SCIENTIFIC TEST REPORT

Completed by:

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Abstract

Three samples of $Cu(OH)_2$ and $FeBr_2$ mixtures, and two samples of FeOOH were tested using DSC here at UIUC. Samples were measured and mixed here on-site and tested in the university DSC lab. Indium calibrations were included in the test series to calibrate the instrument response. $Cu(OH)_2$/$FeBr_2$ samples yielded 101, 143, and 148 J/g irreversible exothermic peaks around 150 °C. FeOOH samples yielded 135 and 125 J/g exothermic peaks near 265 °C. All measured values are far more exothermic than the predicted thermochemistry.

Instrument Information

The instrument used was the Perkin Elmer Diamond DSC pictured below. This is the same system as used previously. The software used for instrument control was Pyris. The system had the following specifications:

- DSC Type: Power-compensation temperature null principle. Measures temperature and energy directly, rather than differential temperature (DT).

- DSC Cell: Independent dual furnaces constructed of platinum-iridium alloy with independent platinum resistance heaters and temperature sensors with furnace mass less than 1g.

  Temperature Sensor: Distributed, Platinum Resistance Thermometers for best linearity.

- Temperature Range: -70 ℃ to 730 ℃

- Calorimetry Accuracy / Precision: < +/- 1% / < +/- 0.1%

- Scanning Rates Heating/Cooling: 0.01 ℃ to 500 ℃/min

Testing Conditions
For all tests, the conditions were as follows:

<div align="center">

Equilibrate at 30 °C for 15 minutes
Heat to the peak temperature at 10 °C/min
Cool back to 30 °C at 10 °C/min
Equilibrate at 30 °C for 10 minutes.

</div>

Peak temperatures were as follows: Indium calibrations: 280 °C, $Cu(OH)_2$/$FeBr_2$: 300 °C, FeOOH: 400 °C.

The tests used gold plated, pressure sealed crucibles from Perkin Elmer, prepared according to the instructions provided by the manufacturer. The only material in contact with the samples was gold.

The experiments were conducted in two stages, with a four test series followed by a three test series.   Each test had a separate indium calibration. Conditions for the test series are as follows:

Series 1:
Indium calibration: 7.3 mg
$Cu(OH)_2$:$FeBr_2$: 6.0 mg
$Cu(OH)_2$:$FeBr_2$: 10.2 mg
FeOOH: 11.6 mg

$Cu(OH)_2$:$FeBr_2$ samples were extracted from larger, hand-mixed mixture of mass ratio 1:2.36.

Series 2:
Indium calibration: 9.3 mg
$Cu(OH)_2$:$FeBr_2$: 12.0 mg
FeOOH: 9.9 mg

$Cu(OH)_2$:$FeBr_2$ sample was extracted from larger hand-mixed mixture of mass ratio 1:2.37.

Results
Results are shown in the appended plots. Indium calibrations were fairly straightforward and showed the expected peaks on heating and cooling. These peaks were used to extract the system constant. The linear background assumption was typically sufficient for these tests.

$Cu(OH)_2$:$FeBr_2$ mixtures showed a sharp exotherm at around 150 °C, with a shoulder at around 135 °C, and another shoulder or separate peak at 170 °C. These tests were typically processed with a quadratic fit, which was performed separately on first and second peaks in cases where the two peaks were resolved. This approach to background is conservative (i.e. yields a weaker exotherm than a linear approximation). All exothermic features were irreversible and did not appear in the cooling traces.   The results for these tests were as follows:

Series	Sample Mass(mg)	Mass Ratio	Heat Release (J/g)
1	6.0	2.36	101
1	10.2	2.36	143
2	12.0	2.37	148

FeOOH samples showed a single, broad, cleanly resolved, irreversible exotherm at 260 °C in both test series. Sample masses of 11.6 and 9.9 mg yielded 135 and 125 J/g heat release.

Analysis:

BLP provided the calculations shown below for the theoretical energy output from these systems.

Table A. Theoretical calculation for maximum energy release from thermal decomposition of FeOOH.

DSC-Perkin Elmer: 101413JH1 (sample 1), FeOOH + Ar					ΔE, J/g	Excess energy, J/g	Energy Gain
Reactant	FeOOH						
quantity, mg	6.30				-158.46	-106.77	3.07
quantity, mmol	0.0708						
	Assumed Reaction I	Energy, kJ/reaction	FeOOH consumed, mmol	FeOOH left, mmol		Energy out, J	theoretical energy, J/g
2FeOOH = Fe2O3 +H2O		-9.20	0.0708	0.0000		-0.33	-51.69

Table B. Theoretical calculation for maximum energy release from chemical reaction of Cu(OH)2 + FeBr2.

DSC-Perkin Elmer: 101413JH2 (sample 2), , Cu(OH)2 + FeBr2										ΔE, J/g	Excess energy, J/g	Energy Gain
Reactant	FeBr2.	Cu(OH)2										
quantity, mg	5.70	2.40								-243.79	-180.52	3.85
quantity, mmol	0.0264	0.0246										
HOF, dH (KJ/mol)	-249.80	-450.00										
Product	Fe(OH)2	CuBr2	Fe2O3	FeBr2.2H2O	CuBr	Cu2O	FeO	H2O	HBr (g)			
HOF, dH (KJ/mol)	-574.00	-141.80	-822.20	-861.40	-104.60	-168.60	-272.00	-285.80	-36.30			
Assumed Reaction I		Energy, kJ/reaction	FeBr2 used, mmol	Cu(OH)2 used, mmol			Cu(OH)2 left, mmol	FeBr2 left, mmol		Energy out, J	theoretical energy, J/g	
Cu(OH)2 + FeBr2 = Fe(OH)2 + CuBr2		-16.00	0.0246	0.0246			0.0000	0.0018		-0.39	-48.62	
10Cu(OH)2+9FeBr2 = 2Fe2O3+5FeBr2.2H2O+8CuBr+Cu2O+3/2 O2		-208.20	0.0222	0.0246			0.0000	0.0043		-0.51	-63.27	
3Cu(OH)2 + 3FeBr2 = Fe2O3 + FeO + 3CuBr + 2H2O + 2HBr + 1/2 Br2		47.40	0.0246	0.0246						0.39		

The calculations for FeOOH are probably too exothermic. Following reference [1], most pathways of decomposition of either FeOOH phase to most phases of Fe_2O_3 and water are endothermic. Indeed two previous studies on DSC of γ-FeOOH showed endotherms at around 260 °C, where we observe exotherms [2,3]. This is quite peculiar. Our results differ significantly from previous published work.

For the copper hydroxide/iron bromide mixture, the analysis seems reasonable, and the experiments are far in excess of any reasonable product pathway for species with known thermodynamic data. There is some uncertainty in the hydrate heats of formation, and other

possible species may exist. In addition, a botallackite-type product (with Br instead of Cl) may be present, though I have been unable to find thermochemistry (heat of formation) for such a product, though other studies of $Cu_2(OH)_3Br$ are presented in the literature.   Still, one would have to find an exothermic pathway far more energetic than the proposed pathways in order to account for the DSC results.

References

[1] Yannick Cudennec, André Lecerf, "Topotactic transformations of goethite and lepidocrocite into hematite and maghemite, Solid State Sciences 7 (2005) 520–529.

[2] A. R. Dinesen, C. T. Pedersen and C. Bender Koch, "The thermal conversion of lepidocrocite (γ-FEOOH) revisited," Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 1303-1310

[3] Rosario Gomez-Villacieros, Lourdes Hernan, Julian Morales, And Jose L. Tirado, "Textural Evolution of Synthetic γ-FeOOH during Thermal Treatment by Differential Scanning Calorimetry," Journal of Colloid and Interface Science, Vol. 101, No. 2, October 1984, 392.

FeBr$_2$ + Cu(OH)$_2$, 2.36:1 mass ratio, 6.0 mg total mass

92.9 J/g (First peak)
7.9 J/g (Second peak)
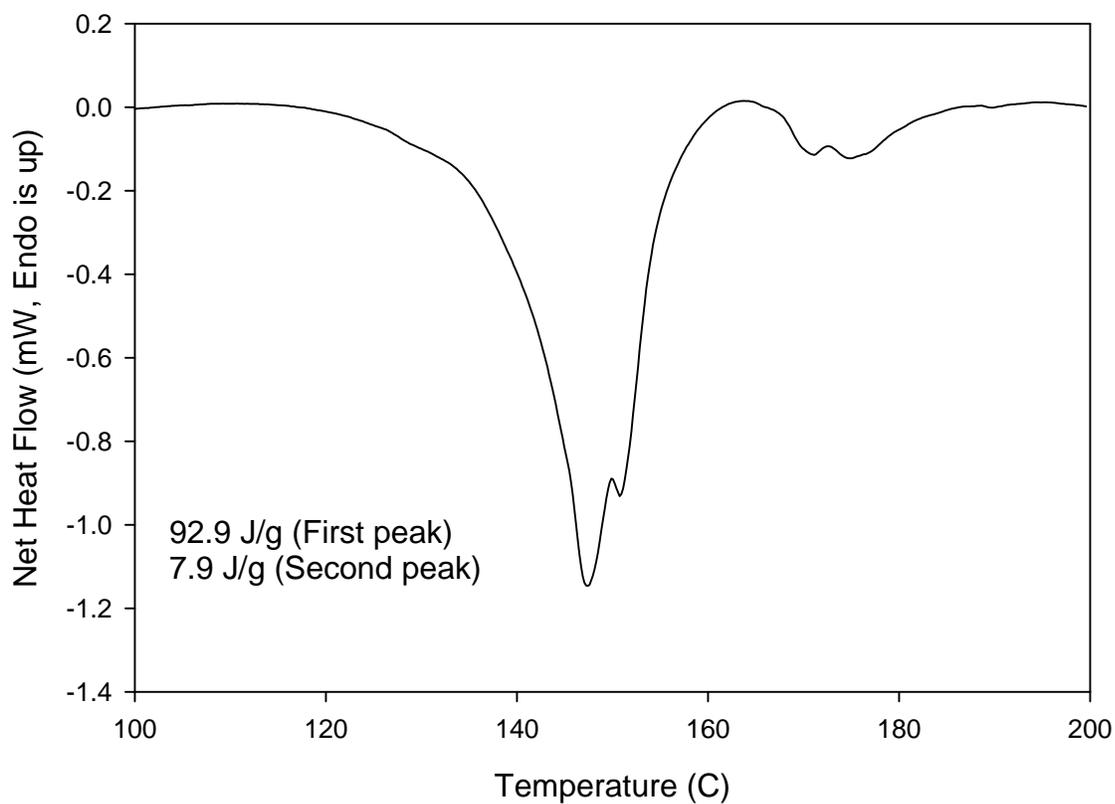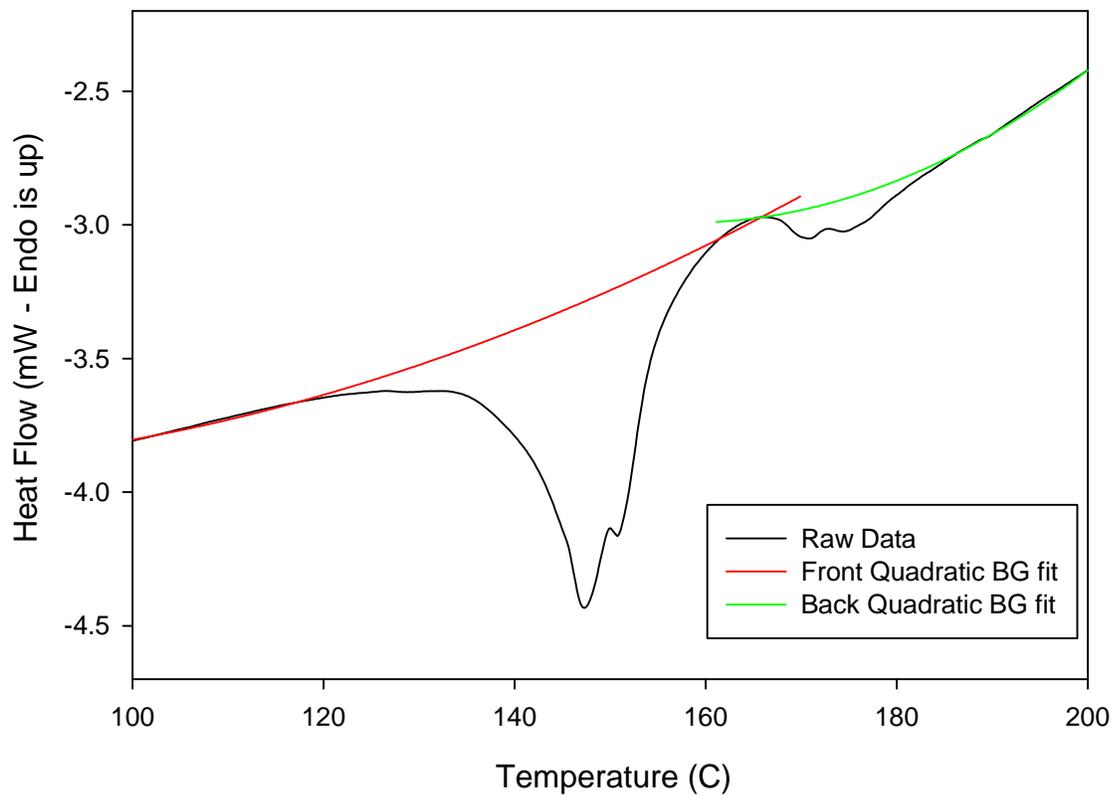
FeBr$_2$ + Cu(OH)$_2$, 2.36:1 by mass, 10.2 mg total

134.9 J/g (First peak)
18.1 J/g (Second peak)
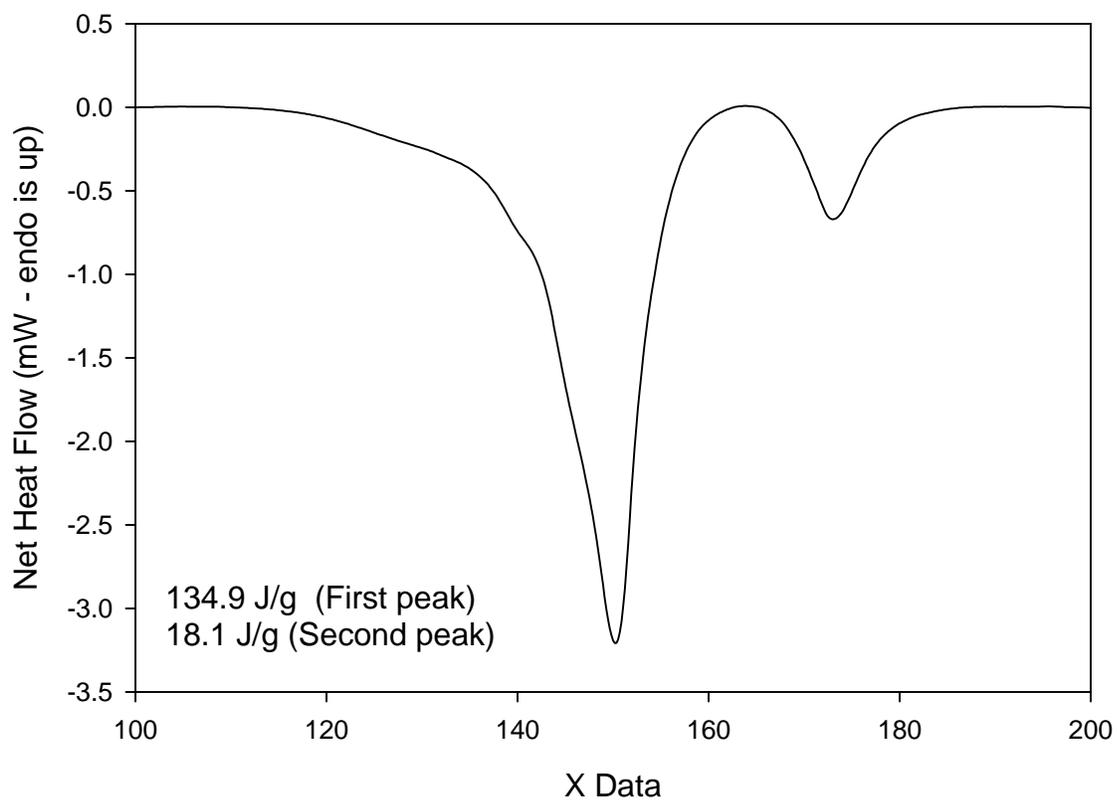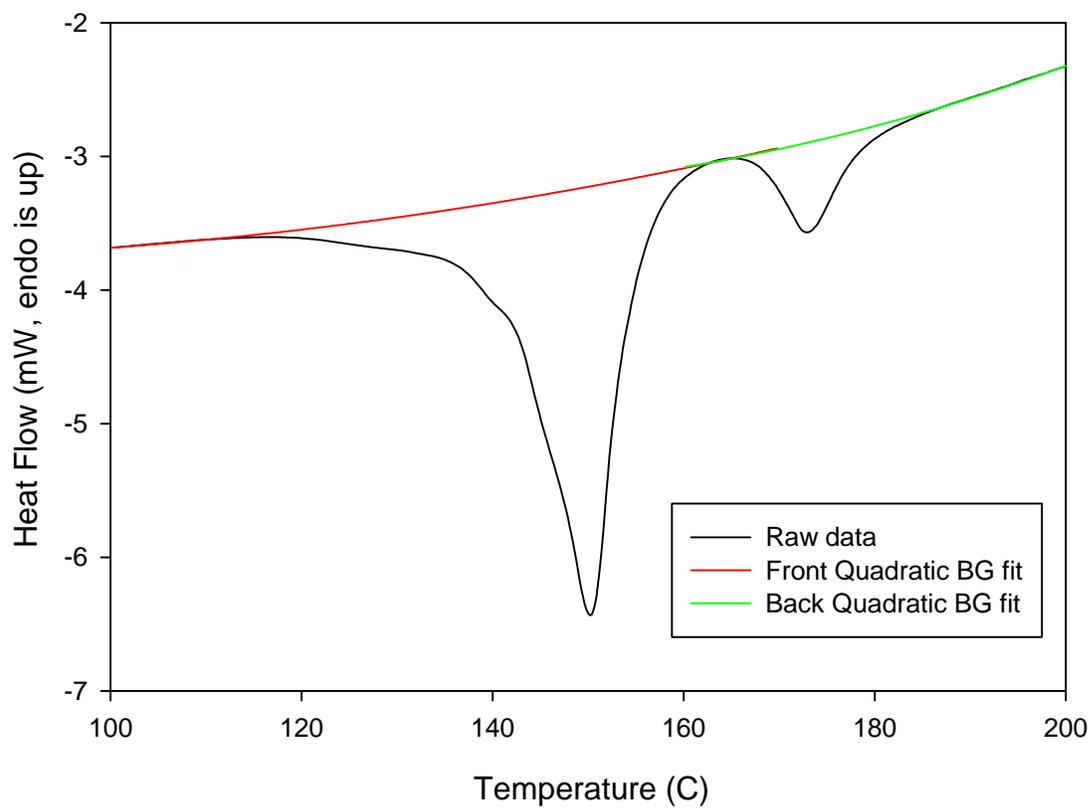
7.3 mg Indium

Indium BG Fit

Integrated Peak = 5.30 mW-K
7.3 mg In @ 28.57 J/g = .20856 J
System Calibration constant: .039351 J/(mW-K)

FeOOH 11.6 mg

FeOOH Quadratic BG Fit
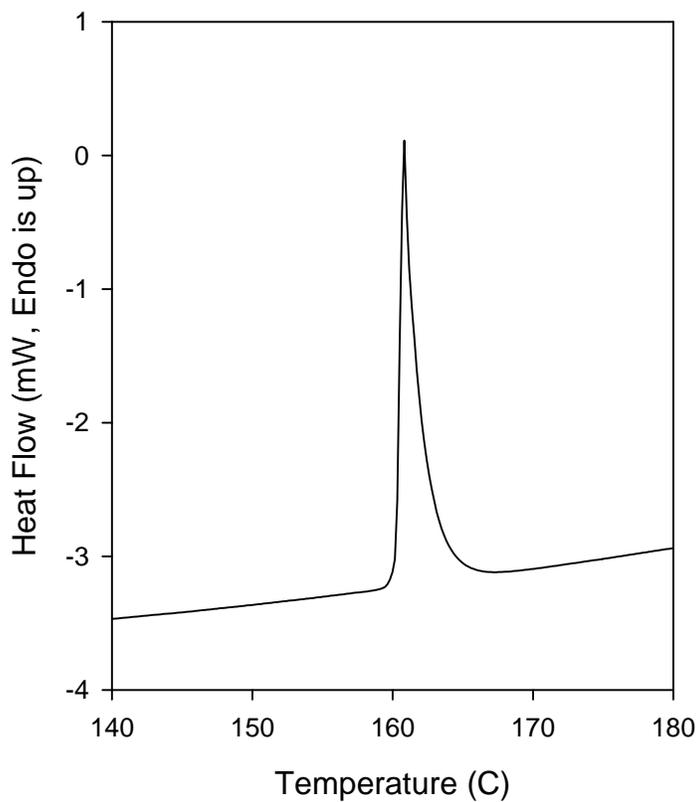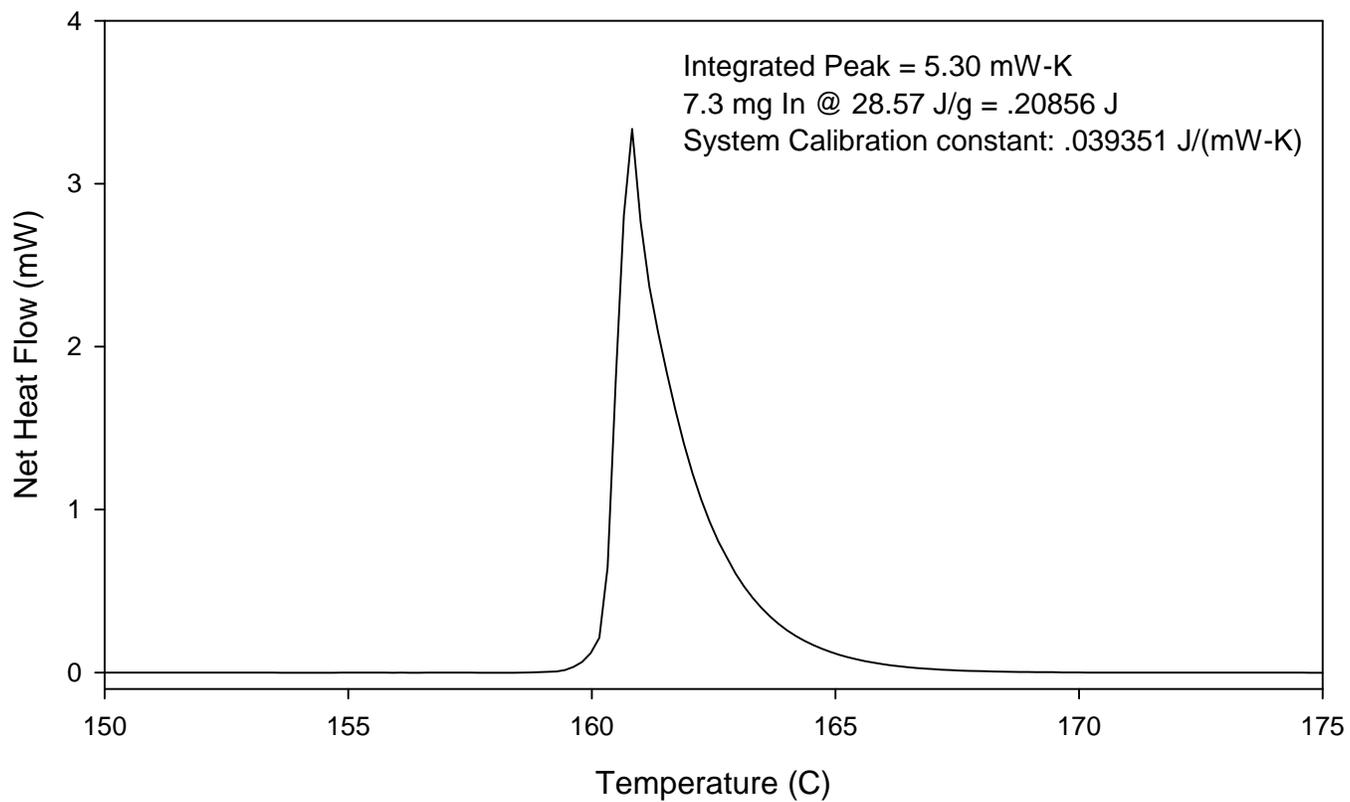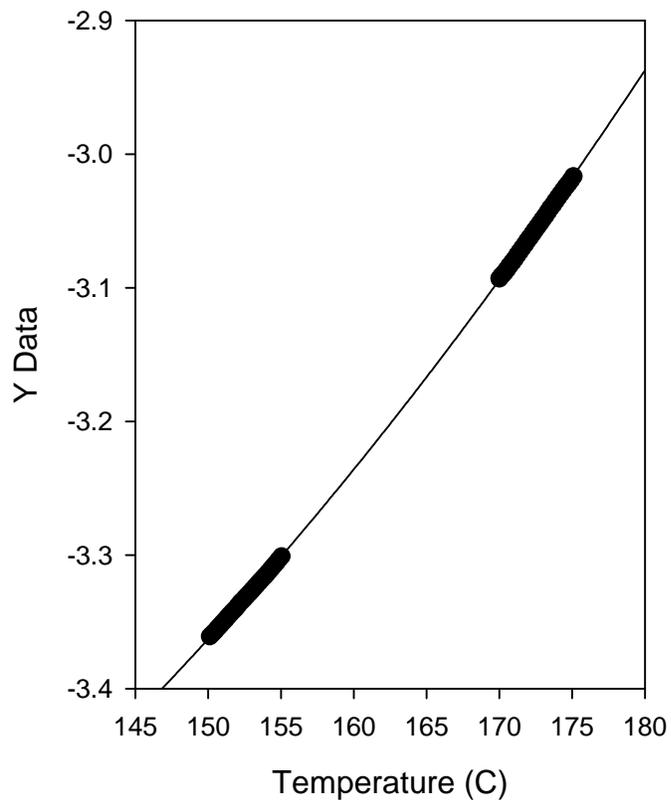
134.7 J/g
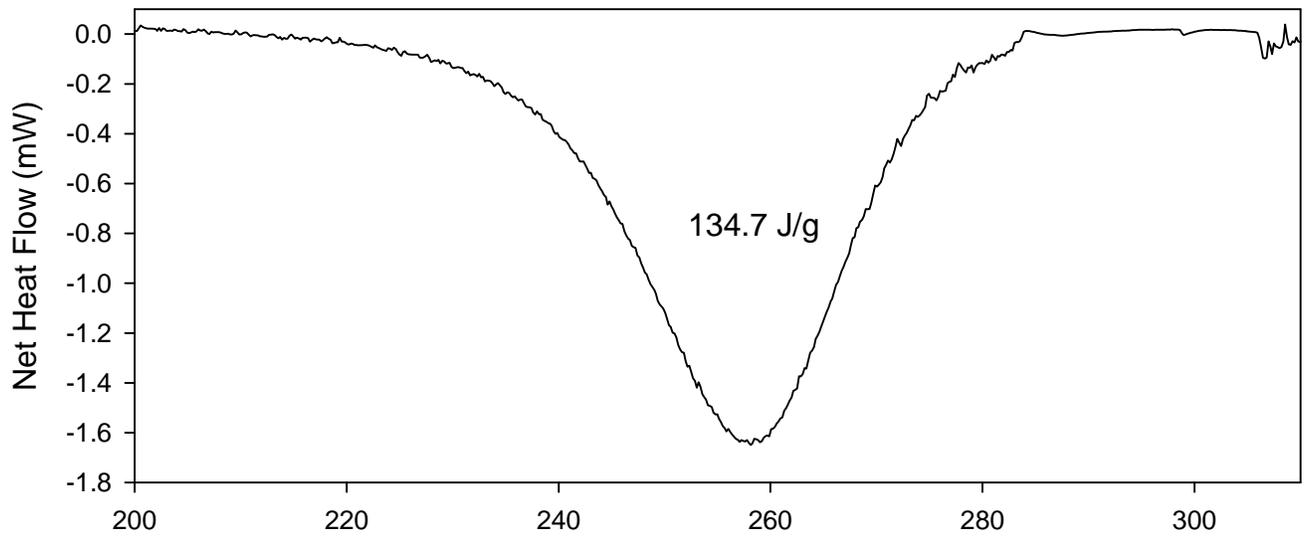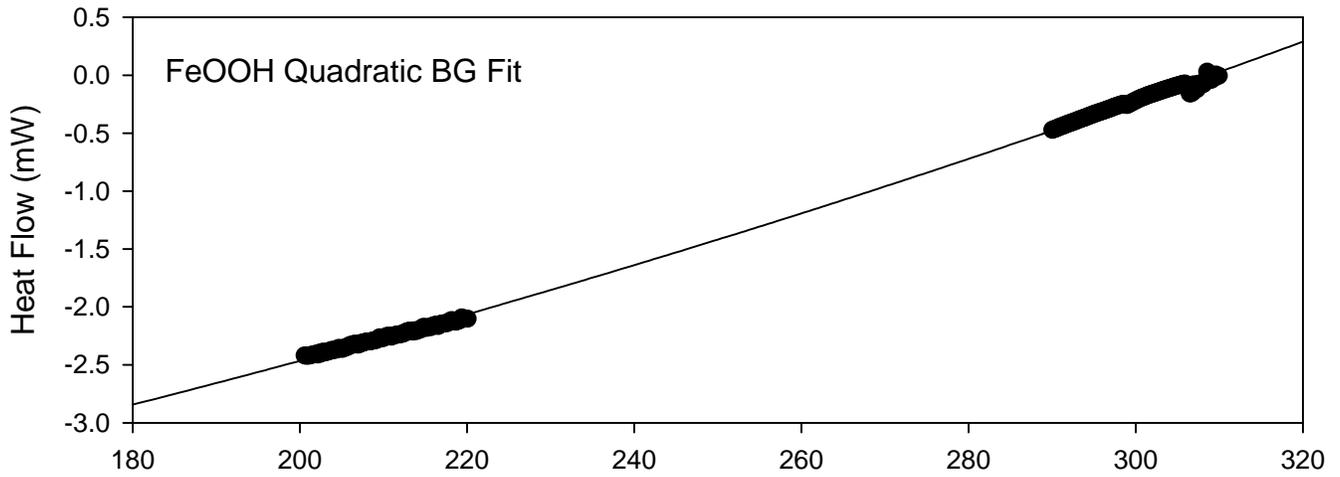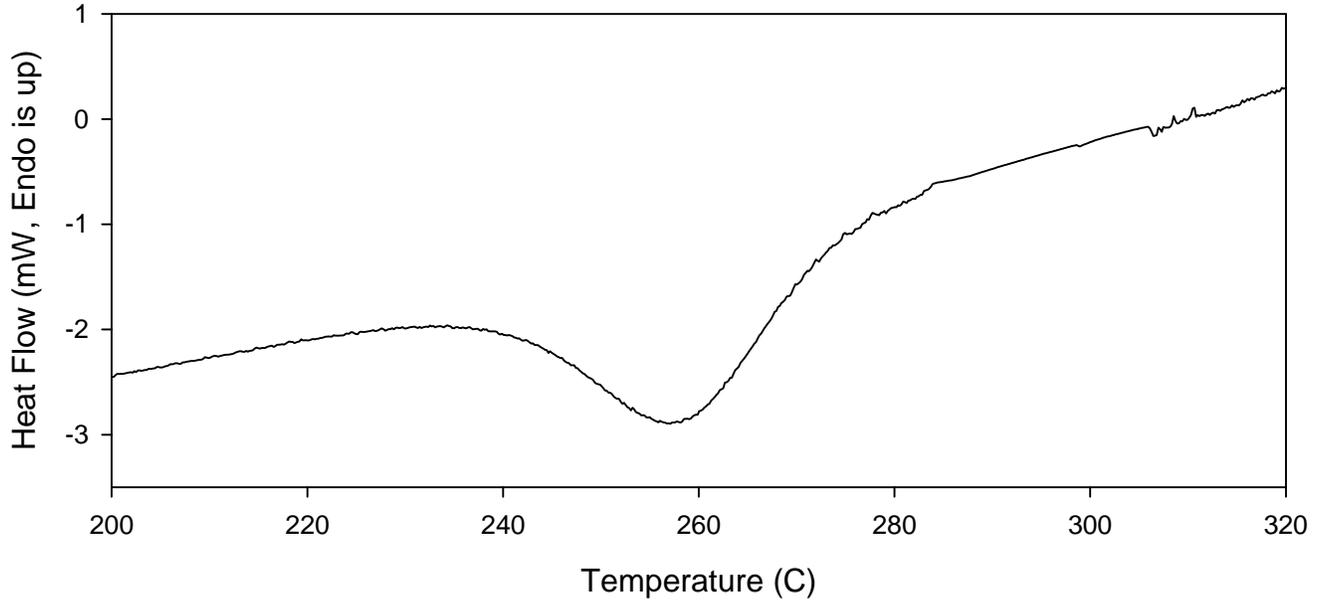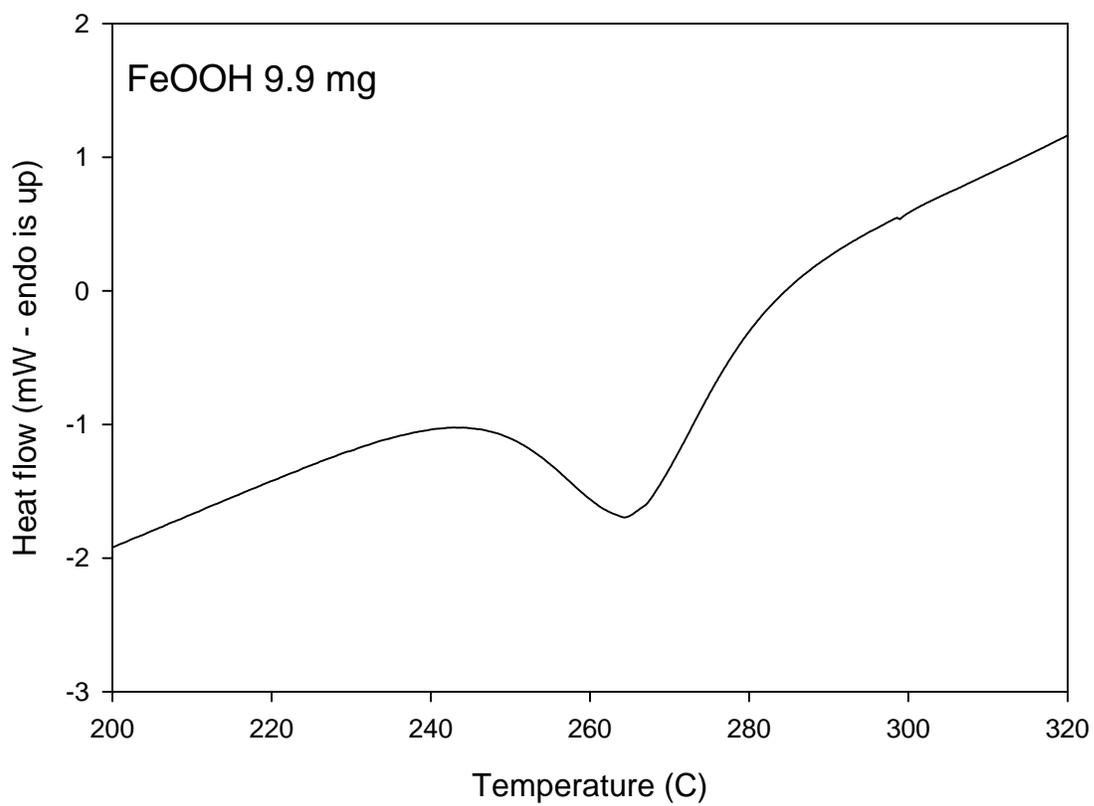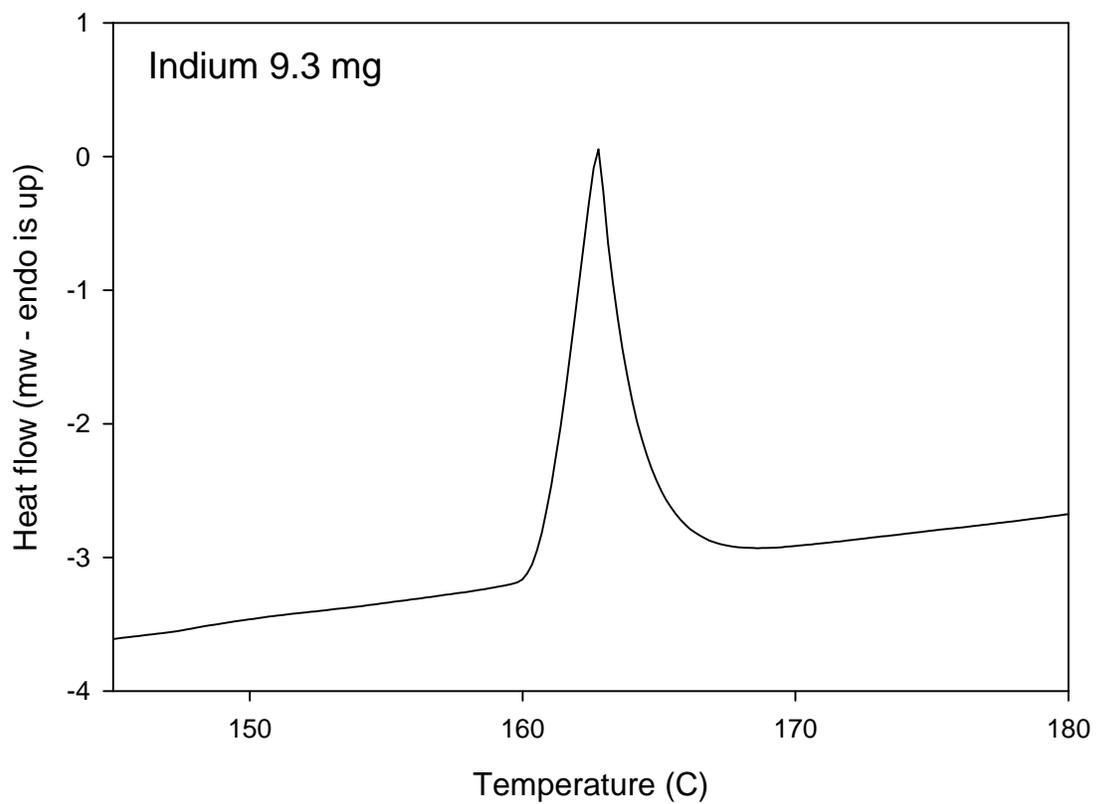
Copper Hydroxide:Iron Bromide; 12.0 mg; 1:2.37 by mass