Measurements of fusion enthalpies by drop calorimetry of laser heated levitated samples

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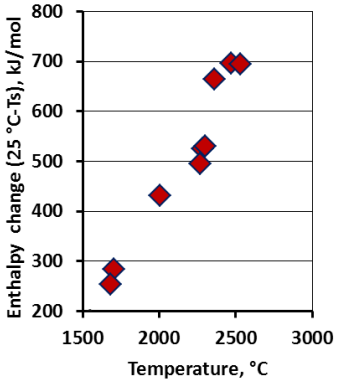
The paucity of experimental data on fusion enthalpies of refractory oxides, such as ZrO_2, HfO_2 and rare earth oxides, hampers accurate calculations of phase diagrams for systems with these components. We developed a new experimental approach to enable these measurements in variable atmosphere. The instrument, which we call a drop-and-catch calorimeter, consists of an aerodynamic levitator with splittable nozzle and catch plates with semiconductor thermopiles. Powder is laser melted into spheroid samples and levitated in a gas stream while being heated with 10.6 μm 400W CO_2 laser. Temperature of the sample surface is measured by spectropyrometer [2]. When the desired temperature is reached, the nozzle is split, sample dropped and caught by catch plates. The heat effect on sample cooling to 25 °C is obtained from the integral value of the peak in thermopile voltage vs. time.



The figure shows drop enthalpies on four Y_2O_3 samples 30-40 mg in weight.

The step at 2400 °C gives the integral value of fusion enthalpy and premeling phase transition in Y_2O_3 (L-C transition) as ~170 kJ/mol. This value is significantly higher than previously assumed (109 kJ/mol) [1]. Although reliable measurements of high temperature heat content values by this method would require emissivity measurements and thermal gradient evaluation, it has the potential to provide reasonable accuracy for measurements of fusion enthalpies of refractory oxides in air, previously experimentally inaccessible.

Possible applications of aerodynamic levitation with laser heating for study of H_2O and CO_2 dissolution in silicate melts will be discussed.

[1] M. Zinkevich, *Prog. Mater Sci.*, **52** [4] 597, 2007 [2] R.A. Felice, *AIP Conference Proc.* **684** [2],711, 2003