

# Harvesting of the infrared energy: Direct collection, up-conversion, and storage

O.P. Dimitriev

V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine,  
41, prosp. Nauky, 03680 Kyiv, Ukraine  
E-mail address: o\_dimitriev@yahoo.com; dimitr@isp.kiev.ua

**Abstract.** Infrared (IR) energy constitutes almost a half of the solar radiation coming to the Earth surface and almost 100% of the outgoing terrestrial radiation. Surprisingly, but such a huge energy flux is mostly considered as thermal waste and is not used for the practical needs on the large scale. Here, two major methods of the IR energy collection have been briefly reviewed, the direct one and harvesting through up-conversion to the visible range, where this energy can be picked up by the conventional solar cells. Advantages and disadvantages of the above methods have been discussed. Potential of application of IR dyes for IR energy collection has been demonstrated. Storage of the IR energy as a delayed way of its consumption has been also discussed.

**Keywords:** IR energy, thermodynamic balance, thermal converters, photoelectric converters, up-conversion, energy storage.

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## 1. Introduction

IR energy constitutes almost a half of the solar radiation reaching the Earth surface. However, even a larger amount of IR energy,  $P_{Earth}^1$ , is re-emitted from the Earth surface in the form of terrestrial radiation, because Earth is heated and therefore emits as a black body with the average temperature of  $T_{Earth} = 288$  K. The amount of this energy is huge and comparable with that coming from the sun to the earth surface in order to provide the thermodynamic balance of the planet (see Fig. 1),

$$P_{Earth}^1 \sim P_{Sun} \sim 10^{17} \text{ W.} \quad (1)$$

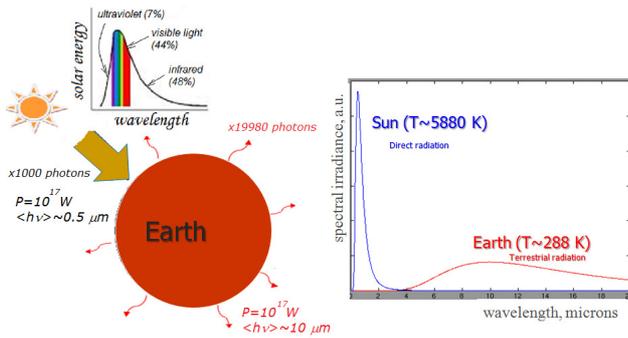
Briefly, the major characteristics of the incoming and outgoing radiation fluxes are as follows. The solar radiation reaching the earth surface has an average power per square meter of about  $230 \text{ W/m}^2$  and its spectrum extends from UV to IR, with the major part of energy which falls in the visible range with the maximum at the wavelength of about  $0.5 \mu\text{m}$  (Fig. 1). Eventually, the same amount of energy must be lost by the “Earth-atmosphere” system, if the internal energy of this system remains constant and the average temperature of the earth surface is unchanged. Therefore, the Earth emits the terrestrial radiation as a heated body. However, the spectral range of this outgoing radiation falls mainly into

the IR range, since the average temperature of the radiative body, *i.e.*, Earth, is far lower than that of Sun and it is 288 K. The peak amount of photons of the outgoing terrestrial radiation (which takes place at the wavelength of *ca.*  $10 \mu\text{m}$ ) is much smaller as compared to the corresponding peak of the incoming solar photons at *ca.*  $0.5 \mu\text{m}$ , being  $7 \cdot 10^{-3}$  versus  $1.5 \cdot 10^3 \text{ W}/(\text{m}^2 \cdot \mu\text{m})$ , respectively [1]. The total amount of photons incoming to and outgoing from Earth is also different according to the balance of the incoming and outgoing energy, *i.e.*,

$$E(\nu) = \int h\nu d\nu = (\sum h\nu_i n_i)_{Sun} = (\sum h\nu_k n_k)_{Earth}, \quad (2)$$

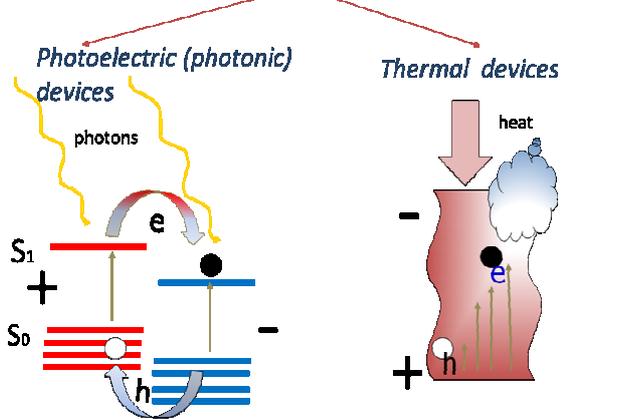
where  $n_i$  is the amount of photons with the frequency  $\nu_i$ ,  $h$  – Planck constant. One can roughly evaluate this relationship as  $N_{Earth}/N_{Sun} = 20$ , where  $N_{Earth}$  is the average total amount of photons emitted by the “Earth-atmosphere” system and  $N_{Sun}$  – total average amount of photons coming from Sun. However, the outgoing radiation has a much wider spectral range, so that the total amount of outgoing energy is equal to the incoming one in accordance with the thermodynamic balance of the planet (Eq. (2)).

Therefore, the IR energy plays a significant role to keep the thermodynamic balance and climate sustainability on our planet. At the same time, IR terrestrial radiation is among the major energetic fluxes



**Fig. 1.** Scheme of the energy balance on the Earth due to the Sun irradiation and terrestrial re-emission, and comparison of spectra of the solar and terrestrial radiations.

## Harvesting of direct IR radiation



**Fig. 2.** Scheme of harvesting of IR energy by two types of devices.

on the Earth, because its power of  $\sim 10^{17} \text{ W}$  is comparable with the power of direct solar radiation (Fig. 1) and exceeds all other energy fluxes, such as photosynthesis ( $\sim 10^{14} \text{ W}$ ), wind ( $\sim 10^{14} \text{ W}$ ), tides ( $\sim 10^{14} \text{ W}$ ), and river streams ( $\sim 10^{12} \text{ W}$ ) [2].

Taking into account that not only the power of the above fluxes is less than that of IR terrestrial radiation, but also that they have significant local instability and dissipation over the earth surface, one can conclude that the terrestrial radiation is one of the major players not only in thermodynamic balance but also in energetic potential for consumption on our planet.

The advantages of the consumption of the terrestrial radiation are as follows. First, this radiation is almost homogeneously scattered and, therefore, there is no need for surface orientation of the corresponding IR cells to harvest this energy or this orientation is not so critical as compared with the solar cells converting direct solar radiation. Therefore, such IR cells can occupy several levels upward from the earth surface without notable shadow effect. Second, these devices do not compete with the green plants for the solar light, since they operate in the different spectral range.

Surprisingly, but such a huge energy flux is mostly considered as a thermal waste and is not used for the practical needs on the large scale. Here, two major methods of the IR energy harvesting are briefly considered, the direct one and the method of upconversion of IR radiation to the visible range, where this energy can be picked up by the conventional solar cells.

### 2. Direct collection of the IR energy

Direct harvesting of the IR radiation can be fulfilled as based on physical principles of conversion of this energy into electricity or useful work as a result of IR photon absorption. Depending on whether such absorption takes place through phonon/vibronic excitations or through electronic excitations of the absorbing material, the corresponding methods of IR energy harvesting can be conventionally separated into thermal and photoelectric (photonic or quantum) methods, respectively (Fig. 2). It means that harvesting of direct solar or terrestrial radiation can be realized through use of devices of two types.

Thermal devices are based on heating of the working body, where the change in its temperature results in generation of electricity or doing the mechanical work. Examples of these devices are based on pyroelectric and thermoelectric materials, thermocouples, solar collectors, etc., and the natural converters include climate machines and cold-blooded animals.

The photoelectric devices require a light quantum or photon that excites electron across the bandgap of a crystalline semiconductor like Si or a donor molecule like polythiophene followed by drop-off of this electron to lower energetic level of the second semiconductor or acceptor molecule that is in contact with the first one. As a result of this process, a potential difference arises at the interface across the heterojunction, which gives rise to electricity in the electrical circuit. In order to collect IR radiation, photoelectric devices should have small band gaps and, therefore, the corresponding devices are based on materials of the following types: narrow gap inorganic semiconductors and semimetals, inorganic quantum wells and quantum dots, superlattices, and some organic compounds, which can be found particularly in green plants and photosynthetic bacteria.

Despite the fact that there are different classes of materials that can be used as converters of the IR energy to electricity, their proper application in regard to collection of terrestrial radiation has not been developed yet. Below, we consider several classes of materials that can be potentially used for application in the above field for collection and conversion of the IR energy.

#### 2.1. Thermal methods of conversion of IR radiation to electricity

Thermal methods of IR energy conversion are based on temperature change of the absorbing material as a result of its heating, which gives rise to changes in its physical characteristics. In *bolometers*, for example, the change in temperature results in change of electrical conductance. The bolometers are made from a material which has a

very small thermal capacity and large temperature coefficient, so that the absorbed radiation leads to a large change in its resistance. The radiant power produces heat within the material, which in turn produces the resistance change. Most bolometers are made from oxides of manganese, cobalt, or nickel [3]. However, bolometer based on graphene layer was recently reported [4]. Such a bolometer allows one to sense tiny changes in thermal radiation and, therefore, represents a new type of device for quantum sensing and information processing.

In *thermocouples* the temperature change leads to generation of thermoelectromotive force. The thermocouple is usually represents a junction of two different metals or semiconductors. Heat absorbed by the junction causes a temperature rise, and hence a thermal electromotive force is developed, which produces a potential difference. The power of the produced electricity is too low, and therefore, the thermocouples are widely used in spectroscopy. The thermocouples do not possess high sensitivity compared to bolometers and pyroelectric converters, however, they have reliable characteristics and good cost/performance ratio.

In *pyroelectric* devices, the change in temperature gives rise to changing polarization of the material, so that the voltage can be generated upon heating. Advantage of pyroelectric materials for generating electricity as compared to the conventional heat engine coupled to electrical generator is the fact that they can work at lower operation temperatures [5]. Application of pyroelectric generators has been matured due to a few patents filed last decades [6], however, these devices still do not appear to be anywhere close to commercialization.

Another class of devices perspective for harvesting of IR radiation is based on *thermoelectric* materials [7]. The thermoelectric energy conversion unit normally consists of two different (*n*- and *p*-type) semiconducting materials connected together in the form of a thermocouple, so that a thermoelectric generator (TEG), also called a Seebeck generator, converts heat flux due to temperature differences directly into electrical energy through a phenomenon called Seebeck effect (a form of thermoelectric effect). The principle of thermoelectric effect is due to the fact that a temperature gradient in a conducting material results in a heat flow; it leads to the diffusion of charge carriers, with different mobility for electrons and holes, respectively. The flow of charge carriers between the hot and cold ends of the device in turn creates a voltage difference. TEGs function like heat engines, but are less bulky and have no moving parts. However, TEGs are typically more expensive and less efficient. The typical efficiency of TEGs is around 5–8%. Only a few known materials are identified to date as efficient thermoelectric materials. Most of these are based on three semiconductors possessing both low thermal conductivity and high power factor; these are bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ), lead telluride (PbTe), and silicon germanium (SiGe), which have the figure of merit ( $zT$ ) value of around  $\sim 1$ . However, because the elements of these materials are mostly not widespread and toxic, researchers are trying to develop new thermoelectric

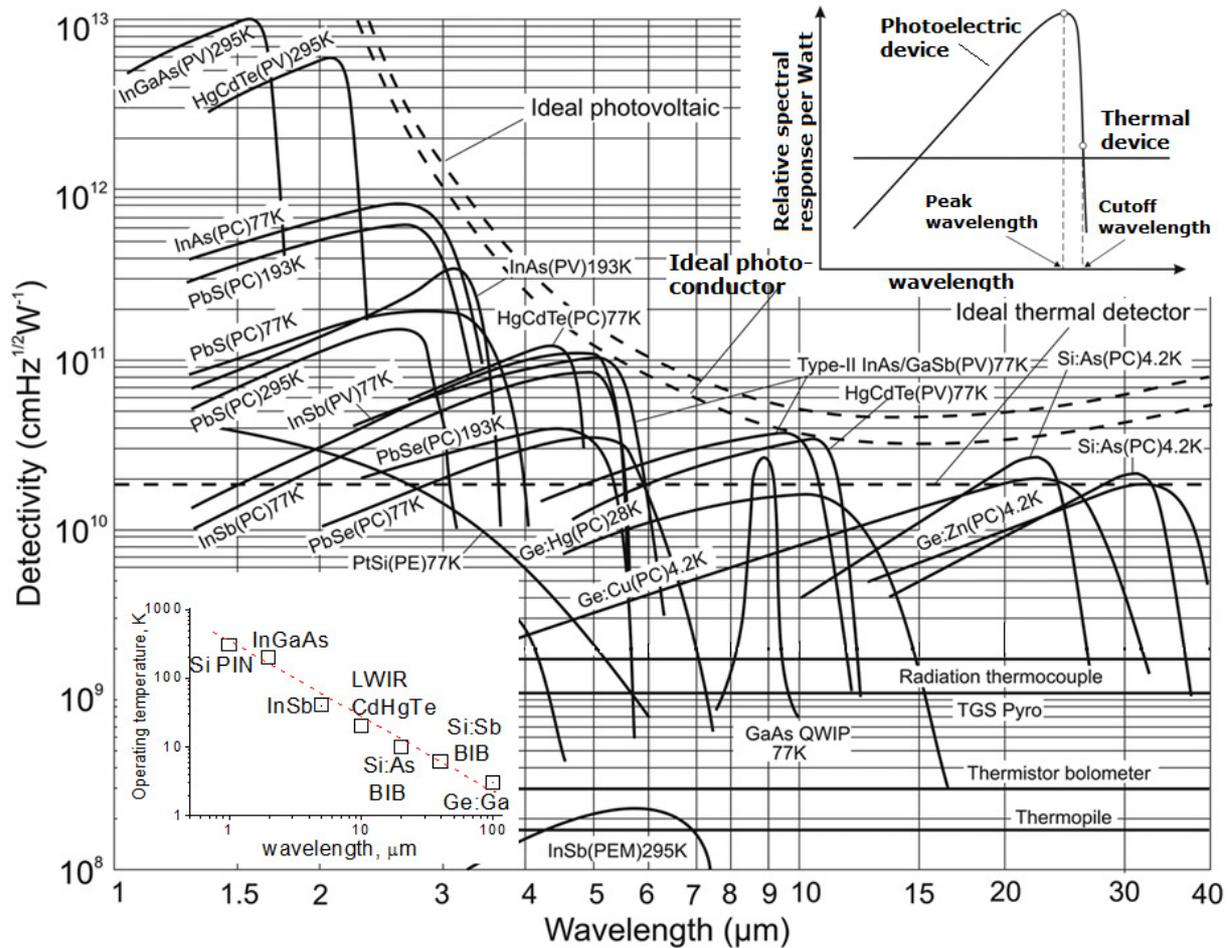
materials with improved  $zT$  for power generation. One example of these materials is the semiconductor compound  $\beta\text{-Zn}_4\text{Sb}_3$ , which possesses an exceptionally low thermal conductivity and exhibits a maximum  $zT$  of 1.3 at the temperature 670 K. This material is also relatively inexpensive and stable up to the above mentioned temperature in vacuum, and can be a good alternative as compared to materials based on  $\text{Bi}_2\text{Te}_3$  and PbTe [9]. The development of tin selenide single crystal that produces a record  $zT$  of 2.6 in one direction is among the most exciting developments for thermoelectric materials [8]. Other new materials of interest include skutterudites, tetrahedrites, rattling ions crystals [9], carbon nanotubes, PEDOT:PSS, hybrid compositions such as poly[KX(Ni-ett)]/poly(vinylidene fluoride) (PVDF) [10], or exotic constructions of  $\text{C}_{60}$  molecules sandwiched between top and bottom graphene electrodes [11]. Despite some new advantages attributed to the recently developed materials, for instance, flexibility, their figure of merit remains low. For example, the highest  $zT$  value 0.42 was achieved at room temperature for PEDOT:PSS films [12].

As alternative to improving the  $zT$ , the development of new materials can be focused on increasing electrical power output, decreasing cost and selecting environmentally friendly compounds. For example, when the fuel cost is low or almost free, *e.g.*, in waste heat recovery, then the cost per watt is only defined by the power per unit area and the operation period. As a result, it has been initiated a search for materials with high power output rather than high conversion efficiency. For example, the rare-earth compounds  $\text{YbAl}_3$  has low figure-of-merit, but it has a power output, which at least doubles that of any other material and can operate over the temperature range of a waste heat source [13].

Despite the fact that the thermoelectric materials are now actively developed, there is some skepticism concerning their perspectives in the energy solution domain [14]. It should be noted that the advantage of thermoelectric devices is that they are nonselective and can consume IR energy within the wide spectral region (Fig. 3) and they also do not have a quantum threshold restriction, from which the device becomes active. However, a sufficiently large thermal gradient is nevertheless needed for their effective work. Also, their response per watt to the incident radiation is several orders of magnitude lower than the peak response of photoelectrical devices.

## 2.2. Photoelectric methods of conversion of IR radiation to electricity

Photoelectric methods are based on electron excitation as a result of absorption of the IR radiation. Since the energy of IR photons is usually low, less than 1.6 eV, narrow gap materials are needed to harvest IR radiation. For this purpose, narrow gap inorganic semiconductors and semimetals, inorganic quantum wells and quantum dots, superlattices, and some organic compounds can be employed (Fig. 4).



**Fig. 3.** Comparison of the spectral response of various thermal and photoelectrical commercially available IR radiation-to-electricity converters, along with the scheme of their relative spectral response and the scheme of operation temperature as a function of wavelength (shown as inserts). Theoretical curves for the background limited detectivity for ideal photovoltaic and photoconductive converters and thermal converters are also shown. Adapted from Ref. [15].

It is well known that some semiconductors are gapless or have a band gap smaller than 1 eV (equivalent to 1.24  $\mu\text{m}$ ), so that they are able to absorb the near-IR (NIR) radiation (Table 1). However, there are few candidates, e.g., HgSe, HgTe,  $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$  that can collect energy from the middle and even far IR range, too. These latter compounds, however, are toxic, and their application, therefore, are to be restricted. Nevertheless, development of these materials in the form of colloidal particles [16] packed in the inert matrix might overcome this problem. The advantage of the nanoparticle application is also due to opportunity to tune their range of absorption by simple changes of the particle size (Fig. 5). Recently, it was reported a successful application of colloidal quantum dots in photovoltaics that demonstrated 4.2% power conversion efficiencies in the IR range, which is even better than for the visible-wavelength PV devices prepared from solution-processed colloidal particles [17]. The best solution-processed photodetectors based on quantum dots have also demonstrated good sensitivities in terms of specific detectivity up to  $10^{13}$  Jones, exceeding the sensitivity of the best epitaxially grown short-wavelength IR (SWIR) photodetectors [17].

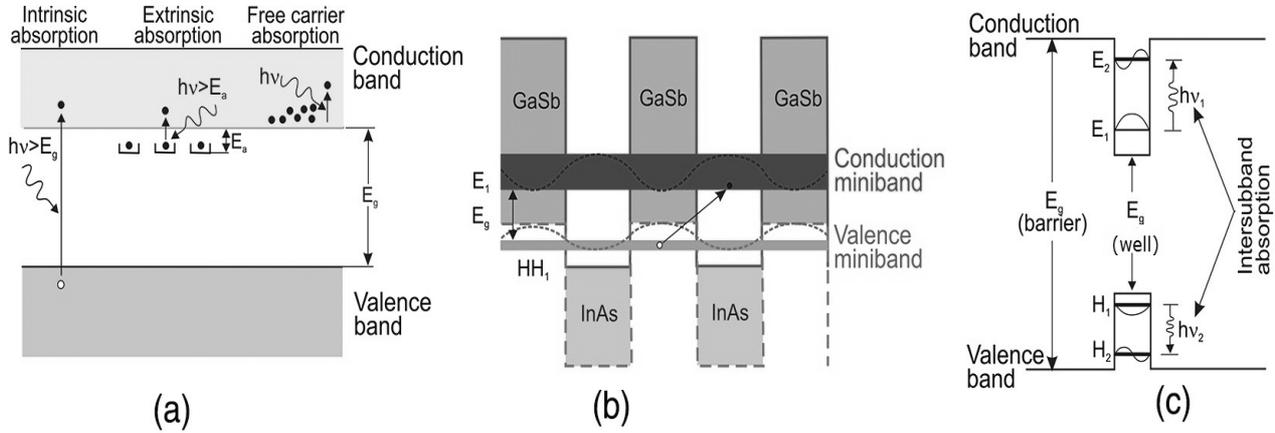
However, to extend the range of absorption of the IR radiation to the middle and far IR ranges, materials with even narrower band gaps are needed; this can be achieved using the energy levels of shallow acceptors within the band gap, for example, in Ge:Cu, Ge:Zn, Si:As semiconductors (Fig. 4a). The other methods include employment of narrow mini-bands formed in semiconductor superlattices and intersubband absorption in semiconductor quantum dots (Figs. 4b and 4c). Since the electronic excitation in the middle and far IR ranges is approaching the thermal energy at room temperature (26 meV), and the vibronic excitations thus affect the operation of the photonic device, efforts should be undertaken to reduce this factor by cooling of the absorber. The longer the wavelength of the IR absorption, the deeper the cooling should be (Fig. 3).

Although the peak quantum efficiency of the best photoelectric converters exceeds 80% [18], low operation temperatures remain the greatest disadvantage of the photoelectric systems for harvesting IR radiation, since cooling requires additional energy.

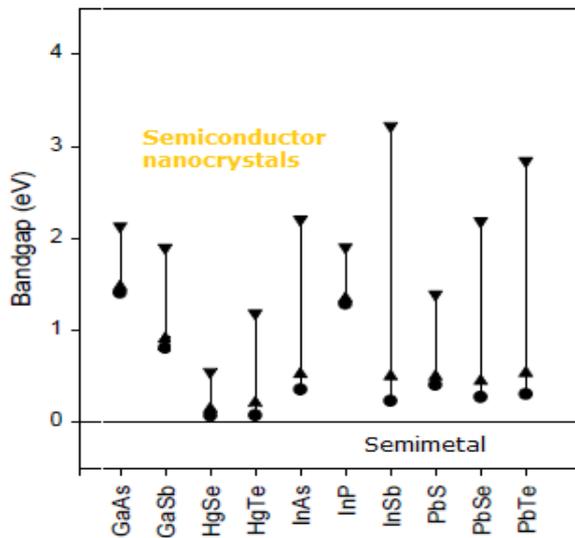
Except for inorganic IR materials, some organic molecules with extended  $\pi$ -conjugated chains can also absorb NIR light with the wavelengths up to 1  $\mu\text{m}$  [19].

**Table 1.** Some bulk semiconductor crystals with intrinsic absorption of the IR radiation.

Semiconductor crystals	InAs	PbTe	PbSe	SnTe	InSb	Hg <sub>0.84</sub> Cd <sub>0.16</sub> Te
$E_g$ , eV	0.36	0.31	0.27	0.18	0.17	0
Absorption edge, $\mu\text{m}$	3.5	4.0	4.6	6.9	7.3	apparently all IR range



**Fig. 4.** Electronic excitation processes in: (a) bulk semiconductors, (b) quantum wells, and (c) type-II InAs/GaSb superlattices.



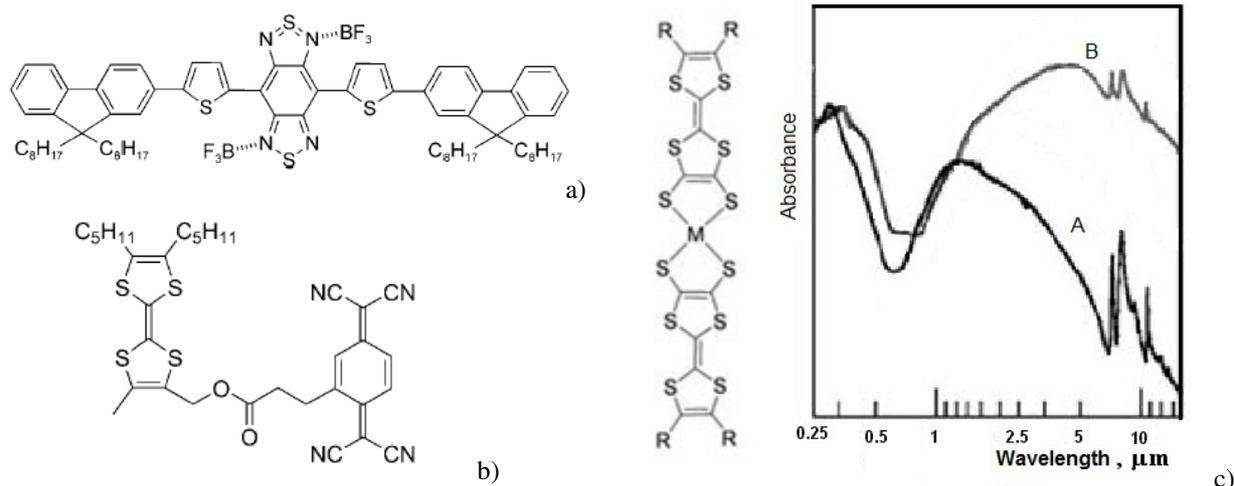
**Fig. 5.** Variation of the band gap of some semiconductor crystals controlled by the crystal size. Adapted from ref. [16].

This class of materials includes metal-organic complexes, ionic dyes, extended  $\pi$ -conjugated chromophores, and donor-acceptor charge transfer chromophores. Very promising results were obtained through development of a new series of donor-acceptor and donor-acceptor-donor D- $\pi$ -A- $\pi$ -D NIR compounds (Fig. 6), where absorption can be tuned within the wavelength range 0.6...1.4  $\mu\text{m}$  [19]. Donor-acceptor compounds of tetrathiafulvalene-tetracyanoquinodimethane (TTF- $\sigma$ -TCNQ), fused porphyrin ribbons and TTF-dithiolato metal complexes represent even more promising examples,

because their absorption spectra extend to the middle-IR and demonstrate the absorption maxima at 1.6, 2.9, and 4.6  $\mu\text{m}$ , respectively, where the thermo-excited electron transfer can take place [20]. Great opportunity can be expected also from the carbon materials and particularly graphene [21] that has a zero band gap and, therefore, can absorb photons from the broad IR range. Thus, design of energy converters based on organic materials that combine high stability and electronic absorption extended to the middle and far IR ranges is an exciting and challenging problem.

### 3. Storage of the IR energy

Storage of the IR energy is a strategy for its accumulation and a subsequent release upon request, so that it can be considered as a delayed IR energy conversion to the consumable form such as electricity. Again, we can consider two different processes of IR energy transformation. Majority of the IR photons that do not excite electrons but phonons, produces heat to be converted and stored. The methods that use the energy of phonons or vibronic excitations will be referred to further as thermal conversion methods. The thermal conversion methods can be separated into two major groups in accord to physical principles used for energy conversion and storage [22]. The first group is based on a common property of matter to experience bulk heating, where the value of the stored energy is proportional to specific heat capacity of the material used, giving rise to the so-called *sensible heat* [23, 24]. The higher capacity  $C$  of the material is, the higher amount of heat can be accumulated. Here, the energy storage is based on the temperature change in the material upon its heating or cooling, and



**Fig. 6.** Examples of organic compounds with electronic absorption of NIR to middle-IR radiation: a) donor-acceptor-donor D- $\pi$ -A- $\pi$ -D; b) TTF- $\sigma$ -TCNQ; c) TTF-dithiolato metal complex with the absorption spectra indicated for (A) R=H, M=Pd, and (B) R=Me, M=Ni (Adapted from ref. [20]).

its unit storage capacity [J/g] is equal to heat capacity  $C$  of the material, multiplied by the temperature change  $\Delta T$ :

$$Q = m C \cdot \Delta T, \quad (1)$$

where  $Q$  is the stored energy and  $m$  – mass of the material. There is a lot of materials that can produce the sensible heat, with water possessing one of the best specific heat capacity of 4190 J/kg·K.

The second groups deals with the property of materials to absorb/release heat (which is called a *latent heat*) upon phase transitions [25-27]. If heating results in a certain phase transition of the material, the reverse phase transition will release the same amount of energy in the form of heat, so that the IR energy can be stored as long as a certain phase of matter is sustained. The storage capacity of the phase-change materials (PCMs) is proportional to mass ( $m$ ) and specific latent heat of the phase change ( $L$ ):

$$Q = m L. \quad (2)$$

Examples of PCMs are water/ice, paraffins, metals, metal eutectics, fatty acids, salt hydrates, *etc.*

The third group of methods should be assigned to photonic ones, because IR photons here are able to induce electronic excitation of the absorber which may store part of the IR energy as chemical energy through photochemical reactions that lead to new chemical compounds with high-energy chemical bonds as a result of electron transfer (such as splitting of water to hydrogen and oxygen). The created chemical bonds can further release their energy upon disruption [28, 29], as shown in reaction (3),



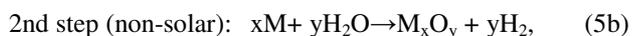
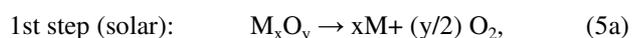
These methods also can be potentially used for charging the electrochemical batteries through photovoltaic cells, and chemical fuel generation. However, because the energy of IR photons is low, the above methods are not so efficient as compared to those employing photons of visible light. For example, it was reported the development of transparent solar cells that operate using predominantly IR light [30]. The authors demonstrated power efficiencies of 1.3% with simultaneous average visible transmission of >65%. By incorporation of NIR distributed-Bragg-reflector mirrors they were successful to increase the efficiency up to 2.4% for the opaque cell, while maintaining high visible-transparency of more than 55%.

Another potential field of application and storage of IR energy is the production of hydrogen as a fuel, which possesses one of the highest energy storage density of 530 kWh/m<sup>3</sup>. The energy necessary to split water into O<sub>2</sub>/OH<sup>-</sup> and H<sup>+</sup>/H<sub>2</sub> pairs is 1.23 eV, which lies in the NIR region. So, NIR semiconductors with suitable redox potentials, such as InP, can be used for this purpose. However, the most relevant application of IR energy here is thermal-assisted splitting of water or thermolysis. The single-step thermal dissociation of water is known to proceed as follows,



Reaction (4) requires a high-temperature heat source at above 2500 K for achieving a reasonable degree of dissociation, and it also requires an effective technique for separating H<sub>2</sub> and O<sub>2</sub> to avoid formation of the explosive mixture. In recent years, significant progress has been achieved in the development of *photothermal systems* for large scale solar concentration that exceeds 5000 Suns with corresponding temperatures above 3000 K, which are capable of water thermolysis [31].

More efficient 2-step water thermolysis requires catalysts like metal oxides for intermediate redox reactions, which was originally proposed by Nakamura [32] by using the redox pair  $\text{Fe}_3\text{O}_4/\text{FeO}$  as follows:



where M denotes a metal and  $\text{M}_x\text{O}_y$  the corresponding metal oxide. The first (endothermic) step is the solar thermal dissociation of the metal oxide to the metal or the lower-valence metal oxide. The second, non-solar (exothermic) step is the hydrolysis of the metal to form  $\text{H}_2$  and the corresponding metal oxide. Since  $\text{H}_2$  and  $\text{O}_2$  are formed in different steps, there is no need for high-temperature gas separation in the net reaction. The use of sunlight to obtain the required temperature of 800 to 1,200 °C to heat up water resulted in launching of the commercial project Hydrosol-2 in 2008 in Spain, with a 100-kilowatt pilot plant erected. It was proposed that this technology could be readily scaled up to the megawatt range by multiplying the available reactor units and by connecting the plant to heliostat fields of a suitable size [33].

#### 4. Collection of the IR energy through up-conversion

Up-conversion or anti-Stokes photoluminescence (ASPL) is a phenomenon of conversion of low-energy photons to photons of higher energy, which requires additional energy gain induced by multiple photon or thermal (phonon) energy absorption [34]. This is a process in which the sequential absorption of two or more photons or photon plus phonons leads to the emission of light at shorter wavelength than the excitation wavelength. Very often, the processes of simultaneous absorption of two or more photons in non-linear media, which results in lifting an electron to higher energy levels, are also considered as photon up-conversion. Below we consider both multi- and single-photon processes leading to conversion of the absorbed light to photons of higher energy.

##### 4.1. Multiphoton up-conversion

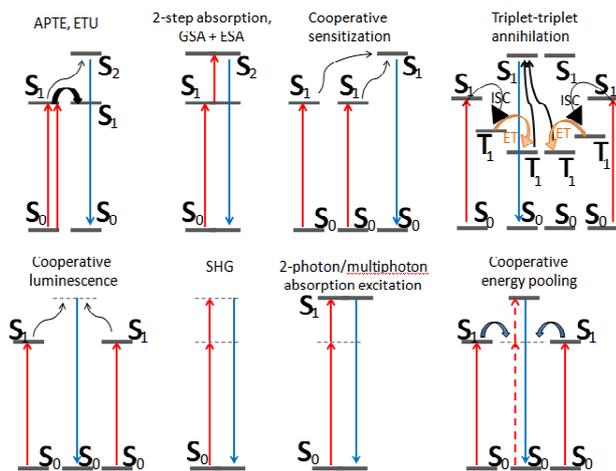
Multiphoton up-conversion processes are based on either sequential or simultaneous absorption of two or more photons; however, the probability of a multiphoton process decreases as the quantity of photons involved in the process increases. These processes can be separated into the two groups: in one group, the excitation to the upper energy level proceeds sequentially through the real electronic levels; in another group, the absorption of two photons is practically simultaneous, at least several orders of magnitude faster than in the first group, and it proceeds through the virtual levels, respectively. Therefore, the first group normally requires long-lived intermediate electronic state in order to be able to accept and then lift a transferred electron after the excitation of a neighboring donor (sensitizer) of energy before the excited intermediate state relaxes back to the ground state. The first group of processes includes APTE (addition de photon par transferts d'energie) or ETU

(energy transfer up-conversion), ground state absorption (GSA) followed by an excited state absorption (ESA), and cooperative sensitization that can be provided either due to singlet-singlet or triplet-triplet annihilation (TTA) (Fig. 7, top row). Usually, these processes need at least two players (except for ESA): one serves as a donor (sensitizer) of energy and the second as an emitter (activator), as well as relatively long lifetime of electron at the intermediate level in order it could pick up the second photon. For example, the known rare-earth ion systems have characteristic lifetimes of 4f-4f inner shell transitions as long as micro- to milli-seconds. In up-conversion through TTA, lifetime of triplet states lies in the range of microseconds, therefore, TTA is a much more efficient process than the other cooperative sensitization that proceeds via singlet-singlet annihilation (Fig. 7).

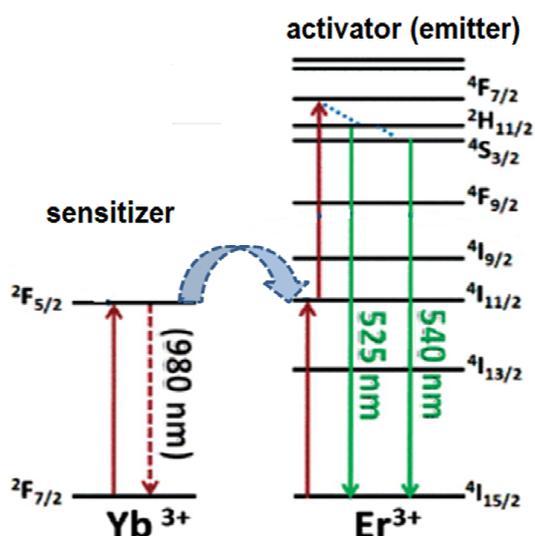
The second group of multiphoton processes includes cooperative energy pooling, second-harmonic generation (SHG), two-photon absorption (TPA), cooperative luminescence; all proceed through intermediate virtual or upper virtual level, or both (Fig. 7, bottom row). The probability for electron to be caught on the virtual level is too low and proceeds within a femtosecond time scale, therefore, high light intensity or concentration of photons is needed in order to electron will be able to take an additional photon to be excited to the higher level. For example, SHG occurs only at excitation intensities up to  $10^{13} \text{ W/m}^2$  [35], which corresponds to about  $10^{10}$  times of the integrated intensity of the terrestrial solar spectrum.

Currently, there are few material systems that are able to convert IR radiation to the visible range. The most known systems are based on the pairs of rare-earth metal ions, such as Yb-Er, Yb-Tm, *etc.*; one of the ions serves as a donor or sensitizer and the other one as an acceptor or emitter, respectively. The donor provides excitation in the red or IR range and subsequent excitation energy supply to the acceptor via a two-step process: first, excitation of the acceptor to the intermediate energy level followed by excitation from this intermediate level to the higher energy level, from which the system emits a high-energy photon (Fig. 8). The disadvantages of using the rare-earth metals in up-conversion systems is that they have small absorption cross section, spectrally narrow absorption and emission bands, and low emission quantum yield overall. To overcome the drawback due to the weak and narrow band NIR absorption, dye sensitizers connected to suitable up-converters have been recently designed [36]. The IR dye antenna assists in collection of NIR energy from the broad spectral range, however, the rare-earth up-converter still emits in the narrow band.

Recently, in order to overcome the above-mentioned drawbacks, new up-conversion systems based only on organic molecules begin to be developed. The advantage of organic dyes is that they normally have broad absorption and emission spectra and high absorption cross section as well [37]. There are two well-known mechanisms of up-conversion in organic materials, which proceed due to a TPA [38] or TTA [39].



**Fig. 7.** Schematic two-photon up-conversion processes. Real electronic levels are shown by solid bars, while virtual levels by the dashed-line ones.



**Fig. 8.** Example of the ETU process in the rare-earth system consisted of  $\text{Yb}^{3+}$  sensitizer and  $\text{Er}^{3+}$  activator.

Although both are related to nonlinear two-quantum process and need focusing excitation light, TPA and TTA are very different in details. The first mechanism requires extremely high light intensities, of the order of  $10^{10}$  of the usual solar intensity on a sunny day [40], and therefore can be ruled out as a viable mechanism for application in solar cells. The second mechanism is based on energy transfer and requires two players in the system, *i.e.*, a donor (sensitizer) and an acceptor (emitter), respectively, as it has been mentioned above. The TTA mechanism of up-conversion has certain advantages over TPA, because it does not require high excitation power density (solar light is sufficient), it possesses relatively high up-conversion quantum yield, and it allows one to readily tune excitation/emission wavelengths and strong absorption of the excitation light [41]. On the other hand, the TTA mechanism normally requires the presence of heavy

atoms in organic chromophores, such as rare-earth metals, which induce strong spin-orbit coupling responsible for the efficient intersystem crossing from excited singlet to triplet levels. Efficient intersystem crossing in heavy metal-free organic chromophores is rare and was found only in few compounds [42], so the absence of heavy atoms normally leads to the lack of strong spin-orbit coupling effects and the lack of phosphorescence in organic compounds, respectively. The other drawback of TTA mechanism of up-conversion is its vulnerability in respect to molecular oxygen that is an ultimate quencher of the photon up-conversion process. In order to overcome this restriction, protective matrices with high barrier properties against oxygen should be designed [43]. A problem with TTA up-converters is the spectral range as well. The longest wavelength at which the TTA system can be excited was reported to be close to 780 nm for the pair of PdTAP-rubrene [44]; it means that these systems are not able to capture the IR photons. Because no efficient up-conversion of near-IR radiation at the wavelengths beyond 800 nm has been found for the above systems, the use of TTA up-converters is limited to solar cells with relatively wide band gaps only.

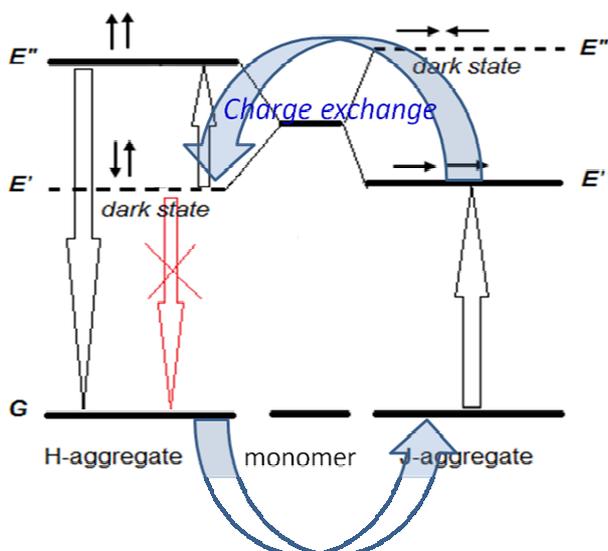
To summarize, the drawbacks of the known up-conversion systems are as follows (see also Table 2):

1) Inorganic rare-earth based materials possess small absorption cross sections, narrow absorption and emission bands, low emission efficiency.

2) Organic TPA is an intramolecular process with relatively low efficiency, so it requires extremely high light intensities, of the order of  $10^{10}$  of the usual solar intensity ( $>10^8 \text{ W/m}^2$ ).

3) Organic TTA represents a bimolecular system (sensitizer + emitter) and usually requires the presence of heavy atoms to facilitate intersystem crossing, it is vulnerable to molecular oxygen, it has limited excitation wavelengths below 800 nm and small anti-Stokes shift.

However, molecular up-conversion via novel mechanisms becomes a subject of recent research trends. Particularly, it was proposed a novel up-conversion mechanism due to the unique ability of specific IR dye to form both J- and H-aggregates in the condensed state, which play the role of sensitizer and emitter, respectively, between which the energy transfer (charge exchange) occurs through the dark states (Fig. 9) [45]. However, the quantum yield of this process is too low, and the mechanism still needs confirmation. Cooperative energy pooling (CEP) is another energy transfer mechanism that provides an alternative route towards efficient and applicable photon up-conversion [46, 47]. CEP is the process, where two photoexcited sensitizer chromophores non-radiatively transfer their energy to a single higher-energy state in an acceptor chromophore (Fig. 7). CEP is different from the Förster resonance energy transfer process, because it is carried out via coupling of the emissive states of both sensitizers with the TPA tensor of the acceptor and thus occurs through the virtual state of the latter [48]. In this way, both sensitizers act as photon storage centers that facilitate to achieve TPA in the acceptor and thus to enable up-conversion with greater efficiency and at reduced excitation intensities.



**Fig. 9.** Proposed up-conversion scheme through electron exchange between H- and J-aggregates of the IR dye. Adapted from Ref. [45].

#### 4.2. Thermal-assisted up-conversion

Thermal-assisted or hot-band absorption (HBA) assisted ASPL is a one-photon process that does not require sensitizer or intensive excitation conditions, but employs additional energy of vibronic modes at environmental temperatures [49]. HBA assisted ASPL has attracted growing interest in recent years due to potential application in various fields, such as photovoltaic energy conversion [50], photoluminescence bioimaging [51], thermal probes [52], optical refrigeration of solids [53-56], etc. It was shown that this type of up-conversion can take place both in inorganic materials, such as rare-earth-doped crystals [57-59], II-VI [60, 61], InP [62], PbS [63] semiconductor quantum dots, InP and GaAs bulk semiconductors [64], inorganic perovskite nanoparticles [65-67], carbon nanotubes [68], and some organic dyes based on rhodamine [69], porphyrin [70], spirolactam moieties under acidic conditions [71], polymethine [72], fluorescein and oxazine [49].

Again, application of organic dyes in this process has some advantages, since they normally possess a broad absorption with high molar extinction coefficient. However, the organic dyes very often can absorb only in the visible range. Therefore, employment of NIR dyes for up-conversion of IR energy is needed. The additional advantage of NIR dyes is relatively large distance between hot absorption and anti-Stokes emission wavelengths. Since the energy difference between hot absorption and emission in ASPL phenomenon is dictated by the energy of vibronic modes, which in organic molecules usually lie in the range of 600 to 1600  $\text{cm}^{-1}$ , the anti-Stokes shift in the visible region (at absorption around  $\sim 500$  nm) is about 15 to 40 nm, while for absorption in the NIR region (near  $\sim 800$  nm) the anti-Stokes shift will be in the range of  $\sim 38$  to 102 nm.

Therefore, the wavelength resolution in the NIR region increases as compared to the visible, and also laser cooling effect that accompanies the ASPL phenomenon becomes more efficient, since it depends on the ratio of the HBA wavelength to the ASPL one [73].

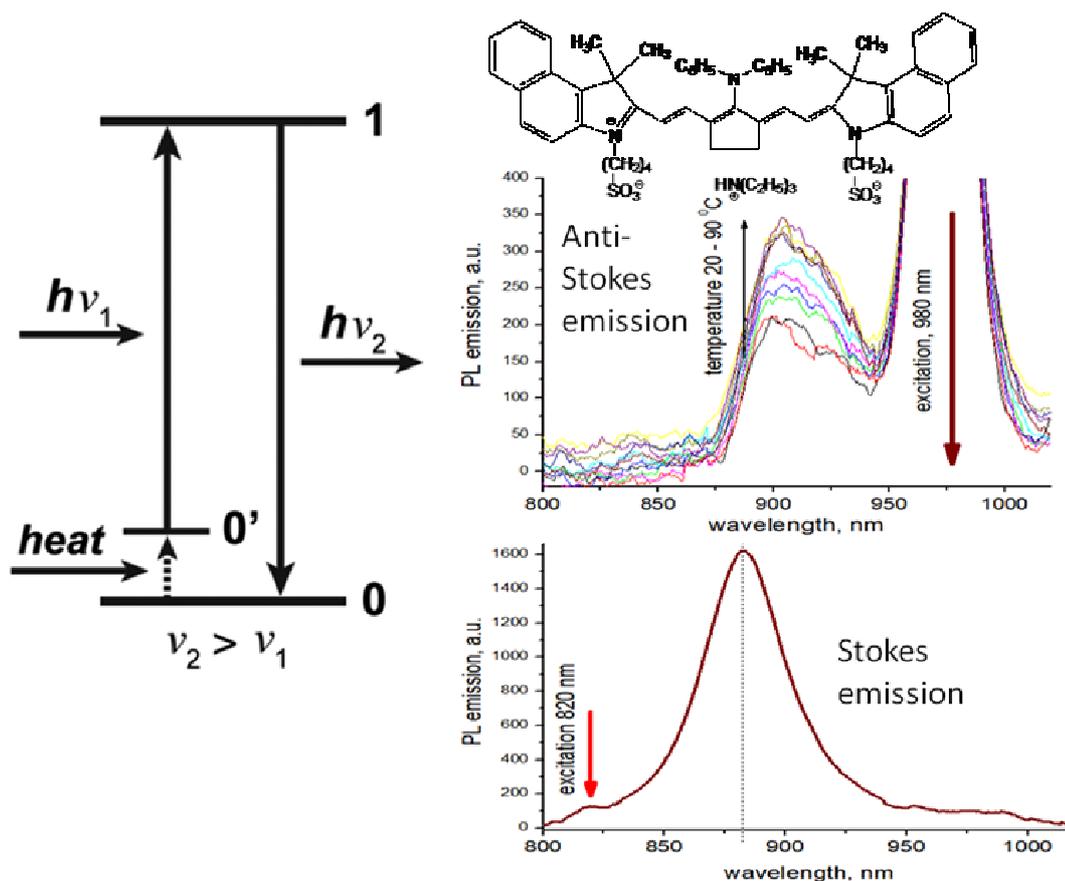
Indeed, the expected anti-Stokes shift was observed recently in novel NIR tricarbocyanine dyes that are able to produce HBA assisted ASPL and thus to convert absorbed NIR energy to the higher energy region; in this process, both excitation and emission of the dye molecules take place in the NIR region, *i.e.*, at 980 and  $\sim 880$  nm, respectively (Fig. 10). This relatively deep shift of the HBA assisted ASPL phenomenon to the NIR region is demonstrated for the first time, which makes the used dye unique due to certain advantages. First, the anti-Stokes shift relatively to the HBA or excitation wavelength reaches here the magnitude of up to 100 nm, which is the record one for the HBA assisted ASPL phenomenon and which is comparable with the up-conversion wavelength shift through triplet-triplet annihilation process [41]. In terms of energy, the above shift (144 meV) is still low as compared to the triplet-triplet annihilation systems (which demonstrate typically 300 to 700 meV), as the latter up-converts energy mostly in the visible region of the spectrum. The second advantage is the laser cooling efficiency, which showed a better net cooling power and faster cooling speed as compared to another organic dye rhodamine. Potential application of dyes of this type for the NIR imaging, however, requires further chemical modification of their structure to shift the ASPL emission to the visible range.

Overall, both multi-photon and phonon-assisted up-conversion processes have certain advantages and disadvantages, which are summarized in Table 2.

#### 5. Conclusions

IR radiation represents a huge domain of energy, which can be exploited by the mankind for its needs, but which still remains unused on the large scale. The feasible devices that are able to harvest IR radiation have been classified here as two types consisted of thermal and photoelectrical converters, respectively. Briefly, the thermal converters are able to collect IR radiation in a broad spectral range, and they normally do not require cooling, but their efficiency is low. Therefore, they can be used in locations where the IR energy represents a waste heat, for example, near car exhaust pipes, *etc.* On the other hand, photoelectric converters of IR energy are more efficient devices, which quantum efficiency can reach up to 100%. However, the disadvantage of the photoelectric converters is that they can work only in the limited, often narrow spectral range to collect IR photons. They also need low operation temperatures, since the bandgap in the far IR range approaches the energy of thermal noise that can be reduced only by freezing of the phonon continuum.

The IR energy can also be collected through up-conversion methods. Although their efficiency is usually



**Fig. 10.** Stokes (lower spectrum) and anti-Stokes (upper spectrum) PL emission of solutions of dye 1859SL [74]. As shown, ASPL phenomenon is more distinct upon heating, which allows one to populate vibronic levels of the ground state. The energy scheme of the ASPL process is shown at the left.

**Table 2.** Major materials used for up-conversion, the up-conversion mechanisms and their main drawbacks.

Materials	Excitation mechanism	Drawbacks
Inorganic rare-earth based materials	Donor (sensitizer) to acceptor (annihilator) energy transfer	Small absorption cross-sections narrow absorption and emission lines, low emission efficiency
Organic molecules (Rhodamine B, PYC, APSS, D- $\pi$ -A chromophores, <i>etc.</i> )	Two-photon absorption	Intramolecular process, the efficiency is relatively low and requires extremely high light intensities, of the order of $10^{10}$ ( $>10^8$ W/m <sup>2</sup> ) of the usual solar intensity.
Donor (sensitizer) and acceptor (emitter) pair	Triplet-triplet annihilation	The bimolecular system (sensitizer + emitter), usually requires the presence of heavy atoms to facilitate intersystem crossing, it is vulnerable to molecular oxygen, has a limited excitation wavelength $<800$ nm, small anti-Stokes emission.
Inorganic rare-earth based materials, semiconductor quantum dots, organic molecules (rhodamine, merocyanines, <i>etc.</i> )	Hot-band absorption	Small up-conversion shift, normally no more than 100 nm, low efficiency.

low, they become a subject of the increasing research attention in recent years, particularly because they can be integrated with the conventional solar cells to increase their efficiency due to the added up-converted photons from the IR range.

Direct consumption of the IR energy has further advantages as compared to the visible photons, which are the major “fuel” of the conventional solar cells. First, the quantity of IR photons is much larger as compared with photons of the visible light from the solar spectrum (see Fig. 1); therefore, the IR devices can potentially collect more photons and produce a larger amount of electron-hole pairs as compared with the conventional solar cells operating in the visible region. On the other hand, development of efficient devices that can respond in the middle and far IR ranges and which are able to collect light quanta from a more extended spectral range still is the challenging task today.

Second, consumption of the IR energy can render a certain influence on the climate changes. In this regard, there is a question which part of the IR spectrum is most suitable to be used. If, for example, the corresponding devices will collect IR energy that normally leaves Earth through the transparency window of the atmosphere (*i.e.*, within the wavelength range of 8 to 13  $\mu\text{m}$  or energy range 0.1...0.15 eV), their work then can provoke the increase in the temperature regime at the earth surface. On the other hand, if the IR converters will collect energy in the region of absorption of greenhouse gases and scatter it in the transparency window of the atmosphere, their application could weaken the greenhouse effect and decrease the average earth temperature, respectively. Therefore, the use of the above IR converters could help in controlling the climate changes. However, these effects, if any, can be expected only if the converters of IR energy will be applied on the large scale.

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#### Authors and CV



**Oleg Dimitriev** is the senior researcher at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. His professional interests cover a wide range of topics, namely: organic electronics, energy conversion issues and ecological ones. He is

the fellow of Swedish Institute, Fulbright Foundation and DAAD, the author of books “Sensible Universe” and “What does your clock show?” (in Russian).