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Correlation between high-pressure electrical properties of ZrO_2 and its crystallite size

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A relation between crystallite size and electrical properties of ZrO_2 has been investigated by measurements of high-pressure electrical resistance. The resistance of nanocrystalline praseodymium-doped zirconia powders has been measured in the pressure and temperature ranges between 15 and 50 GPa, and 77 and 400 K, respectively. Around 30–37 GPa the resistances of all samples decrease by 3–4 orders of magnitude. Therefore, the anomalies in the pressure dependence of the resistance and of parameters depending on the concentration, mobility and activation energy of the charge carriers were found at ca. 40–45 GPa. The activation energy of the charge carriers depends on the crystallite size.

Key words: zirconium dioxide; electrical properties; pressure-induced phase transition; nanocrystalline sample

1. Introduction

Zirconium dioxide, a major component of the best fuel cell materials [1], exhibits quite interesting properties. Studies on the high pressure behaviour of pure ZrO_2 revealed the presence of successive transformations to two different orthorhombic phases (Ortho-I and Ortho-II) [2]. Ortho-I is a distorted fluorite structure and Orhto-II is a densely packed $PbCl_2$-type structure. In his recent work Ohtaka et al. [3] suggest that the monoclinic-to-Ortho-I and Ortho-I-to-Ortho-II phase transitions occur at about 4 GPa and 12 GPa, respectively, for pure ZrO_2 near room temperature. However, the latter (reconstructive) transition is extremely sluggish and the metastability is observed over a wide pressure range.

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In this paper, supplementing our earlier publication [4], we report on the results of investigation of a correlation between electrical properties and crystallite size of ZrO_2 in the pressure range between 15 and 50 GPa and temperature range between 77 and 400 K. Size of crystallites changed from 10 to 500 nm. Our experimental data reveal that the smaller crystallite size, the higher is the transformation pressure.

2. Experimental

The d.c. conductivity measurements were carried out in a diamond anvil cell (DAC) with anvils of the “rounded cone-plane” (Verechagin–Yakovlev) type made of synthetic carbonado-type diamonds [5], consisting of dielectric grains of synthetic diamonds in layers of conducting materials. These anvils are relatively good conductors, thus permitting measurement of the resistances of samples placed between the anvils in the DAC by using the anvils as the electrical contacts to the sample. The procedure for the determination of the pressure reached in a DAC of the “rounded cone-plane” type has been described in [6, 7].

Measurements were made with powder samples of ZrO_2 with various crystallite sizes and with a “bulk material” samples of zirconia containing 5 mole % of $Y_2O_{3.}$ The crystallite sizes in the “bulk” samples amounted ca. 500 nm. The sample was synthesized by the Daiichi Kigensou Company in Japan (Lot # NEY-5M LO524). Moreover, we used nanocrystalline praseodymium-doped zirconia powders, produced using a microwave driven hydrothermal process under pressures up to 8 GPa. Nanopowders of ZrO_2 containing 0.5 mole % of Pr were synthesized in the High Pressure Research Center of the Polish Academy of Sciences [8].

3. Results and discusstion

The pressure dependences of the electrical resistivities of nanocrystalline ZrO_2 are shown in Fig. 1. At ca. 30–37 GPa, the resistances of all samples decrease by 3–4 orders of magnitude. Based on the fact that this result could be reproduced using different samples and different DACs, we are sure that the effect is not due to a short-circuit between the anvils nor to a dielectric breakdown of the sample. Furthermore, we found that the value of this pressure increases with the decrease of the crystallite size. Further anomalies have been found at ca. 40–45 GPa.

The temperature dependence of the resistance of the nanocrystalline samples at most pressures can be fitted by the equation

$$R = R_0 \exp\left(\frac{E_a}{kT}\right) \tag{1}$$

E_a standing for the activation energy, and R_0 being a parameter depending on the mobility and concentration of the charge carriers.

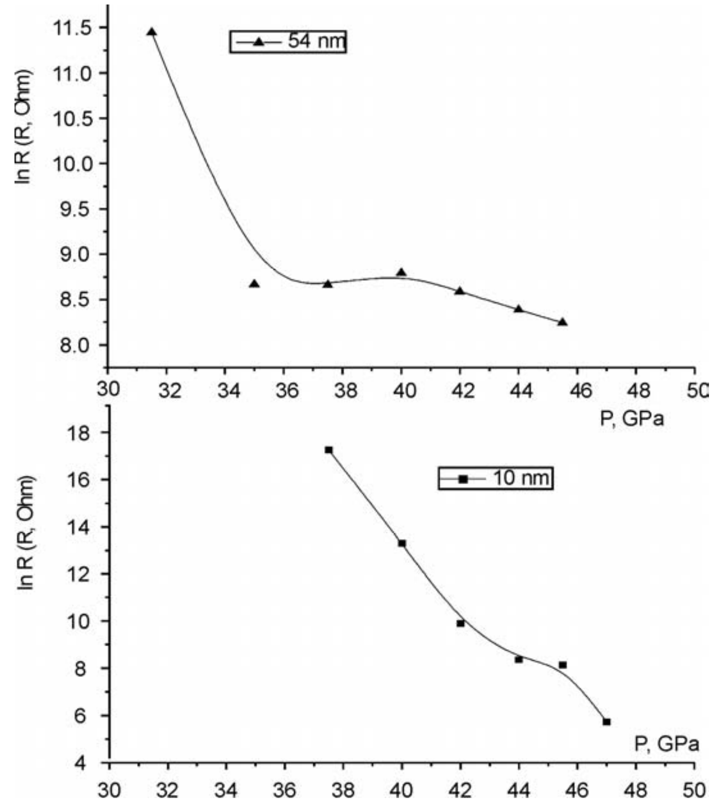

Fig. 1. Pressure dependences of the electrical resistance in nanocrystalline ZrO$_2$ samples detemined for two average crystallite sizes. The measurements were taken at 290 K

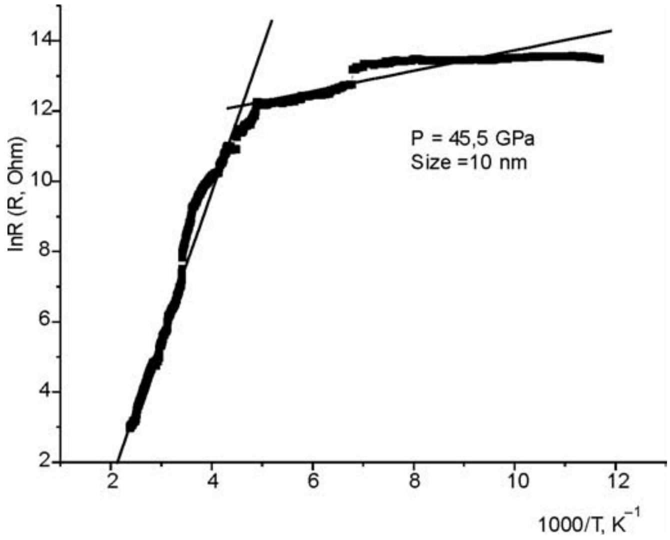

Fig. 2. A typical temperature dependence of resistance in a 10 nm sample

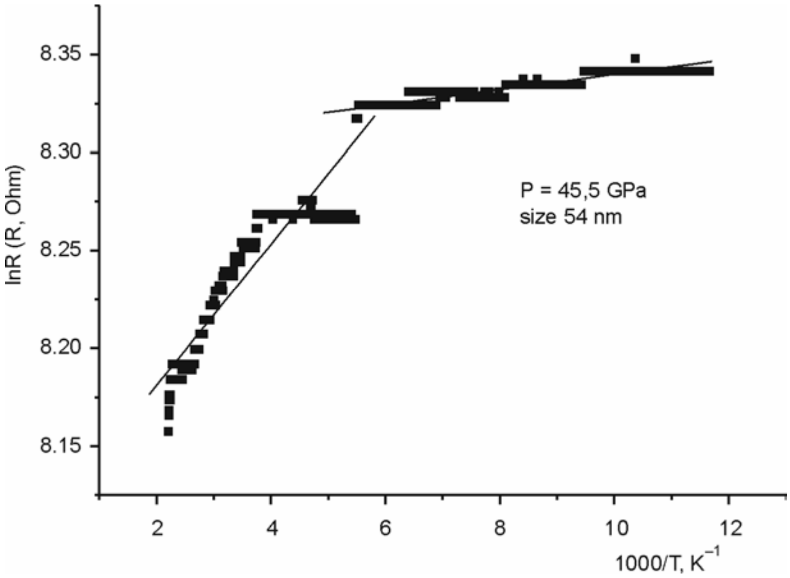

Fig. 3. A typical temperature dependence of resistance in a 54 nm sample

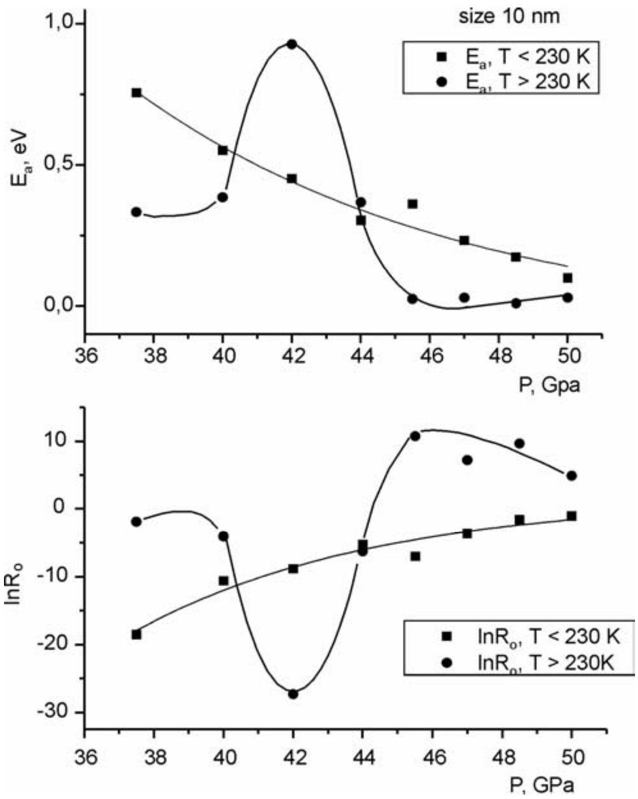

Fig. 4. The pressure dependence of E_a and R_0 in a 10 nm sample

The temperature dependences of the resistance for samples 10 nm and 54 nm at 45.5 GPa consist of two regions characterized by different slopes (Figs. 2 and 3). In a 10 nm sample the crossover appears at 230 K, whereas in a 54 nm sample – between 230 and 250 K. The temperature dependence determined in a 12 nm sample at 42 GPa consists of three regions: below 230 K, between 230 and 310 K, and above 310 K.

The temperature dependence of the resistance of the bulk material varies qualitatively with the pressure applied. At 40 GPa the depencence consists of two regions, between 80 and 180 K, and between 180 and 400 K, corresponding to two different activation processes described by Eq. (1). Above 47 GPa, however, the dependence exhibits a metal-like character (with the positive temperature coefficient) at temperatures exceeding 320 K.

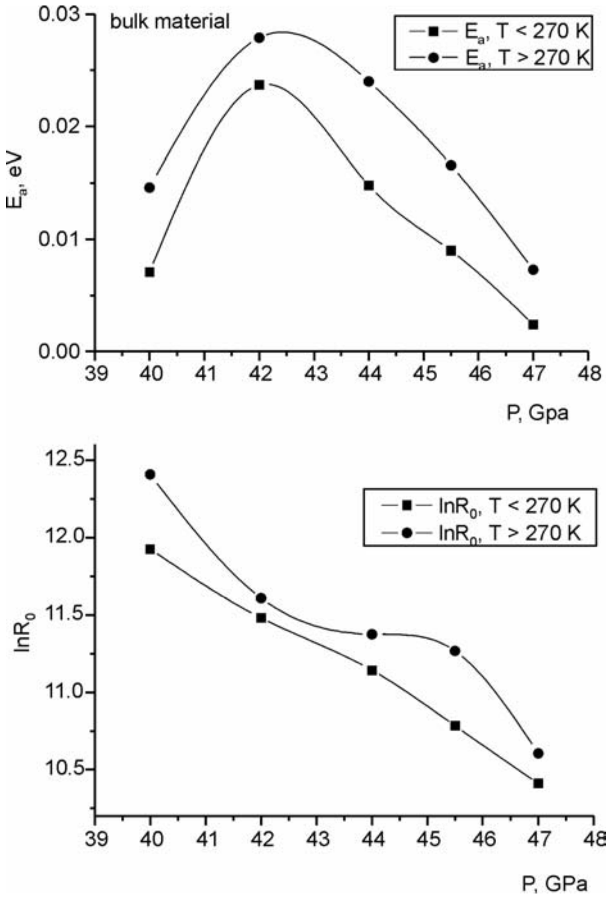

Fig. 5. The pressure dependence of E_a and R_0 in a bulk sample

Pressure dependences of E_a and R_0 are shown in Figs 4 and 5. Around 40–44 GPa maxima of the activation energy have been found in all samples, accompanied in some cases by local minima of the pre-exponential factor. This feature might be associated with a structural phase transition occurring in ZrO_2 in this pressure range. As R_0 is connected with the concentration and mobility of charge carriers, the decrease of R_0 may be associated with an increase of the mobility and/or the concentration of the charge carriers.

Our results indicate that the activation energy dependents on the average size of crystallites: qualitatively, E_a was found to increase with decreasing crystallite sizes, ranging between 0.01 and 1 eV for a 10 nm sample, and between 0.001 and 0.01 eV for a 56 nm sample, whereas its value for bulk ZrO_2 equals approximately 0.01–0.03 eV. One may speculate that surface effects essentially change the conductivity mechanism of ZrO_2 at high pressures.

Our results provide a first hint that a structural phase transition occurring in ZrO_2 may be connected with changes in the electronic structure but a further work is necessary to corroborate this claim and to determine the nature of the electronic changes.

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