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HIGH-PRESSURE DC RESISTANCE OF ZrO₂

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The resistance and thermoelectromotive force (TEMF) of Y₂O₃-stabilized ZrO₂ have been investigated in the pressure and temperature range between 15 and 50 GPa, and 77 and 400 K, respectively. At a pressure of about 35 GPa the resistance of the sample decreases by 3–4 orders of magnitude. At a pressure of about 42 GPa the anomalies in the pressure dependence of the resistance, TEMF and of the parameters which depend on the concentration, mobility, and activation energy of the charge carriers were found.

1. Introduction

Zirconia has rather interesting properties. This material is the major component in the best-known fuel cell materials. Furthermore, it has been suggested that high-density ZrO₂ is a candidate for potentially very hard materials [1]. At high temperatures, pure ZrO₂ crystallizes in the cubic fluorite structure. On cooling, it undergoes a displacive transformation to a related tetragonal fluorite structure and then, via a martensitic transition, to a monoclinic baddeleyite-type structure. The cubic and tetragonal fluorite phases, which exhibit the highest ionic conductivities, can be stabilized at room temperature by the addition of a small amount (< 15 mol %) of Y₂O₃ (or other oxides). Previous studies on the high-pressure behavior of pure ZrO₂ indicate successive transformations to two different orthorhombic phases (ortho-I and ortho-II) [2]. Ortho-I is a distorted fluorite structure and ortho-II is a dense PbCl₂-type structure. Recent work by Ohtaka et al. [1] suggests that the monoclinic-ortho-I and ortho-I-ortho-II phase boundaries occur at about 4 and 12 GPa, respectively, for pure ZrO₂ near the room temperature. However, the latter (reconstructive) transition is extremely sluggish and a large pressure range of me-

tastability is observed.

In this paper we report the results of an investigation of the electrical properties of Y_2O_3 -stabilized ZrO_2 in the pressure range between 15 and 50 GPa and temperature range between 77 and 400 K.

2. Experiment

The *dc* 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 [3], consisting of dielectric grains of synthetic diamonds in layers of conducting materials. These anvils are good conductors, permitting measurement of the resistance of samples placed between the anvils in the DAC by using the anvils as the electrical contacts to the sample. The resistance of the anvils in a *dc* setup does not exceed 10 Ohms and has a negligible temperature dependence. Each anvil has two wires attached, but the sample is only in contact with the anvils. Therefore we do not perform strictly four-point measurements and the contact resistance is not eliminated. Before the resistance measurements the voltage-current characteristic of the system is determined and the resistance measurements are then done in the linear region at a *dc* voltage below 10 mV. This is important because a larger voltage can lead to a breakdown of the sample due to the fact that it is very thin.

The determination of the pressure in the DAC is not easy, since the applied pressure depends on the elastic properties of the compressed layer and anvils as well as on the anvil geometry. The procedure for the determination of the pressure reached in a DAC of the «rounded cone-plane» type has been described in [4,5].

Measurements were made on a compacted powder sample of «partially stabilized» tetragonal ZrO_2 containing 5 mol % Y_2O_3 . The sample was synthesized by the Daiichi Kigensou Company (Japan, lot # NEY-5M LO524).

3. Experimental results and discussion

In Fig. 1 the pressure dependence of the resistance of ZrO_2 is displayed. At a pressure of about 35 GPa the resistance of the sample decreases 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 this effect is not caused by a shortening of the anvils nor by a dielectric breakdown of the sample with increasing pressure.

In Fig. 2 the temperature dependence of the resistance at constant pressure is shown. It can be seen that the temperature dependence of the resistance has regions characterized by different slopes when displayed in a $\log-1/T$ plot. They correspond to activation processes described by

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

with E_a , the activation energy and R_0 , a parameter which depends on the mobility and concentration of the charge carriers. The curves change with increasing pressure. At temperatures above ~ 320 K the resistance increases again with increasing temperature.

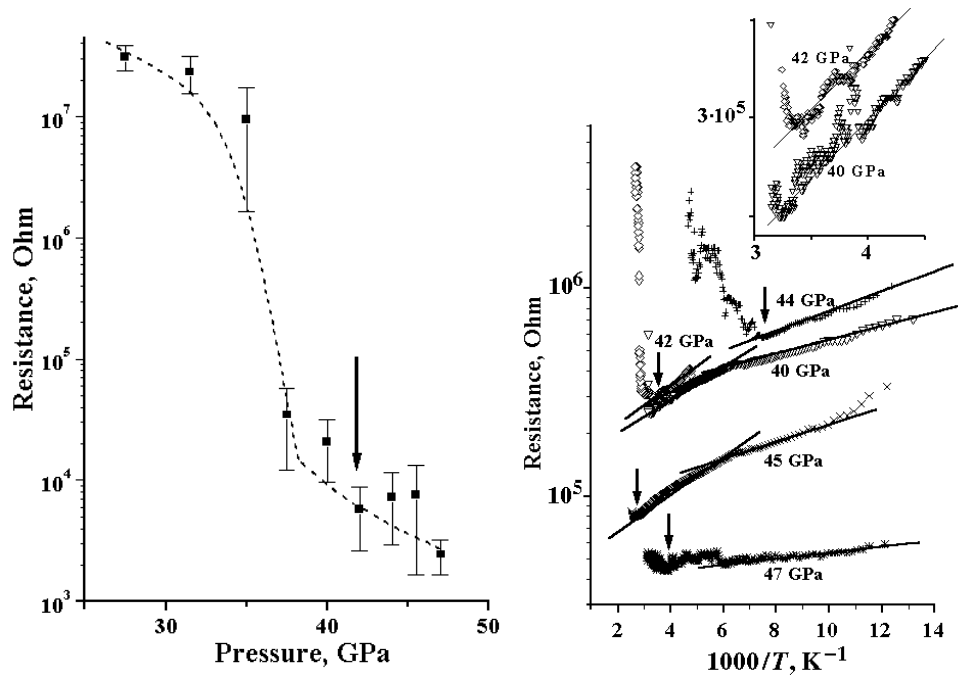


Fig. 1. Resistance of ZrO_2 in the pressure range between 25–48 GPa at ambient temperature. The errors are estimated by averaging results obtained on different samples. The arrow indicates the pressure at which anomalies of the parameters R_0 and E_a (see the text and Figs. 3 and 4) are found

Fig. 2. Isobaric temperature dependence of the resistance of ZrO_2 . The arrows mark the temperature where the resistance starts to increase again with increasing temperature. (Insert – resistance at 40 and 42 GPa at temperatures close to ambient)

In Fig. 3 the pressure dependence of E_a and R_0 are shown. It is well known that R_0 is connected with the concentration and mobility of the charge carriers. A decreasing value of R_0 is usually accompanied by an increase of the mobility and of the concentration of the charge carriers. One can see in Fig. 2, that E_a and R_0 have anomalies near 42 GPa. At the same pressure the features in behavior of resistance and TEMF are found (Fig. 4).

The large drop in the sample resistance may be associated with the ortho-I–ortho-II phase transformation. Although the equilibrium phase boundary in pure

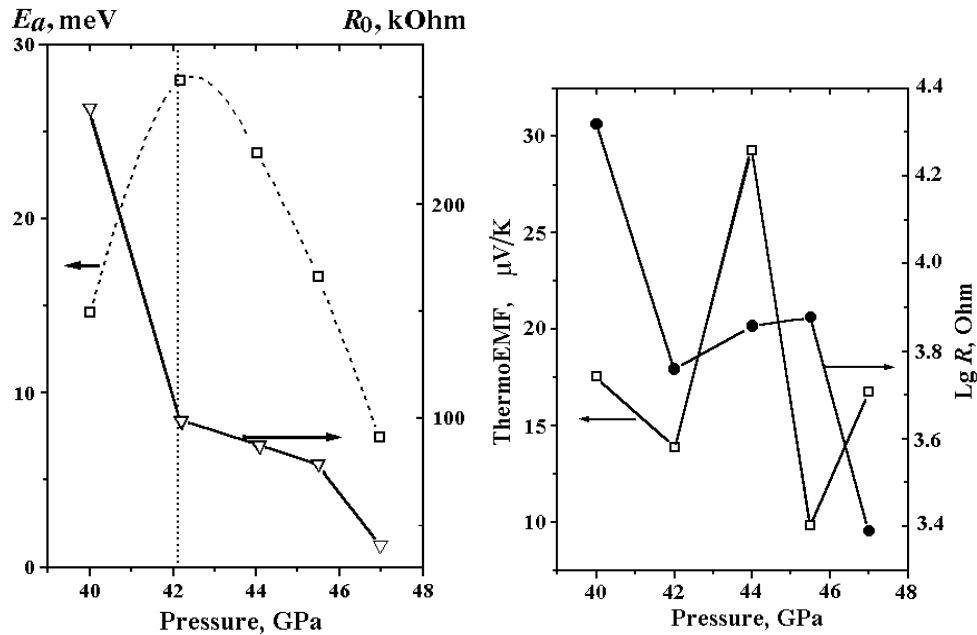


Fig. 3. Pressure dependence of parameters E_a and R_0 , in Eq. 1. Right arrows on curves indicate curves to correspond to R_0 , left arrows indicate curves to correspond to E_a

Fig. 4. Resistance and TEMF of ZrO_2 in the pressure range between 40–48 GPa at ambient temperature

ZrO_2 occurs at much lower pressures (~ 12 GPa), this transition is extremely sluggish at room temperature and is reported to appear above 30 GPa under room temperature compression [6].

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

Acknowledgments

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