Thermodynamic Assessment of the PbO-ZrO$_2$ System

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The thermodynamic properties and phase diagram of the PbO-ZrO$_2$ system have been critically assessed using the Thermo-Calc program. Excess Gibbs energies were expressed by Redlich-Kister polynomials for the solid phases, by the two-sublattice ionic liquid model for the liquid phase and by the compound energy model for the solid solution phase. All solid phases were treated as stoichiometric compounds

Key words : PbO, ZrO$_2$, Thermodynamic Assessment, Thermo-Calc program

I. Introduction

Accurate experimental thermodynamic information forms the basis of the CALPHAD method.[1] The current use of this method consists of evaluating a small number of thermodynamic parameters required to describe binary systems and derive the description of a ternary system from the properties of its constituent binary ones.[1-3]

Recently the thermodynamic modelling of PbO-bearing system has received considerable attention because of the difficulties in constructing PbO-based phase diagrams and evaluating thermodynamic properties by means of experimental methods, and modelling has been justified by its ability to reproduce experimental data in binary systems and to predict experimental result in ternary systems with high certainty.[4,5]

The perovskites of solid solution series PbZr$_x$Ti$_{1-x}$O$_3$ have been of considerable interest for many years for their technological application, which result from their piezoelectric, ferroelectric and pyroelectric properties.[6] Lead zirconate(PbZrO$_3$) is an end member of the technologically important lead zirconate-titanate(PZT) solid solution system. At room temperature, PbZrO$_3$, has an antiferroelectric orthorhombic perovskite structure with an antipolar arrangement along the [110] direction.[7]

Phase diagrams of PbO-ZrO$_2$ system have been published by several authors,[8,9] but the phase relationships in this system were subject to disputes. And the thermodynamic data of PbO-ZrO$_2$ system are not enough.[9-13]

The purpose of the present study is to obtain a consistent thermodynamic description of the PbO-ZrO$_2$ system at 10^5 Pa(1bar), which can be used for calculations of phase equilibria and thermodynamic properties of the PbO-ZrO$_2$-TiO$_2$(PZT) system. The phase diagrams and thermodynamic properties are recalculated and compared with experimental data.

II. Experimental Data

1. PbO

Lead monoxide(PbO) has two stable modifications: tetragonal PbO-L(litharge, red PbO, α-PbO) stable at the lower temperatures, and orthorhombic PbO-M(massicot, yellow PbO, β-PbO) stable at the higher ones.[14] The transition temperature between PbO-L and PbO-M has been studied by several authors and large differences were observed as can be seen from Table 1.[15-22]

Experimental data of the melting point of PbO-M are summarized in Table 2.[15,16,23-27] All data range between 1143-1159 K which probably cover the temperature range of the L$_3$ (liquid)+PbO-M liquids from the monotectic temperature (1143 K) to the congruent melting point of PbO-M(1159 K).

Table 1. Temperature of the PbO-L ↔ PbO-M Transformation at 1 bar

T[K]	Method	Ref.
860	optical	[9]
762	optical	[16]
803	dilatometry	[17]
763	optical	[18]
759-762	optical	[19]
816	XRD	[20]
763	HTXRD	[21]
802-825	XRD	[22]

Table 2. Melting Temperature of PbO-M

| T[K]	Ref.
1161	[23]
1150-1152	[15]
1157	[16]
1159	[24]
1170	[25]
1158	[26]
1143	[27]

2. ZrO₂

There exist in three polymorphic modifications in ZrO_2; monoclinic (m), tetragonal (t), and cubic (c) symmetry. ZrO_2(m) transforms to the tetragonal form, ZrO_2(t), at 1273 K and then to the cubic form having the fluorite-type structure at 2643 K[28] The high temperature forms cannot be retained at room temperature because these transformations are reversible.

3. PbZrO₃

The pure $PbZrO_3$ is known to exhibit three phases: an antiferroelectric, orthorhombic phase between room temperature and from 504 K, a ferroelectric, rhombohedral phase from 504 K to 507 K and a paraelectric, cubic phase above this temperature.[7] The space group of cubic $PbZrO_3$ is P_{bam}.[29] Schmahl *et al.*[13] reported a heat of formation of $PbZrO_3$ from solid PbO and ZrO_2 (monoclinic) to be +5240 $Jmol^{-1}$ based on emf measurements on a cell using CaO-ZrO_2 and PbF_2 electrolytes. Jacob *et al.*[9] reported that the differential thermal analysis(DTA) gives an endothermic peak starting around 1073 K, when an equimolar mixture of solid yellow PbO and ZrO_2(monoclinic) is heated.

The phase diagram by Fushimi and Ikeda[8] for PbO-ZrO_2 suggests the decomposition of cubic $PbZrO_3$ to tetragonal ZrO_2 and a liquid phase containing 93 mol% PbO at 1843 K. Assuming that the activity of PbO in the liquid phase obeys Raoult's law, the Gibbs energy change for the reaction[9],

$$PbO(liquid) + ZrO_2(tetragonal) \longrightarrow PbZrO_3 (cubic)$$
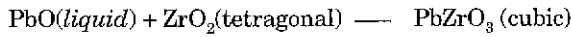
is given by

$$\Delta G^\circ(1843K) = RT\ln(a_{PbO}) = RT\ln 0.93 = -1112.0 \ J \cdot Mol^{-1} \quad (1)$$

The Gibbs energy for monoclinic-to-tetragonal transformation of ZrO_2 and of fusion of PbO at 1843 K can be estimated from the enthalpy change for these transformations[9] as

$$ZrO_2(m) = ZrO_2(t)$$
$$\Delta G^\circ = 6880 - 4.76T \ J \cdot Mol^{-1} \quad (2)$$

$$PbO-M = PbO(l)$$
$$\Delta G^\circ = 26190 - 22.58 \ T \ J \cdot Mol^{-1} \quad (3)$$

From equations (1) to (3), the standard Gibbs energy of formation of $PbZrO_3$ from solid PbO and the monoclinic form of ZrO_2 at 1843 K is obtained as -18429.6 $J \cdot Mol^{-1}$.

The XRD analysis of an equimolar mixture of PbO and ZrO_2 heated to 1223 K indicated the presence of $PbZrO_3$, PbO(ss), and ZrO_2(ss).[9] The PbO solid solution had a tetragonal structure(PbO_tss), rather than the orthorhombic structure of yellow PbO. These observations are not in accordance with the phase diagram by Fushimi and Ikeda .[8]

III. Thermodynamic Models

The liquid phase is described by the two-sublattice model

for ionic liquids.[30] The tetragonal solid-solution phase PbO_tss is described by the compound energy model. The lead monoxide and zirconium oxide and $PbZrO_3$ phases are treated as stoichiometric compounds.[31-33]

1. Liquid Phase

The two-sublattice model for an ionic liquid provides a continuous description from a metal liquid to an oxide liquid. In the ionic liquid model, cation and anions are assumed to mix in their respective sublattice. The liquid can then be represented by the formula $(Pb^{+2}, Zr^{+4})_p(O^{-2}, V_a^{-q})_q$, where p and q are the number of sites on the cation and anion sublattices, respectively, and vary with composition, to maintain electroneutrality. That sublattice will thus contain ions, denoted by a, vacancies denoted by V_a, and neutral atoms denoted by b. Hypothetical vacancies with an induced charge are introduced in the second sublattice to make the model continuous to the metal liquid. In this case, p and q are given by the equation:

$$p = 2y_{O_2} + qy_{Va} \quad (4)$$
$$q = 2y_{Pb^{+2}} + 4y_{Zr^{+4}} \quad (5)$$

where y_s is the site fraction, i.e., the fraction of the species s in a particular sublattice.

The molar Gibbs energy of the liquid is given by[31]

$$^CG_m^{\ Liq} = y_{Pb^{+2}}y_{O^{-2}}\ ^oG_{Pb^{+2}O^{-2}}^{Liq} + y_{Zr^{+4}}y_{O^{-2}}\ ^oG_{Zr^{+4}O^{-2}}^{Liq}$$
$$+q(y_{Pb^{+2}}y_{Va}\ ^oG_{Pb^{+2}O^{-2}}^{Liq} + y_{Zr^{+4}}y_{Va}\ ^oG_{Zr^{+4}Va}^{Liq})$$
$$+pRT(y_{Pb^{-2}}\ln y_{Pb^{+2}} + y_{Zr^{+4}}\ln y_{Zr^{+4}})$$
$$+qRT(y_{O^{-2}}\ln y_{O^{-2}} + y_{Va}\ln y_{Va}) + {}^EG_m^{\ Liq} \quad (6)$$

where the excess Gibbs energy, $^EG_m^{\ Liq}$, is given by

$$^EG_m^{\ Liq} = y_{Pb^{+2}}y_{O^{-2}}y_{Va}L_{Pb^{+2}O^{-2},V_a}^{Liq} + y_{Zr^{+4}}y_{O^{-2}}y_{Va}L_{Zr^{+4}O^{-2},V_a}^{Liq}$$
$$+qy_{Pb^{+2}}y_{Zr^{+4}}y_{Va}\ ^2L_{Pb^{+2},Zr^{+4}V_a}^{Liq} + y_{Pb^{+2}}y_{Zr^{+4}}y_{O^{-2}}L_{Pb^{+2},Zr^{+4}O^{-2}}^{Liq} \quad (7)$$

A comma is used to separate species on the same sublattice, and a colon is used to separate species on different sublattices. The terms $L_{Pb^{+2}O^{-2},V_a}^{Liq}$ and $L_{Zr^{+4}O^{-2},V_a}^{Liq}$ represent interactions in the binary Pb-O and Zr-O systems and were taken from Risold[5] and coworkers[34], respectively. The term $L_{Pb^{+2},Zr^{+4}O^{-2}}^{Liq}$ represents the interaction between PbO and ZrO_2, and ragular interaction parameter is estimated.[2]

2. PbO_tss Phase

As previously mentioned the PbO solid solution containing a few mole percent of ZrO_2 has a tetragonal structure rather than an orthorhombic structure of yellow PbO. The small solubility of ZrO_2 on PbO can be modeled with the compound solution model. The model is then represented by the formula $(Pb^{+2}, Zr^{+4})_p(O^{-2}, Va)_q$. The molar Gibbs energy of the PbO_tss is given by

$$G^m_{\ tss} = y_{Pb}y_O\ ^oG_{PbO} + y_{Pb}y_{Va}\ ^oG_{PbVa} + y_{Zr}y_O\ ^oG_{ZrO} + y_{Zr}y_{Va}\ ^oG_{ZrVa}$$
$$+RT(y_{Pb}\ln y_{Pb} + y_{Zr}\ln y_{Zr} + y_O\ln y_O + y_{Va}\ln y_{Va}) + {}^EG_m \quad (8)$$

The RT term comes from the entropy of mixing under the assumption of random mixing within each sublattice. The four first terms can also be justified on the assumption of

random mixing if it is assumed that all the nearest neighbors are situated on the other sublattice and furthermore, that the nearest neighbour bond energies are constant. Finally, the last term is an excess Gibbs energy which to the first approximation may depend upon the interactions between atoms in the same sublattice,

where

$$^{E}G_{m} = y_{Pb}y_{Zr}L_{Pb,Zr\ Va} + y_{Pb}y_{Zr}L_{Pb,Zr\cdot O} + y_{Pb}y_{Va}y_{O}L_{Pb\ Va,O}$$
$$+ y_{Va}y_{O}L_{Zr\ Va,O} \tag{9}$$

Here y_i denotes the site fraction of component i on the relevant sublattice. And the parameter $^{o}G_{i,O}$ is the Gibbs energy of a hypothetical state where all the interstitial sites are filled with oxygen. L parameters represent the interaction energy between components. L parameters can be expressed as a function of composition using a Redlich-Kister polynomial. Each coefficient in the polynomial may have a linear temperature dependence.[3]

3. Stoichiometric Phase

The only ternary oxide, PbZrO$_3$, is described as a stoichiometric compound. The Gibbs energy of PbZrO$_3$ is given relative to PbO, ZrO$_2$ and O$_2$(1bar):

$$G_{m}^{PbZrO3} = G_{PbO} + G_{ZrO2} - 4540 - 6.76\ T \quad J \cdot Mol^{-1} \tag{10}$$

where G_{m}^{PbZrO3} is the molar Gibbs energy of the PbZrO$_3$

phase. G$_{PbO}$ and G$_{ZrO2}$ are the Gibbs energy of PbO and ZrO$_2$ respectively. And the last two terms are the Gibbs formation energy of PbZrO$_3$.[9]

IV. Data Assessment and Parameter Optimization

Optimization of thermodynamic parameter , as well as all calculations was performed with the Thermo-Calc databank system.[3] Thermodynamic description of pure elements used in the present work is from the SGTE(Scientific Group Thermodata Europe) databank.[3-5] The binary description of Pb-O and Zr-O systems were adopted, as has been already mentioned by Risold et al.[5] and Liang et al,[34] respectively. For the stoichiometric phases PbZrO$_3$ and the two solution phases, including the ionic liquid, the parameters were tested by trial and error to see if they could fit to experimental data of the PbO-ZrO$_2$ system. The thermodynamic parameter set of the PbO-ZrO$_2$ system is listed in Table 3.

V. Results and Discussion

1. Thermodynamic Properties of PbZrO$_3$

In Fig. 1, the calculated heat capacity of PbZrO$_3$ cubic phase is compared with the estimated values.[10] The calcu-

Table 3. Thermodynamic Parameters for the PbO-ZrO$_2$ System Estimated in the Present Work

IONIC_LIQ	
$(Pb^{+2})_p(O^{-2},V_a^{-q})_q$	$G^{Liq}Pb^{+2}, O^{-2} = 2G^{Liq}{}_{PbO} = -438420 + 720T - 130TLn(T)$
	$^{o}L^{Liq}Pb^{-2}, O^{-2}, V_a = 168750 - 61T$
	$^{1}L^{Liq}Pb^{-2}, O^{-2}, V_{a} = 29510 - 20T$
$(Zr^{+4})_p(O^{-2},V_a^{-q})_q$	$G^{Liq}Zr^{+4}, O^{-2} = -1931250.3 + 272.52T + 2G^{Liq}{}_{Zr} + 4GHSEROO^{1)}$
	$^{o}L^{Liq}Zr^{+4}, O^{-2}, Va = 75000$
	$^{1}L^{Liq}Zr^{+4}, O^{-2}, Va = -80000$
	$^{1}LiqZr^{+4}, O^{-2}, O + 50000$
$(Pb^{+2},Zr^{+4})_p(O^{-2},V_a^{-q})_q$	$L^{Liq}Pb^{+2}, Zr^{+4}, O^{-2} - 30000 + 20T$
PbO_tss	
$(Pb_{+2},Zr_{+4})(O^{-2},Va)$	$G(PbO\_tss, PbO;0) = -235043 + 250.4T - 46.2TLn(T) - 0.008T2 - 225000T^{-1}$
	$G(PbO\_tss, ZrO_2;0) = -1143377 + 247.6T - 8.076TLn(T)$
	$L(PbO\_tss, PbO, ZrO_2;0) = -30000$ (estimated)
PbZrO$_3$_CUB	
	$G(PbZrO_3\_CUB, Pb:Zr:O;0) = GPbOYEL^{3)} + GZrO_2\_MONO^{2)} - 4540 - 6.76T$

1) GHSEROO
     $298.15 < T < 1000 - 3490.87 - 25.50T - 11.136TLn(T) - 0.0051T^2 + 6.62X10^{-7}T^3 - 38365T^{-1}$
     $1000 < T < 3300 - 6568.76 + 12.66T - 16.81TLn(T) - 5.96X10^{-4}T^2 + 6.78X10^{-9}T^3 + 262905T^{-1}$
     $3300 < T < 6000 - 3986.7 + 31.26T - 18.95TLn(T) - 4.25X10^{-4}T^2 - 1.07X10^{-8}T^3 + 4383200T^{-1}$

2) GZrO$_2$_MONO
     $298.15 < T < 6000 - 1103376.9 + 247.58T - 8.07TLn(T) + GHSERZr^{4)} + 2GHSEROO^{1)}$

3) GPbOYEL
     $298.15 < T < 3000 - 232910 + 244.7T - 45.9TLn(T) - 0.0067T^2 + 178000T^{-1}$

4) GHSERZr
     $298.15 < T < 2128 - 7827.6 + 595.125T - 24.16TLOG(T) - 4.3779X10^{-3}T^2 + 34971T^{-1}$
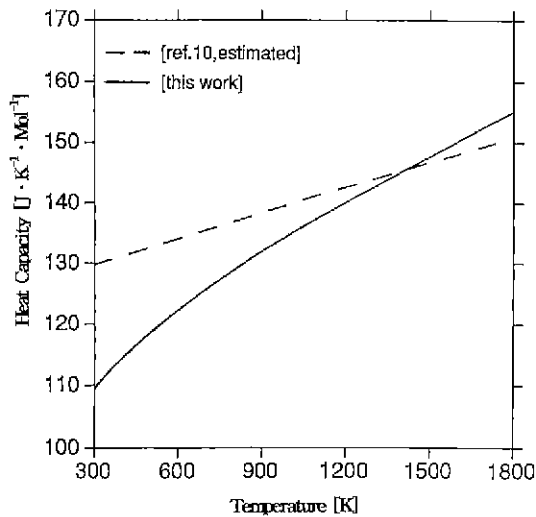 $2128 < T < 6000 - 26085.9 + 262.7T - 42.144TLOG(T) - 1342.9X1028T^{-9}$

Fig. 1. Comparison of the calculated with estimated[10] heat capacities of $PbZrO_3$.
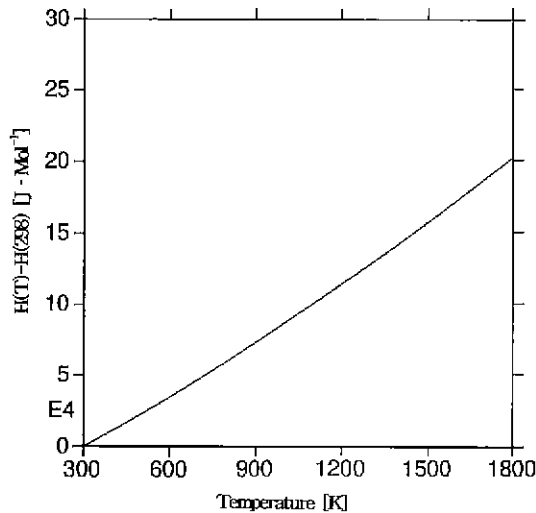
Fig. 2. Calculated enthalpy increment of $PbZrO_3$.

Fig. 3. Calculated entropy of $PbZrO_3$.

Fig. 4. Comparison of the calculated with experimented[10,11,13] temperature dependence of PbO pressures over $PbZrO_3$.

Fig. 5. Calculated PbO-ZrO_2 phase diagram with the experimental phase diagram data.[8]

lated value is lower than estimated values at below 1400 K, but higher above 1400 K. We deduced the heat capacity of $PbZrO_3$ as follows;

$$C_p(PbZrO_3\text{-Cub})$$
$$=110.6+2.5\times10^{-2}\,T-7.8\times10^5T^{-2}\,\text{J}\cdot\text{K}^{-1}\cdot\text{Mol}^{-1} \qquad (11)$$

The calculated molar enthalpy and entropy for $PbZrO_3$ are presented in Fig. 2 and Fig. 3, respectively. Since the heat content and entropy of $PbZrO_3$ are not known, we are not able to compare the present work with experimental values.

In Fig. 4, the calculated PbO pressure with temperature is compared with the several experimental data. All of the experimental data can be reproduced by the calculation.

2. Phase Diagram of PbO-ZrO₂ System

Calculated phase diagram of the PbO-ZrO_2 system is shown in Fig. 5. Here, the experimental data by Fushimi *et al* are also included.[8] In our assessed phase diagram of
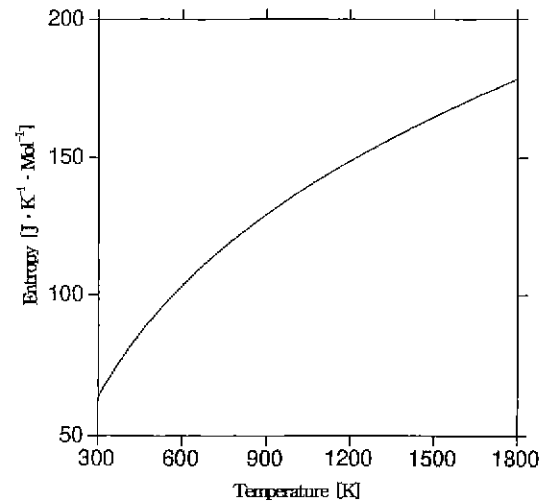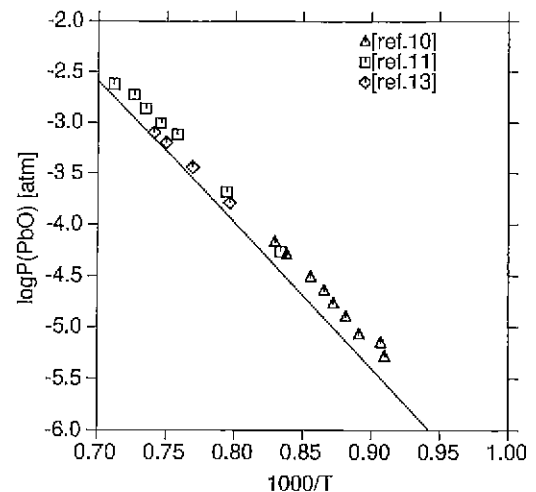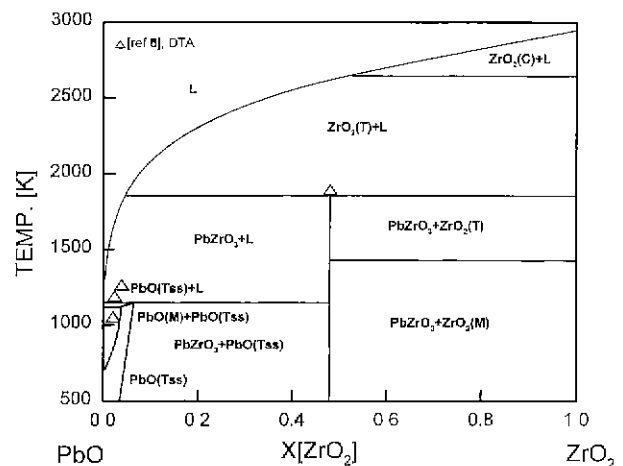
PbO-ZrO_2 system, $PbZrO_3$ melts incongruently at 1811 K. This incongruent melting point is lower than the experi-

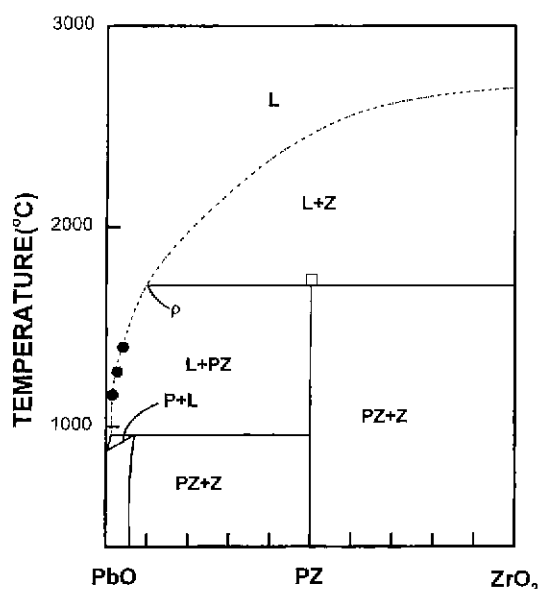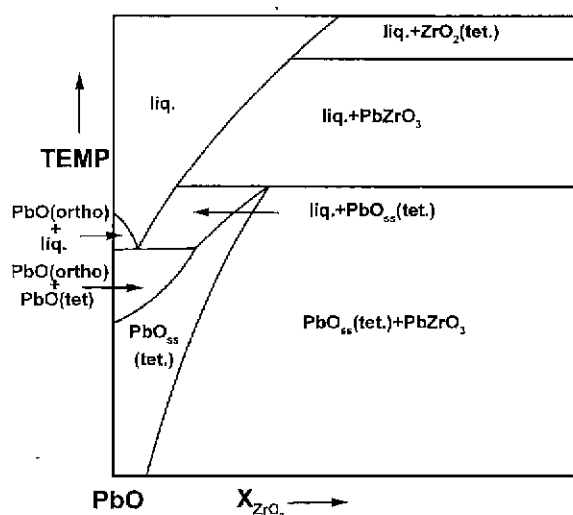**Fig. 6.** PbO-ZrO$_2$ phase diagram of Fushima and Ikeda.[8]

Fig. 7. Schematic phase diagram for PbO-rich side of the PbO-ZrO$_2$ system.[11]

mental one (1843K), but the difference is very small.

In the PbO-rich side of the phase diagram, there are some differences from experimental information (Fig.6), but it is very similar to the estimated phase diagram(Fig.7) except for the orthorhombic solid solution phase.

VI. Conclusion

Thermodynamic properties and the phase diagram of the PbO-ZrO$_2$ system have been critically assessed using the Thermo-Calc program. The heat capacity of PbZrO$_3$ was estimated to be $110.6+2.5 \times 10^{-2}\ T - 7.8 \times 10^5 T^{-2}$ J · Mol^{-1} · K^{-1}. Experimental data on PbO vapor pressure with temperature are reasonably well reproducible. The incongruent melting temperature of PbZrO$_3$ was estimated to be 1811

K. In the PbO-rich side, the tetragonal phase PbO solid solution appeared , but the phase equiliblia at high PbO contents were determined not accurately enough.

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