Heat capacity and thermodynamic functions of γ -Al₂O₃

Jason J. Calvin, Megan Asplund, Ying Zhang, Baiyu Huang, and Brian F. Woodfield*

*Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602,
U.S.A.*

*Corresponding author. Tel.: +1 801 422 2093; fax: +1 801 422 0153

Email address: brian_woodfield@byu.edu (B. F. Woodfield)

Abstract

Alumina (Al_2O_3) can be synthesized with a variety of crystalline structures, each with unique physical properties. Although the corundum phase ($\alpha\text{-Al}_2\text{O}_3$) has been well studied, the other phases of alumina have had limited attention over the years. One of the low-density phases of alumina, $\gamma\text{-Al}_2\text{O}_3$, is important in a variety of technical applications, largely because of its large surface area, pore volume, and high thermal stability when compared to mesoporous silicas. The mesoporous structure of $\gamma\text{-Al}_2\text{O}_3$ causes it to be hygroscopic, and samples that are calcined at different temperatures can have widely varying amounts of water adsorbed to their surfaces as well as subtle changes in structure. We have measured the constant pressure heat capacities of four $\gamma\text{-Al}_2\text{O}_3$ samples that were calcined at (300, 600, 900, and 1100) $^\circ\text{C}$ and have the chemical formulas $\text{Al}_2\text{O}_3 \cdot 1.540\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot 0.811\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot 0.537\text{H}_2\text{O}$, and $\text{Al}_2\text{O}_3 \cdot 0.204\text{H}_2\text{O}$, respectively. Molar heat capacities were measured from 1.8 to 300 K using a Quantum Design Physical Property Measurement System (PPMS), and the data was fit to a sum of theoretical functions below 15 K, orthogonal polynomials from 10 K to 60 K, and a combination of Debye and Einstein functions above 50 K. These fits were then used to generate $C_{p,m}^\circ$, $\Delta_0^\text{T} S_m^\circ$, $\Delta_0^\text{T} H_m^\circ$, and Φ_m° values at smoothed temperatures from 0 K to 300 K for all samples. The differences in the thermodynamic functions for the samples is attributed to the differing amounts of water adsorbed to the surfaces and the corresponding change in the strength of water interactions with the surface.

KEYWORDS: $\gamma\text{-Al}_2\text{O}_3$, Heat Capacity, Thermodynamic properties

1. Introduction

The physical properties of alumina make it a versatile material with a wide variety of applications, such as the production of aluminum metal, abrasion protection, as an abrasive, in catalytic supports, and as a thermal conductor or insulator depending on the structure [1-6]. Alumina can be found virtually everywhere as it almost instantly forms when aluminum metal is in contact with oxygen [7]. This thin covering of aluminum oxide passivates aluminum and gives aluminum its resistance to corrosion [8]. Often, manufacturers wishing to give their aluminum products increased protection will thicken the layer of aluminum oxide via anodizing [9].

Alumina's great versatility arises primarily from its structure. It has at least fifteen different phases (alpha, gamma, delta, kappa, *etc.*), but each phase has a distinct physical structure with a different set of properties [10-14]. One of the most common forms of alumina is $\alpha\text{-Al}_2\text{O}_3$, also known as corundum or sapphire. Another common phase of alumina, $\gamma\text{-Al}_2\text{O}_3$, is valuable in the field of catalysis because of its porous structure and excellent thermal stability [15-17]. This phase of alumina generally has large surface areas ranging from (160 to 400) $\text{m}^2\cdot\text{g}^{-1}$ [18, 19], which is one of the factors that makes it significantly more hygroscopic than many of the other alumina counterparts [20].

The water that is adsorbed to the surface of $\gamma\text{-Al}_2\text{O}_3$ influences its properties appreciably. Investigations into the nature of the water-surface interactions in high-surface area materials have been reported previously for TiO_2 anatase and rutile and for SnO_2 cassiterite [21-24]. Essentially, these studies found water is adsorbed in layers, typically with a tighter bound "inner" layer of water and more loosely bound "outer" layers of water [21-24]. These adsorbed water layers can significantly affect the properties of the materials. The adsorbed water on these $\gamma\text{-Al}_2\text{O}_3$ samples is thought to behave in a similar manner. After calcination at different

temperatures, γ - Al_2O_3 samples possess different amounts of adsorbed water, which contributes to the differences in properties. In a previous study, it has been shown that the presence of adsorbed water on γ - Al_2O_3 stabilizes the materials [25].

Corundum has long been a reference material for calibrating or demonstrating the accuracy of heat capacity measurements [26]. Because of this, a significant number of thermodynamic measurements have been collected for α - Al_2O_3 [27-34]. Some of the other phases of alumina have been characterized by heat capacity measurements, but to a lesser extent [35-37]. This data is important to those who wish to use γ - Al_2O_3 in technological and industrial processes and to understand the variance in the thermodynamic properties of γ - Al_2O_3 as a function of calcination temperature and water content [38, 39]. In a previous paper, we compared the heat capacity and inelastic neutron scattering data for a series of γ - Al_2O_3 as a function of pore size but no thermodynamic functions were calculated [37]. In this paper, we present heat capacity data for a series of γ - Al_2O_3 samples calcined at different temperatures but prepared from a single aluminum alkoxide precursor synthesized using a solvent deficient precipitation method [18]. The focus is on studying the effect of calcination temperature and water content on the intrinsic thermodynamic properties of γ - Al_2O_3 .

2. Experimental

2.1 Sample preparation and Characterization

Alumina samples were prepared using a method previously described by Huang et al using aluminum iso-propoxide ($\text{Al}(\text{OCH}(\text{CH}_3)\text{CH}_3)_3$) purchased from Alfa Aesar [18]. In the final step of the synthesis, aliquots from a common boehmite precursor are calcined in a muffle furnace for two hours at different temperatures, 300° C, 600° C, 900° C, or 1100° C, respectively. Note that for these particular γ - Al_2O_3 samples, the transition to α - Al_2O_3 begins at

1150 °C and is complete by 1200 °C. These samples will be subsequently referred to as AIP (for aluminum iso-propoxide precursor) followed by the temperature at which they were calcined. For example, the sample that was calcined at 300° C will be referred to as AIP 300.

To verify the structures of these aluminas, each sample was analyzed by powder X-ray diffraction (XRD) on a Panalytical X'Pert Pro X-ray diffractometer with Cu-K α radiation (λ = 0.15418 nm) at a scanning rate of 0.02° s⁻¹ in the 2 θ ranges from 10° to 80°. A fixed power source was used (40 kV, 40 mA). The XRD spectra are included in Figure 1, and these measurements confirmed that the samples are pure phase γ -Al₂O₃. Specific surface area was determined using the Brunauer-Emmett-Teller (BET) method, with a P/P₀ range between 0.05 and 0.2 using a Micromeritics TriStar 3000, and the pore size distribution is calculated using a Slit Pore Geometry (SPG) model [40]. The purity of these samples was verified by inductively coupled plasma optical emission spectrometry (ICP-OES). Further details on the characterization and synthesis of the samples can be found elsewhere [18], and a summary of this characterization data is included in Table 1.

As mentioned above, an important feature of these samples is the amount of water that has been adsorbed onto the surface of the aluminas. To accurately determine the effect of the tightly bound “inner” layers of water on these samples, each sample was first dried in an oven at 150° C for 24 hours to remove the “outer” layers of adsorbed water, as only this outer water would be liberated from the surface at this temperature, leaving the inner layers of water on the sample. Immediately after the samples were dried, they were stored in an argon atmosphere with less than 1 ppm O₂ and H₂O to prevent adsorption of additional water before they were measured. Each sample was then subjected to thermogravimetric analysis by a Netzsch STA 409PC. Approximately 20 mg of sample was loaded into a platinum pan and heated from room

temperature to 900° C with a ramp rate of 3° C·min⁻¹ under a 20 mL·min⁻¹ flow of helium gas.

The measured mass of these samples was constant with increasing temperature by the end of the measurement, and the graphical data of the mass of these samples as a function of temperature is included in Figure 2. The calculated amount of water adsorbed to these samples is also included in Table 1.

2.2 Calorimetric Measurements

Constant pressure heat capacities were measured with a Quantum Design Physical Property Measurement System (PPMS) from (1.8-300) K. The powdered alumina samples were encased in copper foil (99.999% Alfa Aesar) in order to improve the thermal conductivity of the samples. The method is described in more detail elsewhere [41, 42]. The pellets were attached to the sample platform by a small amount of Apiezon-N grease, and their heat capacity measured under high vacuum. The sample masses as well as the copper foil masses for the pellets are included in Table 2.

The heat capacity of the copper, as well as the contribution of the grease used to attach the samples to the sample platform in the PPMS, was subtracted from the total heat capacity that was measured. Any contribution to the heat capacity due to the sample holder or calorimeter was accounted for by addenda measurements prior to the sample measurements.

3. Results

The measured molar heat capacity values for the four γ -Al₂O₃ samples (AIP 300, AIP 600, AIP 900, and AIP 1100) are given separately in Tables 3, 4, 5, and 6 and summarized graphically in Figure 3. The inset in Figure 3 shows the heat capacity data below $T = 10$ K. The heat capacities of these samples are smooth without any obvious anomalies or transitions, but the

heat capacities do decrease as the calcination temperature increases, which corresponds to the decreasing amount of water on the sample.

4. Discussion

4.1 Data Fitting

In general terms, the heat capacity is a measure of the occupancy of the various energetic states of a material as a function of temperature [38]. Using theoretical functions to model heat capacity data, information about the electronic, vibrational, and magnetic properties of a sample can be deduced. Because individual contributions to the overall heat capacity of the sample are dependent on of temperature, we can separate the heat capacity data into three different temperature regions and fit the data in these regions using different sets of functions. At low and high temperatures, we use theoretical models to fit the data, and for temperatures in between we use a polynomial function to overlap with these regions.

The contributions to the heat capacity data in the low temperature region, below about $T = 15$ K, are mostly dominated by the lattice vibrations but electronic and magnetic contributions can also be important. The function used to model the lattice vibrations contains odd powers in temperature.

$$C_{Lat} = \sum_{n=3,5,7,\dots} B_n T^n \quad (1)$$

A linear dependence on T , or γT , is typically associated with an electronic contribution to the overall heat capacity; however, for insulating materials, such as these γ -Al₂O₃ samples, a linear term can be necessary due to defects in the lattice or oxygen vacancies [30, 41].

The data from the temperature region (10-60) K was fit to a polynomial function. The fitting region was chosen to overlap with the low temperature and high temperature fits and to fit the inflection point around 100 K. The fits were of the form:

$$C_{mid\ T} = \sum_{n=0,1,2...6} A_n T^n \quad (2)$$

The high temperature data (above 50 K) was fit to a sum of Debye and Einstein functions. These functions are often used to represent the lattice contribution for simple solids, and are of the form

$$C_{high\ T} = m \cdot D\left(\frac{\Theta_D}{T}\right) + n \cdot E\left(\frac{\Theta_{E,1}}{T}\right) + A_1 \cdot T \quad (3)$$

where $D(\Theta_D / T)$, and $E(\Theta_E / T)$ are the Debye and Einstein functions respectively, the variables m , n , Θ_D , Θ_E , and A_1 are all adjustable parameters, and $(m+n)$ should be approximately equal to the number of atoms in the formula unit. The linear term, $A_1 \cdot T$, approximates for the conversion of $C_{V,m}$ to $C_{p,m}$.

The best parameters for each of these functions for the different samples, as well as the regions for which they are valid and the %RMS of the fits, are given in Table 7. Lines representing the fitting functions are also included in Figure 3. Plots of the deviations of the function from the measured data are given by Figures 4-7 and show that the deviations are generally random and are representative of the data.

4.2 Thermodynamic Calculations

Fits representing the data were used to generate the standard molar thermodynamic functions $C_{p,m}^\circ$, $\Delta_0^\circ S_m^\circ$, $\Delta_0^\circ H_m^\circ$, and Φ_m° at smoothed temperatures from 0 to 300 K. These data sets are given in Tables 8, 9, 10, and 11 for AIP 300, AIP 600, AIP 900, and AIP 1100 respectively. The standard state molar entropies are $93.350 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$, $78.908 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$, $69.765 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$, and $61.201 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$ for AIP 300, AIP 600, AIP 900, and AIP 1100 respectively.

As expected, the molar entropies of the samples decrease as the calcination temperature increases and the water content is reduced. As a comparison, the standard state molar entropy of α -Al₂O₃ is 50.950 J·K⁻¹ mol⁻¹ [35], which is significantly less than the standard state molar entropies of all of the γ -Al₂O₃ samples. This should be expected since γ -Al₂O₃ is considerably less dense than α -Al₂O₃. However, another more relevant comparison would be to look at the entropies for the high-surface area TiO₂ nanoparticles previously measured [21, 22] with similar amounts of adsorbed water. A sample of TiO₂·0.532H₂O anatase has a standard state molar entropy of 66.072 J·K⁻¹ mol⁻¹, compared to a standard state molar entropy of 69.765 J·K⁻¹ mol⁻¹ for Al₂O₃·0.537H₂O (AIP 900). A sample of TiO₂·0.244H₂O rutile nanoparticles has a standard molar entropy of 58.035 J·K⁻¹ mol⁻¹, compared to a standard state molar entropy of 61.201 J·K⁻¹ mol⁻¹ for Al₂O₃·0.204H₂O (AIP 1100). Other TiO₂ nanoparticles measured previously did not have similar amounts of adsorbed water compared to AIP 300 and AIP 600.

These results show the importance of water on the surfaces of mesoporous materials and how the water is bonded. Previously, we have developed models to account for water adsorbed onto the surfaces of nanoparticles [21-24], however, in this instance the water is integral to the structure of these alumina samples, and the water can behave differently for the different samples. To illustrate this, the smoothed molar heat capacity values for the AIP 600, AIP 900, and AIP 1100 found in Tables 9, 10, and 11, respectively, were individually subtracted from the smoothed heat capacity values of AIP 300 found in Table 8, since the AIP 600, 900, and 1100 samples had less water adsorbed to their surfaces than AIP 300. Similarly, the smoothed heat capacity values for AIP 900 and AIP 1100 were subtracted from the smoothed heat capacity values for AIP 600, and finally the smoothed heat capacity values for AIP 1100 was subtracted from the smoothed heat capacity values for AIP 900. The difference in water content for each

subtraction was used to determine the molar heat capacity of the water adsorbed to the surfaces of the samples, and thus the resulting heat capacity differences, to a great extent, should represent the behavior of water on the surfaces of the alumina surfaces. These calculated values for the molar heat capacity of the adsorbed water on the surfaces, as well as the molar heat capacity of hexagonal ice for a comparison [43], are plotted in Figure 8.

If the differences in heat capacities were caused only by there being more water on some of the samples, the resulting molar heat capacity of the water from each subtraction should be nearly the same. However, there are large differences in the calculated molar heat capacity of the water, which indicates that the water that is bonded to the surface behaves differently on each sample. What is even more interesting is that the molar heat capacities of the subtracted water do not have any obvious trends relative to each other, that is, water that comes off at higher temperatures is not necessarily more tightly bound than water coming off at a lower temperature. It is true that the water heat capacities for all of the adsorbed water are below the heat capacity of hexagonal ice [43], indicating that the adsorbed water is more tightly bonded and likely contributes to the thermal stability of these catalyst support materials [25]. However, the behavior of the water at different calcination temperatures is not systematic, thus suggesting that the γ - Al_2O_3 samples calcined at different temperatures are unique.

In a previous study we conducted, the heat capacities were compared between four γ - Al_2O_3 samples as a function of pore size [37]. These samples were prepared using a variety of methods and were all calcined at 700 °C, and they had molar water contents between 0.48 and 0.69 moles of water per mole of alumina. The values of the constant pressure heat capacity at 298.15 K were 112.156 J·K⁻¹ mol⁻¹ for $\text{Al}_2\text{O}_3 \cdot 0.69\text{H}_2\text{O}$, 122.461 J·K⁻¹ mol⁻¹ for $\text{Al}_2\text{O}_3 \cdot 0.59\text{H}_2\text{O}$, 129.982 J·K⁻¹ mol⁻¹ for $\text{Al}_2\text{O}_3 \cdot 0.50\text{H}_2\text{O}$, and 112.938 J·K⁻¹ mol⁻¹ for $\text{Al}_2\text{O}_3 \cdot 0.48\text{H}_2\text{O}$, which were

all larger than the value of the constant pressure heat capacity of $95.056 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$ for $\text{Al}_2\text{O}_3\cdot 0.537\text{H}_2\text{O}$ (AIP 900) at 298.15 K. Although the samples in that study had a similar amount of water adsorbed to their surfaces as AIP 900, differences in the calcination temperature or pore sizes may explain the difference in heat capacities. This study claimed that neither the pore diameter nor the water content influenced the thermodynamic properties of the materials, however as we have seen in this study that the water content does have an appreciable effect.

5. Conclusion

The heat capacities of several $\gamma\text{-Al}_2\text{O}_3$ samples were measured from 1.8 K to 300 K. Fits of each data set were used to generate $C_{p,m}^\circ$, $\Delta_0^T S_m^\circ$, $\Delta_0^T H_m^\circ$, and Φ_m° values at smoothed temperatures from 0 to 300 K. It was shown that the differences in the heat capacities of these materials are due to the variability of the water bound to the surfaces as a function of calcination temperature. This makes each of these samples a unique material, and attempting to subtract the contributions of the water is nontrivial.

Acknowledgements

This work was financially supported by a grant from the U.S. Department of Energy under grant DE-SC0016446.

References

- [1] J.P. Murray, Solar Energy **66**, 133 (1999).
- [2] G. Hass, Journal of the Optical Society of America **39**, 532 (1949).
- [3] J. Su, J. Du, L. Ma, Z. Zhang, R. Kang, Journal of Semiconductors **33**, 106003 (2012).
- [4] H. Adkins, L. M. Richards, and J. W. Davis, Journal of the American Chemical Society **63**, 1320 (1941).
- [5] R. Berman, Proceedings of the Physical Society Section A. **65**, 1029 (1952).
- [6] M. Munro, Journal of the American Ceramic Society **80**, 1919 (2005).
- [7] W. H. Krueger and S. R. Pollack, Surface Science **30**, 263 (1972).
- [8] F. Keller, M. S. Hunter, and D. L. Robinson, Journal of the Electrochemical. Society **100**, 411 (1953).
- [9] Y. Huang, H. Shih, H. Huang, J. Daugherty, S. Wu, S. Ramanathan, C. Chang, and F. Mansfeld, Corrosion Science **50**, 3569 (2008).
- [10] S.J. Smith, S. Amin, B.F. Woodfield, J. Boerio-Goates, B.J. Campbell, Inorganic Chemistry **52**, 4411 (2013).
- [11] I. Levin, D. Brandon, Journal of the American Ceramic Society **81**, 1995 (2005).
- [12] A. Dager, D. Fargeot, and J. P. Laval, MRS Proceedings **21**, (1983).
- [13] Z. Łodziana and K. Parliński, Physical Review B **67**, 174106 (2003).
- [14] A. Boumaza, L. Favaro, J. Lédion, G. Sattonnay, J. B. Brubach, P. Berthet, A. M. Huntz, P. Roy, and R. Tétot, Journal of Solid State Chemistry **182**, 1171 (2009).
- [15] D. L. Hoang, S. H. Chan, and O. L. Ding, Chemical Engineering Journal **112**, 1 (2005).
- [16] N. K. Nag, Catalysis Letters **24**, 37 (1994).
- [17] R. S. Schiffino, and R. P. Merrill, The Journal of Physical Chemistry **97**, 6425 (1993).

- [18] B. Huang, C.H. Bartholomew, and B.F. Woodfield, *Microporous Mesoporous Materials* **177**, 37 (2013).
- [19] C. Márquez- Alvarez, N. Žilková, J. Pérez- Pariente, and J. Čejka, *Catalysis Reviews* **50**, 222 (2008).
- [20] D. S. Maciver, H.H. Tobin, and R.T. Barth, *Journal of Catalysis* **2**, 485 (1963).
- [21] J. M. Schliesser, S. J. Smith, G. Li, L. Li, T. F. Walker, T. Parry, J. Boerio-Goates, B. F. Woodfield, *The Journal of Chemical Thermodynamics*. **81**, 298 (2015).
- [22] J. M. Schliesser, S. J. Smith, G. Li, L. Li, T. F. Walker, T. Parry, J. Boerio-Goates, B. F. Woodfield, *The Journal of Chemical Thermodynamics* **81**, 311 (2015).
- [23] J. Boerio-Goates, G. Li, L. Li, T. F. Walker, T. Parry, and B. F. Woodfield, *Nano Letters* **6**, 750 (2006).
- [24] E. C. Spencer, N. L. Ross, S. F. Parker, A. I. Kolesnikov, B. F. Woodfield, K. Woodfield, M. Rytting, J. Boerio-Goates, A. Navrotsky, *The Journal of Physical Chemistry C* **115**, 21105 (2011).
- [25] J.M.M., A. Navrotsky, A.J. Perrotta, *Journal of Physical Chemistry B* **101**, 603 (1997).
- [26] D. C. Ginnings and G.T. Furukawa, *Journal of the American Chemical Society* **75**, 522 (1953).
- [27] D. A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, and E.D. West, *Journal of Research of the National Bureau of Standards* **87**, 159 (1982).
- [28] D. G. Archer, *Journal of Physical and Chemical Reference Data* **22**, 1441 (1993).
- [29] L. Wang, Z. Tan, S. Meng, D. Liang, and G. Li, *Journal of Nanoparticle Research* **3**, 483 (2001).

- [30] A. J. Leadbetter, Journal of Physics C: Solid State Physics **1**, 1481 (1968).
- [31] Z.-C. Tan, Q. Shi, B.-P. Liu, and H.-T. Zhang, Journal of Thermal Analysis and Calorimetry **92**, 367 (2008).
- [32] A. Inaba, The Journal of Chemical Thermodynamics **15**, 1137 (1983).
- [33] R. Q. Fugate, Journal of Applied Physics **40**, 3034 (1969).
- [34] B. E. Walker, J. A. Grand, and R. R. Miller, The Journal of Physical Chemistry **60**, 231 (1956).
- [35] M. Chase, The Journal of Physical Chemistry Reference Data, Monograph 9, (1998).
- [36] Q. Chen, W. Zeng, X. Chen, S. Gu, G. Yang, H. Zhou, Z. Yin, Thermochemica Acta, **253**, 33 (1995).
- [37] E. C. Spencer, B. Huang, S. F Parker, A. I. Kolesnikov, N. L. Ross, B. F. Woodfield, The Journal of Chemical Physics **139**, 244705 (2013).
- [38] E. S. R. Gopal, Specific heats at low temperatures (Plenum Press New York, 1966), Vol. 227.
- [39] J. B. Ott and J. Boerio-Goates, Chemical Thermodynamics: Advanced Applications: Advanced Applications (Academic Press, 2000), Vol. 2.
- [40] B. Huang, C.H. Bartholomew, and B.F. Woodfield, Microporous and Mesoporous Materials **184**, 112 (2014).
- [41] Q. Shi, C. L. Snow, J. Boerio-Goates, B. F. Woodfield, The Journal of Chemical Thermodynamics **42**, 1107 (2010).
- [42] Q. Shi, J. Boerio-Goates, B. F. Woodfield, The Journal of Chemical Thermodynamics **43**, 1263 (2011).

[43] J. Boerio-Goates, G. Li, L. Li, T.F. Walker, T. Parry, B.F. Woodfield, Nano Letters **6**, 750 (2006).

Table 1. A summary of the masses and characterization data for each of the four γ -Al₂O₃ samples reported in this paper. Chemical purity for all samples was determined using ICP-OES. The estimated standard uncertainty in the water content is $u = 0.01$ mol H₂O·mol⁻¹.

Sample	Water Content/ (mol H ₂ O·mol ⁻¹)	Mass Fraction Purity	Surface Area/ (m ² ·g ⁻¹)	Pore Volume/ (cm ³ ·g ⁻¹)	Pore Diameter/ (nm)
AIP 300	1.540	>0.999	369	1.35	12.5
AIP 600	0.811	>0.999	309	1.49	13.1
AIP 900	0.537	>0.999	179	1.20	18.2
AIP 1100	0.204	>0.999	97	0.43	19.9

Table 2. Details of the PPMS calorimetric measurements including pressures (p), sample mass, (M_s), molar mass (M), and copper mass (M_{Cu}). The estimated standard uncertainties in the masses $M_{s,Cu}$ and pressure p are $u(M_{s,Cu}) = 0.06$ mg and $u(p) = 0.1$ mPa.

	$\text{Al}_2\text{O}_3 \cdot 1.540\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 0.811\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 0.537\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 0.204\text{H}_2\text{O}$
p / mPa	1.2	1.2	1.2	1.2
M_s / mg	14.62	13.16	18.50	21.78
M / $\text{g} \cdot \text{mol}^{-1}$	129.705	116.572	111.635	105.636
M_{Cu} / mg	34.80	30.60	32.80	28.02

Table 3. Measured molar heat capacity values at constant pressure for γ -alumina $\text{Al}_2\text{O}_3 \cdot 1.540\text{H}_2\text{O}$. $M = 129.70 \text{ g}\cdot\text{mole}^{-1}$. Measurements were performed using a Quantum Design Physical Properties Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T = 10 \text{ K}$ and 1% $C_{p,m}$ from $T = (10 \text{ to } 300) \text{ K}$. The standard uncertainty in temperature is about 4 mK.

T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
1.8294	$4.1433 \cdot 10^{-3}$	8.0688	0.077556	77.383	16.938
1.9162	$4.7529 \cdot 10^{-3}$	8.4197	0.087442	84.563	20.589
2.0005	$4.9720 \cdot 10^{-3}$	8.7887	0.094787	92.406	24.672
2.0899	$5.2748 \cdot 10^{-3}$	9.1709	0.11111	100.97	29.080
2.1832	$5.8342 \cdot 10^{-3}$	9.5695	0.12087	111.08	34.630
2.2821	$6.2464 \cdot 10^{-3}$	9.9836	0.12845	121.14	40.459
2.4044	$7.3068 \cdot 10^{-3}$	10.396	0.14252	131.20	46.301
2.5469	$7.7452 \cdot 10^{-3}$	10.788	0.15649	141.31	52.003
2.6535	$8.4031 \cdot 10^{-3}$	11.252	0.17216	151.36	57.971
2.7493	$8.9085 \cdot 10^{-3}$	11.745	0.18830	161.48	63.704
2.8985	$9.3554 \cdot 10^{-3}$	12.266	0.21168	171.53	69.218
3.0038	0.010628	12.812	0.23877	181.61	74.941
3.1484	0.012256	13.379	0.26842	191.67	80.494
3.2879	0.012813	13.965	0.30159	201.80	85.539
3.4145	0.013231	14.593	0.33771	211.88	90.491
3.5730	0.013675	15.233	0.37635	221.89	95.369
3.7214	0.015139	15.737	0.40737	231.96	99.901
3.8892	0.018018	17.215	0.51452	242.02	104.16
4.0572	0.018222	18.799	0.63926	252.17	108.66
4.2365	0.021759	20.512	0.79439	262.24	112.82
4.4203	0.024047	22.453	0.98409	272.31	116.50
4.6169	0.023935	24.515	1.1895	282.29	120.68
4.8255	0.026114	26.765	1.5020	292.44	124.45
5.0389	0.028609	29.235	1.8661	302.52	127.89
5.2570	0.032515	31.937	2.3062		
5.4861	0.034030	34.891	2.8598		
5.7270	0.036533	38.112	3.5181		
5.9762	0.038023	41.638	4.3235		
6.2412	0.045085	45.487	5.3364		
6.5112	0.050237	49.701	6.3804		
6.7915	0.059069	54.300	7.8201		
7.0941	0.061698	59.326	9.5228		
7.4047	0.061290	64.818	11.546		
7.7280	0.070377	70.815	13.964		

Table 4. Measured molar heat capacity values at constant pressure for γ -alumina $\text{Al}_2\text{O}_3 \cdot 0.811\text{H}_2\text{O}$. $M = 116.57 \text{ g}\cdot\text{mole}^{-1}$. Measurements were performed using a Quantum Design Physical Properties Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T = 10 \text{ K}$ and 1% $C_{p,m}$ from $T = (10 \text{ to } 300) \text{ K}$. The standard uncertainty in temperature is about 4 mK.

T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
1.8247	$4.6306 \cdot 10^{-3}$	8.0453	0.061397	77.367	15.043
1.9136	$5.0994 \cdot 10^{-3}$	8.3917	0.058959	84.547	18.283
1.9989	$5.3532 \cdot 10^{-3}$	8.7628	0.074127	92.392	21.734
2.0924	$5.8546 \cdot 10^{-3}$	9.1440	0.077173	100.96	25.516
2.2022	$6.4812 \cdot 10^{-3}$	9.5437	0.085588	111.06	30.149
2.3047	$6.6250 \cdot 10^{-3}$	9.9565	0.098562	121.13	35.135
2.4188	$7.1662 \cdot 10^{-3}$	10.377	0.10224	131.18	39.853
2.5244	$8.0127 \cdot 10^{-3}$	10.776	0.11061	141.30	44.617
2.6216	$8.3186 \cdot 10^{-3}$	11.241	0.12061	151.34	49.585
2.7601	$9.3342 \cdot 10^{-3}$	11.734	0.13114	161.46	53.987
2.8758	$9.5170 \cdot 10^{-3}$	12.253	0.14861	171.51	58.558
2.9922	0.010245	12.800	0.16832	181.59	63.141
3.1283	0.011346	13.366	0.18773	191.65	67.730
3.2607	0.011964	13.948	0.21073	201.78	71.822
3.4043	0.013133	14.584	0.23723	211.85	75.658
3.5526	0.013428	15.221	0.26536	221.86	79.576
3.7058	0.014656	15.711	0.28618	231.93	83.133
3.8682	0.017036	17.202	0.36702	241.99	86.369
4.0414	0.017343	18.761	0.46163	252.13	89.896
4.2165	0.018013	20.485	0.57965	262.20	92.824
4.4056	0.019009	22.447	0.72027	272.26	95.696
4.5993	0.021622	24.489	0.92895	282.24	98.891
4.8020	0.021852	26.742	1.1648	292.42	103.22
5.0181	0.023796	29.228	1.4556	302.54	105.88
5.2339	0.026634	31.915	1.8628		
5.4675	0.028855	34.869	2.3550		
5.7094	0.029819	38.093	2.9510		
5.9567	0.034190	41.618	3.6775		
6.2168	0.035287	45.472	4.6289		
6.4818	0.039861	49.684	5.5686		
6.7740	0.039214	54.283	6.8797		
7.0709	0.044220	59.300	8.4126		
7.3830	0.053752	64.800	10.241		
7.7042	0.055988	70.801	12.429		

Table 5. Measured molar heat capacity values at constant pressure for γ -alumina $\text{Al}_2\text{O}_3 \cdot 0.537\text{H}_2\text{O}$. $M = 111.64 \text{ g} \cdot \text{mole}^{-1}$. Measurements were performed using a Quantum Design Physical Properties Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T = 10 \text{ K}$ and 1% $C_{p,m}$ from $T = (10 \text{ to } 300) \text{ K}$. The standard uncertainty in temperature is about 4 mK.

T/K	$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T/K	$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T/K	$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.8303	$2.4664 \cdot 10^{-3}$	8.0372	0.034744	77.380	12.678
1.9136	$2.6083 \cdot 10^{-3}$	8.3941	0.038167	84.554	15.520
1.9972	$2.7364 \cdot 10^{-3}$	8.7599	0.039742	92.394	18.711
2.0865	$3.0145 \cdot 10^{-3}$	9.1417	0.045237	100.96	22.183
2.1796	$3.1722 \cdot 10^{-3}$	9.5397	0.050929	111.07	26.476
2.2774	$3.3957 \cdot 10^{-3}$	9.9577	0.052647	121.13	31.004
2.3812	$3.5842 \cdot 10^{-3}$	10.374	0.059973	131.18	35.413
2.5320	$4.0125 \cdot 10^{-3}$	10.776	0.066026	141.30	39.850
2.6304	$4.1703 \cdot 10^{-3}$	11.242	0.072119	151.38	44.512
2.7668	$4.3975 \cdot 10^{-3}$	11.735	0.079604	161.47	48.611
2.8602	$4.8795 \cdot 10^{-3}$	12.256	0.090685	171.51	52.980
2.9964	$5.1834 \cdot 10^{-3}$	12.802	0.10315	181.58	57.310
3.1319	$5.7698 \cdot 10^{-3}$	13.364	0.11846	191.65	61.289
3.2563	$5.9625 \cdot 10^{-3}$	13.961	0.13382	201.78	65.178
3.4162	$6.4169 \cdot 10^{-3}$	14.578	0.15047	211.85	68.887
3.5487	$6.7830 \cdot 10^{-3}$	15.209	0.16964	221.86	72.500
3.7087	$7.0645 \cdot 10^{-3}$	15.730	0.18518	231.93	75.819
3.8715	$7.7740 \cdot 10^{-3}$	17.168	0.23876	241.99	78.815
4.0389	$8.2889 \cdot 10^{-3}$	18.796	0.30686	252.14	82.214
4.2177	0.010271	20.542	0.39464	262.20	84.989
4.4039	$9.0607 \cdot 10^{-3}$	22.428	0.50199	272.26	87.762
4.5945	$9.6190 \cdot 10^{-3}$	24.501	0.60224	282.24	90.715
4.7975	0.012090	26.745	0.81760	292.38	93.165
5.0117	0.012749	29.213	1.0531	302.47	95.935
5.2333	0.014574	31.923	1.3438		
5.4646	0.015047	34.876	1.7264		
5.7036	0.016184	38.098	2.1962		
5.9554	0.017458	41.623	2.7840		
6.2186	0.016214	45.477	3.5478		
6.4761	0.019408	49.693	4.3585		
6.7701	0.020881	54.292	5.4730		
7.0670	0.025530	59.313	6.8176		
7.3761	0.027830	64.806	8.4043		
7.6972	0.029963	70.812	10.343		

Table 6. Measured molar heat capacity values at constant pressure for γ -alumina $\text{Al}_2\text{O}_3 \cdot 0.204\text{H}_2\text{O}$. $M = 105.64 \text{ g} \cdot \text{mole}^{-1}$. Measurements were performed using a Quantum Design Physical Properties Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T = 10 \text{ K}$ and 1% $C_{p,m}$ from $T = (10 \text{ to } 300) \text{ K}$. The standard uncertainty in temperature is about 4 mK.

T/K	$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T/K	$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T/K	$C_{p,m}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.8408	$1.8613 \cdot 10^{-3}$	8.0328	0.018257	77.369	10.525
1.9156	$1.9710 \cdot 10^{-3}$	8.3877	0.019846	84.549	13.048
2.0048	$2.0219 \cdot 10^{-3}$	8.7470	0.023498	92.391	15.918
2.0995	$2.0712 \cdot 10^{-3}$	9.1293	0.028371	100.96	19.076
2.1998	$2.2269 \cdot 10^{-3}$	9.5258	0.030510	111.07	23.000
2.3049	$2.3718 \cdot 10^{-3}$	9.9471	0.031589	121.13	27.121
2.4159	$2.3029 \cdot 10^{-3}$	10.366	0.035262	131.18	31.129
2.5286	$2.5059 \cdot 10^{-3}$	10.771	0.038710	141.30	35.159
2.6416	$2.7797 \cdot 10^{-3}$	11.237	0.042484	151.34	39.301
2.7543	$2.7910 \cdot 10^{-3}$	11.731	0.046645	161.46	43.177
2.8609	$3.0467 \cdot 10^{-3}$	12.250	0.054083	171.50	47.060
2.9893	$3.1918 \cdot 10^{-3}$	12.794	0.062205	181.58	50.964
3.1165	$3.3522 \cdot 10^{-3}$	13.360	0.070863	191.64	54.694
3.2613	$3.6422 \cdot 10^{-3}$	13.943	0.080488	201.76	58.236
3.4114	$3.2396 \cdot 10^{-3}$	14.575	0.091860	211.83	61.592
3.5467	$3.4625 \cdot 10^{-3}$	15.215	0.10368	221.85	64.676
3.7046	$4.0716 \cdot 10^{-3}$	15.710	0.11277	231.90	67.712
3.8611	$3.8493 \cdot 10^{-3}$	17.186	0.14742	241.96	70.511
4.0328	$4.7409 \cdot 10^{-3}$	18.763	0.19058	252.11	73.499
4.2136	$5.4852 \cdot 10^{-3}$	20.481	0.24514	262.17	76.088
4.4016	$5.1204 \cdot 10^{-3}$	22.432	0.31815	272.23	78.564
4.5905	$5.6301 \cdot 10^{-3}$	24.477	0.40854	282.21	81.119
4.7941	$5.9969 \cdot 10^{-3}$	26.739	0.53532	292.34	83.284
5.0049	$6.9060 \cdot 10^{-3}$	29.230	0.71504	302.42	85.702
5.2272	$7.9715 \cdot 10^{-3}$	31.910	0.90945		
5.4592	$7.6227 \cdot 10^{-3}$	34.868	1.1882		
5.6962	$8.9379 \cdot 10^{-3}$	38.091	1.5459		
5.9487	$8.4764 \cdot 10^{-3}$	41.616	2.0014		
6.2064	0.010989	45.468	2.6095		
6.4737	0.010983	49.683	3.2799		
6.7586	0.014165	54.283	4.2210		
7.0600	0.014696	59.302	5.3464		
7.3709	0.016581	64.800	6.7364		
7.6919	0.018607	70.803	8.4567		

Table 7. Parameters for low T (< 15 K), mid T ($10 \text{ K} < T < 60$ K), and high T (> 50 K) fits of heat capacity data (in $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) for all γ -alumina samples.

	Parameter	$\text{Al}_2\text{O}_3 \cdot 1.540\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 0.811\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 0.537\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 0.204\text{H}_2\text{O}$
Low T Fits	$\gamma / \text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$	$1.8106 \cdot 10^{-3}$	$2.3019 \cdot 10^{-3}$	$1.2049 \cdot 10^{-3}$	$9.4499 \cdot 10^{-4}$
	$B_3 / \text{J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$	$1.9107 \cdot 10^{-4}$	$1.2846 \cdot 10^{-4}$	$5.6263 \cdot 10^{-5}$	$7.1098 \cdot 10^{-6}$
	$B_5 / \text{J} \cdot \text{K}^{-6} \cdot \text{mol}^{-1}$	$-1.5893 \cdot 10^{-6}$	$-1.1686 \cdot 10^{-6}$	$-2.7605 \cdot 10^{-7}$	$4.0012 \cdot 10^{-7}$
	$B_7 / \text{J} \cdot \text{K}^{-8} \cdot \text{mol}^{-1}$	$9.7195 \cdot 10^{-9}$	$7.2062 \cdot 10^{-9}$	$1.6819 \cdot 10^{-9}$	$-3.0420 \cdot 10^{-9}$
	$B_9 / \text{J} \cdot \text{K}^{-10} \cdot \text{mol}^{-1}$	$-1.9932 \cdot 10^{-11}$	$-1.4524 \cdot 10^{-11}$	$-3.1904 \cdot 10^{-12}$	$7.2731 \cdot 10^{-12}$
	n / mol	$1.1272 \cdot 10^{-4}$	$1.1289 \cdot 10^{-4}$	$1.6572 \cdot 10^{-4}$	$2.0618 \cdot 10^{-4}$
	%RMS	3.99	3.93	4.52	5.75
	Range / K	1.829-11.89	1.825-11.31	1.830-10.67	1.841-12.23
Mid T Fits	$A_0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$6.9436 \cdot 10^{-1}$	$8.6311 \cdot 10^{-1}$	$1.6377 \cdot 10^{-1}$	$2.1960 \cdot 10^{-1}$
	$A_1 / \text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$	$-1.9577 \cdot 10^{-1}$	$-2.3918 \cdot 10^{-1}$	$-4.1986 \cdot 10^{-2}$	$-5.9080 \cdot 10^{-2}$
	$A_2 / \text{J} \cdot \text{K}^{-3} \cdot \text{mol}^{-1}$	$2.1672 \cdot 10^{-2}$	$2.6290 \cdot 10^{-2}$	$4.2491 \cdot 10^{-3}$	$6.1862 \cdot 10^{-3}$
	$A_3 / \text{J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$	$-1.0271 \cdot 10^{-3}$	$-1.3459 \cdot 10^{-3}$	$-1.5631 \cdot 10^{-4}$	$-2.8763 \cdot 10^{-4}$
	$A_4 / \text{J} \cdot \text{K}^{-5} \cdot \text{mol}^{-1}$	$2.91564 \cdot 10^{-5}$	$3.9491 \cdot 10^{-5}$	$4.7829 \cdot 10^{-6}$	$8.2701 \cdot 10^{-6}$
	$A_5 / \text{J} \cdot \text{K}^{-6} \cdot \text{mol}^{-1}$	$-4.03541 \cdot 10^{-7}$	$-5.6321 \cdot 10^{-7}$	$-5.9841 \cdot 10^{-8}$	$-1.0523 \cdot 10^{-7}$
	$A_6 / \text{J} \cdot \text{K}^{-7} \cdot \text{mol}^{-1}$	$2.15701 \cdot 10^{-9}$	$3.1023 \cdot 10^{-9}$	$2.6623 \cdot 10^{-10}$	$4.9964 \cdot 10^{-10}$
	%RMS	0.684	0.726	1.44	0.986
	Range / K	11.89-58.63	11.31-55.68	10.67-53.40	12.23-50.27
High T Fits	m / mol	3.5546	3.1102	2.6902	2.6004
	Θ_D / K	617.25	612.74	585.54	597.49
	n / mol	3.3452	2.5099	2.6552	2.4546
	Θ_E / K	978.8	1024.0	928.86	939.12
	A_I	$5.8894 \cdot 10^{-2}$	$5.1127 \cdot 10^{-2}$	$2.5617 \cdot 10^{-2}$	$8.9594 \cdot 10^{-3}$
	%RMS	0.476	0.985	0.438	0.355
	Range / K	58.63-302.52	55.68-302.54	53.40-302.47	50.27-302.42

TABLE 8. Standard thermodynamic functions of γ -alumina $\text{Al}_2\text{O}_3 \cdot 1.540\text{H}_2\text{O}$. $\Phi_m^\circ = \Delta_f^\circ S_m^\circ - \Delta_f^\circ H_m^\circ/T$. $M = 129.70 \text{ g}\cdot\text{mole}^{-1}$. All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^\circ S_m^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^\circ H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Phi_m^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0	0	0	0	0
1	$2.000\cdot 10^{-3}$	$1.874\cdot 10^{-3}$	$9.528\cdot 10^{-7}$	$9.212\cdot 10^{-4}$
2	$5.100\cdot 10^{-3}$	$4.121\cdot 10^{-3}$	$4.369\cdot 10^{-6}$	$1.936\cdot 10^{-3}$
3	0.01023	$7.077\cdot 10^{-3}$	$1.183\cdot 10^{-5}$	$3.133\cdot 10^{-3}$
4	0.01800	0.01102	$2.571\cdot 10^{-5}$	$4.589\cdot 10^{-3}$
5	0.02869	0.01612	$4.880\cdot 10^{-5}$	$6.364\cdot 10^{-3}$
6	0.04230	0.02252	$8.406\cdot 10^{-5}$	$8.505\cdot 10^{-3}$
7	0.05870	0.03023	$1.343\cdot 10^{-4}$	0.01104
8	0.07794	0.03929	$2.024\cdot 10^{-4}$	0.01399
9	0.10050	0.04974	$2.913\cdot 10^{-4}$	0.01737
10	0.12750	0.06168	$4.049\cdot 10^{-4}$	0.02119
15	0.36159	0.15214	$1.560\cdot 10^{-3}$	0.04817
20	0.74231	0.30501	$4.262\cdot 10^{-3}$	0.09191
25	1.2708	0.52443	$9.228\cdot 10^{-3}$	0.15533
30	1.9758	0.81557	0.01727	0.24007
35	2.8742	1.1851	0.02931	0.34771
40	3.9530	1.6375	0.04631	0.47979
45	5.1760	2.1725	0.06908	0.63740
50	6.5139	2.7861	0.09826	0.82096
60	9.7393	4.2445	0.17874	1.2655
70	13.642	6.0297	0.29505	1.8147
80	18.187	8.1417	0.45372	2.4702
90	23.215	10.570	0.66039	3.2325
100	28.579	13.291	0.91914	4.1000
110	34.157	16.275	1.2327	5.0693
120	39.861	19.491	1.6027	6.1357
130	45.626	22.909	2.0301	7.2933
140	51.404	26.502	2.5153	8.5361
150	57.154	30.245	3.0581	9.8578
160	62.843	34.116	3.6581	11.252
170	68.441	38.094	4.3146	12.714
180	73.924	42.162	5.0266	14.236
190	79.272	46.303	5.7927	15.815
200	84.467	50.502	6.6115	17.444
210	89.499	54.745	7.4815	19.119
220	94.357	59.021	8.4009	20.836
230	99.036	63.320	9.3680	22.589

240	103.53	67.630	10.381	24.376
250	107.85	71.945	11.438	26.192
260	111.99	76.256	12.537	28.035
270	115.95	80.557	13.677	29.901
273.15	117.16	81.909	14.044	30.493
280	119.74	84.843	14.856	31.787
290	123.37	89.109	16.072	33.690
298.15	126.21	92.568	17.089	35.252
300	126.84	93.350	17.323	35.608

Table 9. Standard thermodynamic functions of γ -alumina $\text{Al}_2\text{O}_3 \cdot 0.811\text{H}_2\text{O}$. $\Phi_m^\circ = \Delta_f^\circ S_m^\circ - \Delta_f^\circ H_m^\circ/T$. $M = 116.57 \text{ g}\cdot\text{mole}^{-1}$. All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^\circ S_m^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^\circ H_m^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Phi_m^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0	0	0	0	0
1	$2.429\cdot 10^{-3}$	$2.345\cdot 10^{-3}$	$1.183\cdot 10^{-6}$	$1.162\cdot 10^{-3}$
2	$5.595\cdot 10^{-3}$	$4.939\cdot 10^{-3}$	$5.105\cdot 10^{-6}$	$2.386\cdot 10^{-3}$
3	0.01011	$8.007\cdot 10^{-3}$	$1.282\cdot 10^{-5}$	$3.733\cdot 10^{-3}$
4	0.01635	0.01173	$2.590\cdot 10^{-5}$	$5.251\cdot 10^{-3}$
5	0.02445	0.01621	$4.614\cdot 10^{-5}$	$6.981\cdot 10^{-3}$
6	0.03434	0.02152	$7.539\cdot 10^{-5}$	$8.950\cdot 10^{-3}$
7	0.04588	0.02766	$1.154\cdot 10^{-4}$	0.01117
8	0.05906	0.03462	$1.677\cdot 10^{-4}$	0.01366
9	0.07420	0.04243	$2.341\cdot 10^{-4}$	0.01642
10	0.09216	0.05115	$3.170\cdot 10^{-4}$	0.01944
15	0.25520	0.11483	$1.129\cdot 10^{-3}$	0.03953
20	0.54324	0.22482	$3.075\cdot 10^{-3}$	0.07105
25	0.96877	0.38881	$6.789\cdot 10^{-3}$	0.11724
30	1.5728	0.61587	0.01306	0.18047
35	2.3750	0.91607	0.02285	0.26319
40	3.3539	1.2954	0.03711	0.36768
45	4.4630	1.7534	0.05660	0.49549
50	5.6812	2.2856	0.08191	0.64729
60	8.6107	3.5735	0.15300	1.0234
70	12.066	5.1523	0.25587	1.4971
80	16.070	7.0197	0.39616	2.0677
90	20.464	9.1631	0.57857	2.7345
100	25.100	11.558	0.80624	3.4952
110	29.861	14.172	1.0810	4.3454
120	34.667	16.977	1.4036	5.2800
130	39.462	19.941	1.7743	6.2928
140	44.211	23.040	2.1927	7.3776
150	48.891	26.250	2.6583	8.5282
160	53.483	29.552	3.1702	9.7386
170	57.975	32.930	3.7276	11.003
180	62.355	36.368	4.3293	12.317
190	66.614	39.854	4.9743	13.674
200	70.745	43.377	5.6612	15.071
210	74.742	46.926	6.3888	16.503
220	78.601	50.492	7.1556	17.967
230	82.321	54.069	7.9603	19.459

240	85.901	57.649	8.8015	20.976
250	89.341	61.226	9.6779	22.514
260	92.644	64.794	10.588	24.072
270	95.813	68.351	11.530	25.646
273.15	96.784	69.468	11.834	26.145
280	98.851	71.890	12.504	27.234
290	101.76	75.410	13.507	28.835
298.15	104.05	78.262	14.346	30.147
300	104.55	78.908	14.539	30.446

Table 10. Standard thermodynamic functions of γ -alumina $\text{Al}_2\text{O}_3 \cdot 0.537 \text{H}_2\text{O}$. $\Phi_m^{\circ} = \Delta_f^{\circ} S_m^{\circ} - \Delta_f^{\circ} H_m^{\circ}/T$. $M = 111.64 \text{ g}\cdot\text{mole}^{-1}$. All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^{\circ} S_m^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^{\circ} H_m^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\Phi_m^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0	0	0	0	0
1	$1.261\cdot 10^{-3}$	$1.224\cdot 10^{-3}$	$6.165\cdot 10^{-7}$	$6.072\cdot 10^{-4}$
2	$2.851\cdot 10^{-3}$	$2.558\cdot 10^{-3}$	$2.632\cdot 10^{-6}$	$1.242\cdot 10^{-3}$
3	$5.070\cdot 10^{-3}$	$4.108\cdot 10^{-3}$	$6.529\cdot 10^{-6}$	$1.932\cdot 10^{-3}$
4	$8.165\cdot 10^{-3}$	$5.967\cdot 10^{-3}$	$1.307\cdot 10^{-5}$	$2.701\cdot 10^{-3}$
5	0.01232	$8.215\cdot 10^{-3}$	$2.321\cdot 10^{-5}$	$3.572\cdot 10^{-3}$
6	0.01767	0.01091	$3.811\cdot 10^{-5}$	$4.564\cdot 10^{-3}$
7	0.02435	0.01412	$5.900\cdot 10^{-5}$	$5.694\cdot 10^{-3}$
8	0.03250	0.01789	$8.730\cdot 10^{-5}$	$6.977\cdot 10^{-3}$
9	0.04237	0.02227	$1.246\cdot 10^{-4}$	$8.427\cdot 10^{-3}$
10	0.05434	0.02733	$1.727\cdot 10^{-4}$	0.01006
15	0.16308	0.06668	$6.761\cdot 10^{-4}$	0.02161
20	0.36309	0.13881	$1.954\cdot 10^{-3}$	0.04114
25	0.66947	0.25045	$4.483\cdot 10^{-3}$	0.07112
30	1.1176	0.40973	$8.885\cdot 10^{-3}$	0.11355
35	1.7315	0.62592	0.01594	0.17058
40	2.5121	0.90631	0.02648	0.24433
45	3.4415	1.2545	0.04131	0.33659
50	4.4964	1.6707	0.06110	0.44863
60	6.9887	2.7017	0.11803	0.73455
70	10.082	4.0042	0.20292	1.1053
80	13.669	5.5799	0.32132	1.5634
90	17.610	7.4146	0.47748	2.1093
100	21.786	9.4845	0.67431	2.7415
110	26.109	11.763	0.91369	3.4565
120	30.513	14.223	1.1968	4.2501
130	34.952	16.841	1.5241	5.1170
140	39.388	19.593	1.8958	6.0519
150	43.788	22.461	2.3117	7.0497
160	48.124	25.426	2.7713	8.1051
170	52.372	28.471	3.2739	9.2132
180	56.513	31.583	3.8184	10.369
190	60.530	34.746	4.4037	11.569
200	64.410	37.950	5.0286	12.808
210	68.145	41.184	5.6915	14.082
220	71.729	44.437	6.3910	15.388
230	75.160	47.702	7.1255	16.722
240	78.437	50.971	7.8936	18.081

250	81.563	54.237	8.6938	19.461
260	84.539	57.494	9.5244	20.862
270	87.371	60.738	10.384	22.279
273.15	88.234	61.756	10.661	22.728
280	90.064	63.965	11.271	23.710
290	92.624	67.170	12.185	25.153
298.15	94.615	69.765	12.948	26.337
300	95.056	70.352	13.123	26.607

Table 11. Standard thermodynamic functions of γ -alumina $\text{Al}_2\text{O}_3 \cdot 0.204 \text{ H}_2\text{O}$. $\Phi_m^{\circ} = \Delta_f^{\circ} S_m^{\circ} - \Delta_f^{\circ} H_m^{\circ}/T$. $M = 105.64 \text{ g}\cdot\text{mole}^{-1}$ All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

T/K	$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^{\circ} S_m^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_f^{\circ} H_m^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\Phi_m^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0	0	0	0	0
1	$9.525 \cdot 10^{-4}$	$9.474 \cdot 10^{-4}$	$4.743 \cdot 10^{-7}$	$4.731 \cdot 10^{-4}$
2	$1.959 \cdot 10^{-3}$	$1.911 \cdot 10^{-3}$	$1.923 \cdot 10^{-6}$	$9.501 \cdot 10^{-4}$
3	$3.117 \cdot 10^{-3}$	$2.917 \cdot 10^{-3}$	$4.442 \cdot 10^{-6}$	$1.437 \cdot 10^{-3}$
4	$4.596 \cdot 10^{-3}$	$4.007 \cdot 10^{-3}$	$8.264 \cdot 10^{-6}$	$1.941 \cdot 10^{-3}$
5	$6.640 \cdot 10^{-3}$	$5.239 \cdot 10^{-3}$	$1.382 \cdot 10^{-5}$	$2.474 \cdot 10^{-3}$
6	$9.537 \cdot 10^{-3}$	$6.690 \cdot 10^{-3}$	$2.183 \cdot 10^{-5}$	$3.052 \cdot 10^{-3}$
7	0.01356	$8.447 \cdot 10^{-3}$	$3.328 \cdot 10^{-5}$	$3.693 \cdot 10^{-3}$
8	0.01890	0.01059	$4.940 \cdot 10^{-5}$	$4.417 \cdot 10^{-3}$
9	0.02558	0.01319	$7.153 \cdot 10^{-5}$	$5.243 \cdot 10^{-3}$
10	0.03342	0.01628	$1.009 \cdot 10^{-4}$	6.188v
15	0.09899	0.04009	$4.053 \cdot 10^{-4}$	0.01307
20	0.22987	0.08488	$1.199 \cdot 10^{-3}$	0.02492
25	0.43956	0.15700	$2.835 \cdot 10^{-3}$	0.04361
30	0.75463	0.26319	$5.771 \cdot 10^{-3}$	0.07083
35	1.1996	0.41114	0.01060	0.10834
40	1.7883	0.60812	0.01801	0.15796
45	2.5212	0.85969	0.02872	0.22143
50	3.3878	1.1691	0.04344	0.30023
60	5.5165	1.9657	0.08746	0.50806
70	8.2250	3.0125	0.15572	0.78802
80	11.410	4.3142	0.25355	1.1448
90	14.946	5.8594	0.38509	1.5806
100	18.718	7.6277	0.55325	2.0952
110	22.640	9.5947	0.75995	2.6861
120	26.646	11.736	1.0063	3.3499
130	30.689	14.028	1.2930	4.0823
140	34.730	16.451	1.6201	4.8785
150	38.738	18.984	1.9875	5.7339
160	42.685	21.610	2.3946	6.6436
170	46.550	24.314	2.8409	7.6032
180	50.314	27.082	3.3253	8.6082
190	53.960	29.901	3.8468	9.6545
200	57.478	32.759	4.4041	10.738
210	60.859	35.645	4.9959	11.855
220	64.098	38.552	5.6208	13.003
230	67.193	41.470	6.2774	14.177
240	70.144	44.392	6.9642	15.375

250	72.951	47.313	7.6798	16.594
260	75.619	50.227	8.4227	17.832
270	78.150	53.129	9.1917	19.085
273.15	78.920	54.040	9.4391	19.483
280	80.551	56.015	9.9853	20.353
290	82.826	58.881	10.802	21.632
298.15	84.591	61.201	11.485	22.682
300	84.980	61.726	11.641	22.921

Figure Captions

Figure 1. XRD patterns of all alumina samples.

Figure 2. TGA data showing the mass loss as temperatures increased for all alumina samples.

Figure 3. Plot of the molar heat capacity at constant pressure as a function of temperature for γ - Al_2O_3 with $\text{Al}_2\text{O}_3 \cdot 1.540\text{H}_2\text{O}$ represented by black circles, $\text{Al}_2\text{O}_3 \cdot 0.811\text{H}_2\text{O}$ by red inverted triangles, $\text{Al}_2\text{O}_3 \cdot 0.537\text{H}_2\text{O}$ by green squares, and $\text{Al}_2\text{O}_3 \cdot 0.204\text{H}_2\text{O}$ by yellow diamonds. The inset shows the data at low temperatures ($T < 10$ K). Included behind the data points are the fit functions for the samples

Figure 4. Plot of the percent deviations of the fit functions for samples AIP 300 from the heat capacity data against temperature. Inset shows deviations below 10 K.

Figure 5. Plot of the percent deviations of the fit functions for samples AIP 600 from the heat capacity data against temperature on a logarithmic scale. Inset shows deviations below 10 K.

Figure 6. Plot of the percent deviations of the fit functions for samples AIP 900 from the heat capacity data against temperature. Inset shows deviations below 10 K.

Figure 7. Plot of the percent deviations of the fit functions for samples AIP 1100 from the heat capacity data against temperature. Inset shows deviations below 10 K.

Figure 8. Plot of the calculated molar heat capacity at constant pressure as a function of temperature for H_2O adsorbed onto the γ - Al_2O_3 samples alongside the molar heat capacity of hexagonal ice. Smoothed heat capacity values for the samples with less moles of water adsorbed to their surfaces were subtracted from samples with more moles water adsorbed to their surfaces and were normalized by dividing by the difference in the moles of water. The inset shows the data at low temperatures ($T < 10$ K).

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.