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ELECTRICAL PROPERTIES OF ZrO₂ IN NANO- AND POLYCRYSTALLINE STATES AT HIGH PRESSURE

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We present the results of the research work devoted to the problem: how the crystallites influence the electrical properties of stabilized zirconia at pressures of 22–50 GPa and in the temperature range of 77–450 K. The measurements were conducted in the high-pressure chamber under direct current on nanocrystalline powders of ZrO₂ stabilized by Pr (0.5%) and on compact powder samples of «partially stabilized» ZrO₂ including 5% Y₃P₃. The nanocrystallite size equals 10, 12 and 56 nm. The change of electronic properties of stabilized zirconia at 31.5–37.5 GPa, 40–44 GPa and 45.5–48.5 GPa in nano- and polycrystalline states has been discovered. It gives us a possibility to verify the phase diagram of ZrO₂ at those intervals of pressure. Besides, it has been revealed that stabilization as nanocrystallinity leads to appearance of additional mechanisms of conductivity in ZrO₂.

Introduction

Effects of size in ultradisperse systems attract attention because they lead to new properties that are unordinary for homogeneous macroscopic bodies and so are very important for practice. The results of researching the electrical resistance of stabilized zirconia in nano- and polycrystalline states under pressures of 22–50 GPa and in the temperature range of 77–450 K are presented in the article. The aim of the research work is determination of correlation between electrical properties of ZrO₂, stabilization and sizes of its crystallites in nano- and polycrystalline states under high pressures.

Experiment

The measurements of the resistance under direct current were conducted in a high-pressure chamber (HPC) with anvils «rounded cone-plane» that were made from synthetic carbonado-type diamonds. The anvils resistance under direct current is not higher than 10 Ω and has insignificant temperature dependence.

The error of resistance valuation doesn't exceed 10% under pressures of 15–50 GPa. The investigated samples are about 0.2 mm in diameter and 5–30 μm thick [1].

Measurements were made on a polycrystalline powder sample of not stabilized ZrO₂, polycrystalline samples of zirconium partially stabilized by yttrium (ZrO₂ + 3 mol% Y₂O₃) and nanocrystalline ZrO₂ samples partially stabilized by praseodymium. The nanocrystalline samples stabilized by praseodymium had the crystallite size of 10, 12 and 54 nm.

For each sample, two series of measurements were carried out.

The bulk sample of ZrO₂ + Y₂O₃ was synthesized by the Daiichi Daiichi Kigensou Company in Japan (Lot # NEY-5M LO524) and in the Institute of General and Inorganic Chemistry, NAS of Belarus [2]. Nanocrystalline praseodymium-doped zirconia powders were produced using a microwave driven hydrothermal process under pressures up to 8 GPa. Nanopowders of ZrO₂ with Pr in solid solutions had Pr content of 0.5 mol%. These samples were synthesized at High Pressure Research Center, Polish Academy of Sciences. Polycrystalline powders of not stabilized ZrO₂ were synthesized by DonPTI.

Experimental results and discussion

During the experiment it has been discovered that resistance of all samples is falling by 3–4 orders of magnitude under the rising of pressure from 31.5 to 37.5 GPa.

The temperature dependences of resistance of the samples stabilized by praseodymium and yttrium have activation character and are described by ordinary activation relationship

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

where R_0 – parameter characterized by mobility and concentration of charge carriers; E_a – activation energy; k – Boltzman constant; T – temperature.

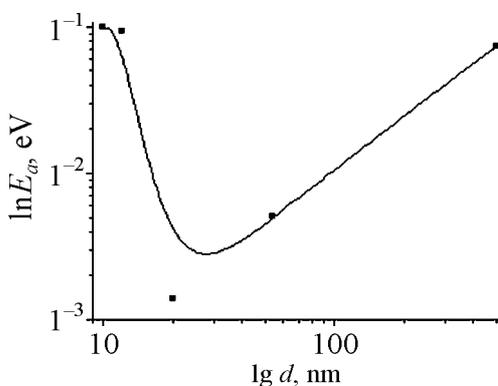


Fig. 1. Dependence of activation energy E_a on the crystallite size d for $T \approx 300$ K

The temperature dependences of resistance for the sample partially stabilized by yttrium had metal-like character to pressure of 45 GPa. Under higher pressure the temperature dependences of resistance had activation character.

We have investigated the influence of crystallite sizes on value of activation energy E_a for nanocrystalline samples [2]. Under pressure of 45 GPa the value of activation energy for 10 and 12 nm was about 0.1 eV, whereas for, 54 nm and for polycrystalline samples – about 10^{-3} eV (Fig. 1).

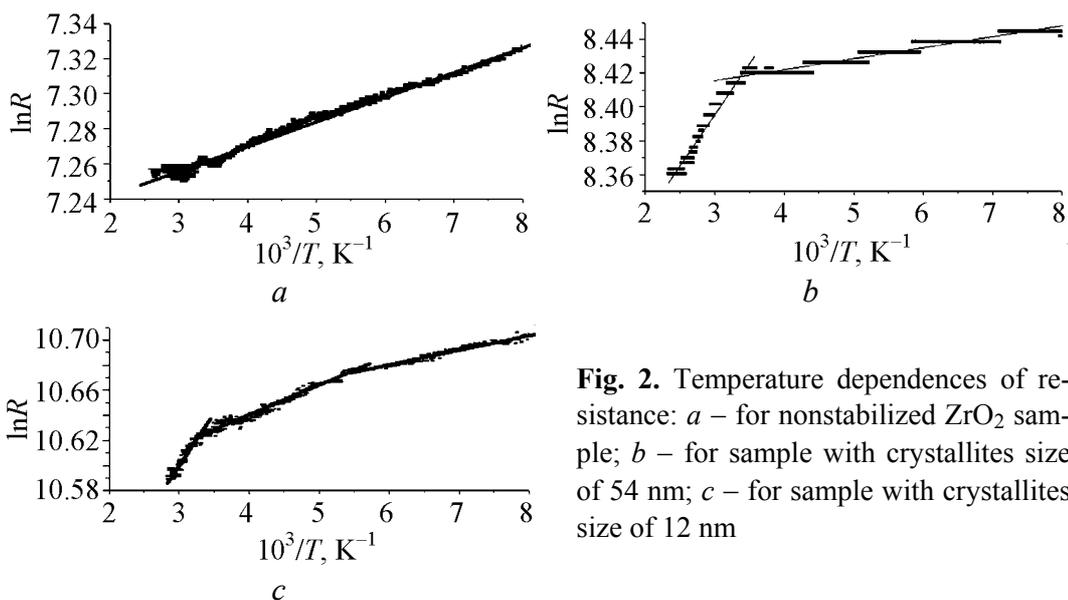


Fig. 2. Temperature dependences of resistance: *a* – for nonstabilized ZrO₂ sample; *b* – for sample with crystallites size of 54 nm; *c* – for sample with crystallites size of 12 nm

Due to our research it is proved that the value of activation energy depends on crystallite sizes in nanocrystalline state and it rises under reduction of the latter [3].

From Fig. 2,*a* it is clear that for the nonstabilized sample there is only one mechanism of conductivity. Stabilization of zirconia leads to appearance of the second mechanism of conductivity (Fig. 2,*b*) developing as changes of the resistance vs temperature curve slope in stabilized ZrO₂. Nanocrystallinity (for 10 nm size) as a stabilization leads to appearance of the activation process that indicates a significant contribution of surface effects to electrical properties of nanoceramics (Fig. 2,*c*).

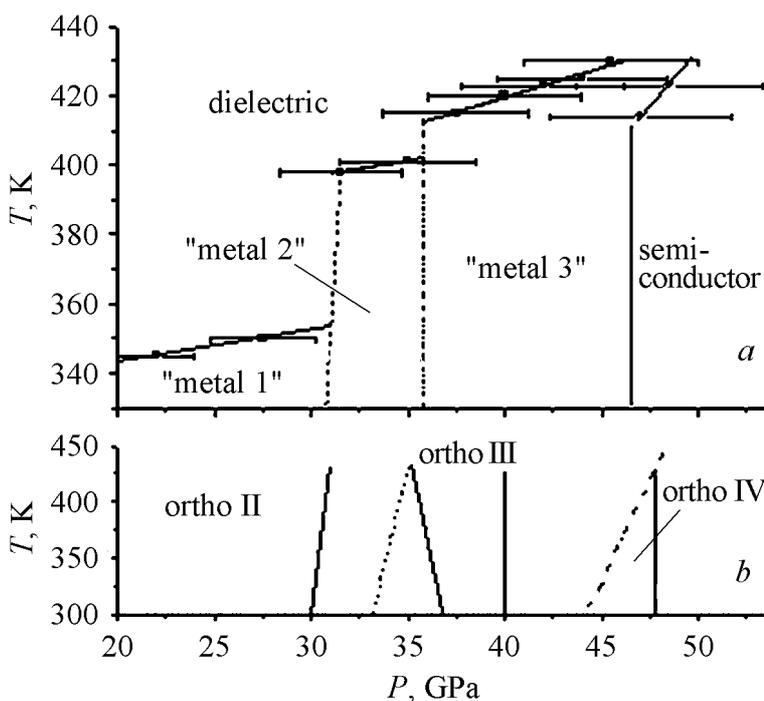


Fig. 3. Fragments of the phase diagram with marked fields of phase transitions: *a* – precised by us, *b* – from Ref. [3]

From the graph of the temperature dependences of resistance it is seen that under pressure of 35 GPa there is the change of the electrical structure. It develops as the changing of signs of the coefficient of line's slope on the logarithm graph of temperature dependences of resistance.

The existence of activation-energy maximum and the change of thermal coefficients of resistance at 31, 35 and 45 GPa prove the existence of structural phase transitions under such pressures in correlation with obtained results (Fig. 3,*b*) [3]. These effects give us a possibility to verify phase diagram of zirconia in this interval of pressures.

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