Thermodynamic Assessment of the \( \text{Y}_2\text{O}_3-\text{Yb}_2\text{O}_3-\text{ZrO}_2 \) System

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Introduction

The rare earth oxide-zirconia systems are used for a variety of applications, such as solid electrolytes and thermal barrier coatings. To gain a better insight into their behavior and further improve their performance, it is essential to understand the thermodynamic properties of these materials. These thermodynamic properties dictate the stability of the oxides in actual service conditions. Today thermodynamics involves both experimental measurements and development of self-consistent databases which contain the Gibbs energies of the individual phases (1). Parameters in various solution models are evaluated based on available experimental data. From a set of relatively simple equations, all phase boundaries and thermodynamic properties can be calculated for a particular system through minimization of the Gibbs energy under given conditions. Further, binary systems are building blocks for higher order systems, which may not be experimentally studied.

Yttria-zirconia (\( \text{Y}_2\text{O}_3-\text{ZrO}_2 \)) is the most widely used of the rare earth oxide-zirconia systems. There are numerous experimental studies of the phase boundaries in this system. In this paper, we assess these data and derive parameters for the solution models in this system. There is current interest in other rare earth oxide-zirconia systems as well as systems with several rare earth oxides and zirconia, which may offer improved properties over the \( \text{Y}_2\text{O}_3-\text{ZrO}_2 \) system. For this reason, we also assess the ytterbia-zirconia (\( \text{Yb}_2\text{O}_3-\text{ZrO}_2 \)) and \( \text{Y}_2\text{O}_3-\text{Yb}_2\text{O}_3-\text{ZrO}_2 \) system. Only limited experimental data are currently available for the \( \text{Yb}_2\text{O}_3-\text{ZrO}_2 \) binary and \( \text{Y}_2\text{O}_3-\text{Yb}_2\text{O}_3-\text{ZrO}_2 \) ternary systems.

There are several calculations of the \( \text{Y}_2\text{O}_3-\text{ZrO}_2 \) system in the literature. Kaufman (2) approaches this type of pseudo-binary by treating each oxide unit (i.e. \( \text{Y}_2\text{O}_3 \) and \( \text{ZrO}_2 \)) as a component. This readily allows development of quite good oxide databases with a minimum number of components. The experimental phase diagram for \( \text{Y}_2\text{O}_3-\text{ZrO}_2 \) is
dominated by a large cubic phase field for ZrO$_2$ as well as a large cubic phase field for Y$_2$O$_3$. Degtyarev and Voronin (3,4) point out that the cubic Y$_2$O$_3$ phase can be derived from the ZrO$_2$ phase by removing two oxygen anions. Thus they treat the two cubic phases as one cubic phase with a miscibility gap. Du et al. (5,6) model the Y$_2$O$_3$-ZrO$_2$ system using the miscibility gap simplification and treating YO$_{1.5}$ and ZrO$_2$ as components. They do a thorough literature survey and derive their model coefficients using experimental data (7). They do not consider experimental data below ~1300 K, due to likely difficulties in attaining equilibria. One of their assessments uses the liquid as the reference state (5) and the other uses the standard element reference state (6). Yokokawa et al. (8,9) calculate the Y$_2$O$_3$-ZrO$_2$ diagram and phase diagrams for a number of other rare earth oxide-zirconia systems. They also treat the oxide units as components and derive solution parameters from both phase boundary data and correlations between ionic radii of metal oxides.

No calculations were found for any ternaries or higher order systems. In this study we assess the Y$_2$O$_3$-ZrO$_2$, Yb$_2$O$_3$-ZrO$_2$, and Y$_2$O$_3$-Yb$_2$O$_3$ binaries from available data. We re-assess the Y$_2$O$_3$-ZrO$_2$ for two reasons—to build a database without the miscibility gap simplification and to include more low temperature data. We do not use the miscibility gap simplification for two reasons. First, the space groups of cubic Y$_2$O$_3$ and cubic ZrO$_2$ are not the same. Second, the use of separate phases makes convergence easier. The oxide units Y$_2$O$_3$, Yb$_2$O$_3$, and ZrO$_2$ are used as components. The model parameters are derived from experimental data. Then these three binary assessments are combined to form the ternary Y$_2$O$_3$-Yb$_2$O$_3$-ZrO$_2$ database.

**Review of Experimental Data**

**Pure Components and Lattice Stabilities**

All data is in the form of Gibbs energies with the standard element reference state (SER). Transition heats and temperatures are given in Table I(a). These data are from the STGE database (10), which in turn were taken from IVTAN database (11). Adjustments are made to the transition temperatures of Y$_2$O$_3$ in order to maintain consistency with the Y$_2$O$_3$-rich data of Stubican et al. (12), which is the most complete dataset for the Y$_2$O$_3$-rich side of the diagram. Further the IVTAN heat of transition between the two solid phases is 54 kJ/mol, which is rather high. A more reasonable estimate for a solid oxide/solid oxide transformation is 20 kJ/mol (13) and this is used in the database.

The SGTE and IVTAN data for Yb$_2$O$_3$ are incomplete. The SGTE database lists only one solid phase for Yb$_2$O$_3$, whereas the IVTAN tables list two solid phases, but with no heat of transition between the two solid phases. In analogy with Y$_2$O$_3$, the lower temperature solid phase is taken as cubic and the high temperature solid phase as hexagonal and the heat of transition is estimated to be 20 kJ/mol. The transition temperatures are taken from IVTAN (11).

Solution database development is based on the determination of lattice stabilities (1). For the pure elements, these have been determined and tabulated. However, when using oxide units as components, these must be estimated. Lattice stabilities are chosen to make the particular phase unstable over the entire range by adding ~20 kJ/mol to the
stable phase's Gibbs energy for a given temperature range. All lattice stabilities are listed in Table II(b).

**Y₂O₃-ZrO₂ System—Phase Boundary Data**

There is a good deal of experimental phase boundary information on this system (12,14-38). The data through 1990 are reviewed by Du et al. (5,6). Figure 1(a) and (b) show two accepted experimental phase diagrams (14,15). Both diagrams are dominated by a large cubic ZrO₂ phase field. Both diagrams contain several invariant points, which are listed in Table II. The differences between the two experimental diagrams indicate the many controversies in this diagram. Du et al. (5,6) state that the difficulty in attaining low temperature equilibria make the low temperature eutectoids unreliable. Therefore they do not use them in their assessment. The Y₂O₃-ZrO₂ system can be viewed as a rigid cation lattice with mobile anions. Due to the low diffusivity of the cations, phase changes are very slow, particularly at the lower temperatures. This fact must be considered in assessing experimental data. In the following discussion we examine available experimental data paying particular attention to the technique and reliability of the data.

There are three measurements of the liquidus line (17-19). Skaggs (19) used a laser heating method to create a 'pendant drop'. Temperature measurements were taken with a small amount of solid in the drop and then again with approximately half the drop solid. The average of these gave the liquidus temperature. However, these data showed a large amount of scatter and are not used in this assessment. Noguchi et al. (17) used a solar furnace in conjunction with a pyrometer. Cooling curves clearly revealed the solification point. Rouanet (18) has used a similar technique and his data are in basic agreement with Noguchi et al. (17). The data of Noguchi et al. (17) are thus used in this assessment.

The ZrO₂-rich side of the diagram is the area of the greatest practical interest. As noted, the equilibrium phases of ZrO₂ are monoclinic, tetragonal, and cubic as temperature increases. In addition, quenched samples also form a persistent, non-equilibrium tetragonal phase (32). The non-equilibrium tetragonal phase has a smaller c axis and generally higher Y₂O₃ contents than the corresponding equilibrium tetragonal phase (37). Some of the discrepancies in reported experimental data are likely due to the formation of this metastable phase (32, 37).

The most well-known transformation of ZrO₂ is the monoclinic to tetragonal transformation, which is accompanied by a 3-5% volume increase. Four measurements were found of this transformation (16, 24, 27, 31)—all show that the transformation temperature decreases with increasing Y₂O₃ content. Duwez et al. (16) observed a sharp change in expansion on the tetragonal to monoclinic transformation. Pascual and Duran (24) used dilatometry and differential thermal analysis (DTA). Ruh et al. (27) used XRD and Yoshikawa and Suto (31) used dilatometry. In the mole fraction of Y₂O₃ from 0.00 to 0.02, these data all show reasonably good agreement. However, Duwez et al. (16) and Pascual and Duran (24) show the transformation temperature continues to decrease to a mole fraction of Y₂O₃ ~ 0.05. Only the mole fraction of Y₂O₃ from 0.00 to 0.02 data are used in this assessment.
There are the most data for cubic/tetragonal equilibria at the ZrO₂-rich side (12, 16, 21, 23-25, 30, 36, 38). Duwez et al. (16) used XRD to determine the cubic/(cubic + tetragonal) boundaries at 1648 and 2273 K. Ruh et al. (27), Pascual and Duran (24), Scott (21) and Stubican et al. (12) have taken similar measurements with XRD. Ruhle et al. (25) and Lanteri et al. (23) used analytical electron microscopy to determine the tetragonal/(tetragonal + cubic)/cubic phase boundaries. Their data indicates these boundaries are temperature independent. Yoshikawa et al. (30) used electron microprobe analysis to determine these phase boundaries. The data points for all these investigations are collected in Figure 2 and show remarkably good agreement with each other at temperatures greater than ~1600 K. At lower temperatures the mole fraction of Y₂O₃ differs by ~0.02.

The cubic phase field on the ZrO₂-rich side occupies a large section of the diagram and extends to low temperatures (33). Stubican et al. (12) has proposed a low temperature eutectoid, as noted in Table II, which is included in this assessment.

There is one confirmed intermediate compound in this system—Y₃Zr₄O₁₂ (12). This is an ordered phase, which decomposes to the disordered cubic solution. As shown in Table II, there is some controversy of its decomposition temperature. Other investigators have reported a pyrochlore-type compound of the form Zr₂Y₂O₇ (24). However the existence of this compound is controversial—many investigators have not observed it, despite careful studies to search for it (34). Therefore it is not considered in this assessment.

As shown in the experimental phase diagram (Figure 1(a) and (b)), there are large cubic ZrO₂ and cubic Y₂O₃ regions, as well as a two phase region. Stubican et al. (12) have determined the phase boundaries of both sides of this two phase field by XRD. Pascual and Duran (24) have also used XRD to determine the cubic ZrO₂/(cubic ZrO₂ + cubic Y₂O₃) boundary. Their data is a mole fraction of Y₂O₃ ~0.08 higher than that of Stubican et al. (12). Jayaratna et al. (36) have also measured these boundaries. Their data for the cubic ZrO₂/(cubic ZrO₂ + cubic Y₂O₃) boundary shows excellent agreement with that of Stubican et al. (12). The data of Stubican et al. (12) is used in this assessment.

Finally, the Y₂O₃-rich side of the diagram is less well studied. It is dominated by the cubic Y₂O₃ phase, which transforms to the hexagonal Y₂O₃ phase at high temperatures. The liquidus data in this region and the phase boundary data is given by Stubican et al. (12). Again, this data is the most complete for this side. As noted, some corrections were made to the Y₂O₃ lattice stabilities for consistency with these data.

**Y₂O₃-ZrO₂ System—Thermodynamic Data**

There is only limited thermodynamic data on this system. Belov and Semenov (39) have measured the activity of ZrO₂ and Y₂O₃ at 2773 K using a Knudsen cell vapor pressure measurement technique. There are some inconsistencies between these data and the reported cubic/liquid phase boundary as shown in Figure 3. Assuming a pseudo-binary, there should be a constant activity in the (liquid + cubic) two phase region. There are two possible reasons for this inconsistency—either the temperature measurement is off or since the system is not truly a binary, but rather a Y-Zr-O ternary, P(O₂) is varying in the
experiment. Following Du et al. (4), we only include the first three ZrO$_2$-rich measurements in this assessment.

One calorimetric measurement was found for the heat of formation of an intermediate compound of the formula Zr$_2$Y$_2$O$_7$ (40) and is given in Table III. However a compound of this stoichiometry has not been observed experimentally. First principles calculations are available for the heat of formation of Zr$_3$Y$_4$O$_{12}$ (41) and are also listed in Table III.

Yb$_2$O$_3$-ZrO$_2$ System—Phase Boundary Data

There is much less experimental data available on this system and only phase boundary information was found. Only one liquidus measurement was found (18). The ZrO$_2$-rich side of the at temperatures below the solidus line has been studied by Corman (26, 29). It is similar to the ZrO$_2$-rich side of the Y$_2$O$_3$-ZrO$_2$ phase diagram and also contains an intermediate compound Zr$_3$Yb$_4$O$_{12}$, which disorders at a higher temperature than Zr$_3$Y$_4$O$_{12}$ as listed in Table II.

Y$_2$O$_3$-Yb$_2$O$_3$-ZrO$_2$ System

The Y$_2$O$_3$-Yb$_2$O$_3$-ZrO$_2$ system appears to be the only pseudo-ternary system with ZrO$_2$ and two rare-earth oxides, which has been experimentally studied. Corman (26) and Corman and Stubican (29) have examined this system at three temperatures from pure ZrO$_2$ to solutions with a mole fraction of Y$_2$O$_3$ equal to 0.5 and a mole fraction of Yb$_2$O$_3$ equal to 0.5. Their diagrams at 1473, 1673, and 1923 K are shown in Figures 4(a), (b), (c), respectively.

The ternaries are characterized by continuous tetragonal ZrO$_2$, cubic ZrO$_2$, and cubic (Y,Yb)$_2$O$_3$ solutions. Further the intermediate line compound, Zr$_3$(Y,Yb)$_4$O$_{12}$, extends across the diagram when both ends are stable (Figure 4(a)). As temperature is raised above 1655 K, the Zr$_3$Y$_4$O$_{12}$ side disappears (Figure 4(b)). Above 1910 K, the compound disappears entirely (Figure 4(c)).

Modeling

As discussed, the oxide units are treated as components. The lattice stabilities are listed in Table I(b).

Each of the solutions are modeled with random mixing term and a Redlich-Kister polynomial (42) to describe the excess free energy:

$$G_m(x, T) = \sum_{i=1}^{2} x_i \, \xi_i G_i(T) + R \sum_{i=1}^{2} x_i \ln x_i + \varepsilon G_m$$

$$\varepsilon G_m = x_i x_j \sum_{j=0}^{n-1} \xi_L (x_i - x_j)^j$$

Here $x_i$ is the mole fraction of component $i$, $\xi_i G_i(T)$ is the lattice stability of that component (Table I(b)), $\xi_L$ are the interaction parameters, $R$ is the gas constant, and $T$ is
the absolute temperature. In this assessment, only the first two terms of the Redlich-Kister polynomials were used:

These interaction parameters were evaluated from the experimental data via the optimizing code Parrot in ThermoCalc and also the optimizing code in WinPhad. First the Y2O3-ZrO2 diagram was obtained by fitting the liquidus and the approximate boundaries of the large cubic phase fields. The smaller phase regions were added by fine-tuning the parameters. A number of optimizations from different starting points were done to get the best fit with no artifacts. The Yb2O3-ZrO2 diagram was done by using the parameters from the Y2O3-ZrO2 system and making adjustments for the differences in the two systems.

ThermoCalc uses the Muggianu approach (43) to extend the binaries to ternaries. This approach gives the correct limits when the ternary solutions reduce to the binaries. In addition a ternary interaction parameter was added of the form:

\[
\text{ex-ten } G_m = x_1 x_2 x_3^0 L(\text{tern})
\]

These parameters were determined by ‘trial and error’ to get the best agreement with the experimental ternary sections.

**Results and Discussion**

The solution parameters for the Y2O3-ZrO2 system and are shown in Table IV. In most cases the \(L^0\) and \(L^1\) parameters are needed; however in some cases only the \(L^0\) parameter is needed. The complete calculated phase diagram is shown in Figure 5(a) with experimental data shown as symbols. Nearly all features of the experimental diagram (Figure 1(a) and (b)) are reproduced including the five invariant points (Table II), the liquidus lines, and the cubic ZrO2/(cubic ZrO2 + cubic Y2O3)/cubic Y2O3 phase boundaries. Only the tetragonal ZrO2/(tetragonal ZrO2 + cubic ZrO2)/cubic ZrO2 does not follow the experimentally measured phase boundaries, as shown in Figure 5(b). The highest temperature points are reproduced, but the calculated diagram does not reproduce the measured lack of temperature dependence of these boundaries. The appearance of the monoclinic solid solution at 1445 K also pushes these boundaries into higher Y2O3 contents.

Figure 6 shows the calculated activities in this pseudo-binary at 2773 K. Note the two phase (liquid + cubic ZrO2) region with constant activity. The experimental data are shown as data points. The measured activity of ZrO2 was used in the assessment and shows very good agreement. The activity of Y2O3 was not used and shows approximate agreement with the calculations.

The enthalpy of formation for Zr3Y4O12 is also extracted from this assessment from:

\[
3 \text{ZrO}_2 + 2 \text{Y}_2\text{O}_3 = \text{Zr}_3\text{Y}_4\text{O}_{12}
\]
The value from the assessment (-45.9 kJ/mol) shows order of magnitude agreement with the calculations from first principles (Table III, ref. (41)).

The parameters for the Yb$_2$O$_3$-ZrO$_2$ system are given in Table V and the calculated phase diagram is given in Figure 7. There is good agreement with the limited experimental data. Due to these limited data, the monoclinic ZrO$_2$ phase was included only as a line compound. The calculated tetragonal ZrO$_2$/(tetragonal ZrO$_2$ + cubic ZrO$_2$)/cubic ZrO$_2$ shows better agreement with experimental data than in the Y$_2$O$_3$-ZrO$_2$ system, as shown in Figures 7 and 5, respectively.

The third binary needed for this study is the Y$_2$O$_3$-Yb$_2$O$_3$ system. This was treated as an ideal solution, in accordance with the limited experimental data (44), which shows a continuous cubic solid solution at 1923 K.

Next the binaries were combined to form the Y$_2$O$_3$-Yb$_2$O$_3$-ZrO$_2$ pseudo-ternary. Additional ternary interaction coefficients were included and given in Table VI. Calculated sections for 1473, 1673, and 1923 K are shown in Figures 8(a), (b), and (c), respectively. The intermediate line compound Zr$_3$(Y,Yb)$_4$O$_{12}$ shows the experimentally observed behavior (Figures 3(a-c)). The tetragonal ZrO$_2$, cubic ZrO$_2$, and cubic (Y,Yb)$_2$O$_3$ phases also show continuous solid solutions, as observed experimentally.

**Conclusions**

Experimental data for the Y$_2$O$_3$-ZrO$_2$, Yb$_2$O$_3$-ZrO$_2$, and Y$_2$O$_3$-Yb$_2$O$_3$-ZrO$_2$ systems has been examined. For the Y$_2$O$_3$-ZrO$_2$ pseudo-binary a good deal of phase boundary data are available, but only limited thermodynamic data. For the other systems, only limited phase boundary data is available. A Calphad-type database was developed for both pseudo-binaries and put together for the pseudo-ternary.

**Acknowledgement**

Partial supported for ZKL by an NSF Career Award under grant DMR-9983532 is greatly appreciated. The work at NASA was supported by the Ultra Efficient Engine Technology (UEET) Program.
References:


15. ibid., Figure 93-055.


44. op. cit. Clevinger, Figure 347.
<table>
<thead>
<tr>
<th>Phase Transition</th>
<th>Temperature of transition (K)</th>
<th>$\Delta_{\text{max}}H$ (kJ/mol)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>ZrO$_2$ monoclinic → tetragonal</td>
<td>1445</td>
<td>8400</td>
<td>(11)</td>
</tr>
<tr>
<td>ZrO$_2$ tetragonal → cubic</td>
<td>2620</td>
<td>21400</td>
<td>(11)</td>
</tr>
<tr>
<td>ZrO$_2$ cubic → liquid</td>
<td>2983</td>
<td>111400</td>
<td>(11)</td>
</tr>
<tr>
<td>Y$_2$O$_3$ cubic → hexagonal</td>
<td>2550</td>
<td>54000</td>
<td>(11)</td>
</tr>
<tr>
<td>Y$_2$O$_3$ hexagonal → liquid</td>
<td>2712</td>
<td>115000</td>
<td>(12)*</td>
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<tr>
<td>Yb$_2$O$_3$ solid → liquid</td>
<td>2783</td>
<td>114000</td>
<td>(11)</td>
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<tr>
<td>Yb$_2$O$_3$ cubic → hexagonal</td>
<td>2663</td>
<td>20000</td>
<td>(11)**</td>
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<tr>
<td>Yb$_2$O$_3$ hexagonal → liquid</td>
<td>2703</td>
<td>12000</td>
<td>(11)**</td>
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</table>

*Values from reference 11 modified to give agreement with data of reference 12.
**Transition temperatures from reference 11 and heats are estimated.

Table I(a). Temperatures and enthalpies of transitions to define lattice stabilities.

<table>
<thead>
<tr>
<th>Phase Abbreviation</th>
<th>Temperature Range (K)</th>
<th>Gibbs energy (J/mol)</th>
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<tr>
<td>ZrO$_2$ monoclinic mz</td>
<td>298-1445</td>
<td>$-1125582.53 + 417508432T + 68.32783T*ln(T) - 0.004651885T^2 + 1.72444167E-10T^3 + 671863.5T^{-1}$</td>
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<td></td>
<td>1445-2620</td>
<td>$1129291.49 + 484.935707T - 78.1T*ln(T) - 1.0845475E-16T^2 + 7.81505167E-08T^3 - 0.622945E-08T^{-1}$</td>
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<tr>
<td></td>
<td>2620-2983</td>
<td>$-1134269.49 + 510.790474T - 80T*ln(T) - 2.0126725E-14T^2 + 9.19196667E-19T^3 - 5.127845E-05T^{-1}$</td>
</tr>
<tr>
<td>ZrO$_2$ tetragonal tz</td>
<td>298-6000</td>
<td>$G_{mz}(T) + 8400 - 5.81314879T$</td>
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<tr>
<td>ZrO$_2$ cubic cz</td>
<td>298-6000</td>
<td>$G_{cz}(T) + 214000.7.7749809T$</td>
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<td>ZrO$_2$ liquid Lz</td>
<td>298-6000</td>
<td>$G_{Lz}(T) + 1114000.9.4599497T$</td>
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<tr>
<td>ZrO$_2$ cubic Y$_2$O$_3$ phase cy</td>
<td>298-6000</td>
<td>$G_{cy}(T) + 21500$</td>
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<td>ZrO$_2$ hexagonal hz</td>
<td>298-6000</td>
<td>$G_{hz}(T) + 22550$</td>
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<td>Y$_2$O$_3$ cubic cy</td>
<td>298-1100</td>
<td>$2.98140E+02 - 19454939.54 + 680.542373T + 113.9721T^2 + 1.49941783E-06T^3 + 813690.5T^{-1}$</td>
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<td></td>
<td>1100-2100</td>
<td>$-2012427.83 + 1275.75211T - 98.0735T*ln(T) + 0.3948891T^2 - 3.688465E-06T^3 + 10928115T^{-1}$</td>
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<td>2100-2599</td>
<td>$-2274854.51 + 2766.12583T - 94.9992T*ln(T) + 1.0031335T^2 - 7.8201833E-06T^3 - 77093000T^{-1}$</td>
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<td>2599-2782</td>
<td>$-2011617.72 + 1043.70289T - 160T*ln(T) + 5.08929E-13T^2 + 2.42719833E-17T^3 - 0.0114311T^{-1}$</td>
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<td>2782-6000</td>
<td>$-2120097.72 + 1399.92055T - 200T*ln(T) + 4.6124375E-16T^2 + 1.38251267E-20T^3 + 3.154309E-06T^{-1}$</td>
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<td>Y$_2$O$_3$ hexagonal hy</td>
<td>298-6000</td>
<td>$G_{hy}(T) + 20000 + 7.69527T$</td>
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<td>Y$_2$O$_3$ liquid Ly</td>
<td>298-6000</td>
<td>$G_{Ly}(T) + 134000 + 48.67307T$</td>
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<td>298-6000</td>
<td>$G_{my}(T) + 22100$</td>
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<td>Y$_2$O$_3$ tetragonal ty</td>
<td>298-6000</td>
<td>$G_{ty}(T) + 21100$</td>
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<tr>
<td>Y$_2$O$_3$ cubic ZrO$_2$ phase cyz</td>
<td>298-6000</td>
<td>$G_{cyz}(T) + 20100$</td>
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<tr>
<td>Yb$_2$O$_3$ cubic cyb</td>
<td>298-2663</td>
<td>$-1858343.67 + 747.941586T - 130.1851T*ln(T) - 0.001896915T^2 + 2.766497333E-12T^3 - 3.079650T^{-1}$</td>
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<td>2663-2798</td>
<td>$-1923755.38 + 1002.70962T - 160T*ln(T)$</td>
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<td></td>
<td>2798-6000</td>
<td>$-2035675.38 - 203.176021T^2 - 200T*ln(T)$</td>
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<td>Yb$_2$O$_3$ hexagonal hyb</td>
<td>298-6000</td>
<td>$G_{hyb}(T) + 200000 - 7.51032T$</td>
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<td>Yb$_2$O$_3$ liquid Lyb</td>
<td>298-6000</td>
<td>$G_{Lyb}(T) + 140000 - 51.82347T$</td>
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<tr>
<td>Yb$_2$O$_3$ monoclinic myb</td>
<td>298-6000</td>
<td>$G_{myb}(T) + 22100$</td>
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<tr>
<td>Yb$_2$O$_3$ tetragonal tyb</td>
<td>298-6000</td>
<td>$G_{tyb}(T) + 21100$</td>
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<tr>
<td>Yb$_2$O$_3$ cubic ZrO$_2$ phase cyzb</td>
<td>298-6000</td>
<td>$G_{czb}(T) + 20100$</td>
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Table I(b). Lattice stabilities.
<table>
<thead>
<tr>
<th>Invariant</th>
<th>Temperature (K)</th>
<th>Composition x(Y$_2$O$_3$)</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutectic liq = cz + cy</td>
<td>2688</td>
<td>0.817</td>
<td>(12)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2603</td>
<td>0.76</td>
<td>(18)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2646</td>
<td>0.825</td>
<td>(19)</td>
<td></td>
</tr>
<tr>
<td>Peritectic cy = liq + hy</td>
<td>2720</td>
<td>0.778</td>
<td>(12)</td>
<td>Introduced, not measured</td>
</tr>
<tr>
<td>Euctectoid cz = delta y + cy</td>
<td>1650</td>
<td>0.435</td>
<td>(27)</td>
<td></td>
</tr>
<tr>
<td>Euctectoid tz = mz + cz</td>
<td>838</td>
<td>0.039</td>
<td>(21)</td>
<td></td>
</tr>
<tr>
<td>Euctectoid cz = mz + delta y</td>
<td>&lt; 673</td>
<td>0.20-0.30</td>
<td>(12)</td>
<td></td>
</tr>
<tr>
<td>Decomposition Temperature of delta y</td>
<td>1523</td>
<td>0.4</td>
<td>(12)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1655</td>
<td>0.4</td>
<td>(35)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1648</td>
<td>0.4</td>
<td>(24)</td>
<td></td>
</tr>
<tr>
<td>Eutectic liq = cz + cyb</td>
<td>2691</td>
<td>0.85</td>
<td>(19)</td>
<td></td>
</tr>
<tr>
<td>Decomposition of delta yb</td>
<td>1898</td>
<td>0.4</td>
<td>(29)</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Experimentally determined invariant points in the Y$_2$O$_3$-ZrO$_2$ and Yb$_2$O$_3$-ZrO$_2$ systems and decomposition temperatures of delta phase.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (K)</th>
<th>Method</th>
<th>ΔH$_f$(from oxides)—kJ/mol</th>
<th>ΔH$_f$(from elements)—kJ/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$Zr$_2$O$_7$</td>
<td>298</td>
<td>Calorimetry</td>
<td>-47.7</td>
<td>-4185.4</td>
<td>(36)</td>
</tr>
<tr>
<td>Zr$_5$Y$<em>4$O$</em>{12}$</td>
<td>0</td>
<td>First Principles—Generalized Gradient Approximation</td>
<td>-20.9</td>
<td>-6454</td>
<td>(37)</td>
</tr>
<tr>
<td>Zr$_3$Y$<em>4$O$</em>{12}$</td>
<td>0</td>
<td>First Principles—Local-Density Approximation</td>
<td>-14.7</td>
<td>-6448</td>
<td>(37)</td>
</tr>
</tbody>
</table>

Table III. Enthalpies of formation of intermediate compound.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameter</th>
<th>Value (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>L</td>
<td>98445 - 45.67T</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>95521 - 30.52T</td>
</tr>
<tr>
<td>Cubic ZrO$_2$</td>
<td>L</td>
<td>-144364 + 24.60T</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>-180000 - 62.25T</td>
</tr>
<tr>
<td>Tetragonal ZrO$_2$</td>
<td>L</td>
<td>-22324 - 32.95T</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>-240000 + 50T</td>
</tr>
<tr>
<td>Monoclinic ZrO$_2$</td>
<td>L</td>
<td>-90000 - 1</td>
</tr>
<tr>
<td>Hexagonal Y$_2$O$_3$</td>
<td>L</td>
<td>-18000</td>
</tr>
<tr>
<td>Cubic Y$_2$O$_3$</td>
<td>L</td>
<td>-30735 - 20.97T</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>99126 - 66.03T</td>
</tr>
<tr>
<td>Zr$_5$Y$<em>4$O$</em>{12}$</td>
<td>A + BT</td>
<td>-45966 + 11.28T</td>
</tr>
</tbody>
</table>

Table IV. Interaction parameters for Y$_2$O$_3$-ZrO$_2$ system.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameter</th>
<th>Value (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>oL</td>
<td>18466 - 15.72T</td>
</tr>
<tr>
<td></td>
<td>oL</td>
<td>-42812 + 26.53T</td>
</tr>
<tr>
<td>Cubic ZrO₂</td>
<td>oL</td>
<td>-116088 + 12.67T</td>
</tr>
<tr>
<td></td>
<td>oL</td>
<td>-296755 + 98.69T</td>
</tr>
<tr>
<td>Tetragonal ZrO₂</td>
<td>oL</td>
<td>-22326 + 33.00T</td>
</tr>
<tr>
<td></td>
<td>oL</td>
<td>-240024 + 50T</td>
</tr>
<tr>
<td>Monoclinic ZrO₂</td>
<td>oL</td>
<td>-90000 - T</td>
</tr>
<tr>
<td>Hexagonal Yb₂O₃</td>
<td>oL</td>
<td>-18000</td>
</tr>
<tr>
<td>Cubic Yb₂O₃</td>
<td>oL</td>
<td>-30735 - 20.97T</td>
</tr>
<tr>
<td></td>
<td>oL</td>
<td>125000 - 66.03T</td>
</tr>
<tr>
<td>Zr₃Yb₄O₁₂</td>
<td>A + BT</td>
<td>-50064 + 11T</td>
</tr>
</tbody>
</table>

Table V. Interaction parameters for Yb₂O₃-ZrO₂ system.

<table>
<thead>
<tr>
<th>Ternary Phase</th>
<th>L(Y₂O₃-Yb₂O₃-ZrO₂) (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal ZrO₂</td>
<td>0</td>
</tr>
<tr>
<td>Cubic ZrO₂</td>
<td>110000</td>
</tr>
<tr>
<td>Zr₃(Y,Yb)O₁₂</td>
<td>-8000</td>
</tr>
<tr>
<td>Cubic (Y,Yb)O₁₂</td>
<td>-100000</td>
</tr>
</tbody>
</table>

Table VI. Ternary interaction parameters for Y₂O₃-Yb₂O₃-ZrO₂
Figure 1. Accepted experimental phase diagrams for the \( \text{Y}_2\text{O}_3-\text{ZrO}_2 \) system (14, 15).
Figure 2—Experimental data for the tetragonal/(tetragonal + cubic)/cubic phase boundaries.

Figure 3. Activity of ZrO$_2$ and Y$_2$O$_3$ at 2773 K from Belov and Semenov (35)
Figure 4. Experimental $\text{Y}_2\text{O}_3-\text{Yb}_2\text{O}_3-\text{ZrO}_2$ ternary at (a) 1473 (b) 1673 (c) 1923 K (29).
Figure 5. Calculated phase diagram for the $\text{Y}_2\text{O}_3$-ZrO$_2$ system. (a) Entire diagram (b) Enlargement of ZrO$_2$-rich region.
Figure 6. Plot of calculated activity in $Y_2O_3$-$ZrO_2$ system vs composition, showing experimental measurements (35).

Figure 7. Calculated $Yb_2O_3$-$ZrO_2$ phase diagram.
Figure 8. Calculated isothermal sections for Y$_2$O$_3$-Yb$_2$O$_3$-ZrO$_2$ at (a) 1473 (b) 1673 and (c) 1923 K.