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Original Article

Preparation of monophasic titanium sub-oxides of Magnéli phase with enhanced thermoelectric performance

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ABSTRACT

Titanium sub-oxides of Magnéli phase are considered as earth-abundant, non-toxic materials for thermoelectric application at high temperature, but very limited investigation has been reported mainly owing to the difficulty lying in obtaining monophasic material. Herein we describe a facile strategy to prepare monophasic Ti_9O_{17} and Ti_4O_7 powder, in which the single Ti_9O_{17} phase is obtained for the first time. After spark plasma sintering, the thermoelectric properties of monophasic Ti_9O_{17} and Ti_4O_7 ceramics are studied comparatively. Despite the one magnitude lower electrical conductivity, Ti_9O_{17} shows higher power factor compared with Ti_4O_7 due to the large Seebeck coefficient. Moreover, with the low electronic thermal conductivity, sub-micron scaled grain size and nano-scaled crystallographic shear plane, the Ti_9O_{17} ceramic exhibits even lower thermal conductivity compared to Ti_4O_7 , leading to a ZT of 0.16 at 764 K, which is the best thermoelectric performance among reported Magnéli phases.

1. Introduction

Titanium sub-oxides with the general formula of $\text{Ti}_n\text{O}_{2n-1}$ have received great attention due to their versatile properties. For instance, Ti_3O_5 shows photoreversible phase transition at room temperature, which is very suitable for optical storage [1]. Ti_4O_7 was found to exhibit high activity and durability for oxygen reduction reaction in either acidic or alkaline solution, which makes it a promising catalytic material for fuel cell and zinc air batteries to replace the less stable carbon based electrode [2,3]. In addition, the Magnéli phases ($4 \leq n \leq 9$) were reported to possess high power factor as well as low thermal conductivity owing to the periodical shear plane in lattice induced by oxygen vacancies, which leads to high thermoelectric figure of merit with respect to other binary metal oxides [4]. Since Magnéli phase $\text{Ti}_n\text{O}_{2n-1}$ is stable until 1923 K and corrosion resistive against alkaline and acid [5,6], there is great potential in this type of material for the thermoelectric application under harsh environment.

Although the thermoelectric properties of titanium sub-oxides with different level of oxygen deficiency have been investigated by a few research groups, in most circumstances they can only be prepared in mixed phases. Very few types of Magnéli phase, such as Ti_4O_7 and Ti_8O_{15} , can be successfully prepared in single phase to date. Harada

et al. synthesized series of TiO_{2-x} compounds by reacting TiO_2 with TiO , but only single phase Ti_4O_7 and Ti_8O_{15} could be attained [7]. More recently, Portehault et al. adopted a sol-gel method to prepare different Magnéli phases by calcining the hybrid gel consisting of C, Ti and O. Although various carbon/Magnéli phase hybrids could be generated due to the carbothermic reduction of TiO_2 , the X-ray diffractions (XRD) patterns clearly indicated that only Ti_4O_7 and Ti_8O_{15} were present in single phase [8]. Likewise, Conze et al. also solely confirmed the successful preparation of C/ Ti_4O_7 and C/ Ti_8O_{15} hybrids, despite the lower carbon content in final products compared to Portehault et al.'s work [9]. In fact, residual carbon is the main disadvantage of carbothermic reduction method, since the malicious effect of amorphous carbon could undermine the thermoelectric performance of Magnéli phase.

In comparison to carbothermic reduction, the hydrogen reduction method is also frequently exploited for its apparent merit of leaving no residual impurity after fabrication. However, it is found that only mixtures of Magnéli phase can be obtained when using H_2 forming gas as reductant [10,11]. In this work, instead of using H_2 forming gas, the pure H_2 gas was selected as reductant to produce Magnéli phase by reducing rutile TiO_2 . Both monophasic Ti_9O_{17} and Ti_4O_7 were obtained by this method. To the best of our knowledge, this is the first example that single phase Ti_9O_{17} without any impurities can be prepared. After

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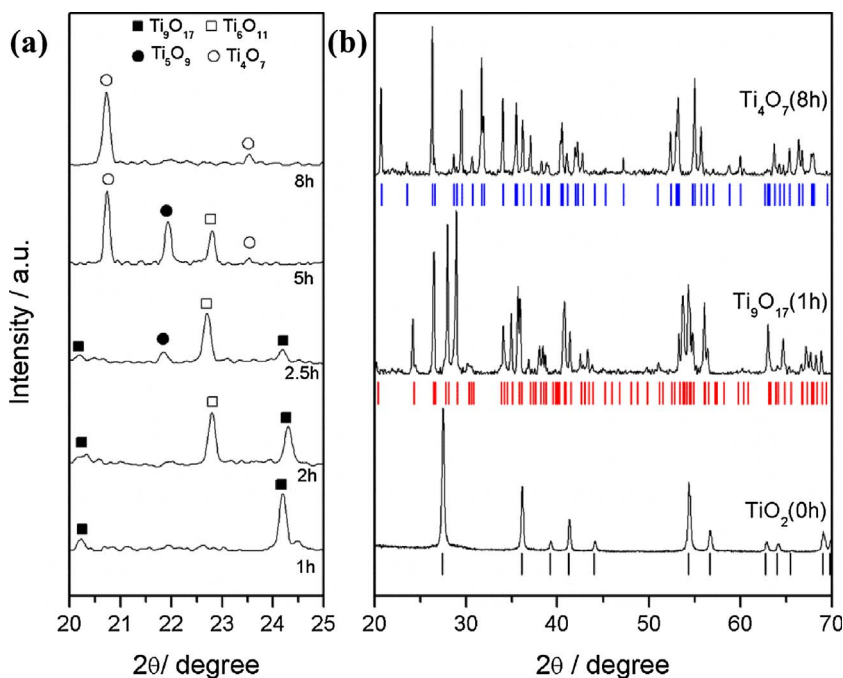


Fig. 1. XRD patterns for pristine TiO_2 and $\text{Ti}_n\text{O}_{2n-1}$ powder. (a) the evolution of XRD peaks at low angle with increasing time of heat treatment under pure H_2 gas (for wide-range spectra see Fig. S1 in Supporting information); (b) the XRD patterns of obtained powders in wide range, showing monophasic rutile TiO_2 (JCPDS#21-1276), Ti_9O_{17} (JCPDS#50-0791) and Ti_4O_7 (JCPDS#50-0787), respectively.

sintered by spark plasma sintering (SPS), the thermoelectric properties of the as-prepared Ti_9O_{17} and Ti_4O_7 ceramics were characterized and compared.

2. Experimental

2.1. Preparation and densification of Magnéli phase $\text{Ti}_n\text{O}_{2n-1}$

The TiO_2 powder of rutile phase was used as starting material. The as-purchased TiO_2 powder was loaded in an alumina crucible and then inserted into a tube furnace with protecting system designed for hydrogen reduction at elevated temperature (LS-09, Japan Pionics co. LTD). The TiO_2 powder was heat treated at 1253 K for 1 h, 2 h, 2.5 h, 5 h and 8 h under pure H_2 gas flow of 50 mL min^{-1} , before cooling down to room temperature in 6 h. The obtained powder was densified by SPS using a super-hard die made of tungsten carbide. The sintering temperature varied from 873 K to 1023 K to find the optimum condition. During sintering, a pressure of 200 MPa was applied from the beginning.

2.2. Characterization

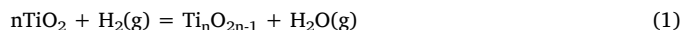
The XRD patterns were collected by a Rigaku Smartlab 9kw diffractometer with $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15418 \text{ nm}$). The transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) observation were performed on a JEOL JEM-ARM200F equipment [12]. For preparing TEM samples, the bulk materials were polished by sand papers to reduce the thickness to $\sim 30 \mu\text{m}$ at first, and then further thinned by ion milling (GATAN PISP Model 691, Gatan Inc.) under a voltage of 4 kV. The sintered samples were ground and polished by the standard ceramographic methods. The SEM observation and electron back-scattered diffraction (EBSD) were undertaken using JEOL JSM-6500F and JEOL JSM-7100F equipment, respectively. The samples for TEM observation were used for EBSD analysis. The electrical conductivity and Seebeck coefficient were measured using a ZEM-3 equipment (Ulvac-Riko) under a low-pressure helium atmosphere. The thermal diffusivity and specific heat were measured using a laser flash method (LFA 457, Netzsch) and a differential scanning calorimeter (DSC 404F3, Netzsch), respectively. The illustration of crystal structure for Ti_9O_{17} was generated by software

CrystalMaker (HULINKS Inc., Japan). The relative uncertainty of the electrical conductivity, the Seebeck coefficient and the thermal diffusivity are 3%, 2% and 5%, respectively. Including measurement errors from C_p and density, the overall uncertainty of ZT is about 10%.

3. Results and discussion

3.1. Preparation of titanium sub-oxide powder by hydrogen reduction

Titanium dioxide can be reduced by hydrogen to generate its sub-oxide according to the following reaction:



Since the oxygen atoms will gradually be deprived from lattice of TiO_2 , theoretically Magnéli phase with different level of oxygen deficiency can be obtained by controlling the reaction time. Upon heat treatment at 1253 K in flowing H_2 gas with increasing time, the phase of TiO_2 changed from rutile to various sub-oxides consecutively, as indicated by XRD patterns (Fig. 1a). After 1 h of reduction, the first observed phase was monophasic Ti_9O_{17} (JCPDS#50-0791), which has rarely been acquired in previous researches. Extending reaction time to 2 h resulted in mixture powder containing Ti_6O_{11} (JCPDS#50-0788) and Ti_9O_{17} , but further increasing reaction time could not lead to monophasic Ti_6O_{11} due to the presence of Ti_5O_9 (JCPDS#51-0641) before Ti_9O_{17} phase was completely disappeared. Similarly, it is found that single phase of Ti_5O_9 also cannot be obtained owing to the simultaneous presence of Ti_6O_{11} , Ti_5O_9 and Ti_4O_7 . After 8 h of reduction, Ti_4O_7 (JCPDS#50-0787) was attained as single phase at last, which is the most frequently reported phase generated by hydrogen or carbothermal reduction. It can be seen that the products of reducing TiO_2 by pure hydrogen were $\text{Ti}_n\text{O}_{2n-1}$ ($n = 4, 5, 6, 9$), among which only Ti_9O_{17} and Ti_4O_7 could be synthesized in single phase (Fig. 1b).

This result can be understood from two aspects. On one hand, from the view of thermal dynamics, Ti_4O_7 is the stable phase while the other phases are metastable under the experimental condition, which is also indicated by thermal dynamic calculation (see Fig. S2). In addition, the stable product of reaction (1) depends on not only the reaction temperature, but also the partial pressure of H_2O which is hardly to control during processing. Thus single phases like Ti_5O_9 and Ti_6O_{11} are difficult to prepare through changing the temperature of reduction alone. On the

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