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硕士学位论文

**BaTiO<sub>3</sub> 片状晶的制备及其在柔性压电发电  
机中的应用**

**The Preparation of BaTiO<sub>3</sub> Platelets and Its Application on  
Flexible Piezoelectric Generator**

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## 摘要

本论文采用熔盐法合成了(001)择优取向生长的  $\text{BaTiO}_3$  片状微晶体, 利用油/水界面自组装的方法获得了具有高度取向性的压电薄膜, 并将其制备成柔性压电发电机用于收集环境机械能。

利用熔盐法在  $1050^\circ\text{C}$  合成了平板状结构的  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  和  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  片状晶体作为前驱体, 熔盐介质分别为  $\text{NaCl-KCl}$  和  $\text{KCl-BaCl}_2$ ; 然后, 在拓扑化学反应阶段  $\text{Ba}^{2+}$  替代  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  中的  $\text{Bi}^{3+}$  形成钙钛矿相的  $\text{BaTiO}_3$ , 反应温度为  $950^\circ\text{C}$ , 熔盐体系为  $\text{NaCl-KCl}$ 。得到的  $\text{BaTiO}_3$  片状晶体具有较大的径厚比(平均尺寸约为  $6\sim 10\ \mu\text{m}$ , 厚度为  $0.5\ \mu\text{m}$ ), 并沿(001)择优生长。

利用界面自组装的方法在水/正己烷界面将制得的规则片状晶体装配成了  $\text{BaTiO}_3$  单层薄膜, 该薄膜不仅具有较好的致密性, 而且片状晶平行于基底表面定向排列。通过理想模型计算了片状晶体在界面以两种不同状态存在时(平行于界面存在、垂直于界面存在)系统界面能的变化量, 证明了界面自组装是一个自发进行的过程, 驱动力为总界面能的减少。

将组装的  $\text{BaTiO}_3$  压电薄膜转移到溅射一层 ITO 的 PET 基底上, 利用 PDMS 封装后制得柔性单层  $\text{BaTiO}_3$  薄膜基压电发电机, 为了提高压电发电机的输出性能, 利用逐层组装——封装的方法制得了多层  $\text{BaTiO}_3$  薄膜基压电发电机。分别测试了两种压电发电机在  $d_{31}$  (弯曲)、 $d_{33}$  (按压) 工作模式下的输出性能, 并分析了其工作原理。

单层  $\text{BaTiO}_3$  薄膜基压电发电机在按压模式下最大开路电压、短路电流分别为  $5.5\ \text{V}$ 、 $30\ \text{nA}$ , 弯曲模式下电压、电流分别为  $6.5\ \text{V}$ 、 $140\ \text{nA}$ ; 将其用于收集风能, 瞬时电压、电流最高可达  $2.3\ \text{V}$ 、 $96\ \text{nA}$ , 当外接  $80\ \text{M}\Omega$  负载时, 它的瞬时、平均输出功率分别为  $0.055\ \mu\text{W}$ 、 $0.021\ \mu\text{W}$ 。

多层  $\text{BaTiO}_3$  薄膜基压电发电机在按压模式下最大开路电压、短路电流分别为  $23\ \text{V}$ 、 $550\ \text{nA}$ , 弯曲模式下电压、电流分别为  $24\ \text{V}$ 、 $280\ \text{nA}$ ; 将其用于收集波浪能, 瞬时电压、电流最高可达  $3\ \text{V}$ 、 $600\ \text{nA}$ , 当外接  $200\ \text{M}\Omega$  负载时, 它的瞬时、平均输出功率分别为  $1.89\ \mu\text{W}$ 、 $0.383\ \mu\text{W}$ 。

制备的  $\text{BaTiO}_3$  薄膜基压电发电机可以驱动数只全屏 LCD 及 LED，证明它具有实用价值。

**关键词：**  $\text{BaTiO}_3$  片状晶、界面自组装、压电发电机

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## Abstract

In this thesis, micron-scale platelet BaTiO<sub>3</sub> with (001) orientation was synthesized using a molten-salt growth method, which was then assembled into film on the oil/water interface by a facile interface self-assembly strategy. Based on the BaTiO<sub>3</sub> piezoelectric film, a flexible piezoelectric generator (PG) was developed to harvest the outdoor renewable energy sources such as wind energy and wave energy.

Aurivillius-structured Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> and BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> platelets crystal were first synthesized as precursor by molten-salt growth method in NaCl-KCl and KCl-BaCl<sub>2</sub> molten salts, respectively. Then, Bi<sup>3+</sup> in BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> was replaced by Ba<sup>2+</sup> and formed perovskite-structure BaTiO<sub>3</sub> through a topochemical reaction at 950 °C in NaCl-KCl molten salt. High aspect ratio BaTiO<sub>3</sub> platelets have an average size of 5~10 μm and a thickness of 0.5 μm, which also exhibits a strong (001) orientation.

Well-defined BaTiO<sub>3</sub> platelets with rectangle shape were self-assembled at a n-hexane/water interface to fabricate a high coverage area ratio mono-layer nanofilm with a preferred [001] orientation. Using an ideal model in which the BaTiO<sub>3</sub> platelets were assumed to be a rectangular platelet, the change in interfacial energy during assembly was calculated exactly, which may be a proof of that it's a spontaneous processes. And the main driving force for the attachment of a BaTiO<sub>3</sub> platelet to the oil/water interface during self-assembly is a decrease in total interfacial energy.

The assembled BaTiO<sub>3</sub> film was transferred onto ITO coated PET substrate and covered with PDMS to develop flexible PG sbased on monolayer BaTiO<sub>3</sub> film and multilayer films with a layer-by-layer method. Subsequently, the output capability of each generator was measured as well as the operating mechanism was analyzed both in  $d_{31}$  mode (under vertical stress) and  $d_{33}$  mode (under parallel shear force).

When the PG based on monolayer BaTiO<sub>3</sub> film working in  $d_{33}$  mode, the output open-circuit voltage and short-circuit current reached up to 5.5 V and 30 nA, while in the mode of  $d_{33}$  they are 6.5 V and 140 nA, respectively. With the aid of windmill, the

PG produced real-time voltage and current outputs that reached 2.3 V and 96 nA when being employed to harvest the wind energy. The instantaneous outpower and average outpower reached the maximum value of 0.055  $\mu\text{W}$  and 0.021  $\mu\text{W}$  at load resistance of about 80  $\text{M}\Omega$ , respectively.

In order to improve the output performance, a novel flexible  $\text{BaTiO}_3$ -PDMS multilayer based PG was fabricated. The output voltage and current of the PG device were 23 V and 550 nA, respectively, which was tapped by a ceramic stack. During the bending deformation, the PG device generated maximum electrical signals of 24 V (open-circuit voltage) and 280 nA (short-circuit current). Moreover, a unique equipment was assembled to convert wave energy into electric energy. Being put into a lake, it was lift up and dropped down by the water wave and produced real-time voltage and current outputs which reached up to 3 V and 600 nA. The instantaneous and average outpower reached the maximum value of 1.89  $\mu\text{W}$  and 0.383  $\mu\text{W}$  at load resistance of about 200  $\text{M}\Omega$ , respectively.

To evaluate the output performance, the PGs were used to harvest ambient energy and successfully drove several LCDs and LEDs. Therefore, the PGs show a promising future for energy generation and self-energy supply.

**Keywords:**  $\text{BaTiO}_3$  platelets crystal; interface self-assembly; piezoelectric generator

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