Heat capacities and thermodynamics of formation of ϵ -Keggin MAI_{12} Selenates (M= Al(III), Ga(III), or Ge(IV))

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Abstract

We report enthalpies of formation from the elements and oxides, $\Delta_f H^\circ = -(22,673.44 \pm 30.19) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_{f,ox} H = -(869.68 \pm 28.75) \text{ kJ} \cdot \text{mol}^{-1}$, for $[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$ (GeAl_{12}) measured using high temperature oxide-melt solution calorimetry. This material is the selenate salt of the germanium-substituted polynuclear Al_{13}^{7+} ion in the ϵ -Keggin structure. We also report heat capacities from temperatures of 2 K to 300 K on this GeAl_{12} selenate and its other heterometal substituted forms, $\text{Na}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$ (AlAl_{12}) and $\text{Na}[\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$ (GaAl_{12}), measured using a Quantum Design Physical Property Measurement System (PPMS). These measurements were used to calculate entropies and subsequently free energies of formation for these three materials. All three MAI_{12} selenates, where M= Al(III), Ga(III), or Ge(IV), have similar heat capacities from temperatures 2 K to 300 K and similar characteristic Debye temperatures, Θ_D , suggesting similar lattice vibrational densities of states.

Keywords: heat capacity, Keggin, Al_{13} , polyoxocation, enthalpy of formation

1. Introduction

The $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{7+}$ polyoxocation [1,2,3] in the ϵ -isomer of the Baker-Figgis-Keggin series [1,4,5] is one of the most studied aqueous molecular clusters because of its relevance to aqueous aluminum chemistry, with applications from environmental science and geochemistry to deodorants [6,7,8,9,10,11,12]. These ions are considered simple model species for the structure and reactivity of larger hydrated nanophase solids in the environment because they contain similar coordinations found in common soil minerals [13,14]. The aqueous $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{7+}$ ion (AlAl_{12}^{7+}) and its heterometal-substituted forms, $[\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{7+}$ (GaAl_{12}^{7+}) [15,16,17,18,19], and $[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{8+}$ (GeAl_{12}^{8+}) [20,21], can be crystallized with sulfate or selenate ions. These crystals are used for structural determination [1,2,3,15,21,22] and recently, for calorimetric studies of heat of formation [23,24]. Crystallization of the AlAl_{12}^{7+} cluster with sulfate is known to produce at least three different phases depending on the synthesis conditions, and obtaining a phase pure product is difficult [15]. Addition of sodium selenate to solutions containing AlAl_{12}^{7+} or GaAl_{12}^{7+} yields tetrahedral crystals [1,2,3,15,22] with space group $F\bar{4}3m$, (Figure 1a) and a stoichiometry of $\text{Na}[\text{MO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot x\text{H}_2\text{O}_{(\text{cr})}$, where $\text{M} = \text{Ga(III)}$ or Al(III) . The Ge(IV) -substituted MAl_{12}^{x+} ion, with its higher valency and slightly larger size, crystallizes with a slight tetragonal distortion upon addition of selenate to aqueous solutions. These GeAl_{12}^{8+} ions produce an overall symmetry of $I4m2$ (Figure 1 b, c.) and a stoichiometry of $[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot x\text{H}_2\text{O}_{(\text{cr})}$ with no sodium co-ions [21].

FIGURE 1.

(a) $F\bar{4}3m$ - $\text{Na}[\text{MO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot x\text{H}_2\text{O}_{(\text{cr})}$, where $M = \text{Ga(III)}$ or Al(III) ; (b) c-axis - $I4m2$ - $[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot x\text{H}_2\text{O}_{(\text{cr})}$; (c) a-axis - $I4m2$ - $[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot x\text{H}_2\text{O}_{(\text{cr})}$; Waters and sodium omitted for clarity. Blue = aluminum, yellow = selenate, purple = germanium (color online).

As part of an ongoing study of the thermodynamic properties of these compounds, we complement recent measurements of enthalpy of formation [23] with low temperature heat capacity measurements. Together these measurements enable complete thermodynamic characterization of standard enthalpies, entropies, and free energies of formation of these solid heterometal-substituted MAI_{12} selenates ($M = \text{Al(III)}$, Ga(III) or Ge(IV)). These data are a starting point for subsequent work on the thermodynamics of large aqueous polynuclear ions and also provide insight into trends in the stabilities of the solids and the role of the heterometal ion.

2. Experimental Methods

2.1 Materials

This is a continuation of previous work [23] and all MAI_{12} selenates were checked with powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA) to ensure the sample integrity was maintained and the hydration state was unchanged. These materials were stored in

a temperature and humidity controlled room for the duration of these studies. XRD showed no changes to the sample integrity, no extraneous peaks were visible, and the TGA results were also consistent with our previous work on these materials, in particular their water content was unchanged[23]. A summary of the sample descriptions and purities can be found in table 1.

TABLE 1.

Sample descriptions and purities from previous work[23].

Sample	Source	Mass fraction purity	Analysis Method
$\text{Na}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$ (AlAl_{12})	synthesis	>0.98	PXRD ^a , SXRD ^b , TGA-EGA-MS ^c
$\text{Na}[\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$ (GaAl_{12})	synthesis	>0.98	PXRD ^a , SXRD ^b , TGA-EGA-MS ^c , SS ²⁷ Al MAS NMR ^d
$[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$ (GeAl_{12})	synthesis	>0.98	PXRD ^a , TGA-EGA-MS ^c , SS ²⁷ Al MAS NMR ^d
aluminum oxide, α - Al_2O_3	Sigma-Aldrich	>0.99	Manufacturer ICP, Fired overnight at 1673K
sodium molybdate dihydrate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	EMD	Reagent grade	Mixed with MoO_3 and heated to 973K
molybdic anhydride, MoO_3	Fisher Scientific	Reagent grade	Mixed with $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and heated to 973K

^aPowder X-ray diffraction

^bSingle Crystal X-ray diffraction

^cThermogravimetric analysis with evolved gas analysis – mass spectrometry

^dSolid State ²⁷Al magic-angle spinning nuclear magnetic resonance

2.2 Enthalpy of formation measurements

The enthalpies of solution, $\Delta_{\text{sol}}H$, of the $\text{Na}[(\text{MO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$, where M = Al(III) or Ga(III), were measured previously [23], and the thermodynamic cycles to calculate the enthalpy of formation, $\Delta_f H^\circ$, for these compounds are found in the prior work. High temperature oxide melt solution calorimetry was used to obtain the $\Delta_f H^\circ$ of $[(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$, as a suitable germanium reference material necessary to the thermodynamic cycle could not be found for room temperature aqueous solution

calorimetry. A custom built Tian-Calvet microcalorimeter described elsewhere [25,26] was used to measure the enthalpy of drop solution, $\Delta_{\text{ds}}H$, of the solid GeAl_{12} compound. The sample was pelletized (~2-3 mg) and dropped from room temperature into molten $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ at $T = 973$ K. The calorimeter was calibrated using the heat content of α -alumina pellets (5 mg). These procedures are standard in our laboratory and have been described previously [25,26]. The chemicals used in the GeAl_{12} selenate thermodynamic cycle were dictated by the availability of pure and stoichiometric reference compounds and knowledge of their enthalpies of formation, as well as by finding conditions for their rapid dissolution in the chosen calorimetric solvent.

2.3 Heat capacity

The low temperature heat capacities of all three samples were measured at $P = 1.2$ mPa using a Quantum Design Physical Property Measurement System (PPMS) with 0.15 K spacing from $T = (1.8 - 10)$ K, logarithmic spacing from $T = (10 - 100)$ K, and 10 K increments from $T = (100 - 300)$ K. Samples were prepared for heat capacity measurement in the PPMS by mixing about (7 to 24) mg of each powder with about 5 mg of copper strips (Alfa Aesar, 0.99999 mass fraction purity) to provide better thermal contact and putting this into copper cups (about 15 mg). The cups were then pressed into pellets approximately 3 mm in diameter and 1 mm in height. After running an addenda measurement, which contains the heat capacities of the calorimeter and the Apeizon N grease used to mount the sample, the samples were successively mounted onto the PPMS puck, and the heat capacities was measured. The PPMS automatically corrects for the addenda heat capacity, and the copper contribution was subtracted using data from ref. [27] yielding the constant pressure heat capacities of MAI_{12} selenates. The uncertainties for the PPMS measurements of the standard molar heat capacities $C_{p,m}^\circ$ following this method are

estimated to be $\pm 0.02 \cdot C_{p,m}^\circ$ for $2 < T/K < 10$ and $\pm 0.01 \cdot C_{p,m}^\circ$ for $10 < T/K < 302$ [28]. Details of the PPMS measurements and sample masses are given in table 2.

TABLE 2.

Details of the calorimetric experiments for the PPMS measurements including pressure, p , sample mass, M_s , molar mass, M , and copper mass, M_{Cu} .

	AlAl ₁₂	GaAl ₁₂	GeAl ₁₂
p / mPa	1.2	1.2	1.2
M_s / mg	16.04	23.66	21.41
M / g·mol ⁻¹	1850.12	1892.86	1872.79
M_{Cu} / mg	18.75	19.80	18.24

^aThe estimated standard uncertainties in the masses $M_{s,Cu}$ and pressure p are $u(M_{s,Cu}) = 0.06$ mg and $u(p) = 0.10$ mPa.

3. Results and discussion

3.1 Heat of formation of GeAl₁₂ selenate

The enthalpy of formation from the elements, $\Delta_f H^\circ$, and oxides, $\Delta_{f,ox} H$, of the GeAl₁₂ selenate was determined using the thermodynamic table presented in table 3. The corresponding enthalpies to the reactions, ΔH_x , in table 3 are listed in table 4, including the drop solution enthalpy, $\Delta_{ds} H$, (Reaction 1 in tables 3 and 4) of the GeAl₁₂ selenate measured in 3Na₂O·4MoO₃ at $T = 973$ K. The $\Delta_{ds} H$ of the GeAl₁₂ selenate is represented as the average of 8 measurements with errors calculated as 2σ of the mean. The reported values for the $\Delta_{f,ox} H$ and $\Delta_f H^\circ$ of the GeAl₁₂ selenate are found in lines 7 and 12 respectively of table 4.

TABLE 3.

Thermodynamic cycle used to calculate $\Delta_f H^\circ$ at $T = (298.15) \text{ K}$ and $p = 0.1 \text{ MPa}$ for $[(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}^a$.

1	$[(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr}, 298 \text{ K})} = \text{GeO}_{2(\text{sol}, 973 \text{ K})} + 4\text{SeO}_{2(\text{sol}, 973 \text{ K})} + 6\text{Al}_2\text{O}_{3(\text{sol}, 973 \text{ K})} + 36\text{H}_2\text{O}_{(\text{g}, 973 \text{ K})} + 2\text{O}_{2(\text{g}, 973 \text{ K})}$
2	$\text{q-GeO}_2_{(\text{cr}, 298 \text{ K})} = \text{GeO}_{2(\text{sol}, 973 \text{ K})}$
3	$\alpha\text{-Al}_2\text{O}_{3(\text{cr}, 298 \text{ K})} = \text{Al}_2\text{O}_{3(\text{sol}, 973 \text{ K})}$
4	$\text{SeO}_{2(\text{cr}, 298 \text{ K})} = \text{SeO}_{2(\text{sol}, 973 \text{ K})}$
5	$\text{H}_2\text{O}_{(\text{l}, 298 \text{ K})} = \text{H}_2\text{O}_{(\text{g}, 973 \text{ K})}$
6	$\text{O}_{2(\text{g}, 298 \text{ K})} = \text{O}_{2(\text{g}, 973 \text{ K})}$
7	$\text{q-GeO}_2_{(\text{cr}, 298 \text{ K})} + 6\alpha\text{-Al}_2\text{O}_{3(\text{cr}, 298 \text{ K})} + 4\text{SeO}_{2(\text{cr}, 298 \text{ K})} + 36\text{H}_2\text{O}_{(\text{l}, 298 \text{ K})} + 2\text{O}_{2(\text{g}, 298 \text{ K})} = [(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr}, 298 \text{ K})}$
8	$\text{Ge}_{(\text{cr})} + \text{O}_{2(\text{g})} = \text{q-GeO}_2_{(\text{cr}, 298 \text{ K})}$
9	$2\text{Al}_{(\text{cr})} + 1.5\text{O}_{2(\text{g})} = \alpha\text{-Al}_2\text{O}_{3(\text{cr}, 298 \text{ K})}$
10	$\text{Se}_{(\text{cr})} + \text{O}_{2(\text{g})} = \text{SeO}_{2(\text{cr}, 298 \text{ K})}$
11	$\text{H}_{2(\text{g})} + 0.5\text{O}_{2(\text{g})} = \text{H}_2\text{O}_{(\text{l}, 298 \text{ K})}$
12	$\text{Ge}_{(\text{cr})} + 12\text{Al}_{(\text{cr})} + 4\text{Se}_{(\text{cr})} + 34\text{O}_{2(\text{g})} + 36\text{H}_{2(\text{g})} = [(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr}, 298 \text{ K})}$

^a Abbreviations: cr = crystalline; l = liquid; g = gas; sol = solution ; q = quartz

TABLE 4.

Measured and calculated enthalpies ($\text{kJ} \cdot \text{mol}^{-1}$) for reactions in table 3.^a

$\Delta H_1 = \Delta_{\text{ds}} H([(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr}, 298 \text{ K})}) = 3906.27 \pm 26.44(8)$
$\Delta H_2 = \Delta_{\text{ds}} H(\text{q-GeO}_2_{(\text{cr}, 298 \text{ K})}) = 73.59 \pm 0.86^b$
$\Delta H_3 = \Delta_{\text{ds}} H(\alpha\text{-Al}_2\text{O}_{3(\text{cr}, 298 \text{ K})}) = 105.80 \pm 1.59^c$
$\Delta H_4 = \Delta_{\text{ds}} H(\text{SeO}_{2(\text{cr}, 298 \text{ K})}) = -49.87 \pm 1.5^d$
$\Delta H_5 = \Delta_{\text{ds}} H(\text{H}_2\text{O}_{(\text{l}, 298 \text{ K})}) = 69^e$
$\Delta H_6 = \Delta_{\text{hc}} H(\text{O}_{2(\text{g}, 298 \text{ K})}) = 21.84^e$
$\Delta H_7 = \Delta_{\text{fox}} H = -\Delta H_1 + \Delta H_2 + 6\Delta H_3 + 4\Delta H_4 + 36\Delta H_5 + 2\Delta H_6 = -869.68 \pm 28.75^f$
$\Delta H_8 = \Delta_f H^\circ(\text{q-GeO}_2_{(\text{cr}, 298 \text{ K})}) = -559.20 \pm 2.27^g$
$\Delta H_9 = \Delta_f H^\circ(\alpha\text{-Al}_2\text{O}_{3(\text{cr}, 298 \text{ K})}) = -1,675.7 \pm 1.3^e$
$\Delta H_{10} = \Delta_f H^\circ(\text{SeO}_{2(\text{cr}, 298 \text{ K})}) = -225.39 \pm 0.6^h$
$\Delta H_{11} = \Delta_f H^\circ(\text{H}_2\text{O}_{(\text{l}, 298 \text{ K})}) = -285.8 \pm 0.1^e$
$\Delta H_{12} = \Delta_f H^\circ([(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr}, 298 \text{ K})}) = \Delta H_7 + \Delta H_8 + 6\Delta H_9 + 4\Delta H_{10} + 36\Delta H_{11} = -22,673.44 \pm 30.19$

^a Expanded uncertainties $U_c(\Delta H)$ are calculated as 2σ of the mean. See Appendix A Tables A1 & A2 for individual experiments.

^b $\Delta_{\text{ds}} H$ at $T = 1073 \text{ K}$ from Reference [31] was corrected to $T = 973 \text{ K}$ using the heat content from Reference[30].

^c $\Delta_{\text{ds}}H$ at $T = 1073$ K measured in our laboratory by K. I. Lilova and J. Qi was corrected to $T = 973$ K using the heat content from Reference[30].

^d Reference[29]

^e Reference[30]

^f Uncertainty of the combined reaction is calculated by error propagation as the square root of the sum of squares of error of each reaction.

^g Reference [31]

^h Reference [32]

3.2 Heat capacity

The measured heat capacities of the MAI_{12} selenates are shown in tables 5 – 7 and figures 2 – 4. All three samples show a decrease in the heat capacity data above about $T = 250$ K as a result of water loss under high vacuum. Data points where the samples exhibited water loss are circled in the figures and were excluded from all data analysis. Figure 5 shows the data below $T = 100$ K, emphasizing the similarity at low temperatures for all three samples.

TABLE 5.

Heat capacity at constant pressure ($p = 1.2$ mPa) for $\text{Na}[(\text{AlO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}$ (AlAl_{12}) from $T = (2 - 300)$ K. $M = 1850.12$ g·mol⁻¹.

T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.9114	0.08773	8.8611	6.1594
2.0385	0.10364	8.9862	6.4250
2.1942	0.12490	9.1433	6.6310
2.3272	0.14565	9.2640	6.9809
2.4545	0.16530	9.4211	7.2277
2.5928	0.19098	9.5441	7.5934
2.7317	0.21958	9.7850	8.0858
2.8705	0.25011	10.886	10.740
3.0099	0.28487	12.100	14.240
3.1519	0.32451	13.429	18.792
3.3061	0.36956	14.926	24.439
3.4403	0.41228	16.581	31.689
3.5792	0.46071	18.411	40.616
3.7152	0.50987	20.520	51.857
3.8504	0.56205	22.777	65.550
3.9576	0.60928	25.297	81.735
4.1115	0.68222	28.099	101.31
4.2515	0.74710	31.223	124.47

1				
2				
3				
4	4.4354	0.83599	34.691	152.00
5	4.5753	0.91560	38.549	184.13
6	4.7358	1.0221	42.835	221.52
7	4.9020	1.1229	47.611	262.85
8	5.0046	1.1996	52.927	311.52
9	5.1451	1.2994	58.836	365.88
10	5.2762	1.4104	65.416	428.39
11	5.4358	1.5192	72.734	497.94
12	5.5948	1.6559	80.882	578.64
13	5.7244	1.7621	89.936	669.16
14	5.8530	1.8863	100.02	762.11
15	6.0222	2.0521	111.24	864.56
16	6.1393	2.1724	121.35	958.75
17	6.2890	2.3236	131.46	1053.3
18	6.4538	2.5137	141.55	1145.2
19	6.5673	2.6475	151.65	1242.9
20	6.7396	2.8524	161.74	1336.8
21	6.8551	3.0003	171.78	1428.1
22	7.0489	3.2096	181.86	1519.6
23	7.1500	3.3616	191.94	1609.5
24	7.3318	3.6028	202.08	1704.7
25	7.4361	3.7792	212.14	1792.2
26	7.6143	4.0148	222.10	1879.2
27	7.7190	4.1981	232.07	1963.3
28	7.8998	4.4466	242.11	2043.1
29	8.0002	4.6683	252.24	2123.0
30	8.1704	4.9075	262.25	2196.4
31	8.2837	5.1342	272.18 ^b	2258.9
32	8.4407	5.4020	281.83 ^b	2300.3
33	8.5607	5.6121	291.27 ^b	2283.2
34	8.7144	5.8677	300.10 ^b	2187.9

^aThe estimated standard uncertainties in the temperature T and pressure p are $u(T) = 0.001$ K and $u(p) = 0.10$ mPa. The expanded uncertainties at approximately 95 percent confidence limits in the values of $C_{p,m}^{\circ}$ are $U(C_{p,m}^{\circ}) = 0.02 \cdot C_{p,m}^{\circ}$ ($2 < T/K < 20$) and $U(C_{p,m}^{\circ}) = 0.01 \cdot C_{p,m}^{\circ}$ ($10 < T/K < 302$).

^bvalues not included in data fitting due to water loss.

FIGURE 2.

Experimental heat capacity from $T = (0 - 300)$ K of $\text{Na}[(\text{AlO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12 \text{H}_2\text{O}$ (AlAl_{12}) including fit. Circled data points (all data above $T = 265$ K) show effect of water loss under high vacuum and were therefore excluded from fitting procedures and thermodynamic calculations. Inset shows values below $T = 10$ K.

TABLE 6.

Heat capacity at constant pressure ($p = 1.2$ mPa) for $\text{Na}[(\text{GaO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}$ (GaAl_{12}) from $T = (2 - 300)$ K. $M = 1892.86 \text{ g} \cdot \text{mol}^{-1}$.

T / K	$C_{p,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.8975	0.09519	8.8039	6.2964
2.0357	0.11199	8.9351	6.5732
2.1766	0.13234	9.0946	6.8311
2.3144	0.15447	9.2223	7.1489
2.4528	0.17896	9.3558	7.4530
2.5910	0.20576	9.5402	7.8437
2.7290	0.23621	9.7346	8.2595
2.8669	0.26901	10.816	10.919
3.0057	0.30587	12.057	14.481
3.1437	0.34536	13.367	18.883
3.2801	0.38858	14.856	24.485

1				
2				
3				
4	3.4183	0.43504	16.525	31.619
5	3.5560	0.48460	18.344	40.550
6	3.6945	0.53949	20.437	51.612
7	3.8342	0.59782	22.696	65.088
8	3.9736	0.66237	25.216	81.286
9	4.1133	0.73113	28.018	100.71
10	4.2536	0.80300	31.142	123.81
11	4.4326	0.90501	34.612	151.02
12	4.5608	0.98011	38.469	183.05
13	4.6896	1.0670	42.762	220.10
14	4.8309	1.1626	47.542	261.57
15	4.9725	1.2647	52.861	309.96
16	5.1205	1.3856	58.769	364.59
17	5.2846	1.5033	65.349	427.07
18	5.4085	1.6043	72.670	496.68
19	5.5407	1.7222	80.823	577.09
20	5.6820	1.8504	89.894	667.34
21	5.8332	2.0017	99.984	761.40
22	5.9964	2.1592	111.21	863.90
23	6.1161	2.2832	121.32	958.40
24	6.2504	2.4334	131.43	1050.3
25	6.3922	2.5951	141.52	1150.1
26	6.5394	2.7512	151.62	1240.4
27	6.7075	2.9678	161.72	1334.1
28	6.8228	3.1186	171.78	1427.2
29	6.9580	3.3001	181.86	1517.4
30	7.1046	3.4713	191.94	1604.2
31	7.2753	3.7237	202.08	1697.3
32	7.3886	3.8967	212.14	1782.0
33	7.5280	4.1085	222.10	1868.5
34	7.6858	4.3577	232.09	1947.4
35	7.8222	4.5595	242.12	2024.0
36	7.9506	4.7871	252.26	2105.5
37	8.0916	5.0260	262.29	2178.5
38	8.2474	5.3358	272.23	2246.4
39	8.3833	5.5226	281.88 ^b	2295.6
40	8.5125	5.7642	291.27 ^b	2284.0
41	8.6716	6.0347	299.93 ^b	2163.3

^aThe estimated standard uncertainties in the temperature T and pressure p are $u(T) = 0.001$ K and $u(p) = 0.10$ mPa. The expanded uncertainties at approximately 95 percent confidence limits in the values of $C_{p,m}^{\circ}$ are $U(C_{p,m}^{\circ}) = 0.02 \cdot C_{p,m}^{\circ}$ ($2 < T/K < 20$) and $U(C_{p,m}^{\circ}) = 0.01 \cdot C_{p,m}^{\circ}$ ($10 < T/K < 302$).

^bvalues not included in data fitting due to water loss.

FIGURE 3.

Experimental heat capacity from $T = (0 - 300)$ K of $\text{Na}[(\text{GaO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12 \text{ H}_2\text{O}$ (GaAl_{12}) including fit. Circled data points (all data above $T = 275$ K) show effect of water loss under high vacuum and were therefore excluded from fitting procedures and thermodynamic calculations. Inset shows values below $T = 10$ K.

TABLE 7.

Heat capacity at constant pressure ($p = 1.2$ mPa) for $[(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12 \text{ H}_2\text{O}$ (GeAl_{12}) from $T = (2 - 300)$ K. $M = 1872.79 \text{ g} \cdot \text{mol}^{-1}$.

T / K	$C_{p,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.9403	0.06980	8.7526	5.3142
2.0693	0.08374	8.8906	5.5414
2.2067	0.10008	9.0306	5.8028
2.3430	0.11792	9.1711	6.0612
2.4825	0.13863	9.3065	6.3005
2.6187	0.16079	9.4446	6.5749
2.7563	0.18559	9.6825	7.0053
2.8964	0.21350	10.761	9.3497
3.0339	0.24460	11.965	12.540
3.1702	0.27746	13.304	16.848

1				
2				
3				
4	3.3073	0.31376	14.794	21.805
5	3.4445	0.35234	16.443	28.499
6	3.5827	0.39562	18.252	37.619
7	3.7206	0.44183	20.370	48.334
8	3.8591	0.49028	22.635	61.539
9	4.0040	0.54768	25.159	77.429
10	4.1399	0.60480	27.966	96.749
11	4.2788	0.66471	31.088	120.04
12	4.4330	0.74131	34.557	147.11
13	4.5705	0.80743	38.418	178.83
14	4.7059	0.88348	42.719	216.11
15	4.8400	0.95985	47.493	258.86
16	4.9808	1.0459	52.828	307.56
17	5.1202	1.1346	58.712	361.57
18	5.2643	1.2267	65.282	421.75
19	5.3957	1.3238	72.596	489.45
20	5.5471	1.4274	80.741	566.41
21	5.6805	1.5331	89.798	651.59
22	5.8197	1.6416	99.867	741.11
23	5.9602	1.7682	111.08	839.99
24	6.1006	1.8943	121.18	924.52
25	6.2404	2.0304	131.25	1014.1
26	6.3806	2.1552	141.30	1100.0
27	6.5202	2.3068	151.40	1189.4
28	6.6595	2.4321	161.51	1273.4
29	6.7997	2.5987	171.55	1362.2
30	6.9396	2.7472	181.63	1451.7
31	7.0796	2.9084	191.77	1545.1
32	7.2181	3.0755	201.87	1639.7
33	7.3587	3.2470	211.96	1732.4
34	7.4977	3.4324	222.04	1829.2
35	7.6372	3.6247	232.11	1926.3
36	7.7731	3.8006	242.19	2021.8
37	7.9167	4.0019	252.21 ^b	2083.3
38	8.0599	4.2214	262.24 ^b	2138.0
39	8.1992	4.4257	272.28 ^b	2210.5
40	8.3371	4.6311	282.10 ^b	2273.7
41	8.4777	4.8389	291.57 ^b	2306.7
42	8.6145	5.0646	300.74 ^b	2285.0

^aThe estimated standard uncertainties in the temperature T and pressure p are $u(T) = 0.001$ K and $u(p) = 0.10$ mPa. The expanded uncertainties at approximately 95 percent confidence limits in the values of $C_{p,m}^\circ$ are $U(C_{p,m}^\circ) = 0.02 \cdot C_{p,m}^\circ$ ($2 < T/K < 20$) and $U(C_{p,m}^\circ) = 0.01 \cdot C_{p,m}^\circ$ ($10 < T/K < 302$).

^bvalues not included in data fitting due to water loss.

FIGURE 4.

Experimental heat capacity from $T = (0 - 300)$ K of for $[(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}$ (GeAl_{12}) including fit. Circled data points (all data above $T = 245$ K) show effect of water loss under high vacuum and were excluded from fitting and thermodynamic calculations. Inset shows values below $T = 10$ K.

FIGURE 5.

Heat capacities of the three MAI₁₂ selenates (M = Al(III), Ga(III), or Ge(IV)) below $T = 100$ K.

3.3 Curve fitting

Heat capacities were fit to a series of overlapping functions in the low ($T < 10$ K), mid ($10 < T < 75$ K), and high ($T > 75$ K) temperature regions. The low temperature heat capacity values were fit to the function:

$$C = \gamma T + B_3 T^3 + B_5 T^5 + B_7 T^7 \quad (1)$$

where γ is proportional to the concentration of lattice vacancies in insulating materials[33], and the B_3 , B_5 , and B_7 terms represent the harmonic-lattice expression [34]. The fitting parameters, % RMS, and ranges of validity for these fits as well as those of the mid and high temperature regions are given in table 8.

The functions used for fitting the mid temperature values were polynomials that have no physical meaning but merely serve to link the low and high temperature fits:

$$C = \sum_{n=0,1,2\dots 7} A_n T^n \quad (2)$$

The high temperature fits consist of a sum of Debye and Einstein heat capacity functions of the form [35]:

$$C = m \cdot D\left(\frac{\Theta_D}{T}\right) + n_1 \cdot E\left(\frac{\Theta_{E,1}}{T}\right) + n_2 \cdot E\left(\frac{\Theta_{E,2}}{T}\right) + A_1 \cdot T + A_2 \cdot T^2 \quad (3)$$

where $D(\Theta_D / T)$, $E(\Theta_{E,1} / T)$, and $E(\Theta_{E,2} / T)$ are Debye and Einstein functions; m , n_1 , n_2 , Θ_D , $\Theta_{E,1}$, and $\Theta_{E,2}$ are all adjustable parameters; $(m + n_1 + n_2)$ should be approximately equal to the number of atoms in the formula unit or unit cell; and the A_1 and A_2 terms represent an approximation to correct for thermal expansion.

TABLE 8.

Summary of the fitting parameters of heat capacity for all samples covering the entire temperature range (1.9 – 300

K. Fits are divided into three overlapping ranges: $T < 10$ K (low T), $6 \text{ K} < T < 75$ K (mid T), and $T > 50$ K (high T).

The %RMS and most valid range for each fit are given along with the fitting parameters.

	Parameters	AlAl ₁₂	GaAl ₁₂	GeAl ₁₂
Low T Fits	$\gamma / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$	0.013339	0.014653	4.842×10^{-3}
	$B_3 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-4}$	8.967×10^{-3}	9.713×10^{-3}	8.269×10^{-3}
	$B_5 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-6}$	4.225×10^{-6}	-1.112×10^{-6}	-1.606×10^{-7}
	$B_7 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-8}$	-9.549×10^{-8}	-8.798×10^{-8}	-6.414×10^{-8}
	Θ_D	324.75	316.21	332.93
	%RMS	0.528	0.531	0.376
	Range / K	1.9 – 7.36	1.9 – 7.12	1.9 – 7.36
Mid T Fits	$A_0 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	1.2871	0.83475	-1.3088
	$A_1 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$	-0.53648	-0.40679	0.65737
	$A_2 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-3}$	0.072795	0.067052	-0.13146
	$A_3 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-4}$	7.721×10^{-3}	7.722×10^{-3}	0.022622
	$A_4 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-5}$	-2.654×10^{-4}	-2.620×10^{-4}	-8.500×10^{-4}
	$A_5 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-6}$	3.428×10^{-6}	3.366×10^{-6}	1.594×10^{-5}

	$A_6 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-7}$	-1.601×10^{-8}	-1.568×10^{-8}	-1.518×10^{-7}
	$A_7 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-8}$			5.799×10^{-10}
	%RMS	0.450	0.315	0.357
	Range / K	7.36 – 58.02	7.12 – 67.55	7.36 – 53.2
High T Fits	m / mol	22.588	26.495	25.647
	Θ_D / K	210.68	232.97	240.17
	n_1 / mol	41.248	41.547	35.751
	$\Theta_{E,1} / \text{K}$	411.71	449.21	468.55
	n_2 / mol	93.033	86.805	95.980
	$\Theta_{E,2} / \text{K}$	980.09	1001.2	1189.2
	T			0.22588
	T ²			4.557×10^{-3}
	%RMS	0.158	0.188	0.147
	Range / K	58.02 – 305	67.55 – 305	53.2 – 305

3.4 Thermodynamic calculations

Once fits to all data were completed, smoothed heat capacities and thermodynamic values were also generated and are given in tables 9 – 11. These thermodynamic values calculated from the fit heat capacity method have an uncertainty of approximately $\pm 2\%$.

TABLE 9.

Standard thermodynamic functions for $\text{Na}[(\text{AlO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}$ (AlAl_{12}) from $T = (0 - 300) \text{ K}$.

$$\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_o^T H_m^\circ / T. M = 1850.12 \text{ g} \cdot \text{mol}^{-1}.$$

T / K	$C_{p,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T H_m^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\varphi_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0	0	0	0	0
1	0.02231	0.01633	8.912×10^{-6}	7.417×10^{-3}
2	0.09854	0.05062	6.259×10^{-5}	0.01932
3	0.28295	0.12090	2.420×10^{-4}	0.04021
4	0.63001	0.24529	6.827×10^{-4}	0.07462
5	1.1933	0.44190	1.574×10^{-3}	0.12706
6	2.0230	0.72841	3.158×10^{-3}	0.20204
7	3.1614	1.1216	5.723×10^{-3}	0.30396
8	4.6283	1.6359	9.591×10^{-3}	0.43698
9	6.4363	2.2820	0.01509	0.60482
10	8.5954	3.0687	0.02258	0.81067
15	24.661	9.2990	0.10210	2.4925

4	20	48.921	19.535	0.28290	5.3899
5	25	79.899	33.671	0.60252	9.5700
6	30	115.81	51.351	1.0901	15.014
7	35	155.03	72.114	1.7661	21.654
8	40	196.40	95.496	2.6439	29.398
9	45	239.32	121.09	3.7326	38.145
10	50	283.71	148.59	5.0396	47.800
11	55	329.77	177.78	6.5725	58.278
12	60	376.46	208.48	8.3385	69.506
13	65	424.16	240.49	10.340	81.419
14	70	472.69	273.70	12.582	93.961
15	75	521.55	307.97	15.067	107.08
16	80	570.36	343.19	17.797	120.73
17	85	618.88	379.23	20.770	134.87
18	90	666.98	415.97	23.985	149.47
19	95	714.59	453.31	27.439	164.47
20	100	761.75	491.16	31.130	179.86
21	110	854.99	568.15	39.215	211.65
22	120	947.39	646.50	48.227	244.61
23	130	1039.6	725.98	58.162	278.58
24	140	1132.1	806.40	69.021	313.40
25	150	1225.0	887.68	80.806	348.97
26	160	1318.1	969.71	93.521	385.20
27	170	1411.1	1052.4	107.17	422.01
28	180	1503.7	1135.7	121.74	459.35
29	190	1595.3	1219.4	137.24	497.14
30	200	1685.6	1303.6	153.64	535.36
31	210	1774.2	1388.0	170.94	573.95
32	220	1860.6	1472.5	189.12	612.87
33	230	1944.7	1557.1	208.15	652.09
34	240	2026.2	1641.6	228.01	691.56
35	250	2105.0	1725.9	248.66	731.24
36	260	2180.9	1809.9	270.09	771.12
37	270	2253.8	1893.6	292.27	811.14
38	273.15	2276.2	1919.9	299.41	823.78
39	280	2323.9	1976.9	315.16	851.29
40	290	2391.0	2059.6	338.74	891.53
41	298.15	2443.5	2126.6	358.44	924.38
42	300	2455.1	2141.7	362.97	931.84
43	305	2486.1	2182.6	375.32	952.01

TABLE 10.

Standard thermodynamic functions for $\text{Na}[(\text{GaO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}$ (GaAl_{12}) from $T = (0 - 300)$ K.

$$\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_0^T H_m^\circ / T. M = 1892.86 \text{ g} \cdot \text{mol}^{-1}.$$

T / K	$C_{p,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_0^T H_m^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\varphi_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0	0	0	0	0
1	0.02427	0.01778	9.701×10^{-6}	8.078×10^{-3}

1					
2					
3					
4	2	0.10691	0.05502	6.800×10^{-5}	0.02102
5	3	0.30589	0.13113	2.623×10^{-4}	0.04369
6	4	0.67804	0.26530	7.375×10^{-4}	0.08092
7	5	1.2773	0.47629	1.694×10^{-3}	0.13746
8	6	2.1518	0.78196	3.384×10^{-3}	0.21797
9	7	3.3393	1.1986	6.102×10^{-3}	0.32689
10	8	4.8475	1.7394	0.01017	0.46832
11	9	6.6912	2.4134	0.01591	0.64572
12	10	8.8778	3.2286	0.02367	0.86205
13	15	24.978	9.5853	0.10475	2.6021
14	20	49.145	19.902	0.28695	5.5549
15	25	79.954	34.071	0.60729	9.7794
16	30	115.66	51.743	1.0946	15.255
17	35	154.69	72.469	1.7694	21.915
18	40	195.88	95.794	2.6451	29.667
19	45	238.67	121.32	3.7309	38.414
20	50	282.98	148.75	5.0343	48.061
21	55	328.99	177.86	6.5635	58.525
22	60	376.70	208.52	8.3271	69.737
23	65	425.37	240.59	10.332	81.638
24	70	473.92	273.89	12.580	94.174
25	75	522.75	308.25	15.072	107.30
26	80	571.18	343.54	17.807	120.95
27	85	619.13	379.61	20.783	135.10
28	90	666.60	416.34	23.997	149.70
29	95	713.67	453.65	27.448	164.72
30	100	760.44	491.44	31.134	180.11
31	110	853.44	568.28	39.203	211.89
32	120	946.28	646.52	48.202	244.84
33	130	1039.3	725.94	58.130	278.79
34	140	1132.6	806.37	68.989	313.59
35	150	1225.8	887.69	80.781	349.15
36	160	1318.7	969.77	93.504	385.37
37	170	1410.8	1052.5	107.15	422.18
38	180	1501.8	1135.7	121.72	459.51
39	190	1591.2	1219.3	137.18	497.29
40	200	1678.9	1303.2	153.53	535.49
41	210	1764.6	1387.2	170.75	574.05
42	220	1848.2	1471.2	188.82	612.91
43	230	1929.6	1555.1	207.71	652.06
44	240	2008.8	1638.9	227.40	691.43
45	250	2085.7	1722.5	247.88	731.00
46	260	2160.5	1805.8	269.11	770.74
47	270	2233.2	1888.7	291.08	810.61
48	273.15	2255.6	1914.7	298.15	823.20
49	280	2303.8	1971.2	313.77	850.59
50	290	2372.4	2053.2	337.15	890.65
51	298.15	2427.0	2119.7	356.71	923.34
52	300	2439.2	2134.8	361.21	930.76
53	305	2472.0	2175.4	373.49	950.83
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TABLE 11.

Standard thermodynamic functions for $[(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}$ (GeAl_{12}) from $T = (0 - 300)$ K.

$$\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_0^T H_m^\circ / T. M = 1872.79 \text{ g} \cdot \text{mol}^{-1}.$$

T / K	$C_{p,m}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_0^T H_m^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\varphi_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0	0	0	0	0
1	0.01311	7.599×10^{-3}	4.488×10^{-6}	3.110×10^{-3}
2	0.07583	0.03173	4.276×10^{-5}	0.01035
3	0.23762	0.08892	1.892×10^{-4}	0.02587
4	0.54740	0.19560	5.673×10^{-4}	0.05376
5	1.0524	0.36796	1.349×10^{-3}	0.09814
6	1.7960	0.62164	2.752×10^{-3}	0.16301
7	2.8148	0.97128	5.033×10^{-3}	0.25228
8	4.1212	1.4293	8.478×10^{-3}	0.36961
9	5.7370	2.0048	0.01338	0.51819
10	7.6887	2.7072	0.02006	0.70088
15	22.766	8.3759	0.09249	2.2101
20	46.270	17.959	0.26185	4.8664
25	76.563	31.430	0.56651	8.7695
30	111.81	48.442	1.0357	13.918
35	150.65	68.555	1.6906	20.252
40	192.25	91.359	2.5468	27.689
45	236.09	116.51	3.6168	36.141
50	281.57	143.73	4.9105	45.523
55	327.15	172.72	6.4332	55.757
60	372.60	203.13	8.1821	66.762
65	419.05	234.78	10.161	78.461
70	466.00	267.55	12.373	90.791
75	513.03	301.31	14.821	103.70
80	559.86	335.92	17.503	117.12
85	606.27	371.25	20.419	131.03
90	652.17	407.21	23.565	145.37
95	697.50	443.69	26.940	160.11
100	742.27	480.60	30.539	175.21
110	830.32	555.49	38.404	206.37
120	916.87	631.46	47.141	238.62
130	1002.6	708.24	56.739	271.79
140	1088.3	785.68	67.193	305.72
150	1174.4	863.69	78.506	340.32
160	1261.3	942.25	90.684	375.48
170	1349.3	1021.4	103.74	411.15
180	1438.6	1101.0	117.67	447.26
190	1529.2	1181.2	132.51	483.77
200	1621.2	1262.0	148.26	520.66
210	1714.4	1343.3	164.94	557.89
220	1809.0	1425.3	182.56	595.46
230	1904.7	1507.8	201.12	633.33
240	2001.6	1590.9	220.65	671.49
250	2099.6	1674.6	241.16	709.94

260	2198.6	1758.8	262.65	748.66
270	2298.7	1843.7	285.13	787.64
273.15	2330.4	1870.5	292.43	799.97
280	2399.6	1929.1	308.63	826.88
290	2501.5	2015.1	333.13	866.37
298.15	2585.3	2085.6	353.86	898.73
300	2604.4	2101.6	358.66	906.10
305	2656.1	2145.1	371.81	926.06

All thermodynamic parameters for the MAl_{12} selenates ($\text{M}=\text{Al(III)}$, Ga(III) , or Ge(IV)) are summarized in table 11, including standard molar entropies, and enthalpies and Gibbs energies of formation from the elements and oxides. Values of $\Delta_{\text{f,ox}}H$ and $\Delta_{\text{f,ox}}G$ are similar for the isostructural Al and Ga compounds but the Ge compound is significantly less stable with respect to the oxide components (table 12). The characteristic Debye temperatures Θ_D of the MAl_{12} selenates are similar but increase slightly from Al to Ga to Ge and the Ge compound has a slightly lower vibrational entropy at 298 K.

TABLE 12.

Thermodynamic parameters at $T = 298 \text{ K}$, $p = 0.1 \text{ MPa}$, for solid $\text{Na}[(\text{AlO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$, $\text{Na}[(\text{GaO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}$, and $[(\text{GeO}_4)\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot 12\text{H}_2\text{O}_{(\text{cr})}^a$.

MAl_{12} Selenate	$S^\circ/$ ($\text{J} \cdot \text{K}^{-1} \cdot$ mol^{-1})	$\Delta_{\text{f,ox}}H^b/$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta_{\text{f,ox}}S^b/$ ($\text{J} \cdot \text{K}^{-1} \cdot$ mol^{-1})	$\Delta_{\text{f,ox}}G^b/$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta_{\text{f}}H^\circ/$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta_{\text{f}}S^\circ/$ ($\text{J} \cdot \text{K}^{-1} \cdot$ mol^{-1})	$\Delta_{\text{f}}G^\circ/$ ($\text{kJ} \cdot \text{mol}^{-1}$)
Al	2126.59 ± 42.53	-1073.21 ± 39.42	-1442.15 ± 42.72	-643.23 ± 41.43	-23363.02 ± 39.60^c	-10141.43 ± 42.55	-20339.35 ± 41.58
Ga	2119.75 ± 42.40	-1107.36 ± 39.95	-1466.04 ± 42.59	-670.25 ± 41.42	-23103.86 ± 40.09^c	-10161.06 ± 42.42	-20074.34 ± 42.04
Ge	2085.58 ± 41.71	-869.68 ± 28.75	-1475.35 ± 41.90	-429.80 ± 31.35	-22673.74 ± 30.19	-10133.77 ± 41.73	-19652.06 ± 32.65

^a Uncertainty of the combined reactions is calculated by error propagation as the square root of the sum of squares of error of each reaction.

^b includes gaseous oxygen and water, see Reaction 7 in Table 3.

^c Recalculated from previous results [23] using $\Delta_{\text{f}}H^\circ(\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O})$ [32] to reduce error.

4. Conclusions

Heat capacity measurements allowed the calculation of standard entropies for a well-known crystalline form (with selenate as anion) of the molecular cluster, $\epsilon\text{-AlAl}_{12}^{7+}$, and its heterometal-substituted forms, GaAl_{12}^{7+} and GeAl_{12}^{8+} . Here we have reported these heat capacity measurements as well as the enthalpies of solution of these materials using various calorimetric techniques. The enthalpies of formation from the oxides and elements were calculated and used in conjunction with the standard entropies to find the free energies of formation of these MAl_{12} selenates, where $\text{M} = \text{Al(III)}$, Ga(III) , or Ge(IV) . We found that the two isostructural heptavalent MAl_{12} selenates ($\text{M} = \text{Al(III)}$ or Ga(III)) were similar in $\Delta_{\text{f,ox}}H$, $\Delta_{\text{f,ox}}G$, and S° , and the GeAl_{12} selenate was significantly less stable than these other two compounds. Our future work is aimed at measuring the energetics of the aqueous $\text{MAl}_{12}^{7/8+}$ ions and these data will be essential towards not only calculating these thermodynamic values, but also towards elucidating how the crystalline framework interacts with the $\text{MAl}_{12}^{7/8+}$ ions. Differences in the stabilities of the constituent $\text{MAl}_{12}^{7/8+}$ ions will become more apparent with these results.

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