On the thermodynamic aspect of zinc oxide polymorphism: calorimetric study of metastable rock salt ZnO

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The enthalpies of dissolution of metastable rock salt (rs-ZnO) and thermodynamically stable wurtzite (w-ZnO) polymorphs of zinc oxide in aqueous H2SO4 have been measured in direct calorimetric experiments at 303 K and 0.1 MPa. Based on the obtained results, the standard enthalpy of the rs-ZnO to w-ZnO phase transition, \( \Delta H = 11.7 \pm 0.3 \) kJ mol\(^{-1}\), has been determined.

Since the discovery\(^1\) of high-pressure polymorph of zinc oxide, \( rs-ZnO \), its synthesis and properties have been intensively studied.\(^2\)–\(^14\) The most of these studies were conducted in situ at high pressure due to the problems of \( rs-ZnO \) recovery under ambient conditions.

Recently, an attempt has been made\(^2\) to extract the thermodynamic data of \( rs-ZnO \) from available ab initio simulations and experimental data on the pressure-induced phase transition of \( w-ZnO \) to \( rs-ZnO \). However, neglecting the strongly pronounced kinetic features of this transition below 1000 K\(^3\) rendered these data ambiguous.\(^3\) As a result, a completely incorrect set of thermodynamic functions of \( rs-ZnO \) still prevails in the literature.

Recently, it was found that single-phase \( rs-ZnO \) synthesized at 7.7 GPa and 800 K could be completely recovered in the form of macroscopic (> 100 mm\(^3\)) bulks under normal conditions.\(^15\) At ambient pressure, these bulks are kinetically stable up to 370 K, which allows the direct measuring of thermochanical properties of metastable \( rs-ZnO \) to be performed by conventional calorimetry. In the present work, enthalpies of dissolution of two ZnO polymorphs in aqueous H2SO4 were measured by solution calorimetry under ambient conditions.

The following reactions occur in the calorimetric vessel at 302.75 K after piercing the membrane between the two cells and mixing the components:

\[
\begin{align*}
rs-ZnO \text{ (nanocrystalline)} + H_2SO_4 \text{ (aq.)} & \rightarrow Zn^{2+} + SO_4^{2-} + H_2O \text{ (solution)} + \Delta H_1 \\
\end{align*}
\]
\[\text{(1)}\]

\[
\begin{align*}
w-ZnO \text{ (nanocrystalline)} + H_2SO_4 \text{ (aq.)} & \rightarrow Zn^{2+} + SO_4^{2-} + H_2O \text{ (solution)} + \Delta H_2 \\
\end{align*}
\]
\[\text{(2)}\]

Experimental heat flow curves of dissolution of nanocrystalline \( rs-ZnO \) and \( w-ZnO \) bulks\(^3\) are shown in Figure 1. The enthalpy values measured in calorimetric runs are \( \Delta H_1 \) and \( \Delta H_2 \) (see Table 1). In both cases, the final state is the same, \( i.e. ZnSO_4 \) solution in aqueous H2SO4. Since the real structure and impurity content for both \( rs-ZnO \) and \( w-ZnO \) samples are almost the same, one can conclude that the \( \Delta H_1 - \Delta H_2 \) value corresponds to the enthalpy of phase transition between two ZnO polymorphs, \( i.e. \) to the \( rs-ZnO \) to \( w-ZnO \) transition enthalpy \( \Delta H \) at 302.75 K.

The \( \Delta H^0 \) value of \( \pm 11.7 \pm 0.3 \) kJ mol\(^{-1}\) determined by solution calorimetry also may include some strain energy that is usual for bulk samples quenched from high pressure–high temperature conditions. However, this contribution should not exceed \( \pm 0.1 \) kJ mol\(^{-1}\).

Table 1 Calorimetric data on the dissolution of nanocrystalline ZnO bulks in 2 N aq. H2SO4 at 302.75 K.

<table>
<thead>
<tr>
<th>Run</th>
<th>m/mg</th>
<th>( \Delta H_1/\text{J g}^{-1} )</th>
<th>m/mg</th>
<th>( \Delta H_2/\text{J g}^{-1} )</th>
<th>( \Delta H/\text{kJ mol}^{-1} )</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>19.64</td>
<td>-1291.6</td>
<td>15.76</td>
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</tr>
<tr>
<td>2</td>
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<td>-1320.5</td>
<td>6.55</td>
<td>-1184.4</td>
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<tr>
<td>3</td>
<td>2.58</td>
<td>-1325.6</td>
<td>4.17</td>
<td>-1171.8</td>
<td>-12.5</td>
</tr>
</tbody>
</table>

Figure 1 Heat flow curves of dissolution of nanocrystalline zinc oxide in 2 N aq. H2SO4 (see Table 1, run 2): (1) bulk \( rs-ZnO \) and (2) bulk \( w-ZnO \).

1 Single-phase nanocrystalline bulk \( rs-ZnO \) was synthesized from \( w-ZnO \) nanopowder at 7.7 GPa and 800 K with subsequent rapid quenching. The details of high-pressure synthesis and characterization of recovered samples were described elsewhere.\(^16\) Nanocrystalline bulk \( w-ZnO \) to be used as a reference sample was produced by a reverse phase transition of nanocrystalline bulk \( rs-ZnO \) as a result of heating from 300 to 523 K with heating rate of 1 K min\(^{-1}\) with DSC monitoring of the transition. This approach was used to eliminate possible influence of grain size and surface contribution on heat effects as the ‘secondary’ bulk \( w-ZnO \) should inherit the whole prehistory of starting \( rs-ZnO \), except for crystal structure. Phase purity of the samples was confirmed by powder X-ray diffraction.
enthalpy.‡ Work gave very close values for the transition enthalpy of 12.0 \pm 0.2 kJ mol\(^{-1}\) for \(P_{tr}\) of 9.6 GPa, which is in excellent agreement with the corresponding value from our isothermal experiments.

Thus, two independent calorimetric techniques used in the present work gave very close values for the \(rs\)-ZnO to \(w\)-ZnO transition enthalpy.\(^\ddagger\)

Earlier,\(^2\) the key thermodynamic value, \(\Delta_m G^0 = 23.12 \text{ kJ mol}^{-1}\), corresponding to the \(w\)-ZnO to \(rs\)-ZnO phase transition at 0.1 MPa and 298.15 K, was estimated exclusively from one of the most questionable values, the room-temperature equilibrium transition pressure, \(P_{tr}\). The choice of \(P_{tr} = 9.6 \text{ GPa}\) based on averaging value of ab initio estimations (that vary from 7.5 GPa\(^2\) to 12.7 GPa\(^3\)) and one randomly chosen value of the onset pressure of kinetically hindered phase transition at 300 K (that also varies from 7.5 GPa\(^2\) to 10.0 GPa\(^4\)). All this leads to completely wrong equilibrium \(P-T\) line in the high pressure–high temperature region, where the transition is governed by thermodynamics, and equilibrium experimental data are available.\(^6,7\)

The standard enthalpy of the \(w\)-ZnO to \(rs\)-ZnO phase transition, \(\Delta_h H^0(298.15 \text{ K}) = 11.7 \pm 0.3 \text{ kJ mol}^{-1}\), derived from our experimental results is two times lower than the ‘recommended’ value, \(\Delta_h H^0(298.15 \text{ K}) = 23.93 \pm 3.11 \text{ kJ mol}^{-1}\) (see ref. 2) under unfounded suggestion that \(P_{tr}\) ≈ 9.6 GPa. Indeed, it is known that \(w\)-ZnO starts to transform into \(rs\)-ZnO already at pressures above 5 GPa.\(^6,8\) At room temperature, this transition is very sluggish due to the existence of a strong kinetic barrier, which hinders the nucleation of a new phase.\(^8\) The transition pressure depends on temperature and shows a substantial (from 9 to 2 GPa at room temperature) hysteresis.\(^5,9\) The hysteresis loop decreases as the temperature rises, and above 1000 K the branches of direct and reverse transitions merge at pressure of about 5.8 GPa, which can be considered as the equilibrium pressure of this phase transition. Based on more reasonable choice of the transition pressure at 300 K, \(i.e. P_{tr} \approx 5.8 \text{ GPa}\), the \(\Delta_h H^0\) value should be about 14 kJ mol\(^{-1}\), which is in agreement with the experimental value of transition enthalpy found in the present work.

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References


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Footnotes

\(^\ddagger\) A Calvet calorimeter (SETARAM C80) operated in isothermal and linear scanning modes was used. Heat flow calibration of the instrument was done using the EJ3 calorimeter unit and Joule effect calorimetry cells (SETARAM S60/1434) and checked with the melting enthalpy of indium. Isothermal experiments were performed at 302.75 K in 2-cell calorimetric vessels made of stainless steel with Teflon membranes. Mixing was performed by reversing the calorimetric block, 2 N \(aq\) H\(_2\)SO\(_4\) was prepared from 95% H\(_2\)SO\(_4\) and deionized water. Initial and final concentrations of H\(_2\)SO\(_4\) were checked by DMA 35 from Anton Paar density meter. Bulk ZnO (from 3 to 20 mg, with \(\pm 0.01 \text{ mg}\) accuracy, see Table 1) was dissolved in 2.0 ml (with \(\pm 0.1 \text{ mg}\) weight monitoring) of 2 N \(aq\) H\(_2\)SO\(_4\) under strictly isothermal conditions (\(\pm 0.01 \text{ K}\)), and the heat production rate was measured. The experimental data were processed using Calisto (AKTS AG) and TDPro (CISP Ltd) software packages.