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ABSTRACT

In this paper, we present results authors published initially on the white light emission with broad band (330-465 nm) excitation of the specially prepared nano-phosphor: Eu^{3+}: ZnS which is capped with sodium methyl carboxylate and on pure red-light emission from the nano-phosphor when capped with alpha methyl acrylic acid and prepared in a different method. Then we discuss possible methods of future improvement of the white light emission from the nano-phosphor. We then present the cost effective and energy efficient method of obtaining highest quality natural white light sources using such nano-phosphor and blue or near UV blue light emitting diodes. The latter discussion includes the driving circuit for the white LED and powering the LED by concentrated solar photovoltaics for both lighting and waste heat energy storage for completely clean energy natural white lighting sources.

Keywords: Natural white light sources; cost effective, energy efficient, Eu^{3+}:ZnS, LED driver circuit, solar concentrator.

1. INTRODUCTION

Lighting accounts for 20% of global building electricity consumption. Nowadays, most of the lighting sources specially, in industrialized and newly industrialized countries, are fluorescent tubes. The latter however contain toxic mercury and the disposal of the tubes poses environmental hazards. Moreover, the radiation from fluorescent tubes causes health problems and the light is not of the same quality as natural white light. Natural white light is found to be the best for the human mind's creativity, efficiency and working functionality. In this regard, energy saving solid state light emitting diodes (LED) offer a great solution. However, none of the phosphor materials available today, except the one invented by us[1-2], produces natural white light as measured in terms of chromaticity coordinates (CC) and color temperatures (CT). The phosphor invented by us is experimentally proven to produce the best quality natural white light (in terms of CC & CT) to date with either a blue LED or a near UV LED. It can produce near natural white light over a broad optical excitation range. This phosphor material has great potential for applications in the future and natural white light sources will consume one-third of the power/energy that is consumed by current fluorescent tubes including compact ones (CFL). At Sustainable Green Power Technologies, we are soliciting grants/support for research with the following objectives: (i) to enable us to improve the nano-phosphor further so that a single nano-phosphor can generate the best quality natural white light when the phosphor is excited by a blue LED or a near UV LED; (ii) to produce a few working prototype models of cost-effective and highly energy efficient natural white light sources using the novel phosphor we have currently invented. Once we carry out (ii), our next goal is to power the light source using first a (iiia) regular solar panel and next a (iiib) small area solar panel combined with a solar concentrator either in the form of a large Fresnel sheet or a parabolic concentrator. The second one will reduce the dependence on silicon for the solar panel and it will also store the solar energy that is otherwise wasted as heat (i.e., the part that is not converted to electric power by the panel). Our research will also explore the possibility of invention of new phosphor that when excited by high power light with wavelength greater than blue light will generate white light through multi-photonic phosphor-up conversion rather than the phosphor down-conversion techniques used by most phosphors. Our studies show that this research when successfully executed can very cost effectively be used in lighting around the world, and this is especially promising

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given the demand for lighting in many parts of Africa and Asia. Also in developed countries like the US, the cost effective natural white light sources will save two thirds of the energy used for lighting and help maintain a cleaner environment. The global market potential for the high-quality natural white light sources is around 100 Billion dollar. Environmental pollution and global warming are related to energy production (most of which gives rise to emissions) which in turn is dictated by energy consumption and development. The solution to this problem lies in enhancing the efficiency of energy utilization and that of energy production so that energy wastage is minimized. The higher the efficiency of energy utilization, the lesser is the effect on environmental pollution and climate change/global warming.

The above-mentioned light source is one of the solutions to environmental pollution and global warming. Our small company is dedicated to finding the most energy efficient and cost effective natural white light source as discussed above.

1.1 Past approaches to generate white light

There are a variety of ways by which white light LEDs are fabricated, among which the colour mixing method and the phosphor down-conversion method are the most commercially viable[5-9]. In the colour mixing approach to white light, three separate red, green and blue LEDs are combined to form white light. The efficiency of the colour mixing approach is high, but the problem associated with obtaining a consistent colour across an array is considerable since the drive voltages for different wavelength differs. This requires a complex drive circuitry with the consequent wastage of significant energy. Also, the maintenance of proper colour balance using this approach is complex as red, green and blue LEDs degrade at different rates over time and with variation in temperature. The appearance of white also changes with viewing angle[5]. In order to overcome these challenges several efforts have been made to produce white light without phosphors, the approach proposed[10] involves stacking two or three InGaN/GaN quanta well structures of different indium content that emits in blue and yellow or blue, green and red. Using a pre-strained metalorganic chemical vapour deposition (MOCVD) growth technique, a low-indium InGaN/GaN QW is grown before the designated light-emitting high-indium InGaN/GaN QWs to create tensile strain in the GaN barrier layer right above the low-indium QW making the incorporation of indium during subsequent growth of QWs more effective. The increased indium content then leads to efficient emission of yellow, orange and red colours. By stacking the yellow- and blue-emitting QWs on a chip[10] produced a white light LED with chromaticity coordinates of (0.334, 0.338) at injection current of 50 mA which is close to ideal condition. The colour temperature at the 50-mA injection current was 5600 K (value at sunlight at noon)[10].

However, for general illumination the warm white colour temperature (2700 K to 4000 K) is preferred. Improvement in the crystal growth of green-red emitting quantum wells is also required for efficiency enhancement and high colour rendition index for general illumination purposes. Quantum dots white-light LEDs have also been fabricated. For example, the homoepitaxial growth of ZnSe on a ZnSe substrate resulted in a self-activated emission that produces white light [11]. Such white light might be the result of combination of blue-green light from ZnSe active layer combined with yellow light from ZnSe substrate. Now CRI of this device is however poor for general illumination, the efficiency of the device is low and it has a shorter lifetime than InGaN white LEDs[11].

The phosphor down-conversion approach is the most common approach. It involves over-coating a blue- LED or UV-LED with a phosphor or mixture of different colour phosphors to create white light [12]. This method produces white LED with high efficiency and long lifespan. It also produces relatively stable colour variation with temperature. Losses in extracted light efficiency in this approach is due to the physical shape of the phosphor, position of the phosphor, the refractive index mismatch which may lead to scattering of light back into the LED and the photoluminescence efficiency of the phosphors. Conventional phosphors are often encapsulated in an epoxy or silicon matrix (glass encapsulation have also been reported[15]. The large differences in the refractive indices of the phosphors and epoxy, together with small particle size and weak absorption of the phosphors give rise to diffuse scattering of incident and emitted light. This scattering caused by the phosphor reduces efficiency due to increased path length for light inside the phosphor, leading to re-absorption losses and decreasing the effective quantum efficiency the phosphor. The longer path lengths caused by randomization of light directionality as it passes through the phosphors increases light contact with high loss areas such as reflectors, phosphor layer, and LED chip which reabsorbs the light [15] In order to minimize losses due to phosphors and enhance efficiency, the use of hemispherical optics and suspended phosphor on semi-transparent host (glass) have been demonstrated by[15] to have satisfied the maximum efficiency requirements of low scattering compared to the conventional phosphor on chip method [15]. Again, there are optical backscattering associated with using conventional bulk phosphors. The losses account for about 50% reduction in the package efficiency of phosphor converted LEDs[7].

Another approach to reducing losses due to backscattering is the use of quantum dots phosphors. Quantum dots have a much smaller size than the wavelength of visible light thereby reducing scattering and associated optical losses [9]. However, for large semiconductor quantum dots (QDs), in addition to scattering of light there is also an overlap between absorbance and emission bands which can lead to strong self-absorption of the emitted lights. The decoupling of this overlap by synthesizing small QDs allows the majority of their atoms to be located at the QD interface, the chemistry of these interface alone determines the emission colour, while the absorption is fixed by the dot size thereby eliminating the effect of self-absorption of emitted light. High-brightness light emitting diodes (or high brightness light emitting diodes) are LEDs that combine the properties of high internal quantum efficiency, high extraction efficiency and high phosphor conversion efficiency to produce high luminous efficacy. At present the commercial high-brightness white LEDs have efficacy above 150 lumen/Watt[4]. Given the challenges associated with developing very efficient white LEDs as enumerated above, it is imperative that developing countries should invest in the research towards the development of efficient white LEDs in their countries/continents rather than relying on the developed nations for breakthroughs. Investment in research and development of efficient high-brightness white LEDs and solar cells would drastically reduce cost of these materials and encourage their deployment in rural areas. In future, development of high-brightness white LEDs and low cost solar cells would eliminate darkness from the villages of developing countries while providing huge cost savings in city-lighting. To explore the possibility of generating white light with high CRI, low CCT and high efficiency using LEDs [1] have recently focused on the studies of synthesis and characterization of Eu-doped ZnS nanoparticle that could serve as a potential candidate for red-emitting phosphor. Their studies have revealed that pure and well-passivated ZnS:Eu^{3+} nano-particles can be synthesized with average nano-particles in the strong quantum confinement regime. The intensity of the red-light emitted from the synthesized ZnS:Eu nanophosphors was found to be size and site dependent. It is expected that further research will improve the intensity of the red-light emission and then ZnS:Eu nanophosphors can become potential candidates for white-light generation using a down conversion method involving pumping a combination of green, yellow and red phosphor with near ultraviolet (UV) LED to generate the white light.

The recent report has it that fabrication of three types of white LED with super-high luminous efficacy (η_L) and luminous flux (φ_v). The first type of white LED with a correlated colour temperature of 4600 K, had η_L of 249 lmW^{-1}, φ_v of 14.4 lm at a forward bias current of 20 mA. It was a phosphor conversion white LED lamp consisting of a blue LED die and a yellow phosphor of YAG (yttrium aluminum garnet). η_L for this white LED reached a maximum 265 lmW^{-1} at 5 mA and then decreased slightly with increasing injection current. However, the white LED was found to be deficient in red light component. To enhance the red component, a red phosphor, SrCaSiN:Eu was added to the YAG white LED. Well-passivated ZnS:Eu^{3+} red nano-phosphors[1] may also be potential candidate that can be added to above mentioned YAG white LED to improve the white light quality. A super high efficiency blue LED which was used in turn to fabricate a high power white LED with output power of 756 mW and luminous flux of 203 lm at 350 Ma [14]. They also fabricated another type of high power white LED using four high-power blue LED dies. φ_v and η_L were 1913 lm and 135 lmW^{-1} at 1 A respectively.

The discovery of a light-emitting diode (LED) with 200% efficiency[16]. When the Led is heated to 135 ºC and biased by low voltage of 70 μV - the output light power was found to be 70 pW when the input power was 30 pW. It is considered that phonons (heat) assist the transitions of electrons from conduction band to valence band (recombination of electron and holes) and increase the emission of photons more than expected from the input electrical energy. Energy conservation is however not violated. Thermally assisted enhanced photon emission has earlier been predicted in the case of picosecond Laser pulse Irradiated semiconductor thin films [17] More research is underway on the newly discovered high efficiency LED which could have tremendous application in high efficiency solid state lighting system in future. Lu et al [13]gave a brief but excellent review (up to date as of 2010) on both organic (polymer based) phosphors and inorganic phosphors for white light applications. The inorganic phosphors have numerous advantages such as simple synthesis, high yield with reproducibility, good stability, and does not disturb the chromaticity. In order to improve the white light generation Lu et al carried out fabrication of white light emitting ZnS:Mn NCs through the surface chelating of 8-hydroxyquinoline-5-sulfonic acid (HQS). They observed that the emission colors of the novel NC composite can be tuned from orange to cyan by carefully controlling the dosage of HQS. They had obtained good white light emission from the NCs with color coordinates (0.35, 0.34) by fine tuning of the surface-coordination emission and the dopant emission of QS-ZnS:Mn NCs. However, the white light emission was obtained by exciting the NCs with light of wave length 365 nm. They had speculated that the white light emission should originate from the cooperative interaction between the surface-coordination emission and the dopant emission of the NC host. The white light emission from the NCs did not seem to be tunable over a broad excitation band.

1.2 Methods of Eu^{3+} doped ZnS nano crystals

Using alpha methyl acrylic acid as the capping agent[1]

Using sodium carboxymethyl cellulose matrix (CMC) as the capping agent[2]

The first type (Type I) of sample gave intense red emission (when excited by blue light) that however was particle size dependent. The second type (Type II) of sample after proper annealing in a sulfur rich environment gave white light which resulted from A combination of the blue-green defect related bands of the host ZnS and the orange-red emission lines of Eu^{3+} ion gave rise to white light. One of the most remarkable findings was that, of all the white light phosphors is that this nano phosphor (Type II) gave white emission when excited by light over a broad excitation band with very good chromaticity coordinates. With fine tuning of the Eu^{3+} concentration, annealing time and temperature etc. it is possible to get the CMC capped Eu^{3+} doped ZnS nano crystals that could give white light with ideal chromaticity coordinates (0.335, 0.335) using UV, near UV and blue LED.

1.3 Synthesis of ZnS: Eu/CMC at different Eu^{3+} concentrations

The synthesis of ZnS:Eu^{3+} embedded in CMC matrix was carried out as follows; 100 ml of $ZnSO_4.7H_2O$ was mixed with 0.1464 g $EuCl_3.6H_2O$ to obtain 1 mol% {molar ratio of $[Eu^{3+}]/[Zn^{2+}]$} in deionized water. The mixture was refluxed at the boiling point of water (100 C) for 1 hour and cooled to room temperature. This was followed by the addition of CMC and the pH adjusted to the required value. Then 100 ml of $Na_2S.9H_2O$ was added drop wise with continuous stirring at room temperature. Stirring was continued for another 15 min after the last drop of S^{2-} precursor solution was added. A powdered sample was obtained by treating the colloid through centrifugation and drying at 90 C for 6 hours. The sample was labeled S1. The same procedure was followed for 5 mol% Eu^{3+} (S2). For purposes of optical characterization, a small quantity of the freshly precipitated sample was dissolved in ethanol solution and spin-coated on a glass slide (thin film). Both the thin film samples of S1 and S2 and their corresponding powdered samples were subjected to post-synthesis annealing in a sulfur-rich atmosphere. The annealing temperature was set at 300 C with annealing time being 35 minutes. The corresponding annealed samples were labeled as S3 (1 mol%) and S4 (5 mol%), respectively.

1.4 Characterization

The as-synthesized (un-annealed) samples and the annealed samples of ZnS:Eu^{3+} nanoparticles embedded in CMC matrix were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), photoluminescence measurements (PLE and PL) and UV-Vis spectroscopy. Optical absorbance measurements for all the samples were carried out to determine their energy band gaps. The UV/VIS spectrophotometer used was JENWAY 6405 spectrophotometer (EMDI laboratory Akure, Nigeria). X-ray diffraction (XRD) measurements were carried out using a PANalyticX'Pert PRO diffraction machine located at the Center for Nanostructured Materials Pretoria, South Africa. Measurements were taken using a glancing angle incidence of 3^o for 2θ value over 5 to 80^o with a scan step of 0.04^o and a time per step of 3 seconds. Photoluminescence excitation and emission spectra of all the samples were recorded using the photoluminescence facility at Laboratoire de Chimie de la matièrecondensee de Paris, France.

1.5 White light emission over broad band with Eu^{3+}: ZnS nano phosphor

Fig.1(b) shows the white light emission on CIE coordinates by nanophosphors of 5 mol% Eu^{3+} doped ZnS capped with CMC when excited over a broad excitation band 330-465 nm[2]. The emission coordinates are close the center coordinates (0.33,0.33) and the quality is high. Our objective is to improve over this so that emissions in the whole excitation occur with the ideal coordinates (0.335, 0.335). These emissions will correspond to high quality natural white light. We give below the approaches to achieve the best nano-phosphor. Fig.1a shows that when Eu^{3+} concentration is changed to 1% the light emission loses the white nature.

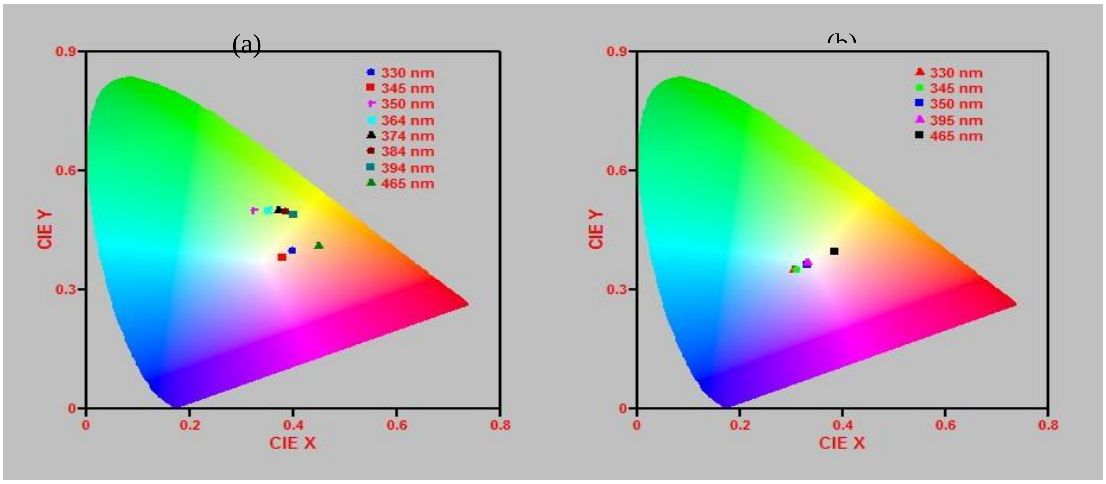

Figure 1. CIE coordinates of Eu^{3+}- doped ZnS nanoparticles (a) 1 mol% Eu^{3+} (b) 5 mol% Eu^{3+} annealed at 300 C in sulfurizing atmosphere [2]

1.6 Fabrication and performance evaluation of high quality white led source (with luminous efficacy 250 lumen/w and > 100 lumen per led) using blue led and a novel phosphor

Using Type I Phosphor:

Use Type I Phosphor that emits intense red light upon excitation by a blue LED, generate white light with a combination of the yellow phosphor YAG containing Ce^{+}. In the original white light emission by Narakuwa et al using a blue LED and the yellow phosphor, YAG containing Ce^{+}, red component is missing and the quality of the light generated is not as high as obtained using Type II [2]. In this method some investigation will be carried out to optimize the red light emission from type I phosphor and the concentration of the type I phosphor and that of the $YAG:Ce^{+}$ so as to generate the white light with ideal chromaticity coordinates (0.335,0.335) upon excitation by a blue LED.

Using Type II Phosphor (See above)

Optimize the Eu^{3+} doped ZnS nano phosphor capped with CMC so as to ascertain the correct Eu^{3+} concentration, annealing time, temperature and the correct sulfur vapor concentration environment, so that the phosphor emits highest quality white light, close to ideal chromaticity coordinates (0.335, 0.335), over the broadest excitation band (which at least 330-465 nm as investigated earlier). To our knowledge only this phosphor has this potential.

Develop the technique of deposition of thin film of this nano phosphor on to microscopic slides and concave glass surfaces, small enough to cap a blue LED.

Ascertain the optimum thickness that will ensure the highest extraction of the resulting white light, using reflector as needed and evaluate the lumen power and the luminous efficacy of the white light.

If process (ii) & (iii) do not seem to be feasible either technologically or for commercial manufacturing, then we shall apply the phosphor to the blue LED with the help of an epoxy and a glass mini cap. Using reflector, as may be needed, for highest light extraction, evaluate the lumen power and the luminous efficacy of the white light that would thus be generated. Use an energy efficient driver circuit to drive the white LED thus prepared and study the power consumption and the characteristics of the white light emission, including the lumen/W.

1.7 Preparation of white LED using the above nano phosphors

We have discussed above approaches to two types of new nano phosphors that can emit high quality white light. Once the nano phosphors are successfully prepared and tested to emit high quality natural white light, our next approach would be to make the white LED. This would be discussed in detail, in a latter paper. The approach would be to minimize the light reflections and scattering to have the highest lumen/watt. The electronics circuit that has been tested in our laboratory to be energy efficient to drive LED bulbs is shown below in Fig.2. For emission, free environment the white LED needs to be driven by solar power. Basically, a solar charge controller that includes battery charger, Load driver, Current limiting (controller),

DC Load Driver circuit

Fig.2 shows the circuit that can be used to drive a DC load (i.e., DC LED bulbs).

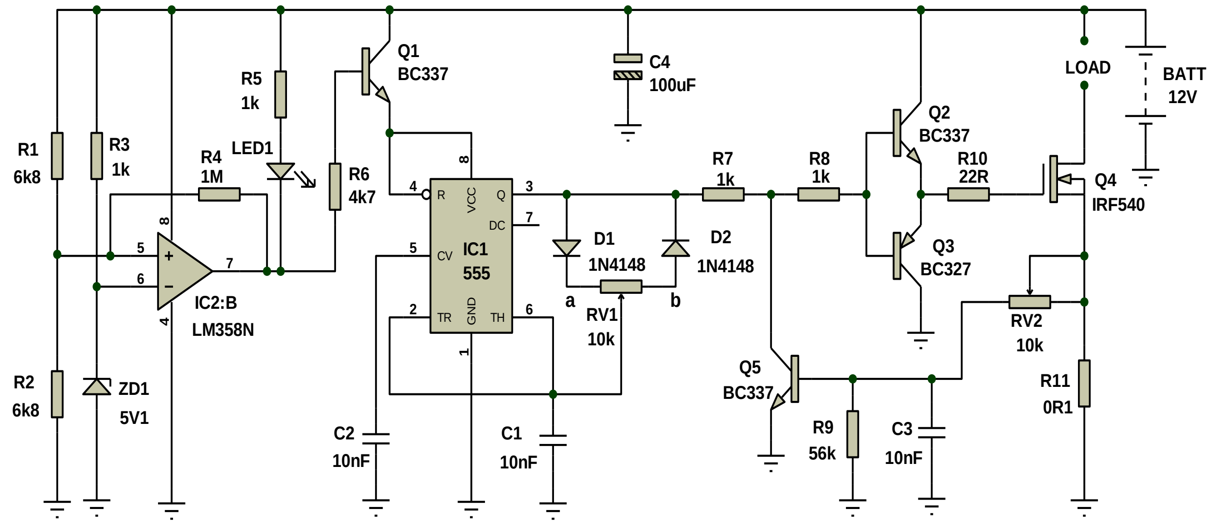

Fig.2 Laboratory tested energy efficient DC LED/LOAD driver circuit

A 555 timer oscillator and a power MOSFET driven by a push-pull low power complementary transistor pair are used for power switching of DC loads such as fans or LED bulbs (Fig.2). The above design easily facilitates the control of the current flowing through the LEDs and hence controls the brightness and dimming. Pulse Width Modulation, PWM, method provides an efficient method of achieving this. The LEDs are turned on and off at a very high frequency such that the strobing effect is not easily perceived. IC1 is a 555 timer chip arranged as an oscillator.

Our next objective is to ensure highest conversion efficiency of solar power to electrical power so that smallest size solar panel can be used to achieve the desired electrical power output and to store away the wasted heat energy from the panel, which otherwise can destroy it. To achieve this, we suggest use of solar concentrators[18] and energy storage device as shown in Fig.3. We use a concentrator so that it concentrates solar energy to 10-30 times more intense on to a solar panel connected on to the top of the copper box, if the concentrator device is a Fresnel sheet lens type or to the base of the box if it is paraboloid mirror. The heat generated from the concentrated solar energy is stored in an efficient way discussed earlier[18]. The box contains oil which takes up the heat of the solar panel. The oil is circulated by motor through coils immersed in the water tank containing phase changing materials. The box should be rotatable along with the concentrator as the sun rotates. The heat energy from the back of the solar panel is directed and stored in the water tank filled with PCM [18]. This way we shall have the most cost effective and high-quality natural white LED lighting source with high energy efficiency.

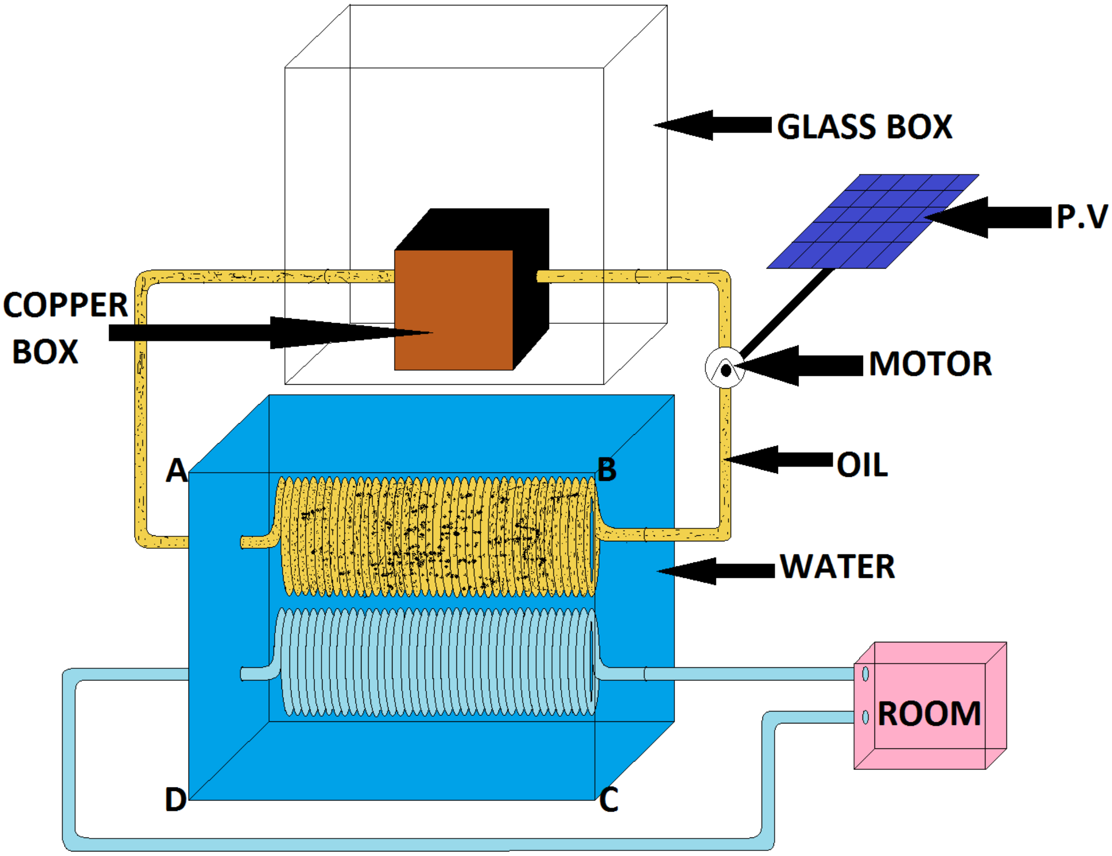

Fig.3. A solar energy storage system to work with parabolic concentrator[18]

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