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## Further insights into thermoelectric properties of nonstoichiometric titanium oxide fabricated by high pressure and high temperature

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### ABSTRACT

The present work explores the feasibility of advancing the thermoelectric properties of nonstoichiometric  $\text{TiO}_{2-x}$  through introducing more and more oxygen deficiencies. Compared with previous work, it is found that this compositional manipulation induces phase transition; in addition, the scattering mechanisms of both carrier and phonon have changed, resulting in the temperature-independent electrical resistivity, inferior electrical performance and an unexpected high thermal conductivity. As a consequence, a moderate  $zT$  value of 0.13 is obtained in  $\text{TiO}_{1.72}$  at 600 °C. Through this work, we understand deeply about thermoelectric properties of nonstoichiometric titanium oxide by high pressure and high temperature, and further investigations about this system have been directed.

### 1. Introduction

Thermoelectric materials are functional ones that can realize the direct converting between heat and electricity. The efficiency of thermoelectric materials is assessed by the dimensionless figure of merit, defined as  $zT = \sigma S^2 T / \kappa$ , where  $\sigma$ ,  $S$ ,  $T$  and  $\kappa$  denote the electrical conductivity, Seebeck coefficient, absolute temperature, and the total thermal conductivity, respectively [1–3]. However, the interdependences of these thermoelectric parameters complicate efforts in upgrading the performance of thermoelectric materials. Improving the electrical conductivity usually leads to the degradation of the Seebeck coefficient. Similarly, decreasing the thermal conductivity often brings about the deterioration of the electrical conductivity.

In the past several decades, the nanostructure has been widely employed to upgrade  $zT$  values through lowering the thermal conductivity. Meanwhile, the multi-scale hierarchical structure has succeeded in further minimizing the thermal conductivity [2–4]. Alternatively, chemical tuning together with both the doping of foreign atoms and the formation of vast intrinsic defects is the most commonly used means to boost the electrical properties of oxides. Also, chemical tuning is effective in reducing the thermal conductivity [5]. Additionally, efforts have been persisted in developing advanced fabrication technologies and exploring new potential thermoelectric candidates with outstanding performances.

Among the advanced thermoelectric materials, transition-metal oxides are paradigmatic at high temperatures because of their good thermal stability and being free of toxic elements that can make up for

the insufficiency of the conventional alloy-based thermoelectric materials [6]. Environmentally friendly  $\text{TiO}_2$ -based thermoelectric materials are typical representatives of oxide thermoelectric materials, with great unexploited thermoelectric properties. Their unique structural and physical properties hint that the thermoelectric performance of this system can be boosted substantially [7]. For titanium oxide, the oxygen content can be altered in a relatively wide range, from  $\text{TiO}$  to  $\text{TiO}_2$ , implying the versatilities of the structures and properties. In particular, nonstoichiometric  $\text{TiO}_{2-x}$  have shown some intriguing properties and been extensively exploited for the thermoelectric performances.  $\text{TiO}_{2-x}$  is formed when reduction happens to  $\text{TiO}_2$ , with crystallographic shear structures being evolved. Herein, dense planar defects are introduced into titanium oxide according to the oxygen deficiency. Encouragingly, the dense planar defects act as important sources for phonon scattering while not for carrier [7,8]. In other words, the synergy between electrical and thermal transport of titanium oxide might be possible by introducing more and more oxygen deficiencies.

Recently, a series of multi-scale hierarchical nonstoichiometric  $\text{TiO}_{2-x}$  ( $\text{TiO}_{1.84}$ ,  $\text{TiO}_{1.80}$ ,  $\text{TiO}_{1.76}$ ) have been successfully prepared by using high pressure and high temperature (HPHT) method and the thermoelectric properties have been advanced via our strategy [8]. In this precursory work, the electrical conductivity was improved while the thermal conductivity was diminished with the increase of the oxygen deficiency [8]. The thermal conductivity would be further reduced by modulating the microstructures and morphologies toward desirable ones. On the other hand, based on the special features of titanium oxide, the thermoelectric performance of titanium oxide might

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be continuously upgraded by introducing more and more oxygen deficiencies in a reasonable manner. Actually, however, there should be an optimum carrier concentration for a given thermoelectric material to achieve its best performance [3,9]. Additionally, the conducting type of a certain titanium oxide, namely n-type or p-type, will also change at a certain temperature when the oxygen content is further reduced [10]. This carrier type-changing thermoelectric material is not useful at all from the application point of view. Therefore, further efforts are needed to verify whether it is feasible to push the  $zT$  value to higher one just through oxygen content manipulation and concomitant modulations of microstructures and morphologies.

In light of the above scenarios, we fabricated nonstoichiometric  $\text{TiO}_{1.72}$  by HPHT, and further reduction of oxygen content and multi-scale hierarchical structure were integrated into a single system to see whether  $zT$  can be further raised. We find that the electrical transport of  $\text{TiO}_{1.72}$  does not exhibit semiconducting behavior any longer and the scattering mechanisms might also have changed. What is more, the thermal conductivity gets higher with the formations of denser planar defects and multi-scale hierarchical structures. Consequently, a moderate  $zT$  of 0.13 was achieved here. We get further insights into thermoelectric properties of nonstoichiometric  $\text{TiO}_{2-x}$  fabricated by HPHT although the  $zT$  value is just moderate.

## 2. Experimental section

Starting materials (Ti (99.99% metals basis, 300 mesh) and  $\text{TiO}_2$  (99.8% metals basis, 25 nm, anatase)) were weighted according to the stoichiometry of  $\text{TiO}_{1.72}$  and mixed thoroughly by an agate mortar. The well-mixed powders were cold-pressed into a cylinder of 10.5 mm in diameter and 7 mm in thickness. This cylinder was then encased with molybdenum foil to avoid probable contamination, and the HPHT reactive sintering assembly was done after these. A China-type large-volume cubic high-pressure apparatus (SPD-6  $\times$  1200) was used to conduct the HPHT reactive sintering. The HPHT reactive sintering conditions used here were identical with those of our this previous work (namely 1080 °C, 3 GPa, and 2 h). [8] The sample chamber was heated by an energized graphite crucible and pressed by the hydraulic-pressed multianvil technique. The temperature of the chamber was told by a platinum–rhodium thermocouple fixed on its surface, while the change of the resistance of standard materials manifests the pressure. High-pressure quenching was undertaken on the chamber before unloading the pressure. Sample of  $\text{TiO}_{1.72}$  was successfully prepared by these procedures, and Fig. 1 is the schematic of our assembly for HPHT.

## 3. Characterization

The phase structures of our sample were analyzed by X-ray diffraction using a Cu K $\alpha$  radiation (D/MAX-RA). The morphologies and detailed microstructures were investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2200FS), respectively. A bar-shaped specimen of 3  $\times$  3  $\times$  8 mm was cut from the disk-shaped sample for the simultaneous measurements of electrical resistivity and Seebeck coefficient from 27 °C to 600 °C by Joule Yacht/Namicro-3L thermoelectric measurement system. The carrier concentration and mobility at room temperature were revealed by Hall measurement. Another disk-like sample being identical to the bar-shaped sample in properties was used for measuring the thermal conductivity. The thermal conductivity was computed in the light of  $\kappa = \lambda C_p D$ , where  $\lambda$  is the thermal diffusivity coefficient obtained by a laser flash method (Netzsch LFA 457) from 27 °C to 600 °C,  $C_p$  denotes the heat capacity estimated by the Dulong-Petit law, and  $D$  refers to the bulk density of the sample measured by Archimedes method.

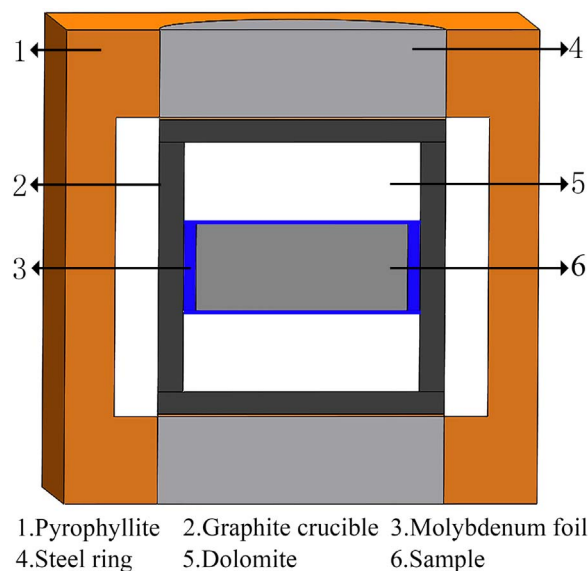


Fig. 1. The schematic of our assembly for HPHT.

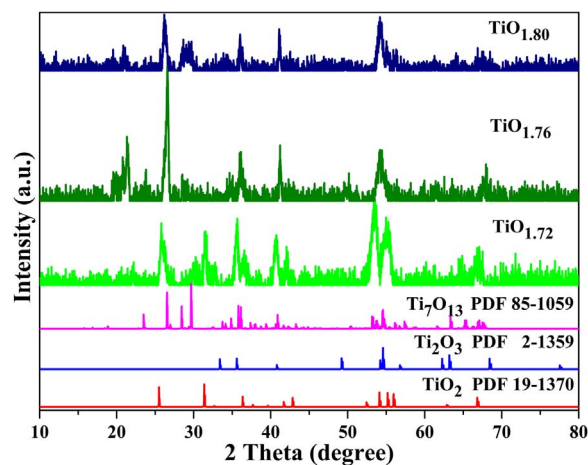


Fig. 2. The XRD pattern of our  $\text{TiO}_{1.72}$  fabricated by HPHT and some standard ones, with the ones of  $\text{TiO}_{1.76}$  and  $\text{TiO}_{1.80}$  from Ref. [8] for comparison.

## 4. Results and discussion

The XRD result of  $\text{TiO}_{1.72}$  fabricated by HPHT and some standard patterns are shown in Fig. 2, with those of  $\text{TiO}_{1.76}$  and  $\text{TiO}_{1.80}$  from Ref. [8] for comparison. Evidently, the peaks of our sample  $\text{TiO}_{1.72}$  are very complicated, the low intensity and broadening of the peaks being the cases for it. All these inevitably make precise identification of the peaks difficult. These might be related to the existences of multi-scale hierarchical structures and plentiful lattice defects, which will be discussed later. Even so, the peaks of  $\text{TiO}_{1.72}$  can be well indexed to  $\text{TiO}_2$  (PDF 19-1370),  $\text{Ti}_2\text{O}_3$  (PDF 2-1359) and  $\text{Ti}_7\text{O}_{13}$  (PDF 85-1059), within the detection limitation of the measurement. Additionally, the resultant sample is dark blue, indicating the formation of oxygen vacancies [11]. Herein, the reducing environment was brought about by the extrusion of high pressure (3 GPa) and the great ability of Ti to pillage oxygen under high temperature. It is noteworthy that the phase constitutions of  $\text{TiO}_{1.72}$  obtained here are different from those of our previous work, as shown in Fig. 2, which should stem from the phase transition driven by compositional manipulation. All these make it clear that nonstoichiometric  $\text{TiO}_{1.72}$  has been successfully prepared by HPHT.

The morphologies of our  $\text{TiO}_{1.72}$  are characterized by SEM, shown in Fig. 3. From the low magnification one, Fig. 3A, we can glimpse general morphologies of  $\text{TiO}_{1.72}$ , particles varying in length scales and pores

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