Thermodynamic Assessment of the ZrO$_2$-TiO$_2$ System

**Jeong-Ho Park[†*], Ping Liang, Hans Jürgen Seifert, Fritz Aldinger, Bon-Keup Koo[**]
and Ho-Gi Kim[*]**

Pulvermetallurgisches Laboratorium, Max-Planck Institute für Metallforshung, D-70569 Stuttgart, Germany
**Department of Materials Science and Engineering, Korea Advanced Institute of Science
and Technology, Taejon 305-701, Korea*
**Department of Material Engineering, Taejon National University of Technology, Taejon 300-170, Korea

A thermodynamic assessment for the ZrO$_2$-TiO$_2$ system has been conducted. An optimal thermodynamic data set for this system is evaluated by the CALPHAD(CALculation of PHAse Diagram) method applied to experimental phase diagram and thermodynamic data. The liquid is described by ionic liquid model with two sublattices. The solubilities of the solid solution phases, tetragonal ZrO$_2$ and TiO$_2$(rutile), were described by subregular substitutional model with one sublattice. Two compounds, ZrTiO$_4$ and ZrTi$_2$O$_6$, are modeled as stoichiometric compounds.

Key words: Thermodynamic assessment, ZrO$_2$-TiO$_2$ phase diagram, CALPHAD, Ionic liquid model

I. Introduction

PZT or modified PZT solid solutions are of interest for many years for their technological applications, which result from theirs piezoelectric, ferroeletric, and pyroelectric properties.[1-3] Nevertheless, attentions were paid mainly to physical properties, kinetics, and device characterizations but a few to phase equilibria and thermodynamic considerations. The quasibinary system ZrO$_2$-TiO$_2$ along with two other quasibinaries PbO-TiO$_2$ and PbO-ZrO$_2$ systems are the edges of the quasiternary system PbO-ZrO$_2$-TiO$_2$ system including the technically important PZT solid solution. Also zirconium titanate solid solutions are of interest for their useful dielectric properties in the microwave frequency regime.[4] Phase diagrams and phase relations of this system have been published by several authors.[5-14] There is, however, no general agreement among the proposed phase diagrams. This is associated with the sluggish kinetics at relatively low temperatures, the formation of metastable phases, the difficulties in conducting experiments at high temperatures, etc. Major discrepancies were concerned with the existence of intermediated compound, the range of homogeneity of the compound and solid solutions. The determination of the phase relations and thermodynamic properties in zirconia systems can be achieved with relatively a few experiments by means of the CALPHAD method.[15] The application of this method to binary systems can be used to check for internal consistency between thermodynamic and phase diagram data and to provide opti-

[†]Corresponding author: pjhqb@kaist.ac.kr

mized thermodynamic functions. The calculated ternary phase diagrams and thermodynamic quantities based on the thermodynamic descriptions of the binary diagrams make it possible to design experiments most efficiently. The same is true of going from a ternary to a quaternary system and so on.

The purpose of the present study is to obtain a self-consistent set of parameters for thermodynamic modeling of the ZrO$_2$-TiO$_2$ system allowing evaluation of phase diagrams and relevant thermodynamic data.

II. Experimental Data

ZrO$_2$ exhibits three polymorphic modifications, which are monoclinic, tetragonal, and cubic forms. For the convenience, they are denoted as ZrO$_2$_m, ZrO$_2$_t, ZrO$_2$_c, respectively. The solid solution based on ZrO$_2$_t is designated as Zss. It is adopted that the monoclinic ZrO$_2$ transforms to the tetragonal at 1478 K and then the tetragonal to the cubic at 2626 K, which agrees reasonably with the data from Ref. 12 and 13 within experimental errrors. TiO$_2$ exhibits three polymorphic forms, anatase, brookite, and rutile, of which the first two are believed to be matastable with respect to rutile.[16] The solid solution based on TiO$_2$ is designated as Tss.

It is known that there are several invariant equilibria such as eutectic, eutectoid, peritectic, and peritectoid reaction, two intermediate compounds(ZrTiO$_4$, ZrTi$_2$O$_6$), and solid solutions of end-members and compounds in the ZrO$_2$-TiO$_2$ system. Some earlier studies of this system have indicated the absence of any compounds in the system and the presence of partial solid solutions.[5,6] Other previous studies
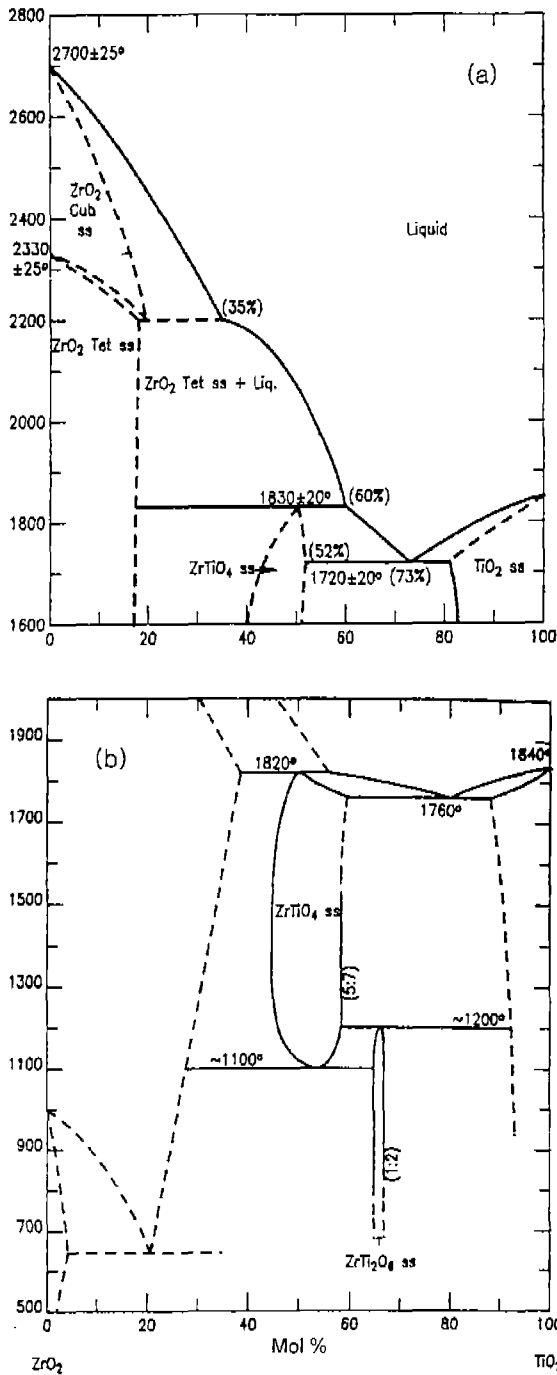
Fig. 1. Phase diagrams of the ZrO_2-TiO_2 system proposed by A. V. Shevchenko *et al.* (a) and A. E. McHale *et al.* (b).

have proposed the phase diagram including intermediate compound of formula $ZrTiO_4$.[7-13] A. E. McHale and R. S. Roth[14] have proposed low temperature phase relations which included new compound $ZrTi_2O_6$ stable below about 1473 K as well as $ZrTiO_4$ stable above about 1373 K. Although investigators agree on solid solution of the end-members and intermediate compound with solid solution, the details of the equilibria are in doubt. Fig. 1 shows some phase diagrams proposed experimentally.

III. Thermodynamic Models

The solution phases including tetragonal ZrO_2 and TiO_2 solid solutions are described by substitutional solution model

$$G_m = x_1{}^{\circ}G_1 + x_2{}^{\circ}G_2 + RT(x_1\ln x_1 + x_2\ln x_2) + {}^E G_m \quad (1)$$

where the parameters $^{\circ}G_i$ represent the lattice stabilities of pure components i and are given relative to the enthalpy of selected reference state of pure element at 298.15 K. the excess Gibbs free energy is described by Redlich-Kister polynomial formula.

$$^E G_m = x_1 x_2 \sum_{i=1}^{n} {}^i L(x_1 - x_2)^i \quad (2)$$

in which the interaction parameter $^i L$ may be also temperature-dependent.

The liquid phase is described by ionic liquid model[17] with two sublattices. The liquid can be represented by the formula $(Zr^{+4}, Ti^{+4})_P (O^{-2}, O, Va)_Q$, where Va represent hypothetical vacancy and P and Q are the number of sites on the sublattices and vary with composition in order to maintain electroneutrality. The values of P and Q are calculated from the following equations.

$$P = 2y_{O^{-2}} + Qy_{Va}$$

$$Q = 4y_{Zr^{+4}} + 4y_{Ti^{+4}} \quad (3)$$

where y denotes the site fraction of a constituent. P and Q are simply the average charge on the opposite sublattice. The hypothetical vacancies have an induced negative charge equal to Q.

$$G_m^l = y_{Zr^{+4}} y_{O^{-2}} {}^{\circ}G_{Zr^{+4}O^{-2}}^l + y_{Ti^{+4}} y_{O^{-2}} {}^{\circ}G_{Ti^{+4}O^{-2}}^l +$$

$$Qy_{Va}(y_{Zr^{+4}} {}^{\circ}G_{Zr^{+4}Va}^l + y_{Ti^{+4}} {}^{\circ}G_{Ti^{+4}Va}^l)$$

$$+ RT\{P(y_{Zr^{+4}}\ln y_{Zr^{+4}} + y_{Ti^{+4}}\ln y_{Ti^{+4}})$$

$$+ Q(y_{O^{-2}}\ln y_{O^{-2}} + y_{Va}\ln y_{Va})\} + {}^E G_m^l \quad (4)$$

where the excess Gibbs energy, $^E G_m^l$, is given by

$$^E G_m^l = y_{Zr^{+4}} y_{Ti^{+4}} y_{O^{-2}} L_{Zr^{+4}, Ti^{+4}:O^{-2}}^l$$

$$+ y_{Zr^{+4}} y_{O^{-2}} y_{Va} L_{Zr^{+4}:O^{-2}, Va}^l$$

$$+ y_{Ti^{+4}} y_{O^{-2}} y_{Va} L_{Zr^{+4}:O^{-2}, Va}^l$$

$$+ Qy_{Zr^{+4}} y_{Ti^{+4}} y_{Va} L_{Zr^{+4}, i^{+4}:Va}^l \quad (5)$$

A colon is used to separate constituents in different sublattice whereas a comma constituents in the same sublattice. The parameter L represents the interaction energy between constituents in the sublattice and can be described as follows.

Table 1. Thermodynamic Description of the ZrO_2-TiO_2 system(in J/mol)

* Ionic-liquid

$^0G^l_{Ti^{+2}:O^{-2}} = 2GTIO2 + 178003 - 62.4769T$

$^0G^l_{Zr^{+4}:O^{-2}} = -1931250.3 + 272.26T + 2GZRLIQ + 4GHSEROO$

$^0G^l_{Zr^{+4}:O} = 2648.0 + 31.44T + GHSEROO$

$^0G^l_{Zr^{+4}:Va} = GZRLIQ$

$^0L^l_{Zr^{+4}, Ti^{-4}:O^{-2}} = -50000 - 25T$

$^0L^l_{Zr^{+4}:Ti^{-2}, Va} = 424351.51 - 215.70189T$

$^0L^l_{Zr^{+4}:Ti^{-2}, Va} = 211955.21 - 77.30708T$

* TiO₂ solid solution(Tss)

$^0G_{TiO_2} = GTIO2 + 22057.5$

$^0G^{Tss}_{ZrO_2} = {}^0G^{ZrO_2\_t}_{ZrO_2} + 25000$

$^0L^{Tss}_{TiO_2, ZrO_2} = -18600 + 4T$

* ZrO₂

$^0G^{ZrO_2\_m}_{Zr,O_2} = -1103376.90 + 247.58658T - 0.076129Tln(T) +$

$\qquad GHSERZR + 2GHSEROO$

$^0G^{ZrO_2\_c}_{ZrO_2} = -1014781.7 - 269.4T + 59.015088Tln(T)$

$\qquad -0.017726352T^2 + GHSERZR + 2GHSEROO$

* ZrO₂_t solid solution(Zss)

$^0G^{ZrO_2\_t}_{ZrO_2} = -1036480.92 - 261.13659T + 59.015088Tln(T) -$

$\qquad 17.726352*10^{-3}T^2 + GHSERZR + 2GHSEROO$

$^0G^{Zss}_{ZrO_2} = {}^0G_{TiO_2} + 35000$

$^0L^{Zss}_{ZrO_2, TiO_2} = -10000 + 15T$

$^1L^{Zss}_{ZrO_2, TiO_2} = 100000$

* Intermediate compounds

$^0G_{ZrTiO_4} = {}^0G^{ZrO_2\_m}_{ZrO_2} + {}^0G_{TiO_4} + 4959 - 12T$

$^0G_{ZrTi_2O_6} = {}^0G^{ZrO_2\_m}_{ZrO_2} + 2{}^0G_{TiO_2} - 31260 + 11T$

GHSERZR

298.15<T<2128.0

$-7827.595 + 125.64905T - 24.1618Tln(T) - 4.37791*10^{-3}T^2 + 34971T^{-1}$

2128.00<T<6000.0

$-26085.921 + 262.724183T - 42.144Tln(T) - 1342.895*10^{28}T^{-9}$

GHSEROO

298.15<T<1000.0

Table 1. Continued.

$-3480.87 - 25.503038T - 11.136Tln(T) - 0.005098888T^2 + 6.61846*10^{-7}T^3 - 38365T^{-1}$

1000.0<T<3300.0

$-6568.763 + 12.65988T - 16.8138Tln(T) - 5.95798E - 4T^2 + 6.781*10^{-9}T^3 + 262905T^{-1}$

3300.0<T<6000.0

$-13986.728 + 31.259625T - 18.9536Tln(T) - 4.25243*10^{-4}T^2 + 1.0721*10^{-8}T^3 + 4383200T^{-1}$

GZRLIQ

298.15<T<2128.0

$+18147.703 - 9.080762T + 1.6275*10^{-22}T^7 + GHSERZR$

2128.0<T<6000.0

$+17804.649 - 8.91153T + 1.343*10^{31}T^{-9} + GHSERZR$

GTIO2

298.15<T<700.0

$-966880.638 + 348.553035T - 57.02081Tln(T) - 0.020171715T^2 + 3.85969167*10^{-6}T^3 + 528343*T^{-1}$

700.0<T<2130.0

$-974253.514 + 461.204893T - 74.51871Tln(T) - 0.0013569695T^2 + 2.101665*10^{-8}T^3 + 1126927T^{-1}$

2130.0<T<4000.0

$-1022606.35 + 679.832804T - 100.416Tln(T)$

$$L_{C_1, C_2:A_1} = {}^0L_{C_1, C_2:C_4} + {}^1L_{C_1, C_2:A_1}(y_{C_1} - y_{C_2}) +$$

$$^2L_{C_1, C_2:A_1}(y_{C_1} - y_{C_2})^2 + \cdots \qquad (6)$$

where the ^1L coefficients can depend on temperature and C_t represent cations C_i and A_i anions. ^0L, ^1L and ^2L are so called regular, subregular and subsubregular solution parameters, respectively.

Gibbs free energy of $ZrTiO_4$ and $ZrTi_2O_6$ which are treated as stoichiometric compounds are given respectively as follows:

$$^0G_{ZrTiO_4} = {}^0G^{ZrO_{2\text{-}}m}_{ZrO_2} + {}^0G_{TiO_2} + 4959 - 12T \qquad (7)$$

$$^0G_{ZrTi_2O_6} = {}^0G^{ZrO_{2\text{-}}m}_{ZrO_2} + 2{}^0G_{TiO_2} - 31260 + 11T \qquad (8)$$

IV. Assessment

The assessment of the model parameters was made by means of Thermo-Calc software and database system.[18] Thermodynamic description of pure elements used in the present work is from the SGTE(Scientific Group Thermodata Europe) databank.[19] $ZrTiO_4$ and $ZrTi_2O_6$ compounds, which were reported to have the range of homogeneity, are treated as stoichiometric compounds.

The binary description of Zr-O and Ti-O systems was adopted, which has been obtained by authors in the previous work and B.-J. Lee,[20] respectively. The accuracies are changed by trial and error until most of the selected experimental information is satisfactorily described. The optimal set of parameters obtained in the current work is given in Table 1.

V. Results and Discussion

The whole ZrO_2-TiO_2 phase diagram calculated from the present set of parameters is given in Fig. 2. The calculated invariant equilibria are compared with the experimental ones in Table 2, which shows fair agreement. The high temperature peritectic reaction, Liquid+ZrO_2_c_↔Zss is a result of the present work. No reliable information about the ZrO_2-rich region above 2500 K has been reported due to the difficulties in conducting experiments at high temperatures. Several authors[7,12,13] have reported tentatively but so much different phase equilibria about this region. Since the
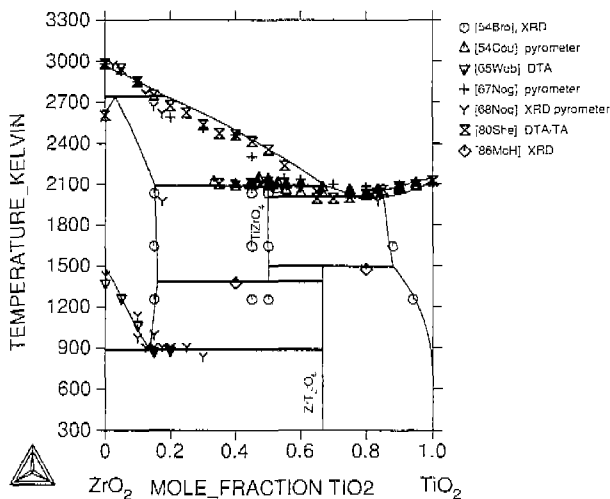

Fig. 2. Calculated phase diagrams of the ZrO_2-TiO_2 system with the experimental phase diagram data. $ZrTiO_4$ and $ZrTi_2O_6$ are treated as stoichiometric compounds.

Table 2. Comparison of Calculated and Experimental In-variant Equilibria

Reactions	Experimental	Calculated
Liq.+Zss↔$ZrTiO_4$	2093 K[9] 2103±20 K[14]	2086.5 K
Liq.↔$ZrTiO_4$+Tss	2033 K[9] 1993±20 K[14]	2005.1 K
$ZrTiO_4$+Tss↔$ZrTi_2O_6$	~1473 K[15]	1497.6 K
$ZrTiO_4$↔Zss+$ZrTi_2O_6$	~1373 K[15]	1382.2 K
Zss ZrO_2_m+$ZrTi_2O_6$	~903 K[13] 953 K[15]	887.6 K
Liq.+ZrO_2_c↔Zss		2744.3 K

low temperature eutectoid reaction, Zss↔ZrO_2_m+$ZrTi_2O_6$ is also very hard to be established experimentally because of the difficulties in achieving equilibrium at low temperatures and the occurrence of a diffusionless transition between ZrO_2_t and ZrO_2_m, there have been no agreement among reaction temperatures and compositions previously reported.[7,12,13] The field of Zss(the boundary between Zss and Zss+$ZrTiO_4$) calculated in the present work agrees with the results of F. H. Brown *et al.*,[7] A. Cocco *et al.*,[9] and T. Noguchi *et al.*[12] but have lower extent than those of L. W. Coughanour *et al.*,[8] and A. E. McHale *et al.*[14] The field of Tss calculated agree with the results of F. H. Brown *et al.*[7] The calculated liquidus curves are nearly in agreement with the experimental ones from Ref. 11-13. The range of homogeneity of intermediate compounds, $ZrTiO_4$ and $ZrTi_2O_6$, considered as stoichiometric compounds is to be calculated by thermodynamic models.

VI. Summary

The phase diagram and thermodynamic data available for the ZrO_2-TiO_2 system have been considered in the present assessment. An attempt has been made to provide the consistent set of thermodynamic parameters describing the system by coupling CALPHAD method using Thermo-Calc software and database system. The set of thermodynamic functions is for a simplified version of the ZrO_2-TiO_2 phase diagram in which $ZrTiO_4$ and $ZrTi_2O_6$ is treated as stoichiometric compounds. Comprehensive comparisons with the experimental data available are made, and it is shown that the set can satisfactorily account for most of the experimental data except for the homogeneity data of $ZrTiO_4$ and $ZrTi_2O_6$.

Acknowledgements

References

1. B. Jaffe, R. S. Roth and S. Marzullo, "Piezoelectric Properties of Lead Zirconate-Lead Titanate Solid-Solution Ceramics," *J. Appl. Phys.*, **25**, 809-810 (1954).
2. I. J. Fritz and J. D. Keck, "Pressure-Temperature Phase Diagrams for Several Modified Lead Zirconate Ceramics," *J. Phys. Chem. Solids*, **39**, 1163 (1978).
3. B. Jaffe, W. R. Cook Jr. and H. Jaffe, "Piezoelectric Ceramics, Academic Press," London-New York (1971).
4. G. Wolfram and E. Göbel, "Existence Range, Structural, and Dielectric Properties of $Zr_xTi_ySn_zO_4$ Ceramics (x+y+z= 2)," *Mater. Res. Bull.*, **16**, 1455 (1981).
5. W. Büssem, C. Schusterius and A. Ungewiss, Ber. "Ueber Roentgenographische Untersu- chungen an den Zweistoff-

systemen TiO_2-MgO, ZrO_2-MgO und ZrO_2-TiO_2(X-Ray Investigations of the binary systems TiO_2-MgO, ZrO_2-MgO, and ZrO_2-TiO_2)," *Deut. Keram. Ges.*, **18**, 433-443 (1937).

6. H. G. Sowman and A. I. Andrews, "A Study of the Phase Relations of ZrO_2-TiO_2 and ZrO_2-TiO_2-SiO_2," *J. Am. Ceram. Soc.*, **34**(10), 298-301 (1951).

7. F. H. Brown and P. Duwez, "The Zirconia-Titania System," *J. Am. Ceram. Soc.*, **37**(3), 129 132 (1954).

8. L. W. Coughanour, R. S. Roth and V. A. DeProsse, "Phase Equilibrium Relations in the Systems Lime-Titania and Zirconia-Titania," *J. Res. Natl. Bur. Std.*, **52**, 37-42 (1954).

9. A. Cocco and G. Torriano, "Relazioni Tra le Fasi allo Stato Solido nel Sistema ZrO_2-TiO_2(Relations between the Solid Phases in the System ZrO_2-TiO_2)," *Annali di Chimica (Rome)*, **55**, 153-163 (1965).

10. A. H. Webster, R. C. MacDonald and W. S. Bowman, "The System PbO-ZrO_2-TiO_2 at 1100," *J. Canad. Ceram. Soc.*, **34**, 97-102 (1965).

11. T. Noguchi and M. Mizuno, "Phase Changes in Solids Measured in s Solar Furnace, ZrO_2-TiO_2 System," *Solar Energy*, **11**(1), 56-61 (1967).

12. T. Noguchi and M. Mizuno, "Phase Changes in the ZrO_2-TiO_2 System," *Bull. Chem. Soc.(Jap.)*, **41**, 2895-2899 (1968).

13. A. V. Shevchenko, L. M. Lopato, I. M. Maister and O. S. Gorbunov, "The TiO_2-ZrO_2 System," *Russ. J. Inorg. Chem.*, **25**(9), 1379-1381 (1980).

14. A. E. McHale and R. S. Roth, "Low Temperature Phase Relationships in the System ZrO_2-TiO_2," *J. Am. Ceram. Soc.*, **69**(11), 827-832 (1986).

15. L. Kaufman and H. Bernstein(Eds.), "Computer Calculation of Phase Diagrams, Academic Press," New York and London (1970).

16. R. D. Shannon and J. A. Pask, "Kinetics of the Anatase-Rutile Transformation," *J. Am. Ceram. Soc.*, **48**(8), 391-398 (1965).

17. M. Hillert, B. Jansson, B. Sundman and J. Agren, "A Two-Sublattice Model for Molten Solutions with Different Tendency for Ionization," *Metall. Trans. A*, **16A**(2), 261-266 (1985).

18. B. Sundman, B. Jansson and J.-O. Andersson, "The Thermo-Calc Databank System," CALPHAD, **9**(2), 153-190 (1985).

19. Scientific Group Thermodata Europe, SGTE substance Database(1994).

20. B.-J. Lee, "Thermodynamic Evaluation of the Ti-O Binary System," *J. of the Kor. Inst. of Met. and Mater.*, **32**(7), 869-877 (1994).