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The Progress of Ferroelectric Materials in the Field of Optoelectronics

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Abstract. Ferroelectric materials are a type of material with a spontaneous polarization (SP) phenomenon. It has excellent piezoelectric, pyroelectric, and photoelectric properties, and it also features a high dielectric constant and high semiconductor compatibility. Therefore, researchers conduct in-depth studies on it and demand commercial uses. This paper reviews the performance of ferroelectric materials in the field of optoelectronics and the application scope based on their optoelectronic properties, and presents specific research findings and breakthroughs in recent years. Firstly, the photovoltaic performance of ferroelectric materials and the solar cells that were improved based on this performance were introduced. Secondly, the electro-optic properties of ferroelectric materials and their applications in electro-optic modulators are introduced. Finally, the application of ferroelectric materials in the field of photoelectrocatalysis is introduced. The application prospects of ferroelectric materials in the photoelectric field are explored, and the current challenges they face are proposed, including the development of new ferroelectric materials to improve the photoelectric conversion efficiency, extend the service life of ferroelectric materials, control the size of ferroelectric materials, and optimize the preparation process of ferroelectric materials, etc.

Keywords: Ferroelectric materials, Photoelectric performance, Photovoltaic effect, Electro-optic effect, Photoelectrocatalysis

1. Introduction

Ferroelectrics are materials that have the characteristic of spontaneous polarization, and the direction of the polarization vector can be switched by applying an electric field [1]. Ferroelectric materials, due to their unique properties, have demonstrated broad application prospects in numerous fields such as memory, dielectric energy storage, piezoelectric devices, and optoelectronics [2]. The core advantage of ferroelectric materials lies in the existence of spontaneous polarization within them that can reverse under the influence of an external field. This characteristic endows them with excellent photoelectric conversion capabilities, enabling them to efficiently convert optical signals into electrical signals. Therefore, ferroelectric materials play a crucial role in the field of optoelectronics and have become key materials for manufacturing high-performance optoelectronic devices such as photovoltaic devices, optoelectronic memory devices, and photodetectors.

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In recent years, many breakthrough achievements have been discovered in ferroelectrics, including photogenerated voltages higher than the band gap, the discovery of low-bandgap ferroelectrics, and higher photoelectric conversion efficiency. The interaction between ferroelectrics and optics is an important driving force behind the development of innovative optoelectronic systems. It plays a significant role in areas such as polarization inversion and phase transition [3]. Although ferroelectric materials have been widely applied in the field of optoelectronics at present, there are still problems, such as insufficient understanding of the photoelectric mechanism of ferroelectric materials, complex and highly uncertain domain structure regulation of ferroelectric materials, and insufficient service life of ferroelectric materials.

Therefore, this article introduces the different properties and applications of ferroelectric materials in the field of optoelectronics, aiming to provide readers with a review of the basic optoelectronic properties and related applications of ferroelectric materials, and offer references for deeper research.

2. The photoelectric properties of ferroelectric materials

The photoelectric properties of materials refer to the electrical characteristics they exhibit under the influence of light. This is specifically reflected in the process and result where matter converts light energy into electrical energy when photons interact with materials. This performance holds a significant position in optoelectronic devices such as solar cells and photodetectors, as it directly affects the performance and efficiency of these devices.

Fridkin proposed that ferroelectrics could be utilized to achieve photoelectric energy conversion, and solar cells could be fabricated based on so-called photoferroelectric crystals [4]. In recent years, researchers have been dedicated to developing new ferroelectric materials to enhance the performance of solar cells. For instance, Deng et al. developed a hydrophobic ferroelectric polymer PVDF with multiple advantages and successfully applied it to the active layer. Based on the multiple advantages of PVDF, the PM6/BTP-eC9 system achieved an excellent efficiency of 18.35% in LBL devices based on BTP-eC9. Through the green solvent scraping printing technology, the large-area (1.21 cm^2) two-component achieved an efficiency of 16.40%, ranking among the top in the performance of this type of device. It is used for developing efficient large-area organic solar cells [5]. It can be seen from this that due to the spontaneous macroscopic polarization of ferroelectric materials, they can be used as optoelectronic materials to process optoelectronic devices. This polarization can change direction under the action of an external electric field, and its non-centrosymmetric crystal structure will generate an internal electric field within the material [6]. Meanwhile, the band gap of ferroelectric materials can be regulated through doping, solid solution design, or an external electric field to optimize their light absorption performance.

3. The photovoltaic effect of ferroelectric materials and its APPLICATIONS

3.1. Photovoltaic effect of ferroelectric materials

The traditional photovoltaic effect relies on two fundamental processes. The first is the generation of photogenerated carriers, which can be achieved by semiconductors absorbing light. Secondly, under the built-in electric field, photogenerated electrons and holes are separated and collected, forming a net current flowing in a specific direction. Utilizing solar radiation through the photovoltaic effect is the most efficient production process, providing huge economic and ecological benefits. However, its photoelectric conversion mechanism determines that its conversion efficiency cannot exceed the

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Shockley-Queisser (SQ) limit. Therefore, the search for new photovoltaic materials to develop solar cells with better performance and more functions has become a research hotspot in this field at present [4].

Due to the high spontaneous ferroelectric polarization intensity of ferroelectric materials, researchers speculate that the ferroelectric polarization in ferroelectric bodies can play the role of an internal electric field, rapidly separating photogenerated carriers and moving them in different directions. Researchers attempt to explore the mechanism of the photovoltaic effect in ferroelectric oxides from the perspectives of fundamental physics and material design, and seek new ways to enhance the photoelectric conversion efficiency. BiFeO3 has become the most favored research object in this direction. Compared with traditional ferroelectric materials, the energy gap of BiFeO3 is reduced to 2.7 eV, but it still maintains a large ferroelectric polarization, and at the same time has strange linear and nonlinear optical responses as well as photovoltaic effects. When Cr replaces part of the Fe in BiFeO3, the optical band gap variation of the formed double perovskite structure Bi2FeCrO6 can reach several eV, increasing the energy conversion efficiency to 8.1% [4]. Compared with the traditional photovoltaic effect, the photoelectric conversion efficiency of the ferroelectric photovoltaic effect is not limited by the SQ limit, and at the same time, an open-circuit voltage above the band gap can be obtained. This phenomenon is called the anomalous photovoltaic effect [7].

3.2. Applications in solar cells

With the continuous increase in energy demand, the development and utilization of clean and renewable energy - solar energy - is extremely urgent. The core concept of traditional solar cells based on semiconductors is to use a p-n junction with a band gap of 1.4eV to absorb solar radiation and have a p-n junction to separate photogenerated electron-hole (e-/h+) pairs and generate current [8]. Photovoltaic technology is an important technique for converting solar energy into electrical energy. Figure 1 is a schematic diagram of the photovoltaic effect, respectively demonstrating the photovoltaic effect of the semiconductor p-n junction and ferroelectricity. Electron-hole pairs are generated in materials exposed to sunlight, and the separation of them creates a potential difference at both ends of the material. To achieve high power output, photovoltaic devices require high photovoltage, photocurrent, and photoelectric conversion efficiency. High open-circuit voltage, good light absorption characteristics, and favorable polar structure are used for the separation of photogenerated carriers.

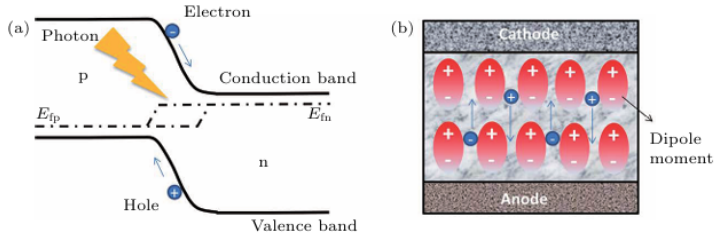


Figure 1. Schematic diagram of photovoltaic effect generation (a) Semiconductor p-n junction; (b) Ferroelectricity-photovoltaic effect [4]

At present, various ferroelectric materials have been applied in the manufacturing of solar cells. For instance, Chen et al. incorporated two-dimensional perovskites into three-dimensional perovskites. The efficiency of this two-dimensional template perovskite solar cell was 24.1%, and it

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demonstrated excellent durability. Even after 1000 hours at 85°C under maximum power point tracking, it still maintained an initial efficiency of 97% [9]. Dong et al. used ferroelectric BiFeO3 nanoparticles and Mg0.07 Zn0.93O/Mg0.12Zn0.88O double window to improve the efficiency of CIGS solar cells. Compared with no polarization state (16.65%), the polarization state of the device efficiency increased by 17.67% [10]. Li et al. modulated the performance of solar cells by polarizing the novel narrow-bandgap ferroelectric semiconductor hexane-1, 6-diammono-pentasmuth, etc. [11]. In conclusion, ferroelectric materials play a role in enhancing the photoelectric conversion efficiency and improving the stability of solar cells in their manufacturing.

4. The electro-optic effect of ferroelectric materials and its applications

4.1. Electro-optic effects of ferroelectric materials

The phenomenon where a medium changes due to the action of an electric field is called the electro-optic effect. This effect is a general term for all kinds of changes in the optical properties of an object under the action of an external electric field. The characteristic of the electro-optic effect is that there is almost no delay time, it can change rapidly with the electric field almost synchronously, and has an extremely high response frequency. The electro-optic effect is divided into the Pockels effect and the Kerr effect. In the Pockels effect, birefringence is directly proportional to the magnitude of the electric field, while in the Kerr effect, the change in refractive index is directly proportional to the square of the electric field. Ferroelectric materials can spontaneously polarize, and applied electric fields can redirect the direction of their polarization vectors, showing hysteresis loops. This characteristic makes ferroelectric materials highly sensitive to changes in external electric fields and light fields, so they exhibit good electro-optic effects. The inherent performance in them can endow crystals with properties similar to electric dipoles. This polarization inversion is usually accompanied by a region transition. The speed and mechanism of regional switching in this process will directly affect the electro-optical properties [12].

4.2. Applications in electro-optic modulators

With the emergence of the 5G era, the demand for high-speed and large-capacity data transmission in optical fiber communication has become increasingly pressing. As a key component in optical communication systems, the performance of electro-optic modulators is critically dependent on the electro-optic coefficient, response speed, and material stability. However, conventional materials, such as lithium niobate, are constrained by their relatively low electro-optic coefficients and high driving voltages, which limit their ability to meet the requirements of future ultra-high-speed communication systems [12]. The Pockels effect is a type of electro-optic effect. As a widely applied nonlinear optical phenomenon, it can achieve nearly instantaneous changes in refractive index by applying an electric field. This characteristic enables it to play a core role in electro-optic modulators, making it possible to achieve modulation bandwidths exceeding 100GHz, and it has important applications in fields such as quantum networks, programmable photonic circuits, and reconfigurable metasurfaces [13].

The electro-optic effect is crucial for controlling optical signals at high speeds. At present, a variety of ferroelectric materials have been applied in the manufacturing of electro-optic modulators. For instance, lithium niobate (LN) and barium titanate (BTO) are two excellent Pockels materials. Figure 2 shows the relationship between the electro-optic effect and polarization regulation, as well as the transition from state 1 to state 2 of the BTO thin film domain under the electric field E.

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Chelladurai, D. et al. experimentally verified the frequency response of the dielectric constant and the Pockels coefficients of LN and BTO covering the range of 100 MHz to 330 GHz. These data cover a wide range of frequencies and are of great significance to various developing technologies, including high-speed communication, quantum networks, programmable photonics, and reconfigurable metasurfaces. They lay the foundation for designing new devices with the highest frequencies [13]. Svetlana P. Kotova et al. discovered a ferroelectric liquid crystal with subwavelength helical spacing as the electro-optical medium for a high-speed phase space light modulator. The electro-optical medium of the helical phase plate can form and reconstruct the vortex light field at frequencies up to 3 kHz [14]. R. Mitra et al. comprehensively studied different ferroelectric perovskite systems serving as modulators in bulk ceramics, thin films, single crystals, and heterostructures [15]. In conclusion, ferroelectric materials have a higher electro-optical coefficient, which can reduce the driving voltage and decrease the device volume, meeting the demand for high-density optoelectronic integration in 5G communication.

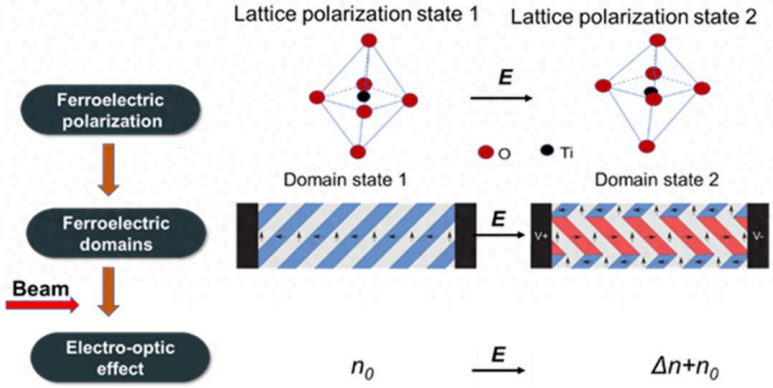


Figure 2. The relationship between electro-optic effect and polarization regulation, as well as the transition of domain state 1 to state 2 of BTO thin films under electric field [12]

5. The application of ferroelectric materials in photoelectrocatalysis

Photoelectrocatalysis is a technology that combines photocatalysis and electrocatalysis. Its main mechanism is to excite electrons through light and transfer them to promote chemical reactions. In the process of photoelectrocatalysis, the adsorption of molecules on the surface of the catalyst will change its potential energy surface, enabling photons to directly interact with molecules and trigger the desired reactions. Unlike simple electrocatalysis, the energy source of photoelectrocatalysis is incident light rather than an applied bias voltage.

The application of ferroelectric materials in photoelectrocatalysis mainly benefits from their spontaneous polarization characteristics, which can effectively separate photoinduced charge carriers and thereby enhance the efficiency of photoelectrocatalysis. At present, a variety of ferroelectric materials have been discovered and applied in the field of photoelectrocatalysis. For instance, Yang et al. utilized ferroelectric-enhanced BiVO4-BiFeO3 photoelectrocatalysis to achieve efficient, stable, and high-current-density oxygen evolution, verifying the significant function of enhancing charge separation and transport characteristics [16]. Qin et al. developed a novel photoelectrocatalytic system using the ferroelectric material BiOIO3 (BIO), achieving excellent degradation and mineralization of antibiotics. BIO possesses unique ferroelectric properties and nanosheet morphology, which can enhance carrier separation and reduce recombination, with a degradation rate 3.46 times that of traditional photocatalysts such as MoS2 [17]. Nassereddine et al.

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developed a low-cost spraying technology for nanostructured BiFeO3 photoelectrodes, demonstrating that applying an external electric field can induce ferroelectric polarization on disordered polycrystalline substrates, thereby achieving effective dipole alignment and enhancing photoelectrochemical performance. This highlights the beneficial role of ferroelectric catalysts and promotes photoelectrocatalysis to surpass traditional semiconductor catalysts. Improving photoelectrochemical properties through polarization [18]. In conclusion, ferroelectric materials can achieve the separation and transfer of photogenerated carriers, thereby enhancing the efficiency of photoelectrocatalysis. At present, researchers are still constantly exploring new ferroelectric materials with the aim of developing more efficient photoelectrocatalytic materials.

6. Conclusion

This article systematically reviews the performance, applications, and challenges of ferroelectric materials in the field of optoelectronics. Ferroelectric materials, due to their spontaneous polarization characteristics, possess excellent photovoltaic, electro-optic, and photoelectrocatalytic properties, demonstrating significant application value in fields such as solar cells, electro-optic modulators, and photoelectrocatalysis. However, there are still many challenges and considerable room for development in the application of ferroelectric materials in the field of optoelectronics. Firstly, it is necessary to search for ferroelectric bodies with smaller energy gaps, thinner thickness, but excellent ferroelectric properties, to achieve higher photoelectric energy conversion efficiency. Secondly, when the thickness of ferroelectric films drops to the nanometer level, the spontaneous polarization intensity significantly decreases, affecting the photoelectric performance. In addition, ferroelectric photovoltaic devices are prone to polarization fatigue under electric field cycling, resulting in a relatively short service life. Researchers can attempt to achieve mass production while controlling size and enhancing photoelectric conversion efficiency by developing new ferroelectric materials, such as two-dimensional ferroelectric materials, and simultaneously optimizing the production and preparation processes of ferroelectric materials. It is believed that in the near future, ferroelectric materials will be further developed and promoted in the field of optoelectronics, playing an important role in the manufacturing, informatization, and intelligence of the new era.

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