

Tm²⁺ luminescent materials for solar radiation conversion devices

Field of the invention

The invention relates to broadband-absorbing Tm²⁺ luminescent materials for solar radiation conversion devices, and, in particular, though not exclusively, solar radiation conversion devices such as photovoltaic cells or luminescent solar concentrators that comprise a broadband-absorbing Tm²⁺ luminescent material, the use of Tm²⁺ luminescent materials in solar radiation conversion devices, methods of synthesizing Tm²⁺ based luminescent materials and a method for forming a Tm²⁺ luminescent (poly)crystalline thin-film layer on a substrate.

Background of the invention

Solar radiation conversion devices such as luminescent solar concentrators (LSCs) aim at lowering cost of solar energy generation by concentrating sunlight using a cheap luminescent plate onto small area strip photovoltaic cells. In such scheme sun light is absorbed by a luminescent material and re-emitted in all directions. A considerable fraction of the light is trapped in the plate that acts as a light guide by total internal reflection. This way the light is guided to the perimeter where photovoltaic cells convert it into electric power. Similarly, simple luminescent conversion layers(LCL) on top of or integrated in a photovoltaic device, e.g. a solar cell, may be used to increase the overall conversion efficiency of the device. In such scheme (part of the) sun light is absorbed by a luminescent material and re-emitted in all directions. A considerable fraction of the light is coupled into the device either directly or indirectly by total internal reflection. This way the absorption

efficiency in the cell is enhanced due to an enhanced optical path length.

While solar panels are already contributing to the world energy production, LSCs and LCLs are still not commercially available. Although the concept is appealing, the production of large sized LSCs and LCLs with sufficient efficiency turns out to be a real challenge. The problems that are encountered mainly concern the shortcomings associated with the luminescent materials that are used in an LSC or LCL.

Ideally, a luminescent material for an LSC or LCL should meet certain requirements. The material should have: a broad spectral absorption, a high absorption efficiency over the whole absorption spectrum, non-overlapping absorption and emission spectra (i.e. a large Stokes' shift), a high luminescent quantum efficiency (percentage of absorbed photons that lead to a newly emitted photon), a photon emission that matches the spectral response of the PV-cell it is coupled to and it should be compatible with materials that form the waveguide.

The most common luminescent material that is used for LSCs are organic dyes. These materials are relatively cheap, easily produced and can be integrated into a waveguide structure in a simple way. The width of their absorption spectrum however is limited and the absorption and emission spectra overlap resulting in substantial losses due to self-absorption.

An interesting group of luminescent materials that are currently investigated for applications in LCSs are the inorganic rare-earth compounds. These materials can exhibit relatively large shifts between absorption and emission. For example, in the article by De Boer et al, "Progress in phosphors and filters for luminescent solar concentrators", 1202, a phosphor based on Sm^{2+} is described that exhibits emission around 700 nm and absorption edge below 600 nm.

Although this material looks promising in view of the re-absorption problems of the conventional dyes, the absorbing properties are relatively poor as it only covers a part of the

total solar spectrum that is available for conversion. Hence there is a need for improved luminescent materials that both exhibit broadband absorption (i.e. absorption over a large part of the solar spectrum), little self-absorption and an emission spectrum that may be easily matched with photovoltaic devices.

Summary of the invention

It is an objective of the invention to reduce or eliminate at least one of the drawbacks known in the prior art. In a first aspect the invention may relate to a solar radiation conversion device comprising a Tm^{2+} based inorganic luminescent material for converting solar radiation of at least part of the UV and/or visible and/or infrared solar spectrum into infrared solar radiation, preferably said infrared solar radiation having a wavelength of around 1138 nm; and, a photovoltaic device for converting at least part of said infrared solar radiation into electrical power.

The Tm^{2+} based inorganic luminescent material exhibits a large Stoke's shift so the problem of self-absorption in the solar radiation conversion device does not occur. The Tm^{2+} based inorganic luminescent material absorbs more than twice the amount of power from the sunlight spectrum when compared to absorption of solar radiation of conventional luminescent materials such as dyes. Contrary to the well-known dye's, Tm^{2+} based luminescent materials are colourless which enhances applicability in the build environment. Further, the infrared emission peak at 1138 nm of the Tm^{2+} based inorganic luminescent materials advantageously coincides with the 1.13 eV bandgap for optimal conversion of the broad solar spectrum (in particular the AM1.5 solar spectrum) on the basis of a single-junction cell. This feature allows for improving the overall conversion efficiency of a LSC or LCL.

In an embodiment, said luminescent material may comprise a binary, ternary and/or a quaternary inorganic crystalline host material that is doped with Tm^{2+} ions. In an

embodiment said luminescence (emission) originations from Tm^{2+} ions. In another embodiment, said Tm^{2+} ions is present in a concentration between 0.1 and 100%. In yet another embodiment, in a concentration between 1% and 90%. In a further
5 embodiment, between 1% and 50% an in yet a further embodiment between 0.2% and 11%.

In an embodiment, said binary inorganic host material may be defined by the general formula ML wherein $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and $\text{L} = \text{Cl}, \text{Br}, \text{I}$. In another embodiment, binary
10 inorganic host material may be defined by the general formula NL_2 wherein $\text{N} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ and $\text{L} = \text{Cl}, \text{Br}, \text{I}, \text{F}$. In yet another embodiment, said binary inorganic host material may be defined by the general formula NI_2 wherein $\text{N} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$. Many host materials may be used for the Tm^{2+} ions. It has been found that
15 in particular CaI_2 or NaI may be used as Tm^{2+} inorganic luminescent converter material. These materials exhibit superior absorption characteristics for the solar spectrum.

The host materials may also be an alloy or mixture described by the general formula $\text{M1}_{(1-x)}\text{M2}_{(x)}\text{L}$ with M1 and M2 any
20 of the elements M , or $\text{ML1}_{(1-x)}\text{L2}_{(x)}$ with L1 and L2 any of the elements L . The host materials may also be an alloy or mixture of the general formula $\text{M1}_{(1-x)}\text{M2}_{(x)}\text{L1}_{(1-y)}\text{L2}_{(y)}$. The host materials may also be an alloy or mixture of 3 or more elements M or L . The host materials may also be an alloy or mixture of the
25 general formula $\text{N1}_{(1-x)}\text{N2}_{(x)}\text{L2}$ with N1 and N2 any of the elements N , or $\text{NL1}_{(1-x)}\text{L2}_{(x)}$ with L1 and L2 any of the elements L . The host materials may also be an alloy or mixture of the general formula $\text{N1}_{(1-x)}\text{N2}_{(x)}\text{L1}_{(1-y)}\text{L2}_{(y)}$. The host materials may also be an alloy or mixture of 3 or more elements N or L .

30 In an embodiment, said luminescent Tm^{2+} doped inorganic material may comprise a (poly)crystalline thin-film layer or crystalline particles, preferably nanoscale particles, wherein said particles are embedded in a matrix material. Tm^{2+} based inorganic luminescent material may be
35 synthesized using different methods, including deposition methods that are compatible with conventional semiconductor processing methods so that the Tm^{2+} based inorganic luminescent

material may be easily integrated in thin-film photovoltaic devices.

In an embodiment said luminescent Tm^{2+} doped inorganic material may be part of or associated with a waveguide structure for guiding said solar radiation of a predetermined wavelength to said photovoltaic device.

In an embodiment, said waveguide structure may comprise a first (top) surface and a second (bottom) surface, wherein a luminescent Tm^{2+} layer is provided over at least part of said first and/or second surface, preferably said layer comprising a (poly)crystalline thin-film layer or a layer of a matrix material in which crystalline (nanosized) particles are embedded. Here, the term nano-sized particles may refer to particles that have an average size of selected between 1 and 1000 nm, preferably between 2 and 800 nm, more preferably between 3 and 500 nm. In a further embodiment, the particles may be selected between 25 and 600 nm, preferably between 50 and 200 nm. The nanosized particles provide the effect that the losses due to scattering in the device are reduced.

In an embodiment, said waveguide structure may comprise a first (top) surface and a second (bottom) surface, wherein said luminescent Tm^{2+} material may be embedded e.g. as (nanosized) particles in said waveguide structure. In an embodiment said matrix material may be a transparent organic polymer. In an embodiment, said transparent organic polymer may be a poly(methyl methacrylate) (PMMA) or a polycarbonate. Hence, the Tm^{2+} based inorganic material as especially suitable for use in luminescent solar energy concentrator.

In an embodiment, said solar radiation conversion devices comprises a wavelength conversion layer wherein said luminescent Tm^{2+} inorganic material is provided over a light receiving face of said photovoltaic device. In an embodiment said photovoltaic device may comprise said luminescent Tm^{2+} inorganic material. In an embodiment, said photovoltaic device may comprise a thin-film layer comprising said luminescent Tm^{2+} inorganic material.

In an embodiment, said photovoltaic device may comprise an infrared absorbing active layer, more preferably said infrared absorbing layer comprising at least one of: a type IV, III-V, or II-VI semiconductor compound, copper indium gallium (di)selenide (CIGS), copper indium (di)selenide (CIS),
5 infra-read absorbing quantum dots, an infrared absorbing polymer, graphene or (carbon) nanotubes. Hence, the Tm^{2+} based inorganic material may be used to extend the efficiency of a simple infrared photovoltaic device thereby effectively
10 converting the infrared photovoltaic device into broad-band solar radiation conversion device.

In an embodiment, in said Tm^{2+} luminescent material solar radiation absorption takes place in the 5d configurations (5d states) of Tm^{2+} while the emission
15 (luminescence) is from the $\text{Tm}^{2+} 4f^{13}(^2F_{5/2})$ to the $\text{Tm}^{2+} 4f^{13}(^2F_{7/2})$ ground state.

In a further aspect, the invention may relate to the use of a luminescent Tm^{2+} inorganic crystalline material in a luminescent solar energy concentrator or a solar cell.

20 In another aspect, the invention may relate to a method for synthesising a luminescent Tm^{2+} doped inorganic crystalline material, wherein the method may comprise: melting an amount of at least a first inorganic ionic compound with a second inorganic ionic compound, said second ionic compound
25 comprising a Tm^{2+} cation in order to form a Tm^{2+} doped a first ionic compound; and, during said melting maintaining the pressure below $5 \cdot 10^{-4}$ mbar, preferably below $1 \cdot 10^{-4}$ mbar.

In yet another aspect, the invention may relate to a method of forming a luminescent Tm^{2+} doped inorganic
30 polycrystalline thin-film on a substrate, wherein the method may comprise: providing a first sputtering target with first sputtering material comprising a first inorganic ionic compound and a second sputtering target with a second sputtering material is thulium; introducing a gas into the
35 sputtering chamber; heating said substrate to a temperature between 10 and 700 °C, preferably 10 and 600 °C; and,

applying an RF electric potential to said first sputtering target and a DC electric potential to said second sputtering target, thereby causing sputtering of said first and second material from said first and second targets onto said
5 substrate in order to grow a (poly)crystalline thin-film of said first inorganic ionic compound that is doped with Tm^{2+} cations.

The invention will be further illustrated with reference to the attached drawings, which schematically will
10 show embodiments according to the invention. It will be understood that the invention is not in any way restricted to these specific embodiments.

Brief description of the drawings

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Fig. 1A-1C depict the absorption, excitation and emission spectra of Tm^{2+} doped inorganic materials according to various embodiments of the invention.

Fig. 2 depicts the absorption spectra of the Red305 dye and the absorption spectrum of Tm^{2+} doped CaI_2 .
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Fig. 3 depicts the loss factor due to self-absorption of a Red305 dye as a function of the diameter of a circular LCS.

Fig. 4A and **4B** show SEM pictures of a crystalline
25 Tm^{2+} doped thin-film layers according to various embodiments of the invention.

Fig. 5 depicts an XRD measurement of a sputtered Tm^{2+} doped NaCl thin film according to an embodiment of the invention.

Fig. 6 depict excitation spectra of an $\text{Tm}^{2+}:\text{NaCl}$ thin film and of a $\text{Tm}^{2+}:\text{NaCl}$ powder sample according to an embodiment of the invention.
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Fig. 7 depicts the emission spectrum of $\text{Tm}^{2+}:\text{NaCl}$ thin-film and of a $\text{Tm}^{2+}:\text{NaCl}$ powder sample.

Fig. 8 depicts a fit of transmission spectrum of a
35 Tm^{2+} doped NaCl film around the $4f^{13}-4f^{13}$ Tm^{2+} absorption region.

Fig. 9A-9C depict schematic cross-sections of luminescent solar energy concentrators comprising a Tm^{2+} doped inorganic material according various embodiments of the invention.

5 **Fig. 10A and 10B** depict cross-sections of schematic solar radiation conversion devices according to another embodiment of the invention.

Detailed description

10 In this disclosure divalent thulium (Tm^{2+}) based inorganic luminescent materials are described that have superior and improved properties when compared to other rare-earth doped phosphors and other luminescent materials for use
15 in luminescent solar concentrator (LSC) or spectral conversion layer on thin-film solar cells devices that are known in the prior art.

 It has been surprisingly found that certain inorganic crystalline host material comprising Tm^{2+} (e.g. Tm^{2+} doped
20 phosphors) exhibit absorbing and luminescent properties that can be advantageously used in LSC devices or SCL's. In particular, it has been found that the Tm^{2+} doped inorganic crystalline materials may absorb the UV and visible part and at least part of the IR part of the solar spectrum (in total
25 more than 60% of the power from the sun) and have a sharp 4f-4f peak emission in the infra-red around 1138 nm. As a result of the large Stokes' shift, the problem of self-absorption does not occur.

 Moreover, the infrared emission peak at 1138 nm
30 advantageously coincides with the 1.13 eV bandgap for optimal conversion of the broad solar spectrum (in particular the unconcentrated AM1.5 solar spectrum) on the basis of a single-junction cell. As will be described hereunder in more detail, this feature allows for improving the overall
35 conversion efficiency of simple single-junction solar cells.

Fig. 1A-1C depict absorption, excitation and emission spectra of doped inorganic materials according to various

embodiments of the invention. In particular, **Fig. 1A** depicts the absorption spectra of Tm^{2+} doped NaCl , NaI , CaI_2 , NaBr and KBr . The spectra exhibit clear crystal-lattice dependent d-band absorption in the VIS and IR. Furthermore, a weak
 5 absorption peak of the parity forbidden 4f-4f absorption around 1138 nm is shown that is relatively independent of the type of host lattice.

In an embodiment, the luminescent material may comprise an inorganic crystalline material (which may
 10 hereafter be referred to as the inorganic host material) that is doped with Tm^{2+} . The inorganic host material may be a binary inorganic host material defined by the general formula ML wherein $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and wherein $\text{L} = \text{Cl}, \text{Br}, \text{I}$. These materials include (but are not limited to) NaCl , NaBr , NaI , KCl , KBr ,
 15 KI , CsCl , CsBr , CsI , RbCl , RbBr , RbI , etc. These materials crystallize at relatively low temperatures (e.g. room temperature) thereby allowing easy formation of Tm^{2+} doped thin films.

The host materials may also be an alloy or mixture of
 20 the general formula $\text{M1}_{(1-x)}\text{M2}_{(x)}\text{L}$ with M1 and M2 any of the elements M , or $\text{ML1}_{(1-x)}\text{L2}_{(x)}$ with L1 and L2 any of the elements L . The host materials may also be an alloy or mixture of the general formula $\text{M1}_{(1-x)}\text{M2}_{(x)}\text{L1}_{(1-y)}\text{L2}_{(y)}$. The host materials may also be an alloy or mixture of 3 or more elements M or L .

25 In another embodiment, a binary inorganic host material may be defined by the general formula NL_2 wherein $\text{N} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ and $\text{L} = \text{Cl}, \text{Br}, \text{I}, \text{F}$. These materials may include (but are not limited to) CaCl_2 , CaBr_2 , CaI_2 , SrCl_2 , SrBr_2 , SrI_2 , BaCl_2 , BaBr_2 , BaI_2 , CaF_2 , SrF_2 , BaF_2 .

30 The host materials may also be an alloy or mixture of the general formula $\text{N1}_{(1-x)}\text{N2}_{(x)}\text{L}_2$ with N1 and N2 any of the elements N , or $\text{NL1}_{(2-2x)}\text{L2}_{(2x)}$ with L1 and L2 any of the elements L . The host materials may also be an alloy or mixture of the general formula $\text{N1}_{(1-x)}\text{N2}_{(x)}\text{L1}_{(2-2y)}\text{L2}_{(2y)}$. The host materials may
 35 also be an alloy or mixture of 3 or more elements N or L .

In an advantageous embodiment, binary iodine inorganic carrier materials given by the general formula NI_2 N

= Mg, Ca, Sr, Ba may be used as the luminescent inorganic converter material. The Tm^{2+} doped iodines exhibit surprisingly good absorption characteristics for the solar spectrum.

In a particular advantageous embodiment CaI_2 or NaI may be used as Tm^{2+} inorganic luminescent converter material. It has been surprisingly found that these materials exhibit superior absorption characteristics for the solar spectrum.

In a further embodiment, a ternary inorganic host material may be used. These ternary materials may include (but are not limited to) CsCaCl_3 , CsCaBr_3 , CsCaI_3 , RbCaCl_3 , RbCaBr_3 , RbCaI_3 , CsSrBr_3 , CsSrI_3 , CsBaBr_3 , CsBaI_3 , RbSrI_3 , KSrI_3 .

It is submitted that the invention is not limited to the above-mentioned inorganic host materials. For example, in an embodiment the invention may also include mixed and/or alloyed forms of the above-mentioned inorganic host materials.

The spectra of **Fig. 1A** show clear 4f-5d ($4f^{13} \rightarrow 4f^{12}(5d)^1$) absorption bands in the visible range of the spectrum, together with 4f¹³-4f¹³ ($^2F_{7/2} \rightarrow ^2F_{5/2}$) absorption in the infrared. The latter absorption bands are relatively independent of the type of inorganic host material. In contrast, the absorption by the 4f-5d transitions are strongly depends on the type of inorganic host material in which Tm^{2+} is present. Mechanisms that determine the 4f-5d transition energy range are determined by the average (centroid) energy and the total crystal field splitting of the 5d-configuration. It appears that the nearest coordination shell of anions around Tm^{2+} determines both aspects. Crystal field splitting is determined by the size and shape of the anion polyhedron. It scales with the the distance to the anions. The centroid shift is strongly determined by the chemical (covalence) and physical (polarizability) properties of the anion ligands.

The broadness of the absorption spectra of the different materials may be further illustrated by the absorption edges of the materials. There the absorption edge may be determined as the wavelengths for with the absorption is 25% of the maximum absorption of the lowest energy 5d state of Tm^{2+} . In the table hereunder the absorption edge for

different Tm^{2+} doped inorganic materials together with their refractive indices are provided:

Luminescent material	absorption edge[nm]	refractive index
$\text{Tm}^{2+}:\text{NaCl}$	710	1.53
$\text{Tm}^{2+}:\text{CaI}_2$	844	1.78
$\text{Tm}^{2+}:\text{NaI}$	831	1.74
$\text{Tm}^{2+}:\text{NaBr}$	810	1.62
$\text{Tm}^{2+}:\text{KBr}$	763	1.54

From the table and the absorption spectra it follows that the Tm^{2+} doped materials exhibit broadband absorption over a range between 200 nm and 900 nm, preferably 220 and 880 nm, more preferably 240 and 860 nm.

Fig. 1B depicts the excitation spectra of the Tm^{2+} doped inorganic materials. The spectra were measured at an emission wavelength of 1138 nm (i.e. at the top of the emission spectra as depicted in **Fig. 1C**).

Fig. 1C depicts the emission spectra corresponding to emission associated with the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of Tm^{2+} doped NaCl, NaI, CaI_2 , NaBr and KBr under 410, 412, 477, 480 and 409 nm excitation respectively. As expected, the transition is relatively independent of the type of host lattice. Further, the graphs reveal that electrons that are excited to a d-band state relax to the $^2\text{F}_{5/2}$ state from where radiative relaxation to the $^2\text{F}_{7/2}$ state takes place. The resulting Stokes-shift between absorption in the UV and visible range of the spectrum and the sharp peak emission in the infrared very well meets the requirements of a luminescent material that is suitable for LSC or SCL applications.

The absorption spectra of these materials are substantially superior when compared to absorption spectra of conventional luminescent materials such as dyes. **Fig. 2** depicts the absorption spectra of the Red305 dye and the

absorption spectrum of Tm^{2+} doped CaI_2 . The solar spectrum as measured on the earth's surface is depicted in the background. The figure shows that the absorption edge of the dye is around 605 nm whereas the absorption edge of Tm^{2+} doped CaI_2 is around 844 nm. Further, the dye absorbs a 30% power fraction of the total solar intensity corresponding to a photon fraction (i.e. the percentage of photons absorbed) of only 18%, whereas Tm^{2+} doped CaI_2 has a power fraction of around 63%, i.e. twice the amount of power compared to the dye, corresponding to a photon fraction of 44%. This figure thus shows that the Tm^{2+} doped materials exhibit substantially superior LCS properties when compared to the state-of-the-art dyes that are currently used for LCS.

Fig. 3 depicts the loss factor due to self-absorption for a Red305 dye as a function of the LCS radius for different LQEs (the loss factor equals 1 minus the transmitted fraction). The fraction of the initially emitted energy that is transmitted through the edges of a circular LCS with a refractive index of 1.5 is depicted for different radii and LQEs. This figures shows that even for a dye with an LQE of 100%, only 20% of the luminescent light is transmitted out of the edges of an LCS with a radius of around 0.56 meter. When lowering the LQE to 80%, only 10% of the luminescent light is transmitted out of the edges of the LCS. This trend is also valid for other dyes or luminescent materials that are based on nano-particles and that exhibit self-absorption. These losses due to self-absorption are eliminated by using luminescent Tm^{2+} doped inorganic materials according to the invention in an LCS structure.

The syntheses of Tm^{2+} doped materials is problematic as often Tm^{3+} instead of Tm^{2+} sites are formed in the inorganic host material. For example, the use of a conventional firing process in a reducing N_2/H_2 atmosphere does not result in stable Tm^{2+} doped materials. Instead, the Tm^{3+} state is formed. For example, heating a mixture of the salt and TmI_2 or TmCl_3 in an alumina crucible in a tube furnace with N_2/H_2 atmosphere at different temperatures (below and above the melting point of

the salts) resulted in the formation of Tm_2O_3 or Tm^{3+} doped CaI_2 or NaCl (according to XRD analyses) and the diffuse reflectance spectra showed the presence of Tm^{3+} rather than Tm^{2+} .

5 Therefore, in order to obtain Tm^{2+} doped inorganic materials that exhibit the above-described advantageous absorption-emission characteristics, a mixture of an inorganic host material (e.g. NaCl) and a Tm^{2+} -based salt (e.g. TmI_2) was contained in a closed quartz ampoule that was under vacuum.

10 The doping concentration of the Tm^{2+} may be varied on the basis of the amount of Tm^{2+} -based salt in the mixture. Heating the ampoule in a furnace however resulted in the formation of Tm^{3+} formation and no Tm^{2+} was found. However, heating the ampoule (with the mixture inside) with a gas burner (a burner that is
15 normally used to melt the quartz) resulted in the formation of Tm^{2+} doped NaCl . On the basis of this process, different Tm^{2+} doped inorganic materials were successfully synthesized, including (but not limiting to) Tm^{2+} doped NaBr , NaI , KBr , CaCl_2 and CaI_2 . Heating a closed vacuum-pumped ampoule had a
20 negative effect on the amount of Tm^{2+} in the final product.

Therefore, during the melting process the ampoule was connected to a vacuum pump, which ensured that the pressure during the firing of the materials was around 10^{-4} mbar or lower. The samples made in this way were all black or greenish
25 black and showed the desired Tm^{2+} f-f emission. Besides the Tm^{2+} doping, only very small amounts of Tm^{3+} was present in some samples. On the basis of this recipe various Tm^{2+} doped inorganic materials were fabricated. For example, for the synthesis of circa 1.5 g of 3% Tm doped CaI_2 the following
30 recipe may be used:

- mixing 1.425 g of CaI_2 with 0.063 g of TmI_2 inside a N_2 filled glove-box;
- transferring the mixture into a dried quartz ampoule;
- 35 - closing the ampoule inside the N_2 filled glove-box with a valve;

- connecting the ampoule, with mixture and N₂ gas inside, to a vacuum pump;
- vacuum pumping the ampoule;
- heating the ampoule with a burner during vacuum pumping until the mixture melts (typically within 1 to 2 minutes).
- stopping the heating, closing the ampoule by melting it, and disconnecting the ampoule from the pump once the quartz has cooled down.
- opening the ampoule in the glove-box by breaking the quartz; and,
- forming a powder of the crystalline material.

On the basis of this fabrication methods Tm²⁺ doped luminescent materials may be fabrications wherein the doping concentration of said Tm²⁺ ions in said host material may vary selected between 0,1 and 100 % depending on the ratio between the amount of Tm²⁺-based salt and the inorganic host material. In an embodiment, the ratio may be selected such that the concentration of said Tm²⁺ ions is between 1 and 50%, more preferably 1 and 30%. Hence, from the above, it follows that stable Tm²⁺ doped crystalline materials in powder form may be synthesized by melting a stoichiometric mixture of salts under vacuum conditions, preferably at a pressure of 10⁻⁴ mbar or less. The crystalline material in powder form may be used in the formation of LSC devices, which will be described hereunder in more detail with reference to **Fig. 9A-9C**.

In some situations, it may be advantageous to use a material synthesis process that is compatible with convention thin-film semiconductor processing technologies so that the formation of crystalline Tm²⁺ doped inorganic materials may be used together with other processing and/or material deposition steps. Hence, in addition to the above-described firing process for producing powder-based Tm²⁺ doped inorganic materials, crystalline Tm²⁺ doped inorganic materials were also synthesized on the basis of a semiconductor deposition technique. In particular, crystalline thin-film Tm²⁺ doped

layers were realized using a sputtering technique. In an embodiment, an RF magnetron co-sputtering technique may be used. In the co-sputtering technique, at least two targets may be used, e.g. a first target comprising an inorganic host material and a second Tm target.

Successful polycrystalline Tm^{2+} doped thin-films of a thickness between 1 and 5 micron were grown on a suitable carrier substrate such as SiO_2 (quartz), Al_2O_3 or various types of glass under different sputtering conditions. In this particular example NaCl was used as the inorganic host material but other binary, ternary or quaternary host materials as described with reference to firing process may also be used without departing from the invention. The pressure during the sputtering process may be selected between 1 and 5 mTorr. The NaCl target was set at an RF power selected between 20 and 50 W (corresponding to a rate between 1 and 5 Å/s) and the Tm target was set at a DC power between 10 and 40 W (corresponding to a rate between 0,05 and 0,08 Å/s). On the basis of these setting, NaCl doped Tm^{2+} films wherein the Tm^{2+} dopant percentage is between 0,2 and 12 % were realized (these values were determined on the basis of EDX measurements). Here a dopant percentage of 1% means that 1% of the cations in the anorganic host material is replaced by a Tm^{2+} cation.

Fig. 4A and **4B** show SEM pictures of crystalline Tm^{2+} doped thin-film layers according to various embodiments of the invention. In particular, **Fig. 4A** and **4B** show SEM pictures of crystalline Tm^{2+} doped NaCl thin-film of a thickness of around 2 micron that were deposited onto an SiO_2 substrate at a temperature of 200°C and 300°C respectively. The presence of Tm^{2+} in the NaCl film gives a greyish/tinted appearance (NaCl films are transparent). A similar effect was observed with the powders that turn from white to greyish/black when doped with Tm^{2+} . Polycrystalline films were grown wherein the grain size may be controlled by temperature. As shown in **Fig. 4A**, when using a deposition temperature 200 °C an average grain size between 200 and 400 nm may be realized. At a deposition

temperature of 300 °C the average grain size is between 600 and 1000 nm as shown in **Fig. 4B**.

Fig. 5 depicts an XRD measurement of a sputtered Tm^{2+} doped NaCl thin film according to an embodiment of the invention. The locations of the peaks in the spectrum match those of NaCl. **Fig. 6** depict excitation spectra of an $\text{Tm}^{2+}:\text{NaCl}$ thin-film and of a $\text{Tm}^{2+}:\text{NaCl}$ powder sample. The spectra are recorded while monitoring the Tm^{2+} line emission around 1140 nm. This figure shows that both the powder and thin-film materials comprise Tm^{2+} that is responsible for absorption of light of the solar spectrum by one or more of its 5d energy bands. Further, it shows that if a Tm^{2+} ion is excited in one of its 5d energy bands by photons of the solar spectrum, a radiation-less relaxation to a lower-level f band takes places before a line emission of photons at around 1138 nm takes place. Hence, the Tm^{2+} doped thin-films exhibit a large Stokes-shift so that no overlap between emission and absorption is present.

Fig. 7 depicts the emission spectrum of $\text{Tm}^{2+}:\text{NaCl}$ thin-film and of a $\text{Tm}^{2+}:\text{NaCl}$ powder sample according to an embodiment of the invention. The spectra were recorded under excitation at 415 nm. This graph shows that for both the powder and thin-film samples, the Tm^{2+} sites are responsible for the photon emission.

Fig. 8 depicts a fit of transmission spectrum of a Tm^{2+} doped NaCl film around the Tm^{2+} absorption region. To quantify the absorption strength, the transmission excluding the dip is fitted and the amplitude of the dip with respect to this fitted line is determined. The inset shows the resulting relative absorption.

Alternative sputtering techniques may be used without departing from the invention. For example, in an embodiment a single target comprising a Tm^{2+} doped target material that was synthesized using the firing method as described above. For example, an $\text{Tm}^{2+}:\text{NaCl}$ or $\text{Tm}^{2+}:\text{CaI}_2$ powder may be synthesized and pressed into a tablet that can be inserted into the target of a sputtering system.

Fig. 9A-9C depict schematic cross-sections of solar radiation conversion devices, in particular luminescent solar energy concentrator devices, comprising a Tm^{2+} doped inorganic material according various embodiments of the invention. **Fig.**

5 **9A** depicts a LSC device according to an embodiment of the invention. The LSC comprises a waveguide structure **902** comprising a first (top) surface **903**, a second (bottom) surface **905** and one or more edges **906**. At least part of the edges **906** of the waveguide structure may be coupled to a
10 photovoltaic cell **908**. In this embodiment, the waveguide structure may be formed of a transparent matrix material in which particles **910**, preferably nano-scale particles, of a Tm^{2+} doped inorganic crystalline material as described in this specification are embedded. When photons **912** from the solar
15 spectrum that enter the waveguide structure are absorbed by one or more 5d energy bands of the Tm^{2+} sites, the excited Tm^{2+} sites transmit photons **914** via an ff-line emission at a wavelength of around 1138 nm. The emitted photons may be guided via the waveguide structure to the edges of the
20 waveguide where a photovoltaic cell **908** that is optimized for converting the photons that are emitted by the Tm^{2+} ions into electrical power.

In an embodiment, the photovoltaic cell may be a Copper Indium Gallium (di)Selenide (CIGS) photovoltaic cell.
25 In another embodiment, the photovoltaic cell may be an Copper Indium (di)Selenide (CIS) photovoltaic cell. These materials are very efficient for converting the emitted 1138 nm (near)infrared solar radiation of the Tm^{2+} sites into electrical energy.

30 In a further embodiment, the photovoltaic cell may comprise a NIR/IR absorbing organic active layer or a NIR/IR dye-sensitized active layer. In an embodiment, the photovoltaic cell may comprise an organic semiconducting layer, e.g. MEH-PV, that is sensitized with NIR/IR absorbing
35 quantum dots. For example, by controlling the size of low-band gap (binary) semiconductors (e.g. PbS, PbSe, InAs and/or HgTe) quantum dots, the quantum dots may be tailored to absorb in

the (near) infrared spectrum between 900 and 2000 nm. See e.g. Sargent et al in "Solution-based Infra-Red Photovoltaic Devices, Nature Photonics 3, 325 - 331 (2009). In another embodiment, the photovoltaic cell may comprise a (single) walled carbon nano-tube layer or a graphene active NIR/IR absorbing layer.

The Tm^{2+} doped particles may be embedded in a transparent matrix material comprising a transparent organic polymer that has excellent transmittance properties in the near-infrared range of the optical spectrum such as poly(methyl methacrylate) (PMMA) or a polycarbonate. In an embodiment, the refractive index of the matrix material may be selected to substantially match the refractive index of the Tm^{2+} doped particles so that losses due to scattering of the emitted light out of the waveguide structure is minimized.

Fig. 9B depicts a LSC device according to another embodiment of the invention. The LSC comprises a waveguide structure **902** comprising a first (top) surface **903**, a second (bottom) surface **905** and one or more edges **906**. At least part of the edges **906** of the waveguide structure may be coupled to a photovoltaic cell **908**. The waveguide structure may be formed of a transparent high-index organic polymer or glass. At least part of the top and/or bottom surface of the waveguide structure may be covered with a luminescent layer **916** that may comprise a Tm^{2+} doped inorganic crystalline material as described in this specification.

In an embodiment, the thin-film luminescent layer may be formed of a transparent matrix material in which particles, preferably nano-scale particles, of a Tm^{2+} doped inorganic crystalline material are embedded. Alternatively, the optically active layer may be Tm^{2+} doped (poly)crystalline thin-film layer that is formed on the waveguide structure. The thin-film layer may be formed onto the waveguide structure using e.g. a (co-)sputtering method as described above. The use of a (poly)crystalline layer that is coupled as an optically active layer to the waveguide structure provides the advantages that the effect of scattering that may occur when

using a matrix layer comprising Tm^{2+} doped particles is eliminated.

In a further embodiment (not shown), both at least part of the top surface and the bottom surface of the waveguide structure may be covered with a thin-film luminescent layer. This way, sunlight that passes the top and bottom side of the waveguide structure may be converted into (near) infrared light that is guided by the waveguide structure towards the photovoltaic cell.

Fig. 9C depicts a LSC device according to yet another embodiment of the invention. In this embodiment, the LSC device comprises one or more luminescent layers that are similar to the ones described with reference to **Fig. 9B**. In this embodiment however, the luminescent layer **916** is embedded in the waveguide structure **902**.

It is submitted that the devices depicted in **Fig. 9A-9C** are non-limiting examples embodying the invention and many variations and/or combinations of features of these embodiments are possible without departing the invention. For example, in an embodiment, a solar radiation conversion device may comprise a waveguide structure comprising Tm^{2+} doped luminescent layers that are provided over the first and/or second surface of the waveguide structure and embedded in the waveguide structure. In a further embodiment, at least part of the photovoltaic cell may be part of the waveguide structure.

Fig. 10A and **10B** depict cross-sections of schematic solar radiation conversion devices according to another embodiment of the invention. In particular, **Fig. 10A** depicts a solar radiation conversion device comprising a broadband-absorbing Tm^{2+} luminescent conversion layer **1002** and a photovoltaic device **1004** comprising a first surface **1001** and second surface **1003**. Depending on the configuration, the first (top) surface may be a light receiving surface. In case of a transparent solar cell, both the first and second surface may be light receiving surfaces. The conversion layer may be coated or deposited on the first and/or second surface. In an embodiment, the conversion layer may be a thin-film

(poly)crystalline Tm^{2+} doped luminescent material as described in this disclosure with reference to **Fig. 4-8**. In another embodiment, the conversion layer may be a transparent matrix material comprising particles, preferably nano-particles, of a Tm^{2+} doped luminescent material as described in this disclosure.

In an embodiment, the photovoltaic device may be a silicon photovoltaic device, e.g. a micro-crystalline (thin-film) silicon photovoltaic device. In another embodiment, the photovoltaic device may be an NIR/IR photovoltaic cell (single or multi-junction) for converting at least the (near)infrared part of the solar spectrum **1006** into electric power. Further, light from the UV and visible part **1008** of the solar spectrum is converted by the broadband-absorbing Tm^{2+} luminescent conversion layer **1002** into 1138 nm infrared solar radiation.

Fig. 10B depicts a solar radiation conversion device, e.g. a solar cell, comprising a broadband-absorbing Tm^{2+} luminescent material. The device may comprise a substrate **1012**, preferably a transparent substrate, comprising a multi-layered thin-film photovoltaic device. The photovoltaic device may comprise a first contact layer **1014** formed on a first surface of the substrate. A solar radiation absorbing active layer or multilayer **1018** is formed over the first contact layer and a second layer **1016** is formed over the active layer.

In an embodiment, the photovoltaic device may comprise at least one layer comprising infrared absorbing quantum dots (i.e. nano-particles having a size such that quantum-confinement effects are induced in the particles, i.e. reducing the size of the particles to less than the Bohr radius of the electron and hole functions in the semiconductor) and nano-particles of a broadband-absorbing Tm^{2+} luminescent material as described in this disclosure. In an embodiment, the size of at least part of the infrared absorbing quantum dots may be optimized for absorption of infrared solar radiation that is transmitted by the Tm^{2+} luminescent nano-particles. For example, PbS quantum dots that have a particle size of around 3-4 nm will absorb (near)

infrared radiation around 900-111 nm. Hence, in this embodiment an infrared part **1006** of the solar radiation may be absorbed directly by infrared absorbing quantum dots while the UV and the visible part of the solar radiation may be converted by the Tm^{2+} luminescent nano-particles into infrared solar radiation **1010** of a wavelength of around 1138 nm. This way, the overall conversion efficiency of a simple infrared photovoltaic device may be extended on the basis of visible solar radiation that is converted into infrared solar radiation.

In another embodiment, the photovoltaic device may comprise further comprise a further broadband-absorbing Tm^{2+} luminescent (poly)crystalline thin-film layer. Such layer may be positioned between the substrate and the first contact layer in order to increase the transformation of the radiation of the UV/visible part of the solar spectrum into radiation of the infrared part of the solar spectrum.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a," "an," and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

The corresponding structures, materials, acts, and equivalents of all means or step plus function elements in the claims below are intended to include any structure, material, or act for performing the function in combination with other claimed elements as specifically claimed. The description of the present invention has been presented for purposes of illustration and description, but is not intended to be exhaustive or limited to the invention in the form disclosed. Many modifications and variations will be apparent to those of

ordinary skill in the art without departing from the scope and spirit of the invention. The embodiment was chosen and described in order to best explain the principles of the invention and the practical application, and to enable others
5 of ordinary skill in the art to understand the invention for various embodiments with various modifications as are suited to the particular use contemplated.

CLAIMS

1. Solar radiation conversion device comprising:

a luminescent Tm^{2+} inorganic material for converting
at least part of the UV and/or visible and/or infrared solar
radiation into infrared radiation, preferably said infrared
radiation having a wavelength of around 1138 nm; and,
a photovoltaic device for converting at least part of
said infrared radiation into electrical power.

2. Solar radiation conversion device according to

claim 1, said luminescent material comprises a binary, ternary
and/or a quaternary inorganic crystalline host material, in
which the luminescence (emission) is from Tm^{2+} ions, preferably
said Tm^{2+} ions being present in a concentration between 0.1 and
100% or preferable between 1% and 50% or preferably between 1%
and 30% or preferable between 0.2% and 11%.

3. Solar radiation conversion device according to

claims 1 or 2 wherein:

said binary inorganic host material is defined by the
general formula ML wherein $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and $\text{L} = \text{Cl}, \text{Br}, \text{I}, \text{F}$;
or, by the general formula NL_2 wherein $\text{N} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ and $\text{L} =$
 $\text{Cl}, \text{Br}, \text{I}, \text{F}$; preferably by the general formula NL_2 wherein $\text{N} =$
 $\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ or, by inorganic host material that is defined by
the general formula MNL_3 ; or,

wherein said inorganic host material is an alloy or
mixture of the materials M , N and/or L .

4. Solar radiation conversion device according to any

of claims 1-3 wherein said luminescent Tm^{2+} doped inorganic
material comprises a (poly)crystalline thin-film layer or
crystalline particles, preferably nanoscale particles, wherein
said particles are embedded in a matrix material.

5. Solar radiation conversion device according any of
claims 1-4 wherein said luminescent Tm^{2+} based inorganic

material is part of or associated with a waveguide structure for guiding said solar radiation of a predetermined wavelength to said photovoltaic device.

5 6. Solar radiation conversion device according to claim 5 wherein said waveguide structure comprises a first (top) surface and a second (bottom) surface, wherein a luminescent Tm^{2+} layer is provided over at least part of said first and/or second surface, preferably said layer comprising
10 a (poly)crystalline thin-film layer or a layer of a matrix material in which crystalline (nanoscale) particles are embedded.

 7. Solar radiation conversion device according to
15 claim 5 wherein said waveguide structure comprises a first (top) surface and a second (bottom) surface, wherein said luminescent Tm^{2+} material is embedded in said waveguide structure.

20 8. Solar radiation conversion device according to any of claims 1-7 wherein said matrix material is a transparent organic polymer, preferably a poly(methyl methacrylate) (PMMA) or a polycarbonate.

25 9. Solar radiation conversion device according to any of claims 1-4, wherein a wavelength conversion layer comprising said luminescent Tm^{2+} inorganic material is provided over a light receiving face of said photovoltaic device.

30 10. Solar radiation conversion device according to any of claims 1-4, wherein photovoltaic device comprises said luminescent Tm^{2+} inorganic material, preferably said photovoltaic device comprises a thin-film layer comprising said luminescent Tm^{2+} inorganic material.
35

 11. Solar radiation conversion device according to any of claims 1-10, wherein said photovoltaic device comprises

an infrared absorbing active layer, more preferably said infrared absorbing layer comprising at least one of: a type IV, III-V, or II-VI semiconductor compound, copper indium gallium (di)selenide (CIGS), copper indium (di)selenide (CIS),
5 infra-read absorbing quantum dots, an infrared absorbing polymer, graphene or (carbon) nanotubes.

12. Solar radiation conversion device according to any of claims 1-11, wherein in Tm^{2+} based luminescent material
10 solar radiation absorption takes place in the 5d configurations (5d states) of Tm^{2+} while the emission (luminescence) is from the $\text{Tm}^{2+} 4f^{13}(2F^{5/2})$ to the $\text{Tm}^{2+} 4f^{13}(2F^{7/2})$ ground state.

13. Use of a luminescent Tm^{2+} inorganic crystalline material in a luminescent solar energy concentrator or a solar cell.

14. Method for synthesising a luminescent Tm^{2+} doped inorganic crystalline material comprising:
20 melting an amount of at least a first inorganic ionic compound with a second inorganic ionic compound, said second ionic compound comprising a Tm^{2+} or Tm^{3+} cation in order to form a Tm^{2+} doped first ionic compound; and,
25 during said melting maintaining the pressure below $5 \cdot 10^{-4}$ mbar, preferably below $1 \cdot 10^{-4}$ mbar.

15. Method for forming a luminescent Tm^{2+} doped inorganic polycrystalline thin-film on a substrate that is
30 mounted in an evacuated chamber, comprising:
providing a first sputtering target with first sputtering material comprising a first inorganic ionic compound and a second sputtering target with a second sputtering material is thulium;
35 introducing a gas into the sputtering chamber;
heating said substrate to a temperature between 10 and 700 °C, preferably 10 and 600 °C; and,

applying an RF electric potential to said first sputtering target and a DC electric potential to said second sputtering target, thereby causing sputtering of said first and second material from said first and second targets onto
5 said substrate in order to grow a (poly)crystalline thin-film of said first inorganic ionic compound that is doped with Tm^{2+} cations.