

Thermal analysis of LaAlO₃ and Y₂O₃ melting

Sergey V. Ushakov and Alexandra Navrotsky

Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California at Davis, CA 95616

Fusion enthalpies (ΔH_{fus}) have not been measured previously for any rare earth aluminates. The importance of knowing ΔH_{fus} for key compounds stems from the fact that fusion enthalpy and melting temperature gives the value for fusion entropy ($\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_m(\text{K})$). Since melting temperatures are usually known, common method to assess missing thermodynamic values is to assign identical entropy of fusion to isostructural compounds and calculate unknown ΔH_{fus} as $\Delta S_{\text{fus}} \cdot T_m$. With calculations of phase diagrams (CALPHAD) methods used widely, the errors from estimates of missing data for key compounds are propagating through the literature. First principles calculations would benefit from well-established experimental benchmarks of fusion enthalpies as well.

The fusion enthalpy of LaAlO₃ was measured with a Setaram Setsys 2400 differential thermal analyzer (DTA) using melting of Al₂O₃ ($T_m = 2054$ °C, $\Delta H_{\text{fus}} = 1092$ J/g) for temperature and sensitivity calibration. The instrument was modified to reach 2500 °C and to allow sample temperature monitoring with a spectropyrometer.¹ The samples and standards were pre-melted with a CO₂ laser and arc-sealed in tungsten crucibles under Ar atmosphere. The configuration of thermal analyzer and welding chamber were described earlier.^{2,3} To avoid previously observed large variations in sensitivity and temperature calibration in successive experiments, the new DTA sensor was heated to above 2400 °C before the measurements. Samples were heated and cooled at 10 °C/min with 20 ml/min Ar flow through the sample chamber to a temperature 50-200 °C above melting. Only data on heating were used for calculation of sensor sensitivity, LaAlO₃ fusion enthalpy and melting temperatures. The integration of endothermic peaks of heat flow signal was performed using a linear baseline after slope correction. The absence of reaction with the crucible was confirmed by microprobe analysis on the cross section of the crucibles after measurements.

In our previous work² on La₂O₃, enthalpy of fusion was calculated as average from heat effects on melting and on crystallization. In the case of LaAlO₃ we found this approach not feasible. We used the same heating and cooling rates (10 °C/min) as for La₂O₃, however, the degree of undercooling in LaAlO₃ is drastically different. ~20 °C undercooling was typically observed² for La₂O₃, however for LaAlO₃ 400 to 600 °C undercooling was typical. In the same conditions, Al₂O₃ melt typically crystallized 100 to 200 °C below the melting temperature. With such undercooling, crystallization of LaAlO₃ produced a peak in heat flow signal apparently ~10 times higher in magnitude than on heating, noticeably affecting sample temperature trace as measured by thermocouple located between sample and reference crucible. This feedback rendered it impossible to quantify the heat effect on cooling. Thus, the value for ΔH_{fus} of LaAlO₃ was calculated only from data on heating in 11 experiments.

We confirmed that for W/WRe sensor and W crucibles, a change in heating rate from 10 to 50 °C/min did not change sensitivity calibration within experimental

uncertainty. Sensitivity of the DTA sensor decreases with temperature, as expected due to increase in heat transfer by radiation. Temperature dependence of sensitivity is close to linear in the 1064 – 2054 °C range, however, it is probably not valid to extrapolate this trend to higher temperature as the calibration factor is affected by changes in heat transfer from crucibles to the sensor plate at high temperature, and to changes in mechanical thermocouple contacts with sensor plate.

An attempt has been made to use value the 84 kJ/mol for fusion enthalpy of Y₂O₃ reported by Shpilrain⁴ to extend sensitivity calibration to 2439 °C. However, our measurements of enthalpy of fusion on two Y₂O₃ samples in sealed crucibles gave values of 130 - 150 kJ/mol using Al₂O₃ fusion enthalpy for calibration. If Shpilrain's⁴ value is correct that would indicate significant increase of DTA sensor sensitivity with temperature which is unlikely. Thus, we conclude that fusion enthalpy of Y₂O₃ is higher than previously reported. This partially resolves the apparent "melting entropy deficit" in Y₂O₃ as stated by Zinkevich⁵ when comparing Shpilrain's⁴ measurements to estimations from volume change on melting. However, this also means that melting of Y₂O₃ cannot be used for sensitivity calibration in DTA until its fusion enthalpy will be measured accurately by drop calorimetry or other method. Since melting temperature of LaAlO₃ is only ~80 °C higher than Al₂O₃ and in the absence of reliable enthalpy standards for higher temperature, we rely exclusively on ΔH_{fus} Al₂O₃ value and assign the uncertainty ± 10 kJ/mol to our measurements of fusion enthalpy of LaAlO₃.

We demonstrated capability of thermal analysis to provide essential thermochemical data on fusion enthalpies and melting temperatures above 2000 °C. The main limitation in accuracy of obtained values for LaAlO₃ ($T_m = 2134 \pm 10$ °C, $\Delta H_{\text{fus}} = 124 \pm 10$ kJ/mol) is from uncertainties in values of T_m and ΔH_{fus} of Al₂O₃ used for calibration and absence of enthalpy standards above 2054 °C. Previously reported fusion enthalpy of Y₂O₃ at 2439 °C is underestimated. Measurement of Y₂O₃ ΔH_{fus} by independent method is necessary both for providing standard for calibration of ultra-high temperature DTA instruments and for reevaluating datasets for calculations of phase diagrams.

References

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