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Relaxation processes in ZrO_2 at high pressures[*]

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Relaxation processes in ZrO_2 have been studied at pressures in the range of 22–50 GPa by measurements of high-pressure electrical relaxation of resistance in time. Electrical relaxation in nanocrystalline praseodymium doped zirconia powders and in a bulk material sample of zirconia has been measured in the pressure range from 35.5 to 50 GPa. The time dependence of electric resistance is most precisely described by exponential function up to the pressure of 35.5–50 GPa. The time dependence of electric resistance is most precisely described by exponential function up to the pressure 44–45.5 GPa. After treatment the pressure higher than 45.5 GPa, the character of the relaxation changes and resistance increased with time. Relaxation processes have not been observed in ZrO_2 with 56 nm crystallite sizes.

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

1. Introduction

Zirconium dioxide is an important material with rather interesting mechanical, optical and electrical properties. The material is a major component of the best known fuel cell materials [1]. Previous studies have been devoted to investigation of the behaviour of pure ZrO_2 at a pressure of about 20 GPa, at room temperature [1]. This work shows that for pure ZrO_2 monoclinic-Ortho-I and Ortho-I-Ortho-II phase boundaries occur at about 4 GPa and 12 GPa, respectively. At high temperatures, pure ZrO_2 crystallizes in a cubic fluorite structure. On cooling, it undergoes a displacive transformation to a related structure of tetragonal fluorite and then, via a martensitic transition, to a monoclinic baddeleyite-type structure [2]. However, the behaviour of ZrO_2 at pressures exceeding 20 GPa and at high temperatures has not been extensively studied so far.

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In this paper, we report the results of a study on the electrical relaxation properties of samples of ZrO_2 with different sizes of crystallites in a pressure range between 35.5 and 50 GPa. The size of crystallites was changed from 10 to 500 nm.

2. Experiment

The dc conductivity measurements were carried out in a diamond anvil cell (DAC), with anvils of the “rounded cone-plane” type made of synthetic carbonado type diamonds [3]. Such anvils are good conductors, permitting measurements of the resistance of samples placed between them in the DAC. The procedure for determining the pressure reached in a DAC of the “rounded cone-plane” type has been described in [4, 5].

Measurements were made on powder samples of ZrO_2 with various crystallite sizes. Moreover, we also studied a bulk material sample of zirconia with Y_2O_3 content of 5 mol %. The crystallite sizes in the latter material were near 500 nm. Nanopowders of ZrO_2 contained 0.5mol % of Pr. Their sizes ranged from 10 to 50 nm. The bulk material samples were synthesized by the Daiichi Daiichi Kigensou Company in Japan (Lot # NEY-5M LO524). Nanocrystalline praseodymium doped zirconia powders were produced using a microwave driven hydrothermal process under pressures up to 8 GPa [6]. These samples were synthesized at the High Pressure Research Centre of the Polish Academy of Sciences.

3. Experimental results and discussion

In Figure 1, the dependence of resistance on time for the sample with 10 nm crystallite size has a negative-going exponential mode for pressures below 45.5 GPa

$$R(t) = (R_{\max} - R_{\min})\exp(-t/\tau) + R_{\min} \tag{1}$$

A change in the type of relaxation is observed at a pressure of 45.5 GPa. Resistance increases with time. The latter corresponds to the process described by the equation

$$R(t) = (R_{\min} - R_{\max})\exp(-t/\tau) + R_{\max} \tag{2}$$

For the sample with 12 nm crystallite size (Fig. 2), the relaxation dependencies of the resistance are described by Equation (1) for all pressures. In the sample with 56 nm crystallite size, no relaxation processes were observed (the resistance did not depend on time). In the bulky sample, the relaxation processes are described by Equation (2) and observed only for pressures up to 44 GPa. The baric dependencies of the characteristic relaxation times (τ) for nanosamples with the crystallite sizes of 10 and 12 nanometers and for a polycrystalline sample are shown in Figure 3. As can be seen from these graphs, the represented baric dependencies have their anomaly between 42 and 44 GPa. The latter leads us to suppose the presence of considerable changes in the electronic structure of ZrO_2 at this pressure.

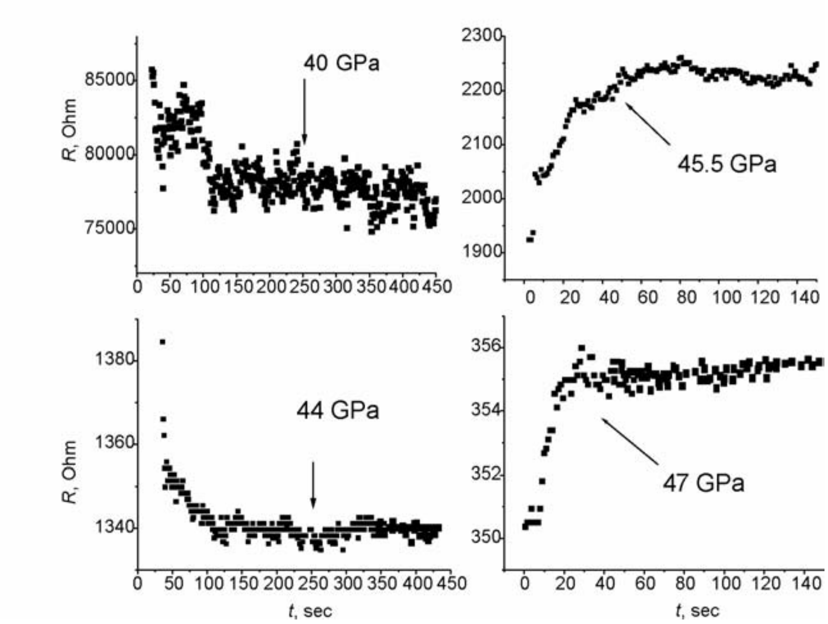

Fig. 1. The relaxation process in ZrO_2 containing 0.5% Pr with 10 nm crystallite size

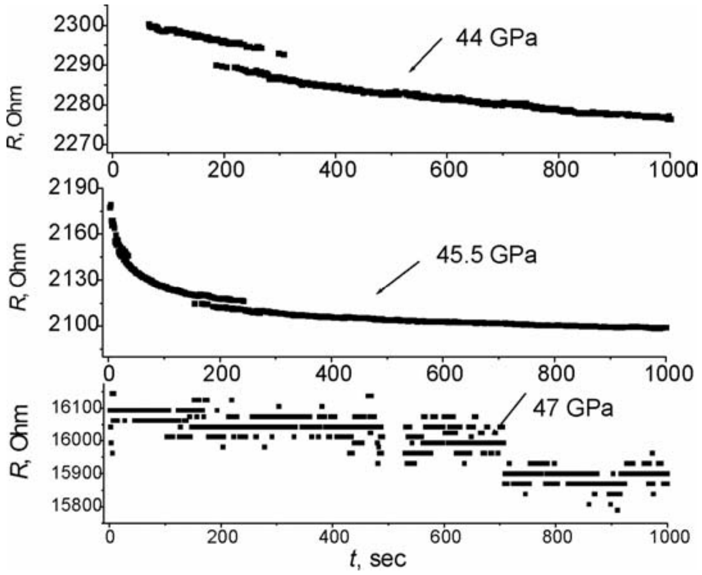

Fig. 2. The relaxation process in ZrO_2 containing 0.5% Pr with 12 nm crystallite size

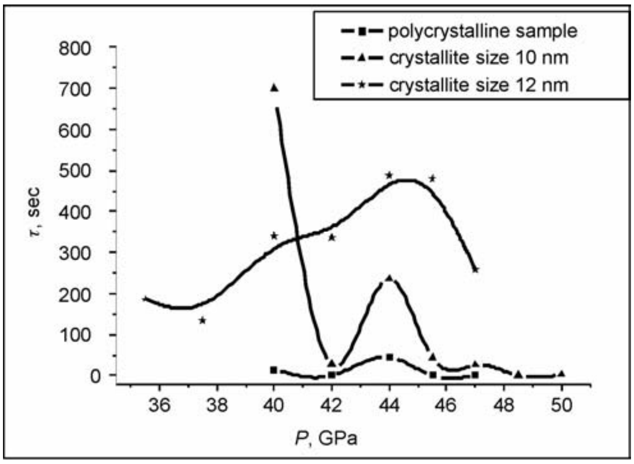

Fig. 3. The baric dependencies of the characteristic relaxation times (τ)
(the error of τ does not exceed 5 sec)

Our results demonstrate that changes in the electronic spectrum may be connected with a structural phase transition in ZrO_2. Furthermore, a substantial increase of the characteristic relaxation time under pressures up to 44 GPa can be associated with structure modifications at these pressures.

Acknowledgements

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