Advances in Perovskite Solar Cells

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Abstract :- The purpose of this review is to take stock of the current situation of research on the new generation of photovoltaic cells based on perovskite materials. A perovskite solar cell is a photovoltaic solar cell that comprises a chemical element having a perovskite structure, most often an organic-inorganic lead or tin halide hybrid, in its active layer. In this paper, the focus will be on analyzing the progression of the yields of these solar cells since their discovery. Indeed, the increase of the yields is a strategic axis to make always more efficient the photovoltaic conversion of the solar energy. This promotes its large-scale development, in order to meet the expectations of the fight against climate change and these numerous negative consequences, which was the subject of the COP21 from November 30 to December 12, 2015 in Paris.

Keywords: Thin film perovskites, Stability, advances, solar cells

1 - Introduction

For almost a decade the arrival on the market of solar photovoltaic power generation technology opens new perspectives for the electrification and the protection of the environment. The photovoltaic conversion of solar energy has become in a few years one of the rising stars of renewable energies. One of the key elements in the progress of the sector concerns research aimed at increasing the efficiency of photovoltaic cells. Its production consists of different sectors such as the silicon sector, the organic sector and thin layers. The most dominant is the silicon sector which saw a new competitor the perovskite sector. However, the big problem with perovskite solar cells remains their stability. This paper is devoted to describe the progress of perovskite solar cells since their appearance.

2 - Stability of perovskite solar cells

The main problems of perovskite solar cells are their structural instability and their low resistance to water and high temperatures [1]. The stability of the perovskite structure is mainly governed by the ionicity and the tolerance factor of Goldschmidt. To understand this phenomenon, Jérôme Lelièvre, as part of his thesis work in 1917 [2], conducted a study on the stability of perovskite-structured materials, including the general formula ABX_3, where X anions are generally oxygen ions O^{2-} or fluoride F^-.

The ionicity reflects the electronegativity gap between the A and O (A-O) cations as well as between the B and O (B-O) cations. The ionic character of this structure can be determined from the difference in mean electronegativity, according to the Pauling scale [3].

$$\delta = \frac{\chi_{A-O}+\chi_{B-O}}{2} \quad (1)$$

Where δ is ionicity, χ_{A-O} and $\chi_{B-O}$are the differences in electronegativity between A and O on the one hand and B and O on the other hand.

The Goldschmidt factor makes it possible to quantify and explain globally the compactness, the existence of the distortions in the perovskite structure as well as the stability of the crystalline structure for different relative values of the ionic rays. Indeed, the size of the element B must be sufficient to be able to form octahedrons with oxygen and thus define the skeleton of the structure. The size of the element A then becomes a preponderant factor, because the distortions that it causes within the skeleton formed by the oxygens can cause a change of space group of the structure. Since the bonds between the oxygen atoms and the atoms A and B are iono-covalent, VM Goldschmidt has stated a stability condition, called the tolerance factor t [4], which makes it possible to link the rays of the cations A and B and anion O by the following relation:

$$t = \frac{r_A+r_O}{\sqrt{2}(r_B+r_O)} \quad (2)$$

where r_A, r_B and $r_O$are, respectively, the ionic rays of the cations A, B and the anion O. Few compounds possess the ideal cubic perovskite structure because the requirements are quite restrictive. The radius r_A of site A must be close to that of oxygenr_O = 0.140 nm, and the ionic radius r_B of site B must be equal to (√2-1) r_O. This factor represents the ideal symmetry deviation, that is, the imbalance between the length of the <A-O> and <B-O> bonds within the perovskite structure. When t is equal to 1, the structure is cubic. If it is little different from 1, a rhombohedral distortion may appear. If t deviates even further than 1 (0.86 <t <0.9), the polyhedron around the A-ions is deformed, the B-O-B angles then take a value less than 180 ° and the symmetry becomes orthorhombic (Pbnm). When t <0.86, the octahedra are replaced by pyramids, the transition cation B is then in square planar coordination thus forming fluorine-type layers. For t> 1, it is the hexagonal structure that appears. Table 1 presents these different symmetries adopted by the perovskite structure as a function of the tolerance factor t.

Table 1: Different symmetries adopted by the perovskite structure as a function of the tolerance factor t.

t value	**Symmetry observed**
$t < 0.85$	Passage from perovskite to fluorite
$0.85 < t < 0.9$	Orthorhombic
$0.9 < t < 1$	Rhombohedral
$t = 1$	Cubic
$1 < t < 1.06$	Hexagonal

One of the solutions to increase the lifespan of perovskite solar cells and improve their stability is the encapsulation of the devices. There are two types of encapsulation: conventional encapsulation that uses simple plastic materials, such as polystyrene and PMMA, and functional encapsulation based on fluorescent materials mixed in a polymer matrix.

Another solution is being refined on the horizon with the advent of tandem cells based on perovskite and silicon. This track is interesting to obtain returns beyond 30%. The architecture of these solar cells makes it possible to limit losses by superimposing two layers of materials that absorb light in different wavelengths. In the case of cells combining silicon and perovskite, the latter absorbs the most energetic photons. Those who are less cross it and are absorbed by the silicon layer below. These two layers can be manufactured separately or together. These are then four or two terminal cells respectively. In the first case, each layer has a higher contact and a lower contact to extract the electrons produced.

III-Progress in the perovskite solar cell sector

Perovskite, named after the Russian mineralogist Lev. A. Perovski, is a crystalline structure common to many oxides. This name first designated calcium titanate ($CaTiO_3$), before being extended to all oxides that have the same structure. Their general formula is ABO_3. They have gained substantial attention because of their high efficiency, low cost and superior optical properties according to the choice of elements A and B: ferroelasticity (example: $SrTiO_3$), ferroelectricity (example $BaTiO_3$), antiferroelectricity (example $PbZrO_3$, ferromagnetism (example $YTiO_3$), antiferromagnetism ($LaTiO_3$). Perovskites have been known since 1830, but it is in 2009 when Tsutomu Miyasaka discover their potential for the realization of photovoltaic cells. Their general formula is ABO_3. They have attracted attention because of their high efficiency, cost and superior optical properties depending on the choice of elements A and B: ferroelasticity (like $SrTiO_3$), ferroelectricity ($BaTiO_3$), antiferroelectricity ($PbZrO_3$), ferromagnetism ($YTiO_3$), antiferromagnetism ($LaTiO_3$): perovskites have been known since 1830, but it is in 2009 that Tsutomu Miyasaka discovered its potential for the realization of photovoltaic cells. The power of photon absorption is 10 times higher. To that of silicon. On the other hand, the good separation of electrical charges and their mobility are the result of a very recent discovery of two experts in the field: Michael Graetzel from the Ecole Polytechnique de Lausanne and Henry Snaith from Oxford University The University of Toin in Japan, which invented the first photovoltaic cell based on perovskite with a yield of 3, 8% in 2009 [5]. During the same period (2008-2009), an another team had the idea of use a lead hybrid of $CH_3NH_3PbI_3$ methylammonium iodide, perovskite structure (similar to $CaTiO_3$ hence their name) and well known for its exceptional optical properties (luminescence) in the visible, to replace the perovskite dyes in the DSSC solar cells sensitized) with a very modest return of 3.8%. This work was taken over by a Korean team, bringing the yield to 6.5% in 2011. In 2012, Michael Graetzel and his team get a 9.7% yield they will improve to reach the value of 15% in 2013 then by 19.3% in 2014. In July 2015 Professor Michael Graetzel announces a record of 20.8% [6]. In 2019, perovskites reached 24.2% [7], catching up with silicon in a very short time. But the big challenge for perovskite solar cells is the long-term stability and the presence of lead in its molecule. Perovskite solar cells are an attractive alternative to silicon cells that dominate the market, but whose performance and stiffness limits have been known for several years. Compared to silicon and perovskites, it took 30 years for the former to reach the record level of 25.7%, but it only took 6 years to reach 20% [8]. A German-Swiss study published in November 2017 in the journal Science shows that the instability of perovskites comes from the degradation of the contact between the active layer (example: CuSCN) and gold during the activity of solar cells [9, 10]. Researchers at the Swiss Federal Institute of Technology Lausanne (EPFL) have developed a simple method for depositing 60 nm thick CuSCN coating layers by accelerated evaporation of the solvent. They also improved the stability of copper thiocyanate doped perovskite cells by protecting them with a thin layer of reduced graphene oxide [11].

A two-terminal tandem cell combining a silicon layer with a perovskite material, provides a cell with a higher efficiency over a longer wavelength range. A 25% yield was thus obtained in June 2018 for a perovskite-silicon cell, by researchers at the Federal Institute of Technology in Lausanne and the Swiss Center for Electronics and Microtechnology [12]. In the same month, Oxford PV announced that it had reached 27.3% for the same type of cell [13]. In September 2018, the Institute of Microelectronics and Components achieved a conversion efficiency of 24.6% with a perovskite-CIGS cell [14]. In March 2019, the Dutch energy research center (Energieonderzoek Centrum Nederland (nl)) achieves a 30.2% efficiency by using a perovskite cell in combination with a two-phase silicon cell from industrial production [15].

The performance of photovoltaic cells based on perovskite materials therefore depends on several parameters, such as the architecture of the cell, the materials used for the active layer, the interfacial layers for ETM electron transport and for HTM hole transport. And the type of electrodes as well as the techniques and the manufacturing conditions. Table 2 gives the performances of some cells of the new generation based on perovskite materials.

Table 2: Comparison of the performances of some cells of the new generation based on perovskite materials. [16-22].

Structure of the solar cell	JCC	VCO	FF	PCE	Ref
FTO/TiO2/$CH_3NH_3PbI_3$/rGO/FTO (rGO pur)	15.86	0.71	45.00	5.10	[16]
FTO/TiO_2/$CH_3NH_3PbI_{3-x}Cl_x$/SpiroOmeTAD/Au	15.30	0.80	55.00	6.70	[17]
FTO/TBD-TiO_2/$MAPbI_3$/Spiro OmeTAD/Au	20.50	1.05	63.10	13.90	[18]
FTO/TiO_2/ $CH_3NH_3PbI_3$/Po-Spiro OmeTAD/Au	22.30	0.98	68.20	15.40	[19]
ITO/SnO_2/ $CH_3NH_3PbI_3$/Spiro-OmeTAD/Au	22.01	1.05	69.00	15.98	[20]
FTO/SnO_2/TiO_2/$MAPbI_{3-x}(Ac)_x$/Au	23.68	1.06	68.00	17.07	[21]
FTO/TT-TiO2/$MAPbI_3$/Spiro-OmeTAD/Au	23.2	1.10	68.00	17.40	[18]
FTO/TiO_2/$CH_3NH_3PbI_3$:TIC/SpiroOmeTAD/Au	23.74	1.00	72.80	17.59	[22]
ITO/SnO_2/$MAPBI_3$-$(Gua_{1-x}MA_x)PbI_3$/Spiro-OMeTAD	22.46	1.10	75.00	18.54	[20]

IV-Conclusion

Perovskites have experienced a meteoric rise in the photovoltaic field which makes them a material of choice in the manufacture of solar cells. Today, they have reached an efficiency of 24.2%, catching up silicon in a very short time. However, their instability undermines large-scale diffusion. Nevertheless, the photovoltaic cell based on perovskite continues to rise in the race for yield and solutions are envisaged to intensify industrial production.

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