetradentate and multidentate organic ligands.
16. The LSC according to claim 15, wherein the organic ligand being a polynuclear heterocyclic aromatic compound, optionally having two or more fused ring structures.
17. The LSC according to claim 16, wherein the aromatic organic ligands being selected from rhodamine, fluorescein, fluorescein, 2-quinolone, 4-quinolone, 4-trifluoromethylcoumarin (TFC), 7-diethyl-amino-coumarin-3-carbohydrazide, 7-amino-4-methyl-2-coumarin, 7-amino-4-trifluoromethyl-2-coumarin, and aminomethyltrimethyl psoralen.
18. The LSC according to claim 15, wherein the organic ligand being selected amongst cryptands, podands, calixarenes, macrocyclic ligands, 1,3-diketones, heterobiaryl ligands, carboxylic acid derivatives, terphenyl ligands, and proteins.
19. The LSC according to claim 18, wherein said ligand being a cryptand.
20. The LSC according to claim 19, wherein said cryptand being selected from bipyridine pentacarboxylates.
21. The LSC according to claim 20, wherein said cryptand being selected amongst cryptands having a cyclic or polycyclic assembly of binding sites.
22. The LSC according to claim 21, wherein the cryptand ligand being selected from tribipyridine pentacarboxylates.
23. The LSC according to claim 22, wherein said ligand being selected from trisbipyridine and pyridine bipyridine.
24. The LSC according to claim 1, being constructed of three plates, each plate consists of two rare earth ions or their complexes.

25. The LSC according to claim 1, being in the form of a stack of several LSC sheets, each sheet being incorporated by two fluorescent species with no overlapping of their absorption or emission spectra.

26. The LSC according to claim 1, comprising three plates, each being incorporated by fluorescence species that absorb the entire solar light in UV and visible part of the spectrum with no overlapping of absorption and emission spectra, thereby circumventing re-absorption losses.

27. The LSC according to claim 26, wherein each of said plates comprising same or different luminescent species.

28. The LSC according to claim 26, wherein in the LSC stack the upper sheet being colored with a fluorescent violet/blue fluorescent species, the middle sheet being colored with a fluorescent green fluorescent species, and the bottom sheet being colored with a fluorescent red fluorescent species.

29. The LSC according to claim 1, further comprising any one or more solar cells, an anti-reflective coating on a top surface and a reflecting coating on a bottom surface.
Fig. 4
Fig. 5

The emission of Ce$^{3+}$ originates from the two transitions:

$5d \rightarrow 2F \frac{5}{2}$

and $5d \rightarrow 2F \frac{7}{2}$
10% Ag-in 50 ml solvent-78 °C (25 min)

$\lambda_{\text{max}} = 405 \text{ nm}$

Polyurethane silica obtained by Sol-Gel polycondensation reaction of Diurethane-siloxane

![Polyurethane silica structure](image)

Fig. 9

Fig. 10
**Fig. 15**

\[ YbTsoxMe \quad T = 295 \text{ K} \quad \lambda_{\text{exc}} = 370 \text{ nm} \]

**Fig. 16**

Absorbance vs. Wavelength (nm)
Excitation of Nd$^{3+}$ (---) and Nd$^{3+}$ + UO$_2^{2+}$ (—). Emission monitored at 1,055 nm.

Fig. 17

2wt\% Nd$^{3+}$

(Excitation 416 nm)

$^4F_{3/2} \rightarrow ^4I_{9/2}$

Fig. 18
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. H01L31/052  H01L31/055

ADD.

According to International Patent Classification (IPC) and both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
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<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>wo 2010/023657 A2 (GREENSUN ENERGY LTD [IL]; REISFELD RENATA [IL]; SHMUELI EITAN [IL]; SA) 4 March 2010 (2010-03-04) figures 2a, 23,24 page 2, paragraph 3 - page 3, paragraph 1 page 3, paragraph 4 page 12, paragraph 2 page 14, paragraph 3-5 page 28, paragraph 1</td>
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<td>A</td>
<td>wo 2012/021460 A2 (YOUNG MICHAEL EUGENE [US]; SRINIVAS ARJUN DANIEL [US]; ROBINSON MATTHE) 16 February 2012 (2012-02-16) paragraphs [0078] , [0079]</td>
<td>1,5,6</td>
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[See patent family annex.]

* Special categories of cited documents:

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**L** document(s) which may throw doubts on priority claim(s) or which are considered relevant to patentability but which are not published with the same introductory passages  
**O** document(s) referred to in the context of priority claim(s)  
**P** document(s) published prior to the international filing date but later than the priority date claimed  

**T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
**X** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is taken alone  
**Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being considered to involve an inventive step when the document is taken alone  

Date of actual completion of the international search: 4 July 2014  
Date of mailing of the international search report: 14/07/2014

Name and mailing address of the ISA:  
European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer: Chao, Oscar
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<td>Y</td>
<td>WO 2010/127348 A2 (BRUER GARRETT [US]) 4 November 2010 (2010-11-04) figures 16, 17, 2, 4, 5 page 3, paragraph 4 page 5, paragraph 2-4 page 10, paragraph 1 page 13, paragraph 3 - page 15, paragraph 1 page 16, paragraph 5 page 17, paragraph 1 page 22, paragraph 2 - page 24, paragraph 1</td>
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