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Concepts

Ferroelectric Oxides for Solar Energy Conversion, Multi-Source Energy Harvesting/Sensing, and Opto-Ferroelectric Applications

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Photoferroelectrics belong to a unique material family that exhibits both photovoltaic and ferroelectric effects simultaneously. The photovoltaic effect is the only known direct method of converting light into electricity and is the basis of solar cells. The ferroelectric effect can induce piezoelectric and pyroelectric effects, which are the working principles of widely used kinetic and thermal sensors, transducers, actuators, and energy harvesters. For a long time, photoferroelectric research was restricted to theoretical investigations only because of either the wide band gap (E_g), which is not able to effectively absorb visible light, or to the weak ferroelectricity caused by a narrow E_g. Recent scientific breakthroughs, however, have opened doors for the development of practical applications. In this article, emerging concepts of creating balanced photovoltaic and ferroelectric properties for photoferroelectrics, as well as those of novel applications in future devices, are presented.

Introduction

While researchers and societies are making efforts to minimize the effect of climate change, development of renewable, zero-emission, clean energy conversion schemes (i.e., electricity production methods) is one of the prior research tasks. The conversion of solar energy into electricity through the photovoltaic effect is considered one of the focuses and, as a result, solar cells/panels made from conventional semiconducting bulk materials and thin-films [e.g., Si, GaAs, CdTe, and copper indium gallium selenide (CIGS)] have reached technological maturity and have thus achieved rapidly growing industrial adoption.

In addition to the above mentioned conventional solar cells that have been developed into large-scale manufacturing, some dye-sensitized and organic solar cells have been developed on a smaller scale.[1] In the most recent decade, perovskite thin-film solar cells fabricated at low temperatures (up to a few hundred degrees Celsius) via wet chemical methods (e.g., sol-gel and spin-coating), especially based on organometal halide perovskites, have been under development at a rocket pace.[2] The record photovoltaic energy conversion efficiency (PCE) has been improved from less than 3% to over 22% within only one decade, compared to the decades' long development of Si-based counterparts.[1, 2] Although the emerging organometal halide perovskite solar cells show a promising energy conversion capability even compared to those conventional, industrially mature counterparts, they struggle with the stability of their excellent performance.[2, 3] Under radiation (i.e., UV), elevated temperature, strain, humidity, and atmospheres containing oxygen, rapid degradation of the performance of these solar cells is commonly observed, owing to the easy decomposition or oxidation of the organometal halide compositions under such environmental conditions.[3] Efforts have been made to improve the stability; however, protection components must be introduced to most organometal halide perovskite solar cells to insulate them from the ambient atmosphere and mechanical/thermal boundary conditions. This hinders their commercialization because of a restriction of the application area and increased manufacturing/maintaining costs.

By contrast, some perovskite oxides possessing non-centrosymmetric unit cells, known as the photoferroelectrics, have shown excellent stability under the above-mentioned conditions.[2] This enables them to work in a normal atmosphere, without the need of special protections. Photoferroelectrics are ferroelectric materials that simultaneously exhibit the photovoltaic effect.[4]

Unlike conventional solar cells made from semiconductors where the theories have been relatively clear, the mechanisms affecting the photovoltaic performance of different photoferroelectrics are not yet well and systematically understood. It is known that photoferroelectrics can exhibit the bulk photovoltaic effect (BPVE), which is a phenomenon that a single-phase noncentrosymmetric bulk material (e.g., a ferroelectric material) generates a steady photocurrent under light excitation. The BPVE enables the open-circuit voltage of photoferroelectrics under illumination to be orders of magnitude higher than the band gap (E_g), introducing the possibility of exceeding the

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Shockley–Queisser (S–Q) limit of the corresponding E_g.[5] It is found that the BPVE is not dependent on the magnitude of spontaneous polarizations (P_s) or remanent polarizations (P_r) in ferroelectric materials in a simple way.[6] On the other hand, because of the noncentrosymmetric nature of the crystal structure of ferroelectrics, the internal electric field is generated from the P_s. This internal electric field acts like an internal p–n junction (termed as a 'self-junction').[7] This may enable the photoferroelectrics to exhibit an interface-related photovoltaic effect that is similar to a conventional p–n junction. In this case, the separation of charge carriers and thus PCE may be positively related to the P_s or P_r in the material. Here, reduction of the E_g to the visible range whilst maintaining the polarization (thus creating the built-in electric field) in the material is likely to increase the PCE.

Photoferroelectrics have been under investigation since the 1970s.[17] Early photoferroelectrics were restricted to conventional ferroelectric compositions, such as the widely used Pb(Zr,Ti)O_3 (PZT)-based and BaTiO_3 (BTO)-based compounds. However, because of their wide E_g, > 3 eV compared to 1.8–3.1 eV (the range of visible light in the solar radiation spectrum), over 90% of the visible-range solar energy cannot be absorbed and effectively converted into electricity.[2,4] Meanwhile, as PZT- and BTO-based materials are typically strong insulators with extremely low conductivity (10^{-9} S m^{-1}), which helps to give them a strong ferroelectricity, the recombination rates of photoexcited charge carriers are high. These lead to low PCEs (at the 10^{-4} level), which are negligible compared to those of conventional semiconductors and organometal halide perovskites (at the 10^{-1} level).[1,2,4] Therefore, early photoferroelectric investigations were mostly theoretical consisting of fundamental studies attempting to reveal and explain the origins and working principles of photoferroelectrics. Fridkin et al.[17–22] have made a great contribution to this knowledge expansion.

Nevertheless, photoferroelectrics have re-attracted attention in recent years thanks to the achievement of 10^{-2} level efficiencies,[5,9,10] largely reduced E_g to cover the entire visible range (as low as 1.1 eV,[11] comparable with that of Si), and the adoption of other practical methods to significantly improve the photovoltaic performance. In particular, the recent second-round bloom of photoferroelectric research is attributed to the further exploration of BPVE. For instance, a poled BTO single crystal could exhibit a PCE of up to 4.8% under standard one-sun illumination (100 mW cm^{-2}, AM 1.5 G), even though less than 10% of the solar spectrum was absorbed.[5] Such a PCE is in the range of practical use of solar energy conversion, and, more importantly, it exceeds the corresponding S–Q limit of 3–4%.[23] This cannot be achieved by a conventional semiconductor solar cell.

Table 1 compares some representative solar energy conversion materials. A review[1] has comprehensively summarized photovoltaic materials other than photoferroelectrics. The photoferroelectrics, especially their physical realizations, have been reviewed[4,24–26] as a relatively independent topic.

On the other hand, apart from the solar panels that aim to produce macro-scale electricity (i.e., > W level power), portable, ubiquitous, and on-demand micro-scale electricity (μW–mW) generation has also attracted great attention in the past two decades[2,27]. This is mainly referred to as energy harvesting (EH) technology, which converts ambient energy (e.g., solar, thermal, and kinetic) existing in the working environment of small electronic components (e.g., sensors) into electricity.[28] This enables those small devices to be self-powered, autonomous, and maintenance-free. Compared to conventional battery-powered counterparts, the self-powered systems provide advantages in terms of long lifespan ("set and forget" solution) and in vivo/in-construction integration/embedment. Meanwhile, an energy harvester can simultaneously be a sensor of the same input energy source, offering the option of system simplification and energy efficient design[27,29,30].

Most developed energy harvesters are single-source, that is, only responding to a certain category of input energy. Consequently, other incident energy sources are wasted. In the meantime, providing enough output power for the corresponding system is challenging for single-source harvesters.[2,27] A multi-source harvester and sensor can solve this issue. Photoferroelectrics are an ideal candidate for the energy conversion material in such systems. Their photovoltaic effect can be used to harvest and detect solar energy (or other visible light) and output DC signals. Their ferroelectricity can give them piezoelectric and pyroelectric effects, which respond to kinetic

Table 1. Summary of some representative solar energy conversion materials in different categories with record PCE, advantages, and drawbacks. The information is extracted from Refs. [1, 2, 5, 8–10].

Material	Sample type	Category	Energy-conversion layer	PCE[a] [%]	Advantages	Drawbacks
polycrystalline Si	bulk	conventional semiconductor	single	21.3	earth-abundant material; mature technology	less likely to break the S–Q limit; theoretical PCE restricted to 33.7%
0.05 (CH$_3$NH$_3$)PbBr$_3$– 0.95 α-(NH$_2$CHNH$_2$)PbI$_3$	thin-film	organometal halide perovskite	single	22.1	flexibility; low-temperature processing; rapidly improved PCE	poor stability
BaTiO_3 (BTO)	bulk single crystal	photoferroelectrics	single	4.8	superior stability; above E_g photovoltage; above S–Q limit PCE	currently low PCE, but rapid progress; of improving PCE is being made
BiMnO_3–BiMn$_2O_5$	composite thin film	photoferroelectrics	single	4.2		
Bi$_2$FeCrO_6 (BFCO)	thin film	photoferroelectrics	multiple	8.1		
[a] Record value.						

and thermal (temperature fluctuation) energy, respectively. Here AC signals will be the output. This unique multi-functionality of photoferroelectrics makes it possible to use photovoltaic, piezoelectric, and pyroelectric effects simultaneously to harvest ambient solar, kinetic, and thermal energy with only a single material. Alternatively, a part of those effects (i.e., photovoltaic) can be used for harvesting energy whilst the others (i.e., piezoelectric and pyroelectric) can be used for sensing, or vice versa, where DC and AC signals can be separated via rectifiers and advanced circuitry. Multi-source energy harvesting/sensing has been presented in some reviews[2, 27] and research papers[13, 30]. However, most photoferroelectrics are not able to provide a balance of ferroelectricity and E_g. They either have strong ferroelectricity, which is preferred for good piezoelectricity and pyroelectricity, but a wide E_g beyond the visible-range, or the E_g engineering considerably degrades the ferroelectricity. Although the photovoltaic effect may be independent of the direction of the P_r,[31] it is largely affected by the magnitude of the P_r.[9] Considering the importance of the E_g as mentioned above, the co-existence of strong ferroelectricity and a narrow E_g is essential for the development of photoferroelectrics either for solar energy conversion or multi-source energy harvesting/sensing applications.

Therefore, this article intends to summarize several emerging concepts of narrowing the E_g or improving the PCEs of photoferroelectrics whilst maintaining their good ferroelectric, piezoelectric, or pyroelectric properties. It also introduces the relatively new concept of using photoferroelectrics in single-material/component, multi-functional, self-powered sensing and opto-ferroelectric devices. The materials covered in this article include single crystals, polycrystalline ceramics, and highly oriented thin-films. Perspectives of future developments of photoferroelectrics are given at the end. The article is expected to stimulate the research progress of photoferroelectric towards practical applications for different potential purposes.

Band-Gap/Gap-State Engineering

Band-gap engineering is the most straightforward method to improve the PCE of photoferroelectrics. It is also the first step to be considered to design an efficient photoferroelectric material or device, because a narrowed E_g gives a much higher S–Q limit (e.g., 33.7 % at 1.34 eV as the maximum S–Q limit at the most ideal E_g compared to only a few percent for E_g ≈ 3 eV).[1] Although strain can be used for partially tuning the E_g, elemental doping into the matrix composition is the fundamental method to reduce E_g by altering the electronic states between atoms/ions. However, E_g reduction derived from doping can easily degrade the ferroelectricity at the same time. For instance, a matrix ferroelectric composition, $KNbO_3$ (KN), has a large ferroelectricity with P_s of about 25 µC cm^{-2} and P_r of about 15 µC cm^{-2} at room temperature.[32] By contrast, when doped with 10–30 mol % $BaNi_{0.5}Nb_{0.5}O_{3-\delta}$ (BNNO; equivalent to 5–15 mol % Ni^{2+}), although the E_g could be reduced to the ideal range of 1.1–1.4 eV (from > 3.5 eV), most of the KN P_s and P_r values at room temperature were found to be sacrificed.[11] As mentioned above, it is believed that both a large ferroelectricity and a narrow E_g are needed for a significantly improved PCE for photoferroelectrics.

The introduction of Ni^{2+} ions and oxygen vacancies is an effective method to reduce the E_g. This is because of the ease of charge transfer from the oxygen $2p$ states at the maximum level of the valence band to the transition-metal (Nb) d states at the minimum level of the conduction band.[11, 12] Despite the above example (KN–BNNO), although the introduction of oxygen vacancies tends to suppress the ferroelectricity through the domain wall pinning effect, a carefully tuned doping level is able to balance between ferroelectricity and the reduction of E_g. For instance, the strong ferroelectric $(K_{0.5}Na_{0.5})NbO_3$ (KNN) was doped with 2 mol % BNNO, equivalent to 1 mol % Ni^{2+}–oxygen vacancy combinations.[13] The doped composition achieved a narrow E_g of about 1.6 eV (down from > 4 eV for pure KNN). In the meantime, a large proportion of the pure KNN's ferroelectricity was retained in the doped composition (KNN–BNNO), with P_s and P_r of about 26 µC cm^{-2} and 11 µC cm^{-2}, respectively.[13] Compared to the values for pure KNN, that is, $P_s \approx 26$ µC cm^{-2} and P_r ≈ 20 µC cm^{-2},[33] there was no compromise on the P_s and the P_r of the KNN–BNNO reached 55 % of that of pure KNN. Considering that both the above mentioned KNN and KNN–BNNO samples were polycrystalline ceramics, and there was some domain wall pinning effect caused by the presence of oxygen vacancies,[12] it can be predicted that KNN–BNNO's ferroelectricity could reach the level of that of pure KNN (i.e., without any compromise) in single crystals and highly-oriented thin-films of the same compositions.

To achieve the ideal balance between E_g and ferroelectricity, the doping concentration must be precisely controlled. For the KNN–BNNO, a slight shift away from the stoichiometry, for example, if more BNNO was added, may degrade the ferroelectricity by a large extent, which is a similar case to that of the above mentioned KN–BNNO. The strategy of using Ni^{2+}–oxygen vacancy combinations for doping to reduce the E_g whilst maintaining strong ferroelectricity has also been proven with another ferroelectric composition, $Na_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ (BNT–BT). The doped composition, 0.95 BNT–0.05 Ba-$(Ti_{0.5}Ni_{0.5})O_{3-\delta}$, achieved a narrow E_g of about 0.9 eV and high P_r of about 31 µC cm^{-2}.[14] Table 2 summarizes different reported compositions doped with Ni^{2+}–oxygen vacancy combinations. It is expected that the same concept would be applicable to other conventional ferroelectric compositions. The composition of $PbNiO_2$–$PbTiO_3$ (listed in Table 2) will be presented in the next section together with the concept of nanolayering.

Among the doping strategies for band-gap engineering, there is an alternative route called gap-state engineering. Instead of tuning the E_g of the entire composition as presented, gap-state engineering creates defect states within the E_g. Half of these defects are filled with electrons. Taking the matrix $BiFeO_3$ (BFO; $E_g \approx 2.7$ eV) as an example, Figure 1 shows the band structures of several options for gap-state engineering based on density functional theory (DFT) calculations.[34] Note that the E_g of 2.8 eV shown in the Figure was obtained from the DFT calculation, compared to the measured 2.7 eV. In

Table 2. Summary of photoferroelectric compositions doped with Ni^{2+} ions and with the presence of oxygen vacancies. The information is extracted from Refs. [11–16].

Composition	Form of material	E_g [eV]	P_r[a] [$\mu C\,cm^{-2}$]	d_{33}[b]	ρ[c] [$\mu C\,m^{-2}\,K^{-1}$]
KN–BNNO $[KNbO_3]_{0.9}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_{0.1}$	polycrystalline ceramics	1.4–1.5	1.7	23	26
KNN–BNNO $[(K_{0.5}Na_{0.5})NbO_3]_{0.98}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_{0.02}$	polycrystalline ceramics	1.6	11	100	128
$[Na_{0.5}Bi_{0.5}TiO_3]_{0.95}[Ba(Ti_{0.5}Ni_{0.5})O_{3-\delta}]_{0.05}$	polycrystalline ceramics	0.9	31	151	–
$Pb(Zr_{0.14}Ti_{0.56}Ni_{0.30})O_{3-\delta}$	thin film	2.9	15–30	–	–
PNT[d] $(PbNiO_2)_x–(PbTiO_3)_{1-x}$	nanoscale heterostructured layer	<2.7	–	–	–

[a] At room temperature. [b] In units of [$pC\,N^{-1}$] or [$pm\,V^{-1}$]. [c] Pyroelectric coefficient. [d] Only by first-principle calculation, no experimental investigation carried out.
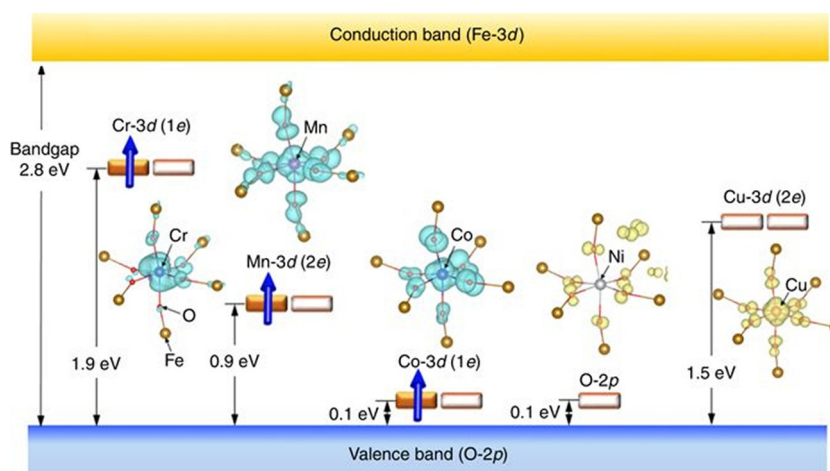

Figure 1. Electronic structures of transition metal doped BFO obtained from DFT calculations. Reproduced from Ref. [34] under the terms of the Creative Commons Attribution 4.0 International License. Copyright 2017, Springer Nature Publishing.

theory, when BFO is doped with a transition metal (i.e., Cr, Mn, Co, Ni or Cu), an in-gap state either half-filled with electrons (e.g., Cr, Mn, Co) or unoccupied by electrons (e.g., Cu) is created. The exception for Ni has been partially discussed above and further details can be found in literature,[34] which is beyond the scope of this article.

When the photon energy of the illumination is smaller than the E_g, those photons that could not be absorbed by the undoped composition can now be absorbed via the gap states. The half-empty states receive electrons from the valance band and the half-filled states supply electrons to the conduction band.

Electron–hole pairs can then be generated. Rather than targeting to improve the above-E_g photovoltaic performance, the aim of the gap-state method is to significantly improve the below-E_g outputs. For instance, the hypothesis has been proven with Mn-doped BFO. Figure 2 clearly shows that 5 mol% Mn-doped BFO (BFMO) outperformed un-doped BFO in the photon energy range of 2.4–3.0 eV of the incident light in terms of the photovoltaic response.[31] The maximum outperformance occurred at below E_g. A similar trend was also observed with a 6 mol% Mn-doped BFO, which reaffirms the con-
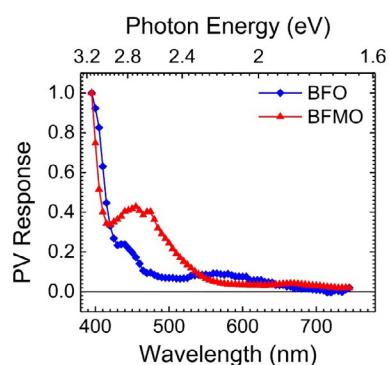

Figure 2. Dependence of photovoltaic response on wavelength and photon energy of incident light for BFO and BFMO thin films. Reproduced from Ref. [31] with permission. Copyright 2017, AIP Publishing.

cept of gap-state engineering.[34] Such a method may compromise up to 50% of the matrix composition's P_s[34] and is a good alternative to the ordinary band-gap engineering via compositional optimization.

Nanolayering and Multilayering

Apart from the record single-layer PCE of photoferroelectrics (4.8%) mentioned above obtained with a 1 mm-thick bulk single crystal (i.e., BTO),[5] most high photoferroelectric PCEs (i.e., >1%) have come from highly-oriented thin-films.[35] This is because photoferroelectrics are different from conventional solid-state solar cells where charges are separated owing to the potential developed at the p–n junction. Instead, one of the theories (ballistic mechanism) believes that, in photoferroelectrics, photoexcited non-thermalized carriers will descend to the bottom of the conduction band through a free path when losing their energy.[5,21,35] Depending on materials, the length of the free path (L_0) is in the range of 10 nm–1 μm. Based on this theory, it is expected that the output photovoltaic electric field can be significantly increased if the thickness of the photoferroelectric material is similar to L_0, with all photoexcited carriers contributing to the BPVE. The thickness of thin films is defined to be <1 μm. Note that this is not saying the thinner the better. As mentioned above, the optimum thickness is material dependent and it does not always show the identical trend of thickness–performance relationship for different materials. This has been discussed in detail elsewhere.[24] It was discussed in the last section that Ni^{2+}–oxygen vacancy doping has proven to be a robust method to reduce the E_g of some photoferroelectric compositions (Table 2). This method can be further combined with the concept of nanolayering. Through first-principle calculations, it was proposed that a 1–2 nm-thick $(PbNiO_2)_x(PbTiO_3)_{1-x}$ (PNT) layer on top of a bulk $PbTiO_3$ layer may increase the photocurrent by up to 43 times.[16] The PNT nanolayer can be potentially made as epitaxially strained or via layer deposition methods. Although no experimental validations were made, the nanoscale heterostructured nanolayer was also expected to be applicable to $Pb(Zr_{0.2}Ti_{0.8})_{0.7}Ni_{0.3}O_{3-\delta}$ and KN–BNNO.[16] Such a concept awaits successful experimental evidence.

In terms of another widely and deeply studied photoferroelectric composition (i.e., BFO), Cr was doped to form Bi_2FeCrO_6 (BFCO), which possessed a tunable E_g as narrow as 1.4 eV by tailoring the Fe/Cr cation ordering and the ordered domain size.[10] The 100 nm-thick single-layer BFCO thin film reached a PCE of 3.3%. Furthermore, similar to conventional tandem solar cells where different layers with different E_g were stacked for optimized absorption and efficiency, a multilayer BFCO cell with a threshold E_g of 1.6 eV achieved a PCE of 8.1% under AM 1.5 G illumination.[10] This is the record among the reported PCEs of all photoferroelectrics (Table 1). Figure 3a shows the structure of the multilayer BFCO cell. By controlling the deposition rate of the pulsed laser deposition (PLD) process, the top BFCO layer yielded the widest E_g whilst the bottom layer yielded the narrowest.[10] Although transferred from conventional solar cells, the multilayering method of creating a tandem structure is still a straightforward concept for improving the photovoltaic performance of photoferroelectrics.

It should be noted that the novel BFCO composition also retained strong ferroelectricity whilst reducing the E_g. Figure 3b
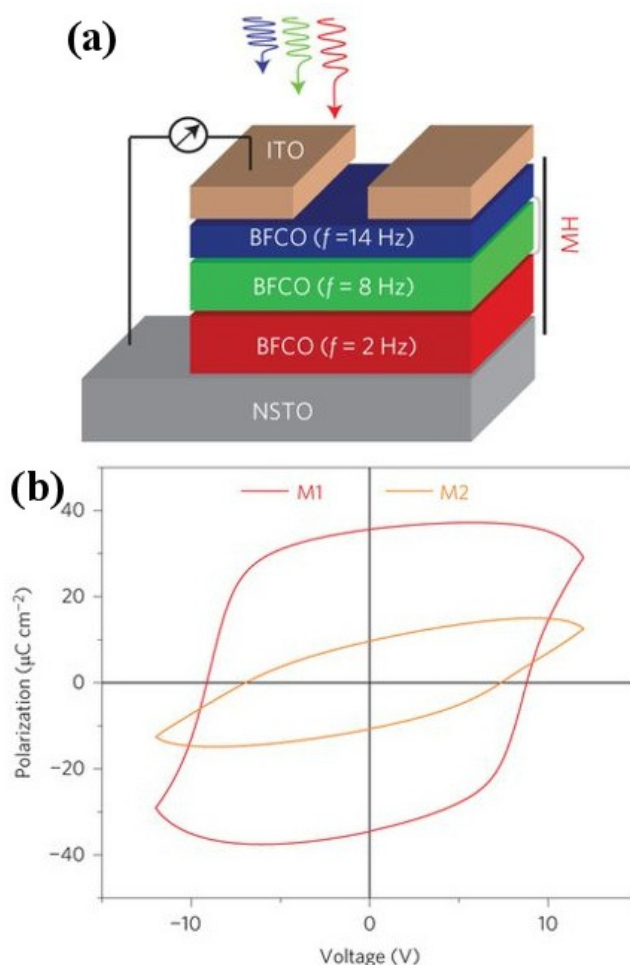

Figure 3. (a) The structure of the multilayer BFCO thin-film solar cell. (b) Ferroelectric hysteresis loops of two multilayer BFCO thin-film structures. Reproduced from Ref. [10] with permission. Copyright 2014, Springer Nature Publishing.

shows well-retained, large P_r (≈ 35 μC cm^{-2}) in spite of the greatly reduced E_g (from 2.7 to 1.6 eV).[10] This is because, crystallized in a double perovskite structure, the ferroelectricity of BFCO was mainly driven by the Bi^{3+} ions. Meanwhile, the interaction between Fe and Cr via oxygen controlled the E_g. The co-exhibition of both narrow E_g and strong ferroelectricity/good piezoelectricity is not only crucial for solar energy conversion, but also important for other potential applications to be presented below.

Polarization/Dipole (Re)Orientation

Although it is not clearly understood how and to what extent ferroelectricity affects the photovoltaic behavior of photoferroelectrics,[31,36] it has been shown that by manipulating the polarization or dipole orientation the photovoltaic performance could be improved by different extents. For instance, in a $Pb[(Mg_{1/3}Nb_{2/3})_{0.68}Ti_{0.32}]O_3$ (PMNT) bulk single crystal where both the directions of the incident light and electrode were perpendicular to that of the P_r, the photovoltaic effect changed in accordance with ferroelectricity.[37] Figures 4 and 5 show the cor-
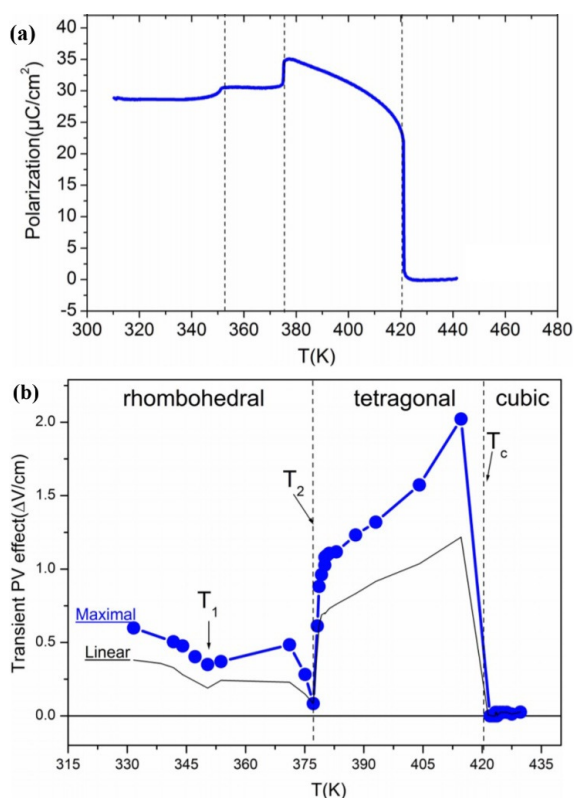
Figure 4. Dependence of (a) polarization and (b) transient photovoltaic effect on temperature for a PMNT single crystal. Reproduced from Ref. [37] with permission. Copyright 2018, American Physical Society.

responding relationship. In Figure 4a, a typical dependence of polarization on temperature measured in the dark reveals the change of polarization caused by phase transition (i.e., dipole reorientation). Before the phase changed to cubic and thus the polarization dropped to zero (below the Curie temperature, 420 K), the photovoltaic effect seemed to be negatively related to the change in polarization (Figure 4b). The maximum transient photovoltaic effect was found to be at around 410 K, just below the Curie temperature (420 K; Figure 4b). When the ferroelectricity vanished at above the Curie temperature, the transient photovoltaic effect correspondingly dropped to zero (Figure 4b). Despite some controversial arguments that have been made about the exact relationship between polarization and photovoltaic effect,[37] it implies that the concept of investigating different photoferroelectric compositions across the phase transition temperatures may help to improve the photovoltaic performance. An optimum working temperature at which the ferroelectricity and photovoltaic effect can be balanced may be defined for a certain composition.

In the above mentioned KNN–BNNO polycrystalline ceramics, the PCE was reported to be positively related to the extent of the domain alignment, when the direction of the incident light was in parallel

with that of the P_r while that of the electrodes was perpendicular.[38] As it was a multi-domain structure, the completion of the domain reorientation along the external electric field during the poling process could represent the extent of domain alignment and could be indicated by different piezo-electric charge coefficient (d_{33}) values. The larger the d_{33}, the better the aligned domain structure (i.e., the more reoriented domains). It can be seen in Figure 5 that the photovoltaic output increased with d_{33}. This was true for any illumination wavelength,[38] implying the concept that multi-domain photo-ferroelectrics may employ the means of improving the domain alignment (e.g., constantly applying an external electric field) to enhance the PCE.

Grain Boundary/Domain Wall Engineering

Although most high PCEs of photoferroelectrics are reported with single crystals and highly-oriented thin-films, no evidence has shown any disadvantage of using polycrystalline structures for PCE improvement. A PCE of approximately 4.2% for a single-layer polycrystalline composite thin film, which is very close to the record of 4.8% for a single layer BTO single crystal, was achieved via grain boundary engineering.[9] Figure 6 shows a transition electron microscopy (TEM) image of the composite film comprising a $BiMnO_3$ phase and a $BiMn_2O_5$ phase. The $BiMnO_3$ phase showed an experimental E_g of about 1.2 eV, and, depending on the selection of electrodes, a P_r of 9–16 μC cm^{-2}.[39] The $BiMn_2O_5$ phase is a semiconductor with 1.23 eV experimental E_g.

In such a concept, with the creation of ferroelectric grains in non-ferroelectric semiconductors, the photoexcited charge carriers prefer accumulation across the grain boundaries to that within the grains. This induced a high PCE, which could also
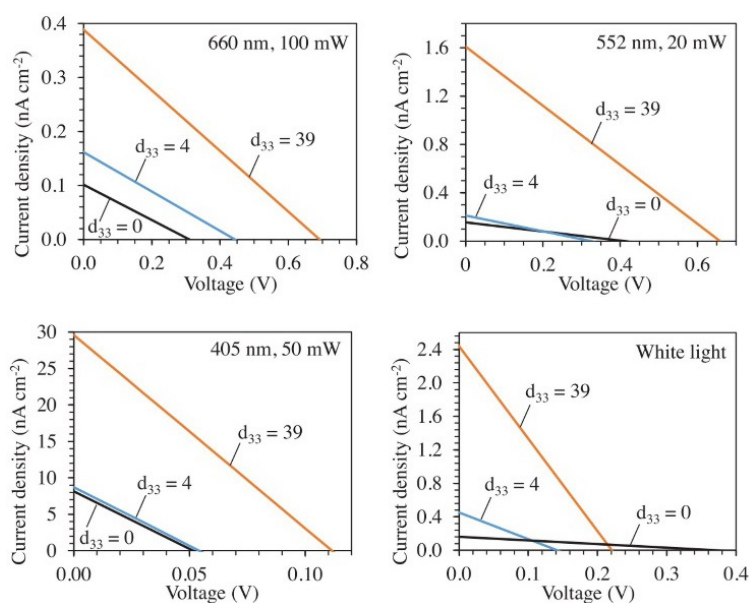

Figure 5. Current density–voltage (J–V) curves of the KNN–BNNO ceramic under different illumination conditions and with different extents of domain alignment (represented by the d_{33} value). Reproduced from Ref. [38] with permission. Copyright 2018, Wiley-VCH.
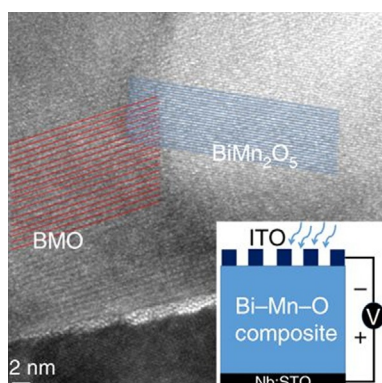
Figure 6. TEM image showing the simultaneous presence of $BiMnO_3$ and $BiMn_2O_5$ phases in a composite (Bi–Mn–O) thin film. The inset shows the device structure made from the composite thin film for electrical measurements. Reproduced from Ref. [9] with permission. Copyright 2018, Springer Nature Publishing.

be tuned by applying a certain number of bipolar pulses of an external electric field.[9] Similarly, it was found that in the 71° domain wall area of BFO thin films, the density of photoexcited carriers was higher than that in other areas.[40] Therefore, the concepts of grain boundary and domain wall engineering imply that nano-sized grains or domains may be created inside certain photoferroelectric materials to increase the ratio of the number of grain boundaries or domain walls to that of grains/domains, thus increasing the density of photoexcited charge carriers and the PCE.

Potential Applications other than Solely Solar Energy Conversion

This article has emphasized the importance of tradeoffs between ferroelectricity and E_g. Such a unique combination of multiple functions does not exist either in conventional solar cells or in organometal halide perovskites. A limited number of materials among the latter were found to be ferroelectric.[2] However, the existence of ferroelectricity in most of them is still under debate, making them unlikely to become robust and practical candidates for ferroelectric and photovoltaic multi-functional materials in the near future.

It is admitted that the PCEs of photoferroelectrics have not yet become competitive with those of conventional and organometal halide perovskite solar cells. Along with the continuous efforts being made to boost the PCEs, attention should also be paid to potential applications of photoferroelectrics other than being used as solar cells. After all, it is their multifunctionality that makes photoferroelectrics unique, rather than the single function of solar energy conversion.

For instance, the most straightforward potential application is multi-source energy harvesting and/or sensing. To the state of the art, most energy harvesters are developed for single energy sources, for example, for harvesting solar, kinetic, or thermal energy via photovoltaic, piezoelectric/triboelectric/ electrostatic/electromagnetic, or thermoelectric/pyroelectric effects, respectively. In some working environments of small-scale electronic devices, such as discrete sensors and wear-

ables, a certain energy source does not always exist, for example, no solar/light energy is available at night/in the dark or if the device wearer is not moving all the time (no kinetic energy). In contrast, in some contexts there is more than one energy source co-existing, for example, the device wearer is doing outdoor activities (kinetic energy) during daytime (solar energy). To make the best use of all available ambient energy and release the largest possible potential of the energy harvesting technology, one may desire to have a multi-source harvester that efficiently responds to different input energy simultaneously.

This demand may be met by physically combining different individual energy harvesters in the same configuration. However, the size and manufacturing costs will increase proportionally with the number of energy sources to be harvested. Additional costs for the device's structural engineering/optimization and wiring between different individual components will also be incurred. Instead, photoferroelectrics co-exhibiting an efficient photovoltaic effect and strong piezoelectric and pyroelectric effects may result in the development of single-material or single-component multi-source energy harvesters. As the harvesting functions can also be used for sensing, including purely multi-source energy harvesting, photoferroelectrics will eventually offer numerous possibilities for the functional design of a self-powered sensing unit. For instance, the DC output from the photovoltaic effect can be used for powering the module and circuitry whilst the AC outputs from the piezoelectric or pyroelectric effects can be used for sensing kinetic or thermal stimuli, respectively.[2, 30] It is also viable to use the AC outputs for harvesting and powering whilst using the DC output for optical sensing. Such a working principle may fundamentally advance the concept of energy harvesters with the same costs as those of single-source counterparts but with tripled functionality and applicability.

Photoferroelectrics may also be used for developing self-powered data storage devices. In most cases of the applications of solar energy conversion, the entire sample surface is illuminated and the output electric signal (i.e., photocurrent) is extracted from the same surface area. In another words, the surface under illumination is covered by a continuous transparent electrode (top electrode). However, in a special case, the top electrode may be only a conductive tip connecting to a much smaller area on the sample surface. As the top electrode area as well as the diameter of the current flow tunnel is largely reduced, the photocurrent density is significantly enhanced. This may induced a local electric field higher than the coercive field (the minimum external electric field to be applied to re-orient ferroelectric domains) of a photoferroelectric material. In such a case, a writing function is solely powered by light, rather than by an electric field.

Figure 7 shows an example architecture of such a device.[41] The photoferroelectric BFO thin film was deposited on top of a patch of $SrRuO_3$ (SRO) bottom electrode coated on a $TbScO_3$ (TSO) substrate. A probe with a conductive tip acted as the tiny-area top electrode. When an area of the BFO was illuminated, the polarization status outside the illuminated area and touched by the conductive tip was able to be switched. The
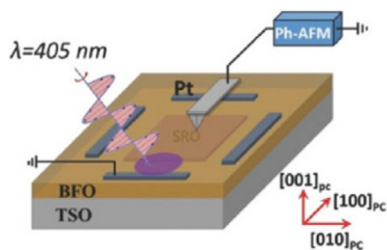
Figure 7. Device configuration with tip-enhanced photovoltaic effect showing light-induced ferroelectric polarization switching. Reproduced from Ref. [41] with permission. Copyright 2018, Wiley-VCH.

Figure 8. Illustration of the poling process assisted by the cumulative effect of light-induced and electrically induced domain switching. The Figure is created according to the description in Ref. [38].

switching was reversible either by tuning the illumination geometry or by rotating the light polarization, which eventually altered the photocurrent direction.[41] It was previously assumed that the reversible manipulation of polarization status in ferroelectrics could only be achieved by an external electric field. Other stimuli, such as temperature and strain, usually cause an irreversible consequence. With the emerging concept of light-induced domain wall motion or polarization switching, the data storage devices may be independent of electric energy sources (e.g., batteries, cable power). Such a self-powered function will open the doors to the development of next-generation opto-ferroelectric devices featuring great freedom in terms of design flexibility, portability, and long life-span.

Beside the example of a highly-oriented BFO thin film, photo-induced and photo-stimulated domain switching was also discovered in polycrystalline photoferroelectric ceramics. When an unpoled sample was placed under white light illumination (without any electric field) for a long enough time (hours), the light source started to pole the sample, increasing the d_{33} from zero to a certain value.[38] Although full domain switching has not been realized, it is expected that photoferroelectric ceramics can possibly be effectively poled solely by light. Compared to conventional electric poling, the light poling (e.g., using solar energy) can save energy for the piezoelectric industry where a large number of products need to be poled with high electric fields (tens of kV cm^{-1}). It can also introduce freedom for the location of the poling—the piezoelectric ceramics can be poled anywhere with a light source, for example, under sunlight, rather than near high-voltage electric sources.

In addition, the cumulative effect of light-induced and electrically induced domain wall motion may help to improve the efficiency of poling of piezoelectric ceramics. Figure 8 suggests that a poling process carried out both under illumination and with an external electric field could induce approximately a 50% higher d_{33} compared to that with an electric field only.[38] Furthermore, the contactless tuning of the conductivity of photoferroelectrics using different light wavelengths to achieve different extents of conductivity change could also stimulate the development of resistive random-access memory (RRAM).[42] Figure 9 gives an example of contactless conductivity tuning solely by light.

Apart from the cumulative effect of light and electric field on ferroelectricity, the synergy between photochemistry and
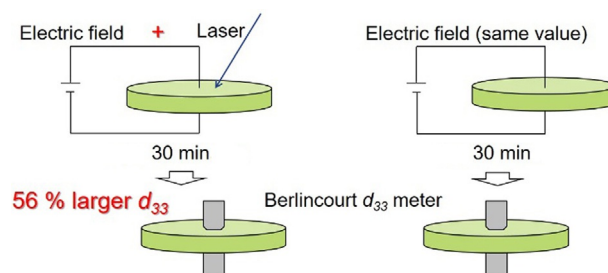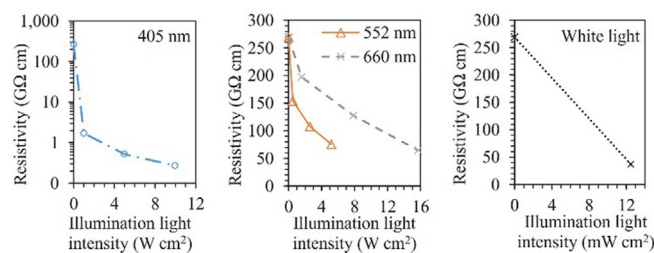

Figure 9. The changes of resistivity of the KNN–BNNO ceramics under illumination with different wavelengths and intensities of incident light. Reproduced from Ref. [38] with permission. Copyright 2018, Wiley-VCH.

photovoltaic activity may also induce disruptive technologies. Using a BTO thin film with La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) and Pt as the bottom and top electrodes, respectively, it was found that the dissociated OH$^-$ and H$^+$ adsorbates between the Pt and BTO layers were able to affect the P_r.[43] Note that the Pt electrode was grown ex situ after ambient exposure. Figure 10 depicts the scenario. In the dark, these adsorbates introduced a dead layer and thus increased the coercive field of the BTO layer. Under illumination, these adsorbates were released and then generated a dielectric dead layer, producing a decreased switchable polarization. This resulted in a substantial reduction of P_r.[43] Such a finding may drive the use of photoferroelectrics as novel chemical sensors. Other potential optical applications of ferroelectric oxides have been reviewed elsewhere.[44]
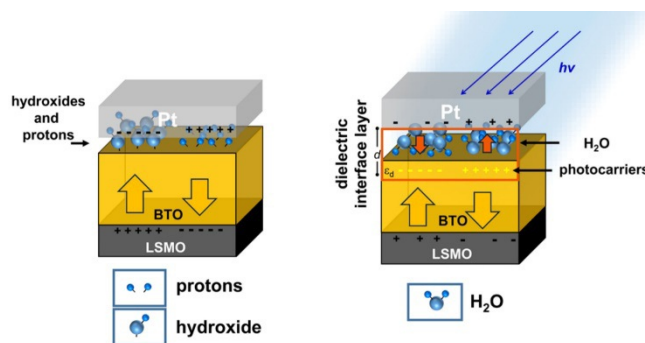

Figure 10. Explanation of the polarization screening mechanism caused by the interfacial layer between Pt and BTO. Reproduced from Ref. [43] with permission. Copyright 2018, ACS Publications.

Summary and Perspectives

The emerging concepts of further developing photoferroelectric materials and devices, with the emphasis of balancing strong ferroelectricity and a narrow band gap (E_g), or improved photovoltaic energy conversion efficiency, have been presented. Although the efficiency has been largely improved, photoferroelectrics still show an order-of-magnitude lower photovoltaic energy conversion efficiency than those of the counterparts made from conventional semiconductors and organometal halide perovskites. With the advantages of potentially above E_g photovoltage and above Shockley–Queisser (S–Q) limit efficiency, photoferroelectrics give hope to developing solar cells with ultra-high efficiency and superior stability compared to those of conventional counterparts. The novel concepts of band-gap/gap-state engineering, nano-/multilayering, polarization/dipole manipulation, and grain boundary/domain wall engineering have been summarized. However, these methods have only been studied individually.

In further research, these methods should be implemented comprehensively by selectively employing two or more concepts of efficiency improvement. For instance, a band-gap and grain-boundary engineered thin film could be tested across the phase transition temperatures and/or with an external electric-field bias (for better aligned domain structures). With these known methods, the practical upper limit of the efficiency of photoferroelectrics may be understood. In the meantime, the interaction of physical, chemical, photovoltaic, and ferroelectric behaviors between atoms, grains, and domains needs to be more deeply explored to discover unknown principles and guide further breakthroughs of efficiency improvement for photoferroelectrics.

Along with the efforts made for photovoltaic energy conversion efficiency improvement, phoroferroelectrics should also be developed for other practical applications, including multi-source energy harvesting/sensing, self-powered and next-generation data storage modules, photo-induced/stimulated piezoelectric effects, and novel chemical sensors. These potential applications benefit from the unique photovoltaic–ferroelectric multi-functionality and definitely indicate a bright future of photoferroelectrics.

With recently discovered narrow E_g and strong ferroelectric materials, important interactions between incident visible light and domain walls/structures that were never realized are now revealed. Further investigations of macroscopic (with bulk single crystals or ceramics) and microscopic (nano-scale) ferroelectric/piezoelectric behaviors with incident light of different wavelengths, polarizations, and intensities should be carried out. Such investigations will enable numerous possibilities for developing next-generation opto-ferroelectric/piezoelectric devices.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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