Phase diagrams of zirconium dioxide systems with yttrium and scandium oxides

P. P. Fedorov, E. V. Chernova

Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilova st., Moscow 119991, Russian Federation

Abstract

The literature data on the study of phase equilibria in systems zirconia with yttria and scandia are analysed. Possible schemes of low-temperature phase equilibria in ZrO$_2$-Y$_2$O$_3$ and ZrO$_2$-Sc$_2$O$_3$ systems are presented taking into account the third law of thermodynamics.

The coordinates of non-variant transformations in these systems are tabulated. A sign of non-equilibrium states is the observation of non-diffusion processes of ordering of solid solutions. The modified cryoscopy method is used to calculate the distribution coefficients of scandia and yttria during the crystallization of the ZrO$_2$ melt.

The possibilities for the existence of a set of ordered phases in the ZrO$_2$-Y$_2$O$_3$ system and diffuse phase transition in the cubic modification of zirconia are discussed.

Keywords: Zirconia, Yttria, Scandia, Solid solutions, Ordering, Phase diagrams, Distribution coefficients

Funding: The study was supported by a grant from the Russian Science Foundation No.22-13-00167 https://rscf.ru/project/22-13-00167


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1. Introduction

Phase diagrams are the physical and chemical basis for the synthesis of functional materials. In addition, they allow predicting the behaviour of the material under operating conditions. Solid solutions of oxides of rare earth elements (REE) \( R_x\text{O}_{2-x} \) in high-temperature cubic modifications of zirconia \( \text{ZrO}_2 \) are among the most refractory oxides with a melting temperature above 2700°C [1, 2]. Materials based on them are widely used as jewellery crystals (fianites) [3, 4] and refractory and corrosion-resistant ceramics [5–9]. The high anionic conductivity of these solid solutions is combined with a low thermal conductivity [10]. These circumstances determine the use of appropriate materials in electrochemical devices (fuel cells, oxygen sensors) [11–13] and also as thermal barrier coatings [14, 15]. Materials based on zirconia are the basis of nuclear fuel with an inert matrix [16].

A lot of studies were dedicated to the study of phase equilibria in \( \text{ZrO}_2 - R_x\text{O}_{2-x} \) systems, but the result of these studies is not satisfactory. These systems have been studied by various groups of researchers. A summary of the data is provided in [17, 18]. The results obtained for different REE do not fit well with each other. Difficulties are associated both with high melting temperatures and with very long time intervals required to achieve equilibrium in the low-temperature region [19–22]. As in previous studies, we will denote regions of phase diagrams where the time required to establish equilibrium exceeds a year as being low-temperature regions. Cubic solid solutions of \( \text{Zr}_{1-x} R_x\text{O}_{2-0.5x} \) are obviously thermodynamically unstable at low temperatures. However, the negligibly small diffusivity of cations [23] prevent the decomposition of solid solutions, which makes the corresponding materials indefinitely stable at ambient temperatures. The insufficiency of the annealing used in a number of studies was demonstrated by researchers from the Tokyo Institute of Technology [24, 25]. In particular, it turned out that the temperature of the eutectoid decomposition of a solid solution based on the medium-temperature tetragonal modification in the \( \text{ZrO}_2 - \text{Er}_2\text{O}_3 \) system, determined in the study [26], was underestimated by about 500 °C [24].

The synthesis of samples under hydrothermal conditions sharply accelerates the processes of phase formation in refractory oxide systems [2, 27]. However, additional problems arise in this case, associated, in particular, with the contamination of samples with hydroxyl ions, which distort the pattern of phase equilibria [28]. In addition, the resulting nanocrystals of intermediate phases often "get stuck" in metastable states [29–30].

The purpose of this study is a critical analysis of the available data on the study of phase equilibria in key \( \text{ZrO}_2 - \text{Y}_2\text{O}_3 \) and \( \text{ZrO}_2 - \text{Sc}_2\text{O}_3 \) systems and construction of assumed phase diagrams with extrapolation to absolute zero temperature in accordance with the third law of thermodynamics.

2. Analysis methodology

In this study, we applied the methodology that we used earlier in [31–33]. According to the consequence of the third law of thermodynamics, as the temperature tends to absolute zero in quasi-equilibrium processes, all phases of variable composition should disappear through the decomposition or contraction of compositions to stoichiometric ones [20, 34]. In this case, the limiting solubility curves should have vertical tangents as the temperature approaches absolute zero [33]. The second important thermodynamic condition is the so-called Hume-Rothery rule, according to which, when an ordered phase with a narrow homogeneity region appears, the region of existence of a neighbouring disordered phase should sharply narrow [35].

The corresponding approach using the extrapolation of the most reliable experimental data in the study of phase equilibria allows by extrapolating phase fields to the region of low temperatures, to obtain information for those regions of phase diagrams where an experiment aimed at realizing equilibrium states is complicated or simply impossible. Previously, using this approach, we outlined the scheme of phase equilibria in the \( \text{ZrO}_2 - \text{Er}_2\text{O}_3 \) system [22].

An alternative technique is the thermodynamic computer simulation of phase equilibria. The construction of thermodynamic models of the studied systems is an ideal goal to strive for [36–38]. However, there are problems associated, among other things, with the determination of the thermodynamic properties of phases of variable composition and with the choice of
3. Results

3.1. ZrO$_2$-Y$_2$O$_3$ system

The ZrO$_2$-Y$_2$O$_3$ system is a classic and model system. It has been studied by various groups of researchers [17, 18, 47]. Solid-liquid equilibria were studied by Rouanet [48], Noguchi et al. [49], Lopato et al. [50]. The most detailed studies of phase equilibria in the solid state were carried out by Pascual and Duran [51] and Stubican et al. [52], with an annealing duration of up to 8 months. These studies provided similar results.

Based on the work data Pascual and Duran, see Fig. 1a. In this study the samples were annealed for 3 hours at 2000°C, 10 hours at 1800°C, and 385 hours at 1450°C, which appears acceptable [22]. However, it is obvious that the 8 months used in this study for annealing at 800°C were completely insufficient. The corrected pattern of phase equilibria is shown in Fig. 1b. At the same time, the designations of the phase composition of the samples annealed and quenched in the study of Pascual and Duran were applied to the figure.

Extensive regions of heterovalent solid solutions based on the high-temperature polymorph of ZrO$_2$ with fluorite structure (phase F, space group Fm$ar{3}$m) and low-temperature cubic modification Y$_2$O$_3$ (phase C, bixbyite type, space group Ia3) were formed in the system. Although the bixbyite type is derived from the fluorite type with an ordered arrangement of vacancies [53], the presence of a two-phase F+C region in the phase diagram was reliably recorded as early as by Duwes et al. [36].

Dissolution of yttrium oxide in high-temperature ZrO$_2$ modification stabilizes the fluorite structure, and a maximum occurs on the liquidus curve. The maximum point on the melting curves of the solid solution is non-variant, and the liquidus and solidus curves merge at it in the presence of a common horizontal tangent. When depicting phase equilibria in this region Pascual and Duran made an unfortunate mistake, which is corrected in Fig. 1b. The course of the liquidus curve in this system was determined using a solar furnace in the studies.

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Fig. 1. Phase diagram of the ZrO$_2$-Y$_2$O$_3$ system according to [51] (a) and its correction taking into account the requirements of the third law of thermodynamics (b)
[48–50], see Fig. 2. When constructing Fig. 1b, we used data of Shevchenko et al. [50].

At a high concentration of yttrium oxide, the melt and three solid phases F, C, and H (a solid solution based on the high-temperature modification of $Y_2O_3$) should provide two three-phase equilibria, displayed as horizontal segments on the phase diagram. Experimentally, the temperatures of these equilibria are not resolved, and computer simulation [43–46] provides a difference in temperatures within 10–25 degrees. Thus, this system at normal pressure is located in the vicinity of the bifurcation point of A II type [54] corresponding to the equilibrium of four condensed phases.

As the temperature decreases, the solid solutions based on the F and C phases undergo ordering with the separation of $Y_4Zr_3O_{12}$ and $Y_6ZrO_{11}$ phases (idealized composition), respectively. The data of [51] and [52] studies agree very well ($\pm 10^\circ C$) in terms of the phase transition temperature $F \leftrightarrow Y_4Zr_3O_{12}$. Our correction in the region of high concentrations of yttrium oxide includes a significant decrease in the region of homogeneity of the ordered phase, which, as the temperature is lowered, must shrink to the ideal $Y_6ZrO_{11}$ composition, as well as the position of the decomposition curve of the solid solution based on the cubic modification of yttrium oxide, which should come to the point of the pure component at $T \to 0 K$.

Fig. 2. Liquidus of the $ZrO_2-Y_2O_3$ system. 1 – data [48], 2 – data [50], 3 – data [49]

Probably, the observation of a wide region of the ordered phase “$Y_6ZrO_{11}$” in the absence of a two-phase region with phase C was caused by the fact that the ordering in this system in an experimental study [51] occurred according to a non-equilibrium non-diffusion mechanism that does not require overcoming the potential barrier to the nucleation of a new phase in the volume of the old one. A similar phenomenon, as shown by the analysis, was observed during low-temperature ordering in the Ni-Pt system [33], as well as in the $HfO_2-R_2O_3$ systems (fluorite-pyrochlore transitions) [22].

The region of low concentrations of yttrium oxide (the decomposition of the tetragonal phase – a solid solution based on the medium-temperature modification of $ZrO_2$) was corrected by analogy with the data of Yashima and others [24], which, when studying equilibria in a similar $ZrO_2-Er_2O_3$ system, annealed samples at 1690 $^\circ C$ for 48 hours and 8 months at 1315 $^\circ C$. At the same time, the temperature of the eutectoid decomposition of the tetragonal phase was raised by us by several hundred $^\circ C$ in comparison with the variants of the phase diagram presented in [51, 52]).

The dotted line denotes the metastable continuation of the curve of the maximum concentration of this solid solution (the solvus curve of phase F). This curve must pass through the origin of the coordinates and have a vertical tangent at this point. This condition can be fulfilled only if there is a point of inflexion on the solvus curve (in this case, on the metastable part of this curve). It should be noted that the eutectoid corresponding to the decomposition of the fluorite phase should be located above the metastable solvus curve. Accordingly, the temperature of the eutectoid decomposition of the cubic solid solution was presumably targeted at $600 \pm 100^\circ C$. This is much higher than is accepted in all studies on phase equilibria in this system, both experimental and calculated.

Thus, the proposed version of the phase diagram of the $ZrO_2-Y_2O_3$ system (Fig. 1b) is characterized by the following non-variant equilibria, presented in Table 1.

5.2. $ZrO_2-Sc_2O_3$ system

Phase equilibria in the $ZrO_2-Sc_2O_3$ system have been studied in numerous papers [55–66]. The approximate phase diagram of $ZrO_2-Sc_2O_3$ system, plotted in accordance with the data of Spiridonov et al. [57], Shevchenko et al. [60–62] and Fujimori et al. [65, 66] with extrapolation to 0 K is shown in Fig. 3. The coordinates of the non-variant points
are summarized in Table 2. Wide regions of solid solutions based on scandia (bixbyite type, phase C) and cubic high-temperature modification of zirconia (phase F) were formed in the system. A maximum was formed on the melting curves of the fluorite solid solution. A comparison of the liquidus curves obtained in [58, 60] is shown in Fig. 4.

With decreasing temperature, the fluorite solid solution (phase F) undergoes ordering with the release of ordered phases, which were originally assigned the designations β, γ, and δ and Zr₅Sc₂O₁₂, Zr₅Sc₂O₁₁ and Zr₃Sc₂O₁₂ compositions (cubic solid solution, phase F was designated as phase α). The decodering of crystal structures [67–69] allowed refining the composition of the b phase: Zr₅₀Sc₁₂O₄₁₁. Compound Zr₅Sc₂O₁₂ was described as a rare mineral found in meteorites [70]. This compound isostructural to the corresponded yttrium phase Zr₅Y₂O₁₂, and forms a continuous solid solution with it [63].

The low-temperature phases β, γ, and δ are characterized by the trigonal distortion of the fluorite lattice due to the ordered arrangement of anion vacancies [61]. The differentiation of cations over crystallographic positions practically does not occur due to frozen diffusion [55], although it is energetically favourable [69].

**Table 1. Non-variant equilibria in the ZrO₂-Y₂O₃ system**

<table>
<thead>
<tr>
<th>Name</th>
<th>Phase balance</th>
<th>Composition, mol % Y₂O₃</th>
<th>Temperature, ºC</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dystectics (maximum on the solid solution melting curve)</td>
<td>L ↔ F</td>
<td>20±2</td>
<td>2750±25</td>
<td>3023</td>
</tr>
<tr>
<td>A,II type bifurcation</td>
<td>L+F+C+H</td>
<td>–</td>
<td>2360±50</td>
<td>2633</td>
</tr>
<tr>
<td>Distectoid</td>
<td>F ↔ Y₅Zr₃O₁₂</td>
<td>40</td>
<td>1380±10</td>
<td>1653</td>
</tr>
<tr>
<td>Distectoid</td>
<td>C ↔ Y₅ZrO₁₁</td>
<td>75</td>
<td>1750±50</td>
<td>2023</td>
</tr>
<tr>
<td>Eutectoid</td>
<td>T ↔ M + F</td>
<td>5±1</td>
<td>950±25</td>
<td>1223</td>
</tr>
<tr>
<td>Eutectoid</td>
<td>F ↔ Y₅Zr₃O₁₂+ M</td>
<td>18±3</td>
<td>600±100</td>
<td>875</td>
</tr>
<tr>
<td>Eutectoid</td>
<td>F ↔ Y₅Zr₃O₁₂+ Y₆ZrO₁₁</td>
<td>45±3</td>
<td>1350±25</td>
<td>1623</td>
</tr>
<tr>
<td>Eutectoid</td>
<td>C ↔ Y₅ZrO₁₁+ F</td>
<td>68±2</td>
<td>1650±50</td>
<td>1923</td>
</tr>
</tbody>
</table>

**Fig. 3. Summary phase diagram of the ZrO₂-Sc₂O₃ system**

**Fig. 4. Liquidus of the ZrO₂-Sc₂O₃ system**

1 – data [60], 2 – data [58]
The transition temperature of the phase β to a disordered state (phase F) is close according to the data of [57, 60–62, 65–66], and is 650±50 °C. Phase disorder temperatures γ and δ indicated in the literature are very different. This may be due to the non-quenchability of the high-temperature disordered cubic phase upon cooling [57]. Data of Zyrin et al. were preferential for the construction of Fig. 4 [61]. In particular, for the transition α→γ, Spiridonov et al. [57] and Ruh et al. [59] reported a temperature of ~1100 °C. The same group of researchers reported a γ phase disorder temperature equal to 1480°C [61] and 1650°C [62]. This region of the phase diagram of ZrO$_2$–Sc$_2$O$_3$ system requires further research.

It should be noted that the continuation of the line of the maximal concentration of the cubic solid solution (solvent curve of the phase F) to zero coordinates (ZrO$_2$) subject to the presence of a vertical asymptote is impossible without the assumption of the presence of an inflection point on the metastable continuation of this curve.

### 3.3. Distribution coefficients

Accurate measurement of the liquidus curve of solid solutions allow calculating the distribution coefficients of the impurity component during the crystallization of the matrix from the melt using the modified cryoscopy method. Previously, such calculations were carried out for a number of ZrO$_2$–R$_2$O$_3$ systems [71]. The basis of the modified cryoscopy method is the Van’t Hoff limit equation:

$$m = \frac{[RT^2_{m}/\Delta H](k-1)}{m_f},$$

where $\Delta H$ and $T_m$ [K] are enthalpy of melting and melting temperatures of the matrix, $R$ is the universal gas constant, $k$ is the impurity distribution coefficient, $m$ is the liquidus slope. This equation is valid for infinite dilution.

In the modified cryoscopy method, the value $m$ is not determined based on precision measurements of small values of temperature depression with the introduction of low impurity concentrations, but by approximating liquidus curves in a wide range of concentrations, followed by differentiation of analytical expressions [72, 73].

Previously, this method was used to process the data of [48, 49] using the liquidus curve of the F phase in the ZrO$_2$–Y$_2$O$_3$ system and study [60] for the ZrO$_2$–Sc$_2$O$_3$ system. In this study, the data of Shevchenko et al. [50] for the ZrO$_2$–Y$_2$O$_3$ system and data of Sekiya et al. [58] for the ZrO$_2$–Sc$_2$O$_3$ system were processed using this method. The points of the liquidus curves in a wide concentration range were processed using the least squares method in the form of a 3rd order polynomial. In this case, the melting point of ZrO$_2$ (2710 °C) was fixed by the provision of a tenfold weight to this point. Primary data were obtained by digitizing the graph provided in [58].

Data for ZrO$_2$–Y$_2$O$_3$ [50] and ZrO$_2$–Sc$_2$O$_3$ [58] systems are well described by third-order polynomials with correlation coefficients of 0.999 and 0.980, respectively. By differentiating the obtained equations for $x = 0$, the values of the liquidus slope (depression) were obtained for an infinitesimal impurity content $m = (\partial T/\partial x)_{x=0}$, namely 594 and 1005 deg/mol, respectively. Hence, according to equation (1) using the enthalpy of ZrO$_2$ melting, $\Delta H = 16.40$ kcal/mol [74], we obtain the distribution coefficients of Y$_2$O$_3$ and Sc$_2$O$_3$ during crystallization of the ZrO$_2$ melt. The obtained value $k_γ = 1.55$ agrees well with
the calculated value obtained from the data of Noguchi et al. [49], but diverges from the value obtained from the data of Rouanet [48], see [22]. The calculated value $k_{Sc} = 1.95$ significantly differs from the value $k_{Sc} = 2.87$ calculated according to Shevchenko et al. [22]. The discrepancies are determined by the complexity of conducting experiments at temperatures above 2700 °C, see Figs. 2 and 4.

4. Discussion

The wide regions of solid solutions formed in ZrO$_2$–R$_2$O$_3$ systems are striking examples of the so-called grossly nonstoichiometry [55]. The maxima on the melting curves of these solid solutions are a characteristic feature of heterovalent isomorphism with a variable number of atoms in the unit cell and correlate with high ionic conductivity and low thermal conductivity [9, 75, 76].

The formation of such solid solutions is characterized by the accumulation of defects associated with charge compensation and the formation of ordered phases with decreasing temperature. This effect that is observed in the studied systems and in this case it is weakened and smeared out due to low cationic diffusion. The absence of pronounced differentiation of cations over crystallographic positions during the formation of ordered fluorite-like phases sharply distinguishes oxide systems from analogous fluoride systems. It can be assumed that the complete cationic ordering will change the thermodynamic stability of the corresponding phases and, thus, it will shift the temperature limits of their existence in the phase diagrams of ZrO$_2$–R$_2$O$_3$. Probably, the observed pattern of ordering (the formation of only two fluorite-like phases Y$_4$Zr$_3$O$_{12}$ and Y$_6$ZrO$_{11}$ in the ZrO$_2$–Y$_2$O$_3$ system and three ordered phases in the ZrO$_2$–Sc$_2$O$_3$ system) is not complete. For comparison, we can refer to the CeO$_2$–Ce$_2$O$_3$ model system, where the set of ordered phases is much richer [77]. In particular, it can be expected that in the yttrium system the same ordered phases as in the scandium system are formed, and the absence of phases of the β and γ types in the ZrO$_2$–Y$_2$O$_3$ system associated only with kinetic difficulties [62]. In addition, the existence of the phase Y$_2$Zr$_5$O$_{15}$, which is isostructural to the erbium analogue can be expected [78].

It should be noted that all thermodynamic models for the ZrO$_2$–Y$_2$O$_3$ system provide for the presence of only one ordered phase Y$_2$Zr$_5$O$_{12}$, which significantly limits their reliability. In this case, the temperature of the eutectoid decomposition of the cubic phase in the ZrO$_2$–Y$_2$O$_3$ system differs according to the data of different models by hundreds of degrees [43–46], and in [46] it falls below absolute zero, which contradicts the third law of thermodynamics. The diagram constructed by us (Fig. 1b) is closest to the thermodynamic model of Degtyarev and Voronin [43].

The inflection points on the extrapolated solvus curves of the F phases deserve special attention. Such points are characteristic of all binary systems with heterovalent solid solutions based on compounds with the fluorite structure [79], which is associated with diffuse phase transitions in fluorite matrices [80, 81]. In particular, such a behaviour of the solvus line takes place in the system UO$_2$–UO$_3$ [82], and the presence of a diffuse phase transition in uranium dioxide is discussed [80, 83–85]. Thus, the results of low-temperature extrapolation of the solvus curves both in the analysed systems and the corresponding curves in other systems with the participation of zirconia and hafnium oxides [22] suggest the presence of a diffuse phase transition in the cubic ZrO$_2$ and HfO$_2$ polymorphs. For zirconium and hafnium oxides, we do not know any indications of its existence.

Conditional estimation of approximate temperature of this transition (since this is diffuse transition, and it is not a phase transition in the thermodynamic sense) based on $T = (0.7–0.8)T_{melt}$ [K] ratio provides a value of 1680–2100 °C, i.e. below the temperature of polymorphic transformation between the cubic and tetragonal modifications of ZrO$_2$ (2170 °C [2]). Thus, probably, all solid solutions of the fluorite structure formed in systems with the participation of zirconia are solid solutions in the disordered initial ZrO$_2$ form. This creates additional difficulties for constructing the corresponding thermodynamic models.

On numerous published "phase diagrams" of (Zr,Hf)O$_2$–R$_2$O$_3$ systems at temperatures below 1350 °C frozen states are shown instead of equilibrium phase regions. The actual behaviour of materials in these systems upon cooling is
determined mainly not by equilibrium phase transformations, but by non-diffusion phase transitions. Accordingly, on phase diagrams, in some cases, two-phase regions degenerate, and instead of them lines of phase transformations of the martensitic type are present.

A scandium solid solution of optimal concentration is thermodynamically stable at temperatures above 700 °C, i.e., the corresponding products are stable in terms of phase composition for an indefinitely long period of time if they are operated at this temperature without lowering it.

5. Conclusions

Phase equilibria at low temperatures in systems involving zirconia and hafnia are among the unresolved fundamental issues. Since the time of achieving equilibrium controlled by cationic diffusion increases exponentially with decreasing temperature, the study of low-temperature equilibria is a very complicated and often unsolvable problem.

It should be noted that ordering processes in systems with zirconia and hafnia oxides have been very poorly studied. Significant discoveries can be expected here. Other methods for the investigation of low-temperature phase formation in the discussed systems are required. It can be expected that the use of salt melts will allow progress to be made in solving this problem. It should be noted that salt melts, in contrast to hydrothermal synthesis, contribute to the formation of micron rather than nanoscale powders, which probably less prone to the formation of metastable equilibria.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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**Information about the authors**

Pavel P. Fedorov, Dr. Sci. (Chem.), Full Professor, Chief Researcher, Prokhorov General Physics Institute of the Russian Academy of Sciences (Moscow, Russian Federation).

https://orcid.org/0000-0002-2918-3926

ppfedorov@yandex.ru

Elena V. Chernova, Junior Researcher, Prokhorov General Physics Institute of the Russian Academy of Science (Moscow, Russian Federation).

https://orcid.org/0000-0001-7401-5019
e-chernova@yandex.ru

Received 20.03.20223; approved after reviewing 18.04.2023; accepted for publication 15.05.2023; published online 25.06.2023.

Translated by Valentina Mittova

*Edited and proofread by Simon Cox*