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Phase transitions in monoclinic ZrO_2

© V.P. Gorelov, S.A. Belyakov, R.K. Abdurakhimova

Institute of High-Temperature Electrochemistry, Ural Branch, Russian Academy of Sciences,
Yekaterinburg, Russia

E-mail: gorelov@ihte.uran.ru

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Zirconia ZrO_2 is one of the most important modern materials, but its use faces the problem of complex polymorphism. It is generally accepted that, under normal conditions, it exists in the monoclinic form $P2_1/c$ (№ 14), which undergoes an extended martensitic transformation into the tetragonal form $P4_2/nmc$ (№ 137) when heated above 1000°C. However, the group-theoretic analysis forbids a direct transition between these space groups and requires at least two intermediate forms. The experiment carried out in this work using structure-sensitive methods (dilatometry and electrical conductivity) indeed revealed the existence of singular points on the temperature dependences of expansion and conductivity in the temperature range of 350 ± 20 and 730 ± 20°C. This agrees with the literature data, which demonstrate singular points on the temperature dependences of the ZrO_2 monoclinic lattice parameters. According to the dilatometry data, these transitions are phase transitions of the second order, which correlates with the obtained Raman data (measurements at temperatures up to 900°C in the range $60-900\,\text{cm}^{-1}$), showing that the local structure changes slightly, therefore, the transitions occur within the framework of the monoclinic syngony.

Keywords: ZrO_2, monoclinic phases, phase transitions, dilatometry, electrical conductivity, Raman spectroscopy.

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1. Introduction

Materials based on zirconium dioxide ZrO_2 possess many outstanding properties that provide their wide and diverse application in different fields [1], including power industry [2,3], catalysis [4,5], healthcare [6], jewellery, etc.

Zirconium dioxide is characterized by a complex polymorphism, including high pressure phases [7–11]. On the one hand, it broadens the range of materials based on the zirconium dioxide, because materials based on different modifications have significantly different properties. On the other hand, the polymorphism creates problems of synthesis and operational problems related to stability.

Under normal conditions a thermodynamically stable form is the monoclinic form of ZrO_2 (baddeleyite) with lattice cell parameters that are determined long time ago at a high accuracy (± 0.00003 nm): $a = 0.51454$; $b = 0.52075$; $c = 0.53107$; $\beta = 99^\circ 14'$ [12].

In 1929 [13], Ruff and Ebert first reported in a large study about the monoclinic-tetragonal phase transition in ZrO_2 detected by X-ray diffraction method in the region near 1000°C. Also, they were the first who investigated the lowering effect of MgO, CaO, Y_2O_3 and Sc_2O_3 additives on the temperature of this transition, as well as found that the high-temperature phase does not become quenched even from the melt temperature of ZrO_2.

The monoclinic-tetragonal transition ($m \leftrightarrow t$) in ZrO_2 takes place with destructive changes in the volume that make it difficult to produce and apply products made of the pure oxide. The transition features a complex kinetics and was extensively investigated by many researches in polycrystalline and single crystal materials using different high-temperature methods [14–31]. It follows from these studies that the $m \leftrightarrow t$ phase transition in ZrO_2 is a diffusionless transition of martensite type [14–22] and is characterized by a strong hysteresis. According to the X-ray diffraction data, with heating the transformation starts near 1000°C, ends near 1200–1230°C; the reverse transition starts near 1000°C and ends near 800°C [14,16,23–30]. It is considered that the divergence between transition temperature ranges reported by different authors is caused mainly by the different thermal history of the samples [16,25,31].

All phase diagrams of systems based on ZrO_2 are built on the assumption of that this transition exists. The monoclinic modification of ZrO_2 has a space group of $P2_1/c$ (№ 14), while the tetragonal modification has a space group of $P4_2/nmc$ (№ 137). However, the problem is that the group-theoretical analysis [32,33] prohibits the direct $m \leftrightarrow t$ transition between these space groups. There should be at least two more intermediate transformation within the monoclinic (or orthorhombic) syngony. The tree of possible transformation paths is presented in [33].

The aim of this study is to detect experimentally the intermediate transformations in the monoclinic ZrO_2 below the temperature of the $m \leftrightarrow t$ transition. We used structure-sensitive methods for the research: dilatometry, electrical conductivity method, as well as Raman spectroscopy.

2. Experimental part

The source material to produce ceramic samples was extra pure grade (99.999%) ZrO_2. For the dilatometric measurements the samples were pressed to obtain briquettes with a length of 40 mm and a cross-section of 4×4 mm, while for the conductivity measurements tablet-shaped samples were used with a diameter of 14 mm and a thickness of 2 mm. The ZrO_2 powder was not ground before pressing to avoid contamination. The samples were sintered in the air at a temperature of 1500°C for two hours at heating and cooling rates of 3°C/min. The geometric density of sintered samples was about 75% of their theoretical density (5.84 g/cm^3 [12]).

The study by scanning electron microscopy (SEM) was performed with the use of a MIRA 3 LMU microscope (TESCAN, Czech Republic).

Thermal expansion of the samples was investigated by an ODP-868 optical dilatometry platform (TA Instruments, USA) in the horizontal mode in a range from room temperature to 1500°C at heating and cooling rates of 1°C/min.

Electrical conductivity of ceramic samples was measured by the two-probe method using a RM 3545-02 resistance meter (Hioki, Japan) in the mode of one range of 100 MOhm to avoid stepwise changes of the measured resistance while switching the ranges (accuracy was ± 0.0001 MOhm). Platinum electrodes were applied by painting method and sintered to the sample at 1000°C for two hours. The measurements were carried out in the dynamic mode under heating from 300 up to 900°C at a rate of 1°C/min in the air dried using zeolites ($pH_2O = 40$ Pa) and in the humidified air ($pH_2O = 610$ and 2800 Pa), as well as in atmospheres of dry argon and oxygen.

Raman spectra in a range of $60-900\,\text{cm}^{-1}$ were measured by a U1000 microscope-spectrometer (Renishaw, United Kingdom) with a Lincam TS1200 high-temperature chamber in a temperature range of 20−900°C with a step of 50°C, and in the region of detected singular points the measurements were carried out with a step of 10°C.

3. Results and discussion

3.1. Microstructure of samples

SEM-images of a ZrO_2 sample (Fig. 1) are obtained after the sample is sintered at a temperature of 1500°C (for two hours), hence these images correspond to a microstructure after direct and reverse $m \leftrightarrow t$ transitions have taken place in the sample. Since the powder was not ground before the sintering, some active-to-sintering dense conglomerates were preserved in it, which resulted in the synthesis of some areas in the ceramic samples with large agglomerates with sizes up to tens of micrometers composed of large grains of $1-5\,\mu$m with a regular shape. The main body of ceramic samples is represented by fine grains with a size of $0.6-1\,\mu$m, that have a rounded shape and form porous regions. The presence of two types of grains made it possible to see better the details caused by the $m \leftrightarrow t$ phase transitions that took place. Large grains make it possible to see well the disconnection of grains along intergrain boundaries caused by the strong stresses arising on them due to the large change in specific volumes of m and t phases, as well as breaking of some grains. This pattern demonstrates at the microlevel the destruction of ceramic products made of pure zirconium dioxide at the $m \leftrightarrow t$ phase transformation. It is worth noting that in single crystals, even in those grown at temperatures below the phase transition, crystallites with low-angle boundaries also are the sources of high stresses causing twinning and cracking at the transition. As a result, after several heating−cooling cycles the single crystal is transformed to a polycrystalline sample [18].

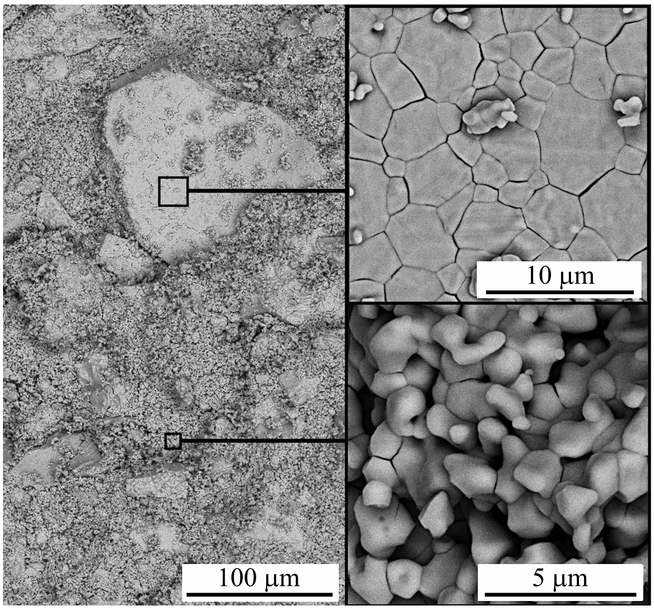

Figure 1. SEM-images of the cross section of a ZrO_2 ceramic sample.

3.2. Dilatometric measurements

Dilatometry is a thermodynamic method of research, because β, the coefficient of volume thermal expansion, is related to F, the free energy. In turn, $\beta = 3\alpha$, where α being the coefficient of linear thermal expansion [34]. In the case of phase transition of the 1-st kind the first derivative of free energy with respect to temperature has a discontinuity, hence a stepwise change takes place, amongst others, in the volume, while transitions of the 2-nd kind are accompanied by a discontinuity of the second derivative of free energy, and a stepwise change takes place, amongst others, in the coefficient of thermal expansion.

The behavior of dilatometric curves for ZrO_2 obtained in our study (Fig. 2) matches well the literature data [16,35,36]. A typical feature of dilatometric curves for ZrO_2 is a sharp,

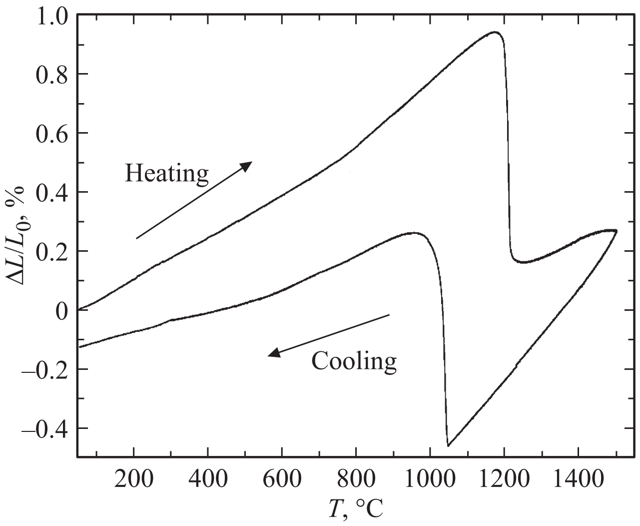

Figure 2. Dilatometric curve of a ZrO_2 sample in the atmosphere of laboratory air in the cycle of heating–cooling from room temperature to 1500°C and vice versa.

almost vertical, stepwise change. In our case this stepwise change is observed near 1200°C while heating and near 1000°C while cooling. The stepwise change while heating is accompanied by a significant decrease in the sample volume, and while cooling it is accompanied by an increase in its volume. These stepwise changes can be interpreted as a direct and a reverse phase transition of the 1-st kind, $m \leftrightarrow t$. In this study we did not plan a detailed discussion of the stepwise changes and the $m \leftrightarrow t$ transition. We just would like to emphasize that these stepwise changes are not monoclinic-tetragonal transitions, they just accompany the transition. This is proved by X-ray diffraction studies that do not show any stepwise changes. According to X-ray diffraction analysis, the $m \leftrightarrow t$ transition runs gradually in a rather wide interval of temperatures, about 150–200°C. In the process of this stretched $m \leftrightarrow t$ transition stresses are accumulated in the ceramics, and as soon as a certain critical limit is achieved, twinning and cracking occur in the material. The microscopy demonstrates such a cracking (Fig. 1). It is the moment of cracking, that is detected by the dilatometer as a stepwise change. However, the phase transition does not end with this. The moment of destruction is also detected by electrical conductivity measurements, for example, Kofstad and Ruzicka [37] reported a stepwise change in electroconductivity at 1200°C as well.

When considering the dilatometric curve (Fig. 2), clearly seen bends can be observed within the sections below the stepwise changes. To detect objectively the bends (singular points), we applied the Suzuki method of differences [38]. For this purpose, a temperature dependence is to be plotted for the differences between experimental values and their approximating trend (in our case — a quadratic polynomial). This method makes it possible to distinguish more clearly the singularities on experimental curves, and it is not sensitive to the scattering of points in contrast to the differentiation method. The difference curves plotted for three successive cycles of thermal expansion (Fig. 3) show conclusively that there are singular points (bends) on the dilatometric curves detected in the region of temperatures near 350, 730°C, as well as in the region of 1050°C. The bends and their positions are reproduced well in successive measurements.

The bend observed near 1050–1070°C is the start of the stretched phase transition to the tetragonal structure. However two other bends near 350 and 730°C are indicative of the presence of two additional phase transitions in the sample. The bends, not the stepwise changes, on the dilatometric curve in these two points and the preservation of the monoclinic syngony in this region are indicative that these are phase transitions of the 2-nd kind [34]. Hence, there are unknown polymorphic modifications of ZrO_2, which existence in a number of not less than two is predicted in [32,33].

The singular points (bends) noted by us near 350 and 730°C are observed in the monoclinic region in structural experiments of other researchers as well, an near the same temperatures. In the study of Haggerty et al. [28], the X-ray diffraction method is used to investigate the temperature anisotropy of parameters of the ZrO_2 monoclinic lattice, which was earlier mentioned by Patil and Subbarao [39], and which was investigated by Simeone et al. [21] by the method of high-temperature

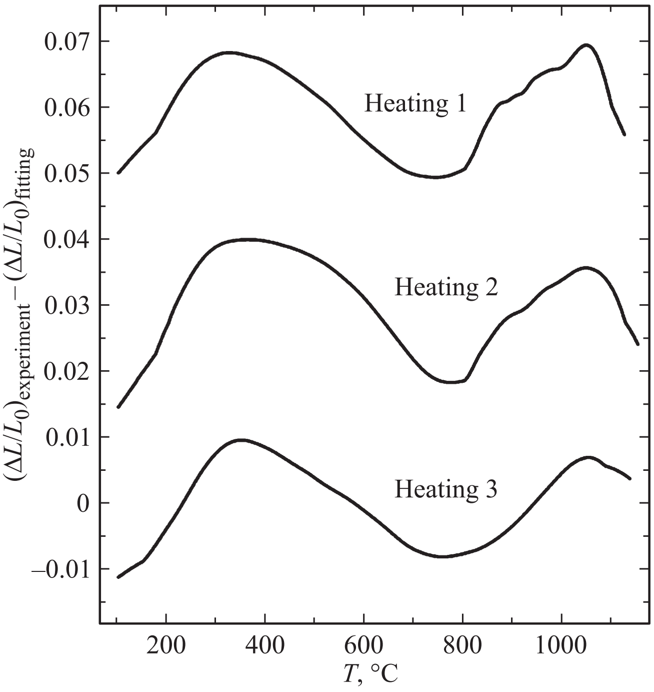

Figure 3. Difference curves (approximated by a quadratic polynomial) for three successive cycles of thermal expansion of ZrO_2 in the atmosphere of laboratory air. The curves are shifted along the ordinate axis for visual convenience.

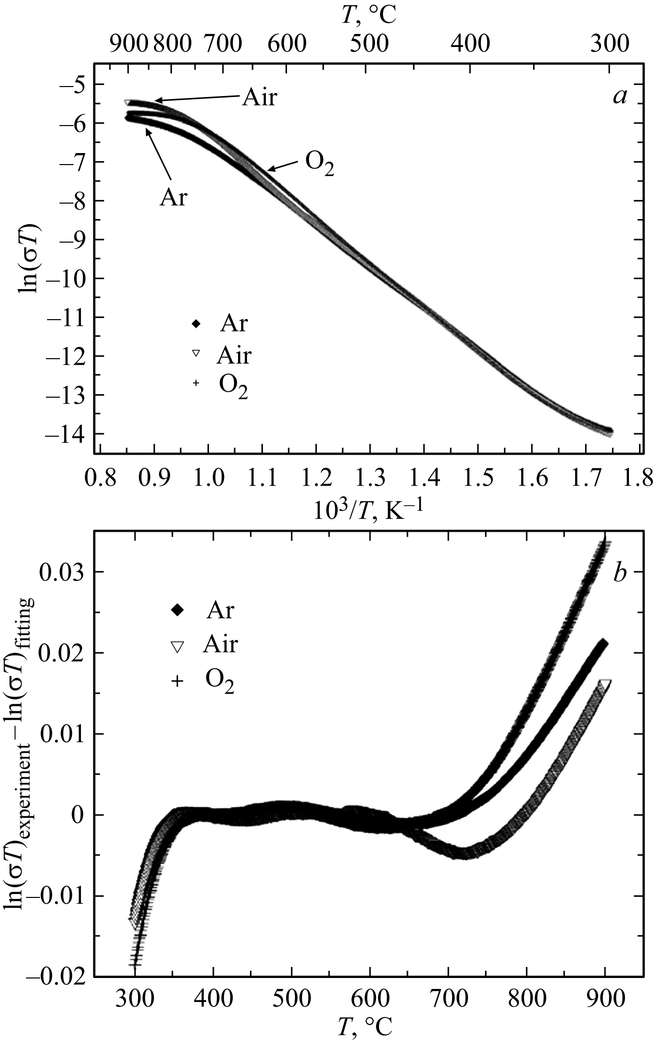

Figure 4. Conductivity of ZrO_2 in Arrhenius coordinates (*a*) and difference curves (*b*) during heating in dry atmospheres of argon, air and oxygen (a linear approximation is used).

neutron diffraction. However, authors of above-mentioned studies, even noting the presence of singular points clearly distinguished on the temperature dependencies of lattice parameters, do not discuss these points as possible phase transformations.

3.3. Electrical conductivity in the monoclinic region

As with the thermal expansion, the electrical conductivity is a structure-sensitive parameter. Therefore, measurements of electrical conductivity of ZrO_2 ceramic samples were carried out in the temperature region of expected phase transitions, 300−900°C, not only to compare them with the dilatometric data, but also as a simple method to study the effect of atmosphere parameters on the detected transitions (Fig. 4, *a*). The difference curves of electrical conductivity, as well as in the case of dilatometry, show two clearly seen bends as well (Fig. 4, *b*). The measurements were carried out in atmospheres of oxygen, air and argon, as well as at different air humidity ($pH_2O = 40$; 610; 2800 Pa). It was found that air humidity has no effect on the electrical conductivity in this temperature range. The partial pressure of oxygen (pO_2) has no effect on the conductivity only up to temperatures of about 500°C, hence it has no effect of the transition in the region of 350°C. However, above the ∼ 500°C a change in pO_2 starts to have a noticeable effect on the conductivity, including the effect on the transition near 730°C. This can be clearly seen on the difference curves of conductivity (Fig. 4, *b*). At the same time, no

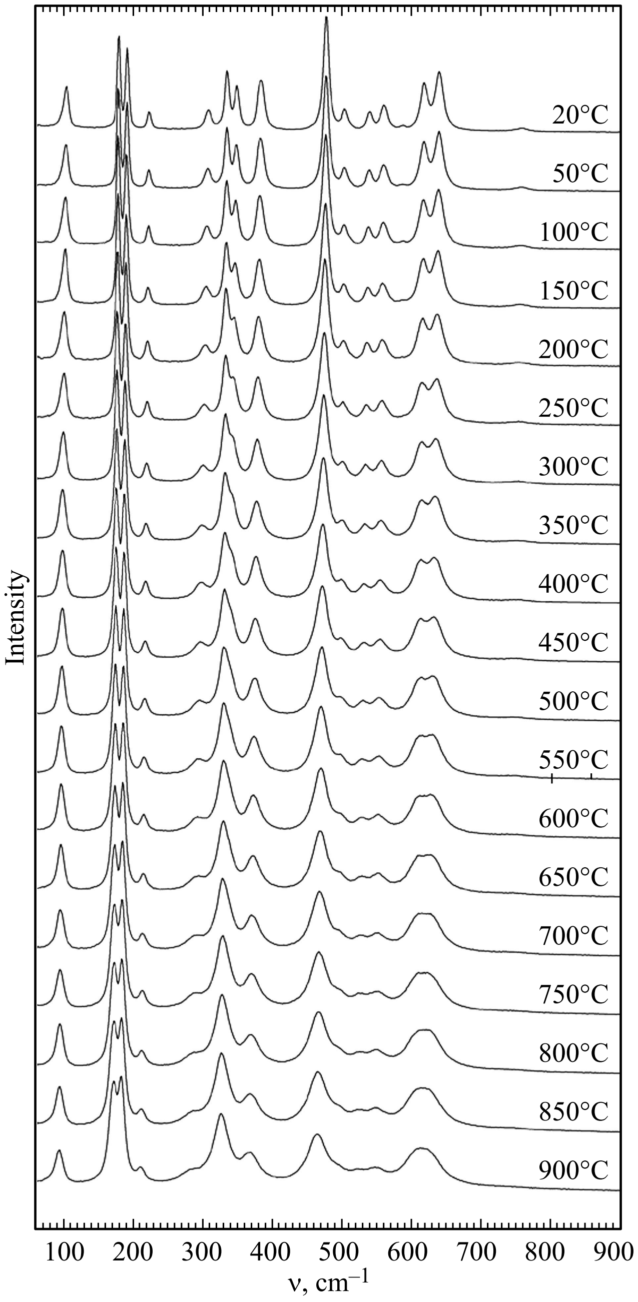

Figure 5. Evolution of Raman spectra for ZrO_2 in the temperature range of 20−900°C.

regular effect of pO_2 on the conductivity is noted. But the same lack of regular effect has been observed by Kofstad and Ruzicka [37] when studied a defect structure of ZrO_2 by the electrical conductivity method, and they explained this lack of regularity by the replacement of the model of interstitial oxygen with the model of oxygen vacancies. As a result, the conductivity in the atmosphere of air becomes higher than that in oxygen.

3.4. Raman spectroscopy (20−900°C)

The Raman spectroscopy as a method of local structure investigation was used in a number of studies [26,27,40] to investigate the $m \leftrightarrow t$ transition. However, in the above-specified studies Raman spectra in the range of temperatures below 1000°C are presented with a very large temperature step or are not presented at all. We have investigated more thoroughly the temperature behavior of Raman spectra in a temperature range of 20−900°C with a step of 50°C (Fig. 5). The regions of supposed transitions of 290−420°C and 680−800°C were investigated in more details with a step of 10°C (Raman spectra are not presented). The spectrum at 20°C shows 15 bands of 18 theoretical bands for the C_{2h}^5 symmetry [41], which is due to the proximity of frequencies of some oscillations [40]. With a temperature increase up to 900°C only a smooth shift and broadening of the bands is observed. It shows that the local structure in the studied temperature interval changes weakly confirming that the detected transitions run within the monoclinic syngony.

4. Conclusion

It is found by the dilatometry method and confirmed by the electrical conductivity method, that there are two phase transitions in the region of existence of the ZrO_2 monoclinic phase at temperatures of 350 ± 20°C and 730 ± 20°C. Summarizing this study and the study of [42], it can be said that under a normal pressure the ZrO_2 has six polymorphic modifications: three monoclinic, two tetragonal and one cubic modifications that transform one to another under heating.

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Conflict of interest

The authors declare that they have no conflict of interest.

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