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Semiconducting properties of nonstoichiometric TiO_{2-x} ceramics

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Abstract

Ceramics containing titanium oxides were prepared using extrusion technology and thermal treatment in two stages: sintering at normal atmospheric conditions at 1000 and 1200 °C and annealing in high vacuum conditions at 950 and 1150 °C. Electrical properties such as thermopower and electrical conductivity of cylindrical specimens have been studied at temperature range from the room temperature up to 350 °C. Activation energy of the process has been determined from conductivity curves. Obtained thermopower values are in the range from 68 up to 105 mV at temperature gradient between the hot and cold ends of the samples at 300 °C, while activation energy values are from 0.03 to 1.16 eV.

Keywords: *titania, extrusion, microstructure, thermoelectric properties*

I. Introduction

Thermoelectric materials receive great interest in recent years due to their potential applications such as coolers (or heaters), power generators, electrodes or thermal energy sensors [1,2]. Non-stoichiometric titanium dioxides (TiO_{2-x}) are expected to be an applicable candidate material for thermoelectric applications [3]. Titanium dioxide (TiO_2) ceramics have been widely used in photocatalysts, dye-sensitised solar cells, gas sensors, self-cleaning components and biomaterials because of its low absorption coefficient, high dielectric constant and good biocompatibility [4]. TiO_2 has been found to be an insulator when the crystal structure is perfectly formed, however, the electrical properties of TiO_2 can be controlled by oxygen vacancies [5]. To increase the electrical conductivity, it is necessary to increase the number of oxygen vacancies in the crystal and obtain a non-stoichiometric titanium dioxide, TiO_{2-x} [6]. Non-stoichiometric titanium dioxide (TiO_{2-x}) can be obtained by techniques such as sintering of mixed powder of TiO_2 and TiO, reduction of TiO_2 in carbon or hydrogen reducing atmosphere, among others [7].

In the present research ceramic specimens were prepared using extrusion followed by two stage thermal treatment: i) at normal atmospheric conditions in air and ii) in high vacuum conditions. Electrical properties, such as thermoelectric power, conductivity and electron activation energy of specimens were studied in conjunction with microstructural features.

II. Experimental

2.1 Specimens preparation

Titanium dioxide samples were prepared using industrial scale extruder. Extrusion mass consisted of anatase 79 wt.% (TiO_2, Hombitan, Sachtleben Chemie GmbH), water 19 wt.%, lubricant 1.5 wt.% (Produkt KP 5144) and binder 0.5 wt.% (Zusoplast C 93, Zschimmer & Schwarz GmbH & Co KG). The obtained green bodies (Ø 10 mm) were sintered at 1000 and 1200 °C with 2 °C/min heating rate and 8 h dwell time to burn out additives and complete transformation from anatase to rutile crystal structure occurs. Further, samples were treated in high vacuum conditions ($6.6\cdot10^{-3}$ Pa) at 950 and 1150 °C with 5 °C/min heating rate and 2 h dwell time. The thermal treatment conditions of samples are shown in Table 1. After sintering the samples were cut into 18 mm long rods. Sample ends surfaces were cleaned using vacu-

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Table 1. Thermal treatment conditions of the samples

Designation of the samples	Sintering in air	Annealing in vacuum
C1	1000 °C / 8h	950 °C / 2h
C2	1000 °C / 8h	1150 °C / 2h
C3	1200 °C / 8h	950 °C / 2h
C4	1200 °C / 8h	1150 °C / 2h

um sparking discharge. For better electrode-material contact a thin aluminium film (0.2–0.3 µm) was deposited on the ends of the samples using vapour deposition technique.

2.2 Electrical properties measurement

The obtained specimens were tested using electrical measurement equipment as described before [8]. Thermopower and electrical resistance measurements were made simultaneously. One of the ends of the specimen has been heated up to 350 °C. Temperature has been controlled using thermocouple copper-constantan. PP63 type DC potentiometer has been used for thermopower measurements (accuracy class 0.05) and MO62 type DC Wheatstone bridge has been used for resistance measurements (accuracy class 0.1).

The thermal effect of thermal probe is used for determination of electrical conductivity of a semiconductor [9]. The method is based on Thompson effect in semiconductor. Using this method semiconductor conductivity type can be determined. Magneto's electrical system voltmeter was used for determination of polarity.

2.3 Phase analysis and studies of microstructure

Crystalline phases in the specimens were identified using X-ray powder diffraction (PXRD), using diffractometer PANalytical X'Pert Pro. Cu Kα filtered radiation over 2θ range from 20° to 65° was used. Microstructure of the specimen fracture surface was investigated using FE-SEM (Mira/LMU, Tescan).

III. Results and discussion

3.1 Structural characterisation

Crystalline phases identified in PXRD patterns of the samples are shown in Fig. 1. After sintering in the air, samples C1 and C2 have anatase and rutile crystal phases but the samples C3 and C4 have only rutile phase. After annealing in high vacuum, samples C2, C3 and C4 have rutile crystal phases, but the sample C1 has both anatase and rutile phases. In the obtained PXRD patterns peaks characteristic for non-stoichiometric titanium oxide phases have not been observed. This could be contributed to small quantity of these phases, less than 1%.

Microstructures of all specimens are shown in Fig. 2. Evidently, by increasing the temperature of thermal treatment the grain size of the specimens increases. The thermal treatment temperature at normal atmospheric pressure in air for the samples C1 and C2 is the same (1000 °C) but different in vacuum conditions (950 °C or 1150 °C). Apparently, average crystallite size in the specimen C1 is smaller, less than 2 µm, compared to average crystallite size in the specimen C2 (less than 6 µm). In this case, if temperature

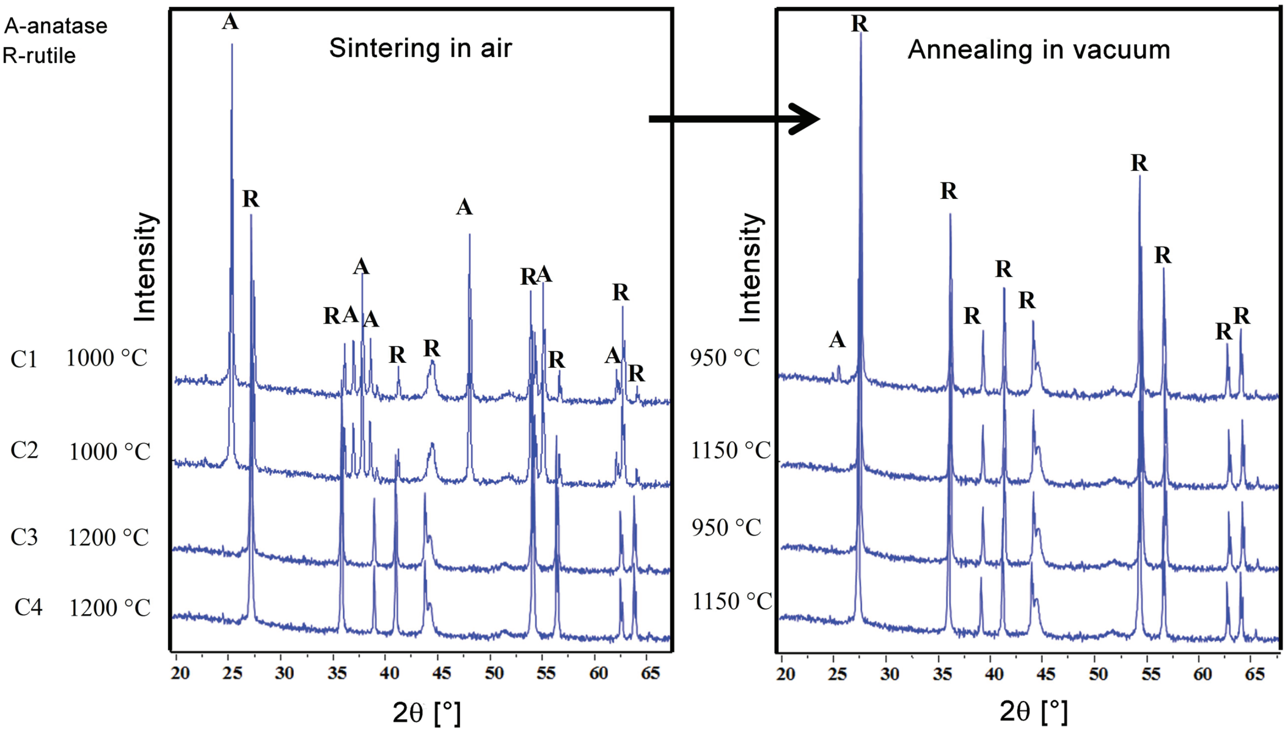

Figure 1. XRD patterns of the samples after sintering in air and additional annealing in vacuum

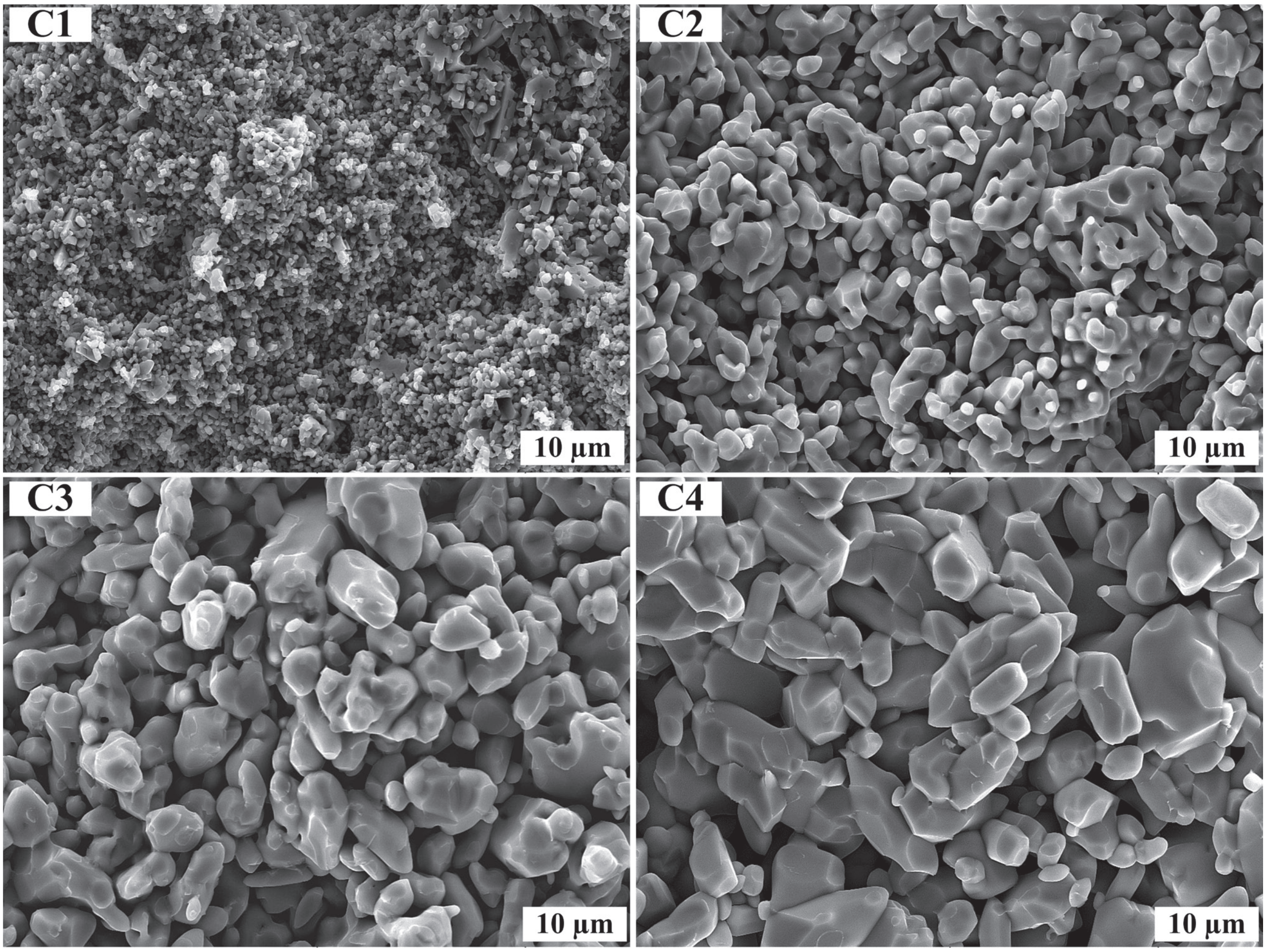

Figure 2. SEM micrographs of specimens fracture surface after sintering in normal atmosphere and annealing in high vacuum conditions

of thermal treatment in vacuum is higher than temperature of thermal treatment at normal atmosphere pressure in air, there is intensive growth of grains in vacuum conditions.

Comparing the specimens C3 and C4, where temperature of thermal treatment in the air is higher than that in vacuum, intrinsic difference of grain size was not observed. Grains of 3–10 µm have been formed in the specimens C3 and C4. Comparing the samples C1 and C3 it can be seen that thermal treatment in air atmosphere has great impact on the microstructure of the obtained ceramics.

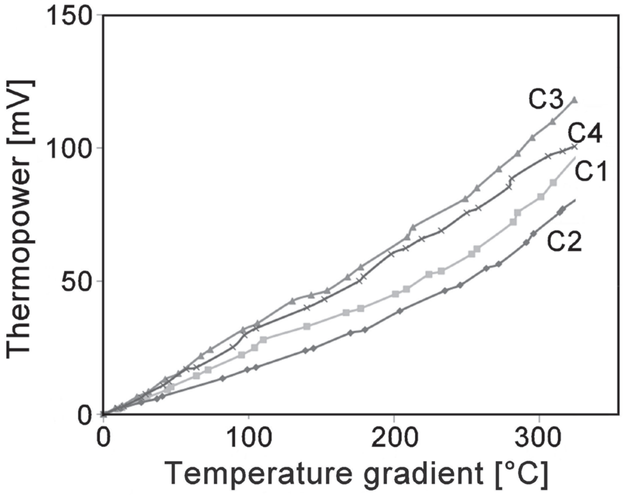

Figure 3. Thermopower as a function of temperature gradient for all specimens

3.2 Thermoelectric power

In all specimens thermopower is in proportional dependence on temperature gradient along ends of the specimens (Fig. 3). The obtained high thermopower values are typical for semiconductor materials. All specimens show *n*-type conductivity. The samples C3 and C4, which were thermally treated in normal atmosphere at 1200 °C before thermal treatment in high vacuum, have higher thermopower values than the samples C1 and C2. It can also be seen from Fig. 3 that samples which were thermally treated in high vacuum conditions at 950 °C, have higher thermopower values than the samples which were thermally treated in high vacuum at 1150 °C. The obtained results have shown that the specimen C3 has the highest thermopower value (105 mV) while, under the same measurement conditions, the specimen C2 has the lowest thermopower value (68 mV). The obtained thermopower values are

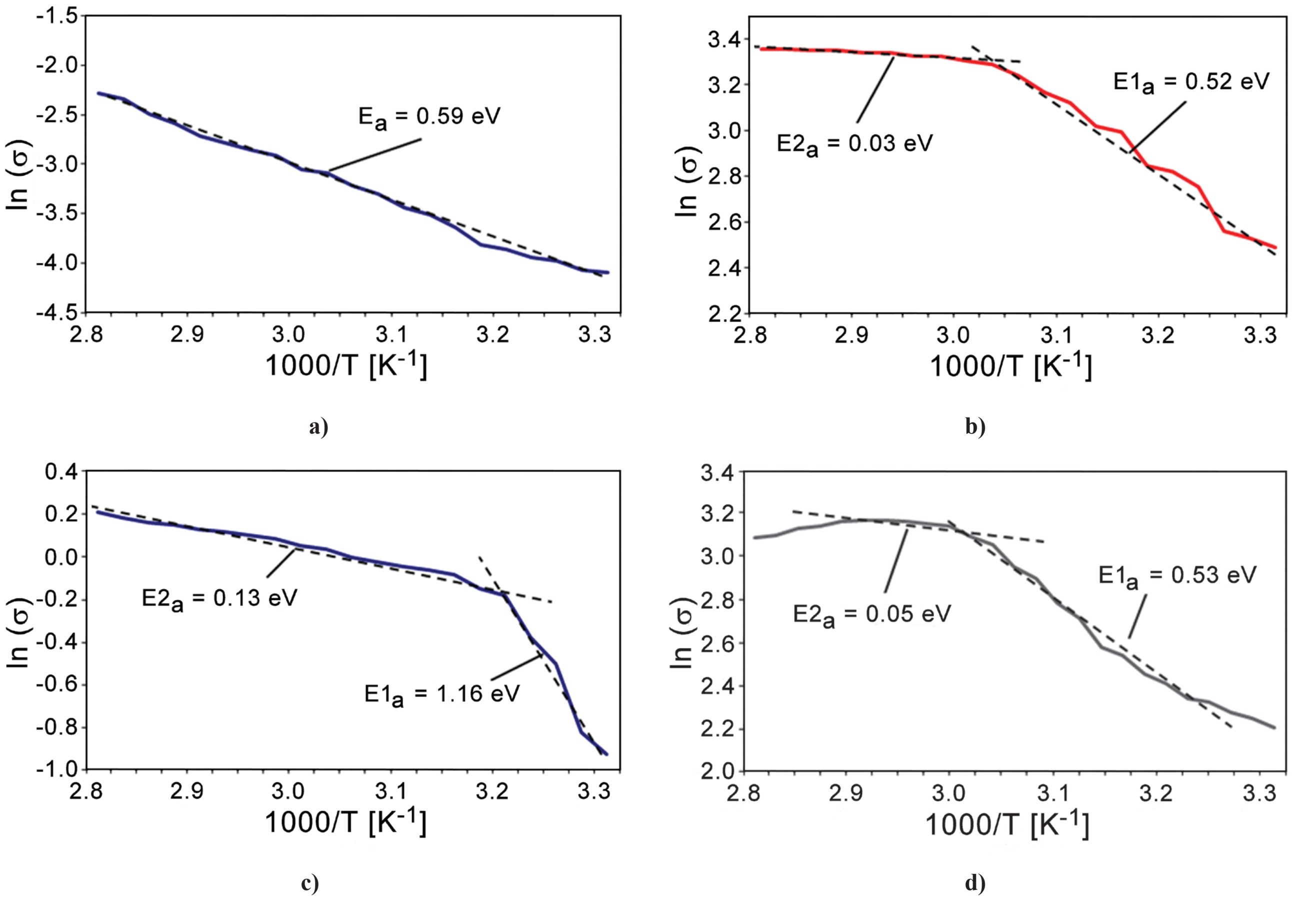

Figure 4. Temperature - conductivity curve of sample: a) C1, b) C2, c) C3 and d) C4

higher than those in our previous publication [8] and comparable with literature data [10].

3.3 Conductivity

Conductivity curves as the function of temperature were constructed for all specimens (Fig. 4). Specimens conductivity significantly improves by means of increasing temperature. In addition, the samples C2 and C4, thermally treated in vacuum at 1150 °C have higher conductivity than the samples treated at 950 °C (C1 and C3). This could be explained with higher concentration of oxygen vacancies obtained at higher temperature. There are two conductivity regions - from 295 to 320 K (region 1) and 320 to 355 K (region 2) in all graphs, except for the sample C1. Activation energy values are significantly lower in region 2 than region 1 because material passes from one conduction mechanism to another. We assume that the bulk conductivity dominates in the region 1 and the surface conductivity dominates in the region 2. We will continue the experiments in order to clarify our assumptions.

IV. Conclusions

Non-stoichiometric titanium dioxide samples were prepared from anatase TiO_2 powder by extrusion followed by two stage thermal treatments in normal atmosphere (air) condition and in high vacuum. The highest thermopower value was obtained for the specimen thermally treated at 1200 °C for 8 h in normal atmosphere and in high vacuum at 950 °C for 2 h. The lower thermopower was obtained for specimens thermally treated at 1150 °C in high vacuum conditions. The obtained thermopower values are higher than those in our previous publication and comparable with literature data.

Conductivity of the prepared samples was also measured and activation energy was determined from conductivity curves. Two conduction mechanisms were observed by activation energy from 0.6 to 1.2 eV, and from 0.03 to 0.13 eV.

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