

PRESENT STATUS OF THE METALLIC INTERMEDIATE BAND SOLAR CELL RESEARCH

A. Martí¹, A. Luque¹, C. Stanley², T. Dittrich⁴, P. Wahnón¹, C. Tablero¹, R. Bayón⁴, N. López¹, L. Cuadra¹, D. Zhou², J. L. Pearson², A. McKee³, A. Belaidi⁴, Y. Milovanov⁴, T. Guminskaya⁴, J.J. Fernández¹, P. Palacios¹ and J. Alonso⁵

¹Instituto de Energía Solar- UPM, ETSIT de Madrid, Ciudad Universitaria sn, 28040 Madrid, Spain.

²Department of Electronics and Electrical Engineering, University of Glasgow, Glasgow, G12 8QQ, UK.

³CST Global Ltd. B-7, Kelvin Campus, West of Scotland Science Park, Glasgow, G20 0TH, UK.

⁴Hahn-Meitner-Institut Berlin, Glienicke Str. 100, 14109 Berlin, Germany

⁵ISOFOTON S.A. Málaga Spain.

ABSTRACT: The metallic intermediate band solar cell (MIBCELL) concept has been researched for the last three years within the 5th Framework Program of the European Commission. This research pursued an ambitious objective: to put this concept into practice and thus approach a long term goal of electricity produced by a cell at a cost of less than 0.5€/Wp. As a result of this work, intermediate band (IB) material candidates have been identified and MIBCELL prototypes have been produced using quantum dot technology. Low cost manufacturing approaches, based on the use of nanoporous materials have also been researched. The quantum dot approach has provided experimental evidence of the performance of the cells under MIBCELL operating principles. The theory underlying the MIBCELL concept is also now better understood.

Keywords: Fundamentals, Devices, III-V semiconductors, Strategy

1 INTRODUCTION

The metallic intermediate band solar cell (MIBCELL, also sometimes referred to by us as the intermediate band solar cell, IBSC) is designed to enhance solar cell efficiency through the absorption of below bandgap energy photons and the extraction of the corresponding photocurrent with no voltage degradation [1,2]. In theory, this would be achieved by means of a semiconductor-like material characterised by the existence of an intermediate band (IB) located within its, otherwise, conventional gap (Fig. 1).

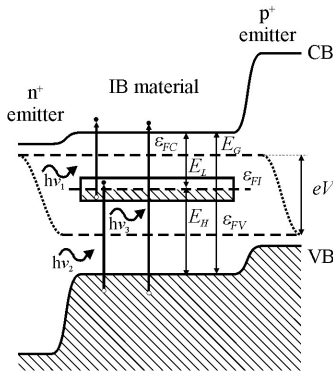


Fig. 1. Basic IBSC energy bandgap diagram showing the photon absorption process involved and the quasi-Fermi level split [2].

The achievement of the current enhancement is easily grasped once it is understood that below bandgap energy photons (photons $h\nu_1$ and $h\nu_2$ in Fig. 1), not absorbed in the absence of the IB, can now contribute to the photocurrent. Hence, in a two step process, photons like $h\nu_2$ pump electrons from the valence band (VB) to the IB and photons like $h\nu_1$ pump electrons from the IB to the CB, the net balance of this process being the creation of electron-hole pairs in the CB and VB. These pairs add to the more conventional and directly generated ones by photons like $h\nu_3$.

It is usually a little more difficult to understand how the cell output voltage may be preserved. In the theory of the IBSC, this is achieved by assuming the existence of three separated quasi-Fermi levels (ϵ_{FB} , ϵ_{FC} , ϵ_{FV}), each one associated with carriers in each of the existing bands: IB, CB and VB respectively. Due to the emitters, the output voltage, V , is ruled by the quasi-Fermi level split $\epsilon_{FC} - \epsilon_{FV}$ and therefore, it is not limited by any of the lowest band-gaps, E_L or E_H , but by E_G . In addition, the IB should be half-filled with electrons in order to provide sufficient empty states to receive an electron from the VB and to supply them for transitions to and from the IB should be of a radiative nature. This implies that the electron energy states forming the IB cannot come about from an arbitrary collection of impurity levels introducing energy levels more or less in the middle of the semiconductor bandgap. Instead, we argue that they should arise from a system that, as in ordinary semiconductors, preserves translational symmetry [3]. This is implicit in the word “band”.

Some other hypotheses complete the description of the ideal device and have been reviewed in detail elsewhere [4,5,6], together with other intermediate band related concepts. Although some of these hypotheses will be re-introduced for discussion purposes, it is not the objective of this paper to list them all.

The optimum device for operation at maximum concentration is found to be one in which $E_L=0.71$ eV and $E_H=1.24$ ($E_G=1.95$ eV) leading to a limiting efficiency of 63.2 % [1,2].

During the past three years, the IB concept has been researched within the framework of the MIBCELL project, supported by the European Commission. The partners involved can be found in the organisation list in the heading of this paper.

The ambitious overall objective of the project was to put this concept into practice and thus approach a long term goal of electricity produced by a cell at a cost of less than 0.5€/Wp. Within this framework, research carried out has fallen into one of the following categories: 1) research into identifying intermediate band

materials and to predict their properties; II) research into showing experimentally the operating principles of the intermediate band solar cell; III) research into early low cost approaches to implement the concept and IV) research into improving our understanding of the operation of the IBSC.

2 IDENTIFICATION OF INTERMEDIATE BAND MATERIALS

By means of direct energy band calculations, this approach has pursued the early identification of intermediate band material candidates. The research in this respect has been successful and several potential material systems have been identified. They are Ga_4X_3M compounds with $X=As$ or P with M being a transition metal. The energy band diagram of one of these materials is shown in Fig. 2a. It was calculated by means of the density functional theory (DFT) using both the local density (LDA) and the semi-local generalized gradient approximation correction (GGA). To assess the results and correct the band-gap problem of the LDA and GGA approximations, the exact exchange method (EXX) [7,8] was also applied.

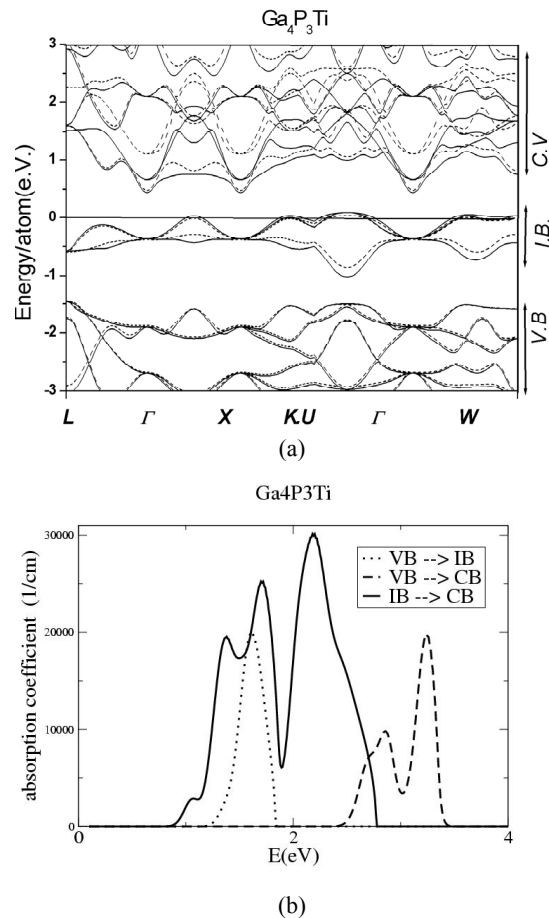


Fig. 2. (a) Band-gap diagram of one IB band material candidates (Ga_4P_3Ti), calculated using the DFT-GGA (solid lines) and the EXX (dashed lines) methods for the exchange potential. Continuous line at 0 eV represents the Fermi level showing the IB is half-filled with electrons. (b) Partial absorption coefficients for the Ga_4P_3Ti system [12].

Results of the calculations, using a double zeta plus polarization basis set, show both direct and indirect band gaps. From this knowledge of the band energy diagrams, it has also been possible to calculate some material parameters such as the density of states [9], the phonon spectra [10], and the direct transition matrix elements [11].

The value of the optical absorption coefficients of the proposed metallic intermediate band materials has also been explored [12]. In this respect, Fig. 2b shows the contribution to the total absorption coefficient obtained when only the upper band (that is, the upper line of the set of lines that form the total valence band set), the lower band of the conduction band and all the bands in the intermediate band are considered.

Further details of the calculation methods used and results obtained using this approach can be found in [13,14].

Results indicate that from the perspective of solid state theory, metallic intermediate band materials can exist. However, the practical synthesis of the materials here identified still remains a challenge.

3 THE QUANTUM DOT APPROACH

The manufacture of quantum dots was chosen as the strategy for an early implementation of a physical system in which the basic operating principles of the IBSC could be tested [15]. Within this approach, the IB would come about from the energy of the confined electrons in the dots (Fig. 3). "Quantum dots" are preferred to other low dimensional structures, such as quantum wells, because in the latter, optical transitions that in theory should lead to the absorption of a photon like $h\nu_i$ (Fig. 1) are forbidden for front illumination [16,17]. Besides, with QDs, the density of states between the intermediate level and the conduction band is truly zero. The phonon bottleneck effect [18] can assist in preventing non-radiative recombination between the CB and the IB.

Some reviews of the IB concept can be found in [19,20,21].

As a result of its mature technology, the InAs/GaAs system was chosen as the one for implementing this approach. It was expected to engineer the IBSC with bandgap values $E_I \approx 0.3$ eV and $E_G \approx 1.4$ eV with this system. As can be seen from the data in the introduction, these values are far from the optimum ones. Hence the use of the InAs/GaAs system was conceived from the beginning as a means of studying experimentally and to prove the principles of operation of the MIBCELL eventually and not as the means of achieving high efficiencies. Furthermore, it was also believed that the QDs, if located randomly, could not possibly lead to an IB with the desired properties but they should also be arranged in a periodical pattern.

QD-InAs/GaAs solar cells were produced using molecular beam epitaxy (MBE) in the Stranski-Krastanov [22] growth method by the University of Glasgow and Compound Semiconductor Technologies. The internal layer structure of the cells is shown in Fig. 4. Fig. 5 shows an atomic force microscope (AFM) picture of a single QD layer in a test sample. The density of dots in the cells is within the range of $4 \times 10^{10} \text{ cm}^{-2}$ and

dot dimensions are of the order 5-6 nm high with base lengths of 25-30nm. The δ -doping layer appearing in the structure, in between two adjacent QD layers, was introduced in order to supply an electron to the IB and, in this way, half-filling it [23]. As mentioned in the introduction, half-filling the IB with electrons is expected to be a necessary condition for obtaining a strong absorption coefficient for transitions from the IB to the CB. A study of the effect of strain on the band-gap structure of the cells can be found in [24]. The role of the space-charge regions that appear next to junctions has been discussed in [25].

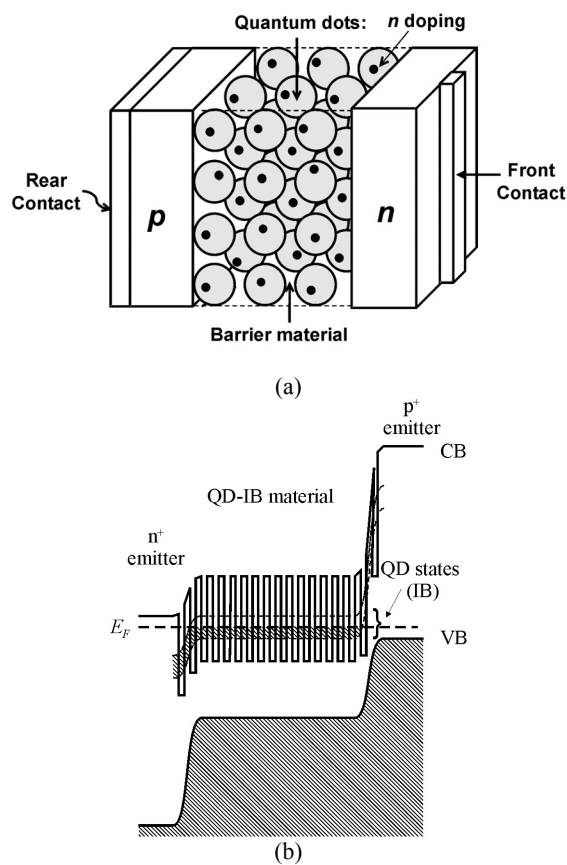


Fig. 3. (a) Artistic representation of a QD-IBSC (b) Simplified energy band diagram to illustrate the formation of the intermediate band from the confined electron energy states in the dots [19].

Concerning the experimental results obtained, Fig. 6 illustrates the current-voltage characteristic of one QD sample as compared with a GaAs reference sample. The structure of this reference sample is identical to the one illustrated in Fig. 4 but without the QD and δ -doping layers.

A strong demonstration of the principles of operation of the IBSC would have required a systematic excess of efficiency of the QD samples when compared with the GaAs references. In this regard, we have not succeeded in providing such proof as shown clearly in Fig. 6. In reality, significant enhancement of the efficiency was not expected because the 1000 Å thick QD region, where the intermediate band absorption occurs, is too thin for substantial sub-gap light absorption.

However, a poorer efficiency does not necessarily imply that the operating principles of the IBSC are not present. The complexity of the QD structure could cause the presence of undesirable effects that would mask these principles. To illustrate our conclusions here, we show in Fig. 7 the normalised quantum efficiency of the QD and reference GaAs solar cell and, in Fig. 8, the electroluminescence (spectrum of the light emitted when the cell is forward biased) for both samples.

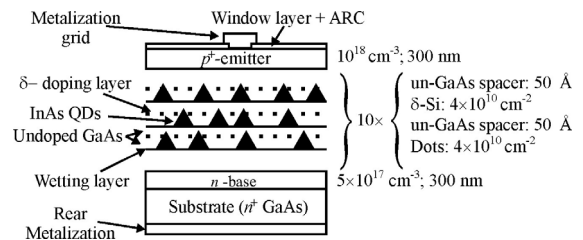


Fig. 4. Internal structure of the QD-IBSCs produced.

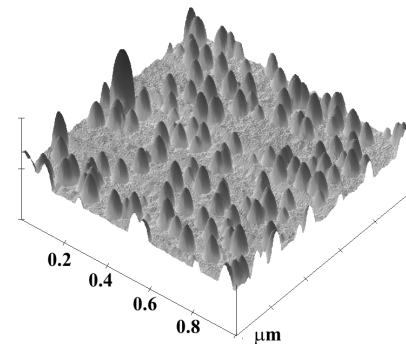


Fig. 5. AFM picture of the dots in one QD layer [26].

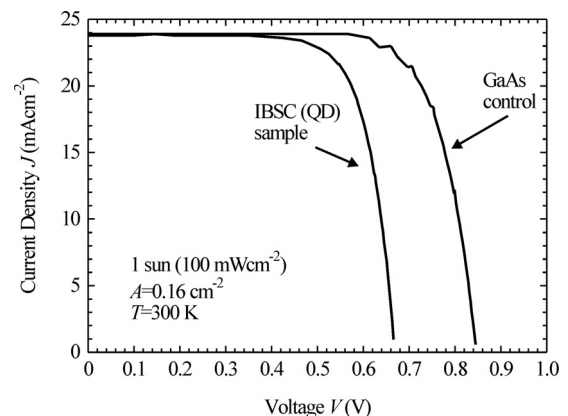


Fig. 6. Current voltage characteristic of a QD-IBSC and a GaAs reference cell [26].

Fig. 7 shows the production of photocurrent from sub-bandgap energy photons. However, it must be emphasised that this result, if not accompanied by voltage preservation, will be useless for photovoltaic applications.

As mentioned in the introduction, the preservation of the voltage requires the existence of three separated quasi-Fermi levels. In this respect, we have formulated in

[26] an equivalent circuit for the IBSC (Fig. 9). In this circuit, diodes are related to recombination processes, independent current generators to photogenerated currents and dependent current generators (elements involving a factor β) to photon recycling processes.

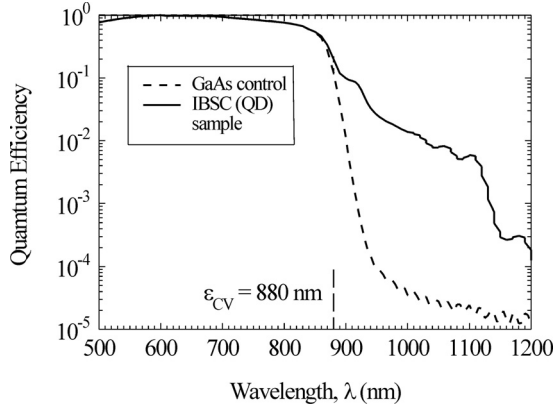


Fig. 7. Normalised quantum efficiency of a QD-IBSC and a GaAs reference cell [26].

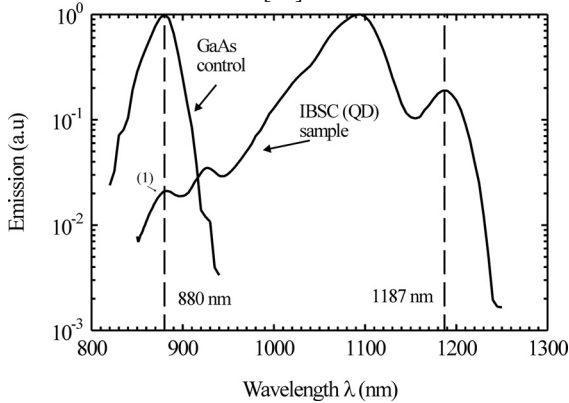


Fig. 8. Electroluminescence spectra of a QD-IBSC and a reference GaAs cell [26].

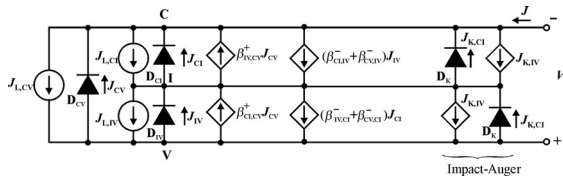


Fig. 9. Equivalent circuit of the QD-IBSC [26].

By multiple fitting the circuit parameters to the experimental results, particularly to those involving the luminescent spectra (Fig. 8) it was found that the diode D_{CV} appeared biased with about 70 mV. This biasing also represented the quasi-Fermi level split between ϵ_{FC} and ϵ_{F1} and was necessary to explain the relatively intense height of the peak (1). This result was considered as indicative of the fulfilment of the second of the operating principles of the IBSC. An enhancement of this split should result from manufacturing QD heterostructures leading to a higher value of the band-gap E_L .

4 LOW COST APPROACHES

Low cost approaches have been researched at the Hahn Meitner Institute by means of the formation of QDs within a nanoporous material.

The nanoporous material chosen, which also plays the role of n contact, was TiO_2 . QDs were formed by filling the nanocavities in this material with PbS (Fig. 10). At an early stage of the research, the lack of a suitable solid state p contact forced the use of an electrolyte. In terms of MIBCELL operation, the resulting system was believed to have a total band-gap, E_G , of approximately 3.2 eV and 1.85 eV for one of the small band-gaps. When CH_3OH was used as an electrolyte, it formed small amounts of HCOOH as result of a photo-catalysis process when the samples were illuminated with below band-gap energy photons. Since the HCOOH formation from CH_3OH requires a higher energy than the one supplied by an individual photon, the formation of HCOOH was taken as indicative of the concurrence of a two photon process in the system [27].

In a second stage of the research, a solid state p type contact was formed by depositing a layer of PEDOT:PSS. Metal contacts were made using Au for contacting on PEDOT and SnO_2 for contacting on TiO_2 . However, no photovoltaic behaviour was observed. Suspecting the problem might lay in an excessive recombination in the PbO_2-TiO_2 interface, an $In(OH)_xS_y$ layer was introduced between (Fig. 11). Photovoltaic behavior was then observed which was enhanced by the manufacturing of several $TiO_2-In(OH)_xS_y-PbO_2$ layers (Fig. 12).

Since the band-gap of the $In(OH)_xS_y-PbS$ is 2.4 eV and the band-gap of PbS is 0.41 eV, the detection of photovoltage for an intermediate value (1 and 1.8 eV) is interpreted as indicative of quantum dot formation. However, no particular evidence of involvement of the specific MIBCELL principles of operation was detected.

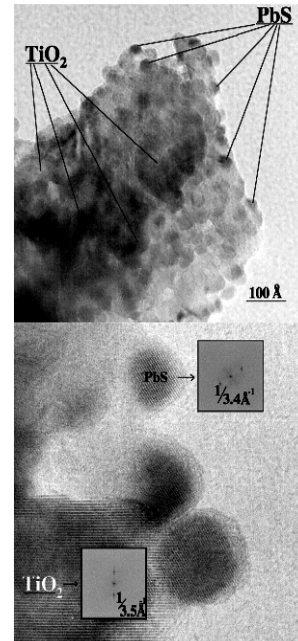


Fig. 10. Detail of the filling of TiO_2 nano-cavities with PbS leading to the formation of QDs

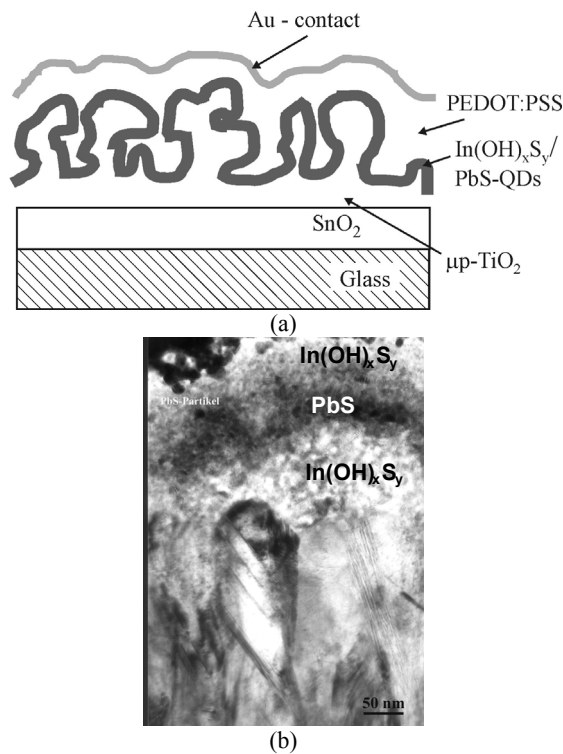


Fig. 11. (a) Structure of the nanoporous approach with solid state p contact. (b) TEM micrograph of an $\text{In}(\text{OH})_x\text{S}_y$ -PbS structure [courtesy of Dr. I.Sieber (BAM) Berlin].

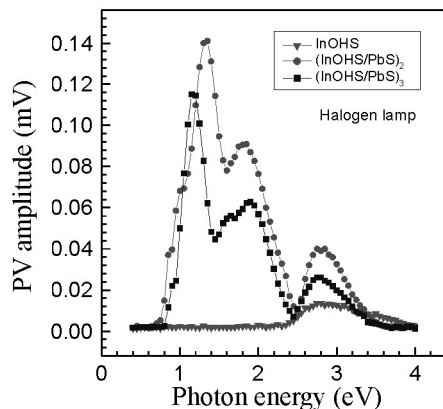


Fig. 12. Photovoltage as a function of the photon energy (measured with a Xe-lamp) as the number of (InOH/PbS) layers increases.

5 ADVANCES IN THE THEORY OF THE INTERMEDIATE BAND SOLAR CELL

In parallel to the experimental research, the theory of the intermediate band solar cell has been revisited regularly during the course of the project, both to include effects not previously considered, as well as approaching them from a different perspective.

In this respect, in [28,29] we have established the thermodynamic consistency of the IBSC concept. In [30] we have analysed the effect of Auger recombination and impact ionisation processes on the performance of the cell (Fig. 13). In [31] we have reformulated the fundamentals of the theory so that the effect of overlap

between absorption coefficients can be taken into account. In [32], we have discussed particular aspects of the implementation of the IBSC concept by means of type II heterostructures. In [33] we have developed a “quasi-drift” diffusion model for the IBSC, useful for studying the case in which the quasi-Fermi levels are not constant within the device.

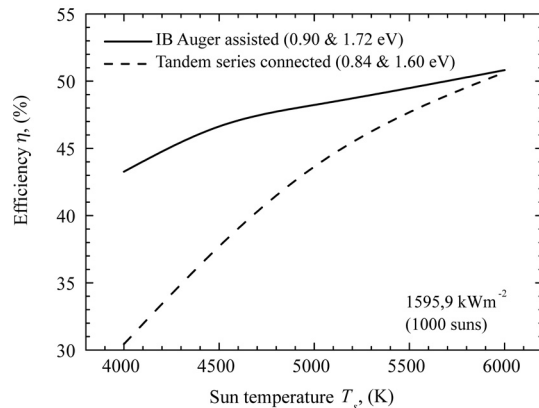


Fig. 13. Dependence of the efficiency of an IBSC assisted by an Auger mechanism with the solar spectrum (represented for different temperatures of the Sun) Comparison with a tandem of two solar cells [30].

6 CONCLUSIONS

“MIBCELL” has resulted in a better understanding of the fundamentals of photovoltaic conversion through an intermediate band and has allowed purely theoretical considerations to be explored through the production and characterisation of the first prototypes.

The work has led to the refinement of the computational techniques suitable for an early identification of intermediate band material candidates. Remarkably, outside the MIBCELL consortium, Yu *et al* have recently synthesised materials based on diluted II-VI oxide semiconductors that exhibit an intermediate band [34].

First MIBCELL prototypes have been manufactured using quantum dot technology and two different approaches. In the first one, MBE has been used to produce InAs QDs in GaAs. The devices made exhibited the production of photocurrent when illuminated with below band-gap energy photons and their electroluminescence spectra have been best explained by the appearance of three quasi-Fermi levels. These are the two working hypotheses that sustained the operating principles of the IBSC.

In the second approach, aimed specifically at low cost, PbS QDs were manufactured by filling the nanocavities produced in TiO_2 . Although it has not been possible to show experimental evidence for the operation of these devices under the operating principles of the IBSC, they have exhibited photovoltaic behaviour and have opened the way for research into a new PV material system.

Acknowledgements

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