Heat capacities, standard entropies and Gibbs energies of Sr-, Rb- and Cs-Substituted barium aluminotitanate hollandites

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Abstract:

Heat capacities of Sr-, Rb-, and Cs-hollandite with the compositions $\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Al}_{2.38}\text{Ti}_{5.59}\text{O}_{16}$, $\text{Ba}_{1.17}\text{Rb}_{0.19}\text{Al}_{2.46}\text{Ti}_{5.53}\text{O}_{16}$, and $\text{Ba}_{1.18}\text{Cs}_{0.21}\text{Al}_{2.44}\text{Ti}_{5.53}\text{O}_{16}$ were measured from 2 K to 300 K using a Quantum Design Physical Property Measurement System (PPMS). From the heat capacity results, the following thermodynamic parameters have been determined. The characteristic Debye temperatures θ_D over the temperature range (30 – 300) K of Sr-, Rb-, and Cs-hollandite are 178.2, 189.7, and 189.2 K, respectively, and their standard entropies at 298.15 K are (413.9 ± 8.3) , (415.1 ± 8.3) , and $(419.6 \pm 8.4) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Combined with previously reported formation enthalpies, their corresponding Gibbs energies of formation from oxides ($\Delta_f G_{\text{ox}}^\circ$) are (-194.9 ± 11.4) , (-195.0 ± 12.8) , and $(-201.1 \pm 12.8) \text{ kJ} \cdot \text{mol}^{-1}$, and those from elements ($\Delta_f G_{\text{el}}^\circ$) are (-7694.6 ± 12.5) , (-7697.0 ± 13.9) , and $(-7697.1 \pm 13.9) \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. The similarities among the obtained $\Delta_f G_{\text{ox}}^\circ$ values suggest that the three substituted hollandites have similar thermodynamic stabilities at standard conditions, which is in agreement with the ease of Cs–Rb–Sr substitutions in the hollandite structure.

Keywords: Heat capacity, Gibbs energy, Entropy, Hollandite, Radionuclide immobilization.

1. Introduction

Nuclear power has been widely used as an alternative energy source to fossil fuels due to its high efficiency, reasonable cost and carbon-free characteristics since the 1950s [1]. As of 2013, over 540

nuclear reactors including power stations were built in 31 countries during the last century [2]; however, safe storage of the radioactive waste from nuclear energy production is a long term issue for human health and environmental protection. In particular, high-level waste (HLW), a byproduct from either used reactor fuel or reprocessed materials [3], needs to be isolated and disposed in a safe manner to avoid infiltration into the nearby soil, water, or air systems. HLW contains approximately 5 % of short and long lived fission products [4] with their half-lives ($t_{1/2}$) ranging from decades to thousands of years [5]. Typically, the shorter the half-life of a radionuclide, the higher its radiation; hence, separation (*e.g.* via ion exchange) and immobilization of short-lived radionuclides, such as ^{90}Sr ($t_{1/2} = 28.9$ year), ^{84}Rb ($t_{1/2} = 33.1$ year), and ^{137}Cs ($t_{1/2} = 23.2$ year), from high level wastes have been considered to be an indispensable treatment to reduce the decay heat load and radioactivity [6].

The conventional route to dispose HLW uses borosilicate glass as a matrix [7], which has good durability and low aqueous solubility; however, there has been concern about its stability during the heat release from radioactive decay of the waste [8]. An alternative strategy is to immobilize the radionuclides as components in the crystal structures of dense minerals, such as silicate, phosphate, and titanate [9-16]. Compared to glass waste forms, these dense minerals have robust thermal stability and aqueous durability rendering them viable candidates for hosting radionuclides.

As a multiphase ceramic waste form, Synroc consists mainly of a mixture of titanate minerals: zirconolite, perovskite, and barium hollandite [9-10]. In particular, barium hollandite is used to immobilize fission products such as Rb, Sr, and Cs, which tend to be water soluble and volatile on heating. Studies have been done for Ba-hollandite waste formed during melt processing and their structure [17-19]. The Ba-hollandite family has the general formula $A_x(\text{Ti}^{4+}, \text{B})_8\text{O}_{16}$ in which Ba

occupies the A site and can be substituted by Cs, Rb, Sr, *etc.*, while the ratio of other B cations (such as Al^{3+} , Fe^{3+} , and Mg^{2+}) to Ti^{4+} can be varied to maintain charge neutrality [20-22]. Hollandites possess a three dimensional (3D) framework composed of $[\text{TiO}_6]$ and $[\text{BO}_6]$ octahedra with A cations encapsulated within the cavity sites. These structural characteristics position hollandites as promising potential waste forms for various radioactive alkali and alkaline earth cations including Cs^+ , Rb^+ , and Sr^{2+} .

To assess further the suitability of hollandites for immobilizing fission radionuclides, it is essential to determine their thermodynamic properties, especially the effects of cation substitutions on phase stability. We have recently measured the enthalpies of formation for two series of Ba hollandites from constituent oxides and/or competing ternary phases using high-temperature oxide melt solution calorimetry [11, 23]. Heats of formation of barium hollandites with Al^{3+} , Fe^{2+} , or Mg^{2+} substituted at the B site indicate that while Al and Fe hollandites are thermodynamically stable phases, Mg hollandite is not an appropriate waste form candidate [23]. More recently, the enthalpies of formation of barium aluminotitanate hollandites with Cs^+ , Rb^+ , or Sr^{2+} substituted at the A site ($\text{Ba}_{1.18}\text{Cs}_{0.21}\text{Al}_{2.44}\text{Ti}_{5.53}\text{O}_{16}$, $\text{Ba}_{1.17}\text{Rb}_{0.19}\text{Al}_{2.46}\text{Ti}_{5.53}\text{O}_{16}$, and $\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Al}_{2.38}\text{Ti}_{5.59}\text{O}_{16}$) were measured [11]. The determined energetics with respect to BaTiO_3 and SrTiO_3 perovskites and other oxides reveals decreased stability from Cs- to Rb- to Sr-hollandite, which is consistent with the phase assemblage observed in Synroc: Cs^+ , Rb^+ , and Ba^{2+} occur in hollandite, whereas Sr^{2+} occurs in perovskite [11].

The aim of this work is to measure low temperature heat capacities (C_p) of the above Cs-, Rb-, and Sr-hollandite and obtain their standard entropies (S°). Combination with the enthalpies of

formation obtained previously [11] yields their Gibbs energies of formation (ΔG_f°) thus providing a complete thermodynamic dataset for these substituted Ba hollandites.

2. Experimental Methods

2.1 Sample synthesis and characterization

The three Cs-, Rb-, and Sr-hollandite samples (table 1) were synthesized using a sol-gel route described in detail in ref [11]. Their compositions were determined to be $\text{Ba}_{1.18}\text{Cs}_{0.21}\text{Al}_{2.44}\text{Ti}_{5.53}\text{O}_{16}$, $\text{Ba}_{1.17}\text{Rb}_{0.19}\text{Al}_{2.46}\text{Ti}_{5.53}\text{O}_{16}$, and $\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Al}_{2.38}\text{Ti}_{5.59}\text{O}_{16}$ using electron microprobe analysis (EMPA). Synchrotron X-ray diffraction (XRD) combined with Rietveld analysis showed that all the three hollandites adopt a tetragonal symmetry with the space group $I4/m$ [11].

2.2 Heat capacity measurements

The low-temperature heat capacities of all three hollandites were measured at $P = 1.2$ mPa using a Quantum Design PPMS with 0.15 K spacing at $T = (1.8 - 10)$ K, logarithmic spacing at $T = (10 - 100)$ K, and 10 K increments at $T = (100 - 300)$ K. Samples used for the heat capacity measurements were prepared by mixing (17 – 26) mg of each powder with about 5 mg of copper strips (Alfa Aesar, 0.99999 mass fraction purity), which were put 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 addendum measurement, which contains the heat capacities of the calorimeter and the Apiezon N grease used to mount the sample, the samples were successively mounted onto the PPMS puck, and the heat capacities were measured. The PPMS automatically corrects for the addenda heat capacity, and the copper contribution was subtracted using data from ref. [24] yielding

the constant pressure heat capacities of Cs-, Rb-, and Cs-hollandite. The uncertainties for the PPMS measurements of the standard molar heat capacities $C_{p,m}^\circ$ are estimated to be $\pm 0.02 \cdot C_{p,m}^\circ$ for $2 < T/\text{K} < 10$ and $\pm 0.01 \cdot C_{p,m}^\circ$ for $10 < T/\text{K} < 302$ [25]. Details of the PPMS measurements and sample masses are given in table 2.

3. Results and discussion

3.1 Heat capacity curve fitting

The experimental heat capacities of Sr-, Rb-, and Cs-hollandite are given in tables 3-5 and shown graphically in figure 1. The smoothness of all the curves indicates that there are no phase transitions or other anomalies in the heat capacities. Heat capacities were fit to a series of overlapping functions in the low ($T < 10$ K), mid ($6 < T / \text{K} < 45$), and high ($T > 30$ K) temperature regions. The low-temperature heat capacity data were fit to the function:

$$C = \gamma T + B_3 T^3 + B_5 T^5 + B_7 T^7 + B_9 T^9 \quad (1)$$

where γ is proportional to the concentration of structural defects (*e.g.* vacancies) in insulating materials [26], and the B_3 , B_5 , B_7 , and B_9 terms represent the harmonic-lattice expression [27]. We note that these samples also exhibit a slight contribution from low-energy modes with a gap in the density of states, but these fits and their interpretation have been published elsewhere [28]. The fitting parameters, % RMS, and ranges of validity for these fits as well as those for the mid- and high-temperature regions are given in table 6.

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

$$C = \sum_{n=0,1,2...8} A_n T^n \quad (2)$$

The high-temperature fits consist of a sum of Debye and Einstein heat capacity functions of the form [29]:

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

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; and $(m + n_1 + n_2)$ should be approximately equal to the number of atoms in the formula unit or unit cell. Generally one Debye and one Einstein function are sufficient to fit data above about 100 K, but to fit a larger T range an extra Einstein function was added. The characteristic Debye temperature Θ_D from the high-temperature fits shows that Sr-hollandite ($\Theta_D = 178.21$ K) has the weakest lattice, Rb-hollandite ($\Theta_D = 189.75$ K) has the strongest, and the Cs-hollandite lattice ($\Theta_D = 189.21$ K) is marginally weaker than Rb-hollandite.

3.2 Thermodynamic calculations

Once satisfactory fits to all the data were obtained, smoothed heat capacities and thermodynamic functions were generated (tables 7 - 9). Thermodynamic parameters calculated following this method have a standard uncertainty of approximately $\pm 2\%$.

The entropies, enthalpies, and Gibbs energies of formation of the three hollandites from oxides and elements at $T = 298.15$ K are summarized in table 10. The standard entropies (S°) calculated from the measured heat capacities are $(413.9 \pm 8.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Sr-hollandite, $(415.1 \pm 8.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Rb-hollandite, and $(419.6 \pm 8.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Cs-hollandite. These entropies are

statistically very similar (though they show slight decreases from Cs- to Rb- to Sr-hollandite); thus the vibrational properties of the three hollandite crystal lattices are similar, which is consistent with their similarities in structures – having the same crystal symmetry ($I4/m$) and small differences in unit cell parameters [11].

The Gibbs energies of formation at standard conditions can be calculated by combining the entropies obtained with the previously determined formation enthalpies and standard entropies of constituent oxides and elements in tables 11 and 12. As shown in table 10, the Gibbs energies of formation from oxides ($\Delta_f G_{\text{ox}}^\circ$) are $(-194.9 \pm 11.4) \text{ kJ}\cdot\text{mol}^{-1}$ for Sr-hollandite, $-195.0 \pm 12.8 \text{ kJ}\cdot\text{mol}^{-1}$ for Rb-hollandite, and $(-201.0 \pm 12.8) \text{ kJ}\cdot\text{mol}^{-1}$ for Cs-hollandite. Similarly, the standard Gibbs energies of formation from elements ($\Delta_f G_{\text{el}}^\circ$) are $(-7694.6 \pm 12.5) \text{ kJ}\cdot\text{mol}^{-1}$ for Sr-hollandite, $(-7697.0 \pm 13.9) \text{ kJ}\cdot\text{mol}^{-1}$ for Rb-hollandite, and $(-7697.1 \pm 13.9) \text{ kJ}\cdot\text{mol}^{-1}$ for Cs-hollandite. Since all these values are highly negative, the three hollandites are thermodynamically very stable relative to their constituent oxides and elements at standard conditions. In addition, the $\Delta_f G_{\text{ox}}^\circ$ values are similar, which is consistent with the ease of Cs–Rb–Sr substitutions in hollandites via accommodating these cations over the cavity sites along the structural tunnels [11]. Lastly, in our previous study [11], enthalpic analysis with respect to BaTiO_3 and SrTiO_3 perovskites and other oxides reveals decreased stability from Cs- to Rb- to Sr-hollandite. Since the enthalpic term plays a more important role than the entropic term, the same trend holds in terms of Gibbs energies for these solid-solid reactions. The revealed stability relation is in agreement with the phase assemblage observed in Synroc where Cs^+ , Rb^+ , and Ba^{2+} enter into hollandite, but Sr^{2+} occurs in perovskite.

5. Conclusions

Low temperature heat capacities of Sr-, Rb-, and Cs-substituted barium hollandites were measured using a Quantum Design PPMS calorimeter, and their standard entropies were deduced. The Gibbs energies of formation of the three hollandite phases were then calculated by combining the obtained entropies with previously determined formation enthalpies. These thermodynamic parameters will enable calculations of the solubilities of radionuclides coming from hollandite dissolution in a variety of aqueous geochemical environments.

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Table 1. Description of the three hollandite samples.

Name	Formula	State	Characterization
Sr-hollandite	$\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Al}_{2.38}\text{Ti}_{5.59}\text{O}_{16}$	Powder	XRD ^a , EMPA ^b
Rb-hollandite	$\text{Ba}_{1.17}\text{Rb}_{0.19}\text{Al}_{2.46}\text{Ti}_{5.53}\text{O}_{16}$	Powder	XRD, EMPA
Cs-hollandite	$\text{Ba}_{1.18}\text{Cs}_{0.21}\text{Al}_{2.44}\text{Ti}_{5.53}\text{O}_{16}$	Powder	XRD, EMPA

^a X-ray diffraction

^b Electron microprobe analysis, the fraction of cations in the formula has a standard uncertainty of about $u = 0.05$.

Table 2. Details of the PPMS calorimetric measurements including pressure (p), sample mass (M_s), molar mass (M) and copper mass (M_{Cu}).

	Sr-hollandite	Rb-hollandite	Cs-hollandite
p / mPa	1.2	1.2	1.2
M_s / mg	18.29	16.53	26.04
M / $\text{g}\cdot\text{mol}^{-1}$	753.10	763.98	776.49
M_{Cu} / mg	22.20	21.16	22.00

^aThe estimated standard uncertainties in the masses $M_{\text{s,Cu}}$ and pressure p are $u(M_{\text{s,Cu}}) = 0.06$ mg and $u(p) = 0.1$ mPa.

Table 3. Heat capacity at constant pressure ($p = 1.2$ mPa) for $\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Al}_{2.38}\text{Ti}_{5.59}\text{O}_{16}$ (Sr-hollandite) from 2 K – 300 K. $M = 753.10$ g·mol⁻¹.

T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.9322	4.5015×10^{-3}	8.7367	0.35485
2.0595	5.2462×10^{-3}	8.8748	0.37995
2.1987	6.2184×10^{-3}	9.0128	0.40397
2.3361	7.0979×10^{-3}	9.1499	0.43012
2.4770	8.4172×10^{-3}	9.2886	0.45603
2.6153	9.5002×10^{-3}	9.4256	0.48410
2.7699	0.011047	9.6608	0.53108
2.9055	0.012468	10.737	0.81381
3.0449	0.014242	11.938	1.2647
3.1809	0.015625	13.277	1.9131
3.3260	0.017961	14.773	2.8263
3.4661	0.019824	16.451	4.0760
3.6014	0.021969	18.306	5.6983
3.7421	0.024729	20.360	7.6889
3.8830	0.026871	22.632	10.159
4.0221	0.029533	25.156	13.103
4.1620	0.032269	27.966	16.570
4.3018	0.035161	31.091	20.719
4.4397	0.038707	34.565	25.628
4.5789	0.042518	38.429	31.287
4.7189	0.046260	42.729	37.925
4.8598	0.050680	47.504	45.282
4.9930	0.054045	52.820	53.849
5.1316	0.058056	58.727	64.095
5.2700	0.064154	65.304	75.919
5.4107	0.068840	72.621	89.911
5.5450	0.074684	80.765	106.86
5.6874	0.078775	89.817	126.64
5.8253	0.084898	99.887	147.78
5.9633	0.092019	111.10	172.04
6.1033	0.097641	121.21	193.40
6.2379	0.10677	131.27	214.92
6.3772	0.11397	141.32	235.70
6.5162	0.12256	151.43	256.21
6.6546	0.13077	161.51	275.40
6.7944	0.14133	171.54	294.81
6.9315	0.15110	181.62	313.97

7.0716	0.16169	191.75	332.16
7.2098	0.17422	201.85	350.01
7.3503	0.18304	211.95	364.21
7.4778	0.19564	222.01	377.52
7.6248	0.21164	232.04	390.67
7.7640	0.22572	242.11	402.38
7.9020	0.24142	252.15	414.81
8.0442	0.25801	262.21	423.98
8.1834	0.27406	272.34	432.84
8.3222	0.29392	282.40	442.08
8.4612	0.31372	292.37	450.15
8.5986	0.33395	302.43	462.68

^aThe estimated standard uncertainties in the pressure p and temperature T are $u(p) = 0.10$ mPa and $u(T) = 0.01$ K ($2 < T/K < 20$), $u(T) = 0.02$ K ($20 < T/K < 100$), and $u(T) = 0.05$ K ($100 < T/K < 300$). The expanded uncertainties at approximately 95 percent confidence limits in the values of C_p° ,_m are $U(C_{p,m}^\circ) = 0.02 \cdot C_{p,m}^\circ$ ($2 < T/K < 10$) and $U(C_{p,m}^\circ) = 0.01 \cdot C_{p,m}^\circ$ ($10 < T/K < 302$).

Table 4. Heat capacity at constant pressure ($p = 1.2$ mPa) for $\text{Ba}_{1.17}\text{Rb}_{0.19}\text{Al}_{2.46}\text{Ti}_{5.53}\text{O}_{16}$ (Rb-hollandite) from 2 K – 300 K. $M = 763.98$ g·mol⁻¹.

T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.9416	3.9416×10^{-3}	8.7744	0.33376
2.0656	4.4797×10^{-3}	8.9281	0.35848
2.2059	5.3334×10^{-3}	9.1014	0.38871
2.3431	6.2539×10^{-3}	9.1926	0.41100
2.4821	7.2517×10^{-3}	9.3454	0.43716
2.6191	8.2734×10^{-3}	9.4886	0.46565
2.7568	9.4457×10^{-3}	9.7514	0.51705
2.8952	0.010665	10.779	0.79182
3.0328	0.012111	12.003	1.2473
3.1691	0.014056	13.345	1.9060
3.3071	0.016058	14.828	2.8144
3.4434	0.017537	16.474	4.0757
3.5817	0.019428	18.314	5.6884
3.7200	0.021325	20.394	7.7724
3.8595	0.023436	22.652	10.245
4.0032	0.026208	25.179	13.243
4.1562	0.029210	27.985	16.770
4.2875	0.032263	31.121	21.007
4.4484	0.033976	34.596	25.945
4.5833	0.036841	38.459	31.761
4.7273	0.039926	42.755	38.461
4.8615	0.044229	47.537	45.730
5.0024	0.048483	52.857	54.494
5.1392	0.051075	58.769	64.563
5.2818	0.056120	65.354	76.534
5.4225	0.060254	72.678	90.578
5.5673	0.064950	80.832	107.70
5.7096	0.071795	89.898	127.76
5.8500	0.075083	99.988	148.80
5.9900	0.080665	111.21	172.44
6.1277	0.088533	121.33	194.77
6.2688	0.096148	131.44	215.60
6.4087	0.10303	141.53	236.96
6.5497	0.11051	151.63	258.12
6.6884	0.11920	161.73	276.42
6.8294	0.12893	171.78	295.24
6.9685	0.13924	181.87	313.08

7.1102	0.14699	191.95	330.32
7.2509	0.15902	202.09	346.58
7.3920	0.17115	212.16	362.67
7.5309	0.18413	222.14	377.72
7.6724	0.19571	232.13	391.88
7.8084	0.21243	242.17	403.51
7.9503	0.22769	252.34	415.97
8.0909	0.24205	262.42	426.26
8.2334	0.25888	272.50	436.31
8.4163	0.28351	282.49	445.99
8.4951	0.29522	292.65	454.28
8.6930	0.31852	302.99	463.47

^aThe estimated standard uncertainties in the pressure p and temperature T are $u(p) = 0.10$ mPa and $u(T) = 0.01$ K ($2 < T/K < 20$), $u(T) = 0.02$ K ($20 < T/K < 100$), and $u(T) = 0.05$ K ($100 < T/K < 300$). The expanded uncertainties at approximately 95 percent confidence limits in the values of C_p° ,_m are $U(C_{p,m}^\circ) = 0.02 \cdot C_{p,m}^\circ$ ($2 < T/K < 10$) and $U(C_{p,m}^\circ) = 0.01 \cdot C_{p,m}^\circ$ ($10 < T/K < 302$).

Table 5. Heat capacity at constant pressure ($p = 1.2$ mPa) for $\text{Ba}_{1.18}\text{Cs}_{0.21}\text{Al}_{2.44}\text{Ti}_{5.53}\text{O}_{16}$ (Cs-hollandite) from 2 K – 300 K. $M = 776.49$ g·mol⁻¹.

T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m}^{\circ} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1.9439	4.3166×10^{-3}	8.8182	0.33258
2.0953	5.0738×10^{-3}	8.9560	0.35703
2.2549	5.8832×10^{-3}	9.0930	0.38166
2.4086	6.8395×10^{-3}	9.2311	0.40760
2.5631	7.8549×10^{-3}	9.3697	0.43343
2.7149	8.8965×10^{-3}	9.5070	0.46245
2.8663	0.010385	9.7442	0.51167
2.9894	0.011554	10.819	0.80052
3.1220	0.012828	12.021	1.2574
3.2660	0.014624	13.358	1.9265
3.4041	0.015849	14.856	2.8518
3.5464	0.017940	16.550	4.1422
3.6900	0.020168	18.388	5.7703
3.8280	0.021934	20.469	7.8184
3.9682	0.023478	22.735	10.281
4.1090	0.025725	25.259	13.243
4.2487	0.027978	28.062	16.750
4.3893	0.031329	31.191	20.891
4.5274	0.035078	34.668	25.804
4.6525	0.036138	38.531	31.499
4.7959	0.040023	42.825	38.137
4.9348	0.043005	47.601	45.493
5.0711	0.046096	52.914	54.273
5.2095	0.051828	58.828	64.483
5.3470	0.055358	65.413	76.622
5.4863	0.058664	72.736	90.647
5.6242	0.063750	80.891	107.71
5.7633	0.069664	89.954	127.88
5.9081	0.073210	100.04	149.54
6.0463	0.079621	111.25	173.76
6.1859	0.084688	121.37	196.01
6.3196	0.092708	131.41	217.83
6.4581	0.10070	141.52	239.65
6.5975	0.10795	151.57	260.34
6.7359	0.11702	161.69	280.40
6.8749	0.12309	171.78	299.94
7.0147	0.13362	181.81	317.32
7.1537	0.14448	191.88	335.50

7.2959	0.15299	201.96	352.62
7.4333	0.16828	212.01	369.04
7.5760	0.17833	222.00	384.48
7.6950	0.19052	231.91	397.63
7.8483	0.20663	241.91	410.34
7.9856	0.22198	252.08	422.68
8.1238	0.23657	262.12	432.14
8.2619	0.25705	272.11	443.11
8.4021	0.27024	282.16	454.32
8.5405	0.29198	292.28	462.87
8.6798	0.31396	302.35	469.72

^aThe estimated standard uncertainties in the pressure p and temperature T are $u(p) = 0.10$ mPa and $u(T) = 0.01$ K ($2 < T/K < 20$), $u(T) = 0.02$ K ($20 < T/K < 100$), and $u(T) = 0.05$ K ($100 < T/K < 300$). The expanded uncertainties at approximately 95 percent confidence limits in the values of C_p° ,_m are $U(C_{p,m}^\circ) = 0.02 \cdot C_{p,m}^\circ$ ($2 < T/K < 10$) and $U(C_{p,m}^\circ) = 0.01 \cdot C_{p,m}^\circ$ ($10 < T/K < 302$).

Table 6. Summary of the fitting parameters of heat capacity data of Sr-, Rb- and Cs-hollandite covering the entire temperature range (1.9 – 300) K. Fits are divided into three overlapping ranges: $T < 10$ K (low T), $6 \text{ K} < T < 45$ K (mid T), and $T > 30$ K (high T). The %RMS and most valid range for each fit are given along with the fitting parameters.

	Parameters	Sr-hollandite	Rb-hollandite	Cs-hollandite
Low T Fits	$\gamma / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$	6.9299×10^{-4}	3.8849×10^{-4}	8.9963×10^{-4}
	$B_3 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-4}$	4.5425×10^{-4}	4.4525×10^{-4}	3.5331×10^{-4}
	$B_5 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-6}$	-3.9943×10^{-6}	-6.1202×10^{-6}	-3.2575×10^{-6}
	$B_7 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-8}$	9.4963×10^{-8}	1.3654×10^{-7}	9.1518×10^{-8}
	$B_9 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-10}$	-3.9946×10^{-10}	-6.3516×10^{-10}	-3.7776×10^{-10}
	Θ_D / K	476.04	480.74	518.52
	%RMS	0.680	1.26	1.14
	Range / K	1.9 - 7.46	1.9 - 7.60	1.9 - 7.56
Mid T Fits	$A_0 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	-1.7075	-1.8020	-1.8368
	$A_1 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$	0.88203	0.92442	0.95032
	$A_2 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-3}$	-0.16900	-0.17596	-0.18271
	$A_3 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-4}$	0.014863	0.015293	0.016018
	$A_4 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-5}$	-5.2876×10^{-4}	-5.3975×10^{-4}	-5.7450×10^{-4}
	$A_5 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-6}$	8.8622×10^{-6}	8.9838×10^{-6}	9.7114×10^{-6}
	$A_6 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-7}$	-5.7267×10^{-8}	-5.7728×10^{-8}	-6.3224×10^{-8}
	%RMS	0.483	0.634	0.625
	Range / K	7.46 - 37.06	7.60 – 39.28	7.56 – 39.45
High T Fits	m / mol	2.8385	3.2743	3.2156
	Θ_D / K	178.21	189.75	189.21
	n_1 / mol	7.1860	8.6766	8.3772
	$\Theta_{E,1} / \text{K}$	345.68	384.03	377.88
	n_2 / mol	14.345	13.135	13.811
	$\Theta_{E,2} / \text{K}$	713.30	778.65	759.13
	%RMS	0.476	0.337	0.290
	Range / K	37.06 - 305	39.28 – 305	39.45 – 305

Table 7. Standard thermodynamic functions of $\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Al}_{2.38}\text{Ti}_{5.59}\text{O}_{16}$ (Sr-hollandite) from 0 K – 300 K. $\varphi_{\text{m}}^{\circ} = \Delta_o^T S_{\text{m}}^{\circ} - \Delta_o^T H_{\text{m}}^{\circ}/T$. $M = 753.10 \text{ g}\cdot\text{mol}^{-1}$.

T / K	$C_{p,\text{m}} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_o^T S_{\text{m}}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_o^T H_{\text{m}}^{\circ} / \text{kJ}\cdot\text{mol}^{-1}$	$\varphi_{\text{m}}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0	0	0	0	0
1	1.143×10^{-3}	8.436×10^{-4}	4.594×10^{-7}	3.842×10^{-4}
2	4.904×10^{-3}	2.573×10^{-3}	3.163×10^{-6}	9.918×10^{-4}
3	0.01357	6.002×10^{-3}	1.191×10^{-5}	2.033×10^{-3}
4	0.02920	0.01186	3.263×10^{-5}	3.699×10^{-3}
5	0.05440	0.02087	7.348×10^{-5}	6.172×10^{-3}
6	0.09377	0.03400	1.461×10^{-4}	9.650×10^{-3}
7	0.15561	0.05274	2.685×10^{-4}	0.01439
8	0.25202	0.07936	4.689×10^{-4}	0.02075
9	0.40038	0.11701	7.899×10^{-4}	0.02923
10	0.61692	0.16974	1.292×10^{-3}	0.04050
15	2.9690	0.79077	9.342×10^{-3}	0.16799
20	7.3286	2.2013	0.03438	0.48236
25	12.968	4.4260	0.08475	1.0359
30	19.261	7.3390	0.16512	1.8351
35	26.105	10.814	0.27826	2.8634
40	33.381	14.775	0.42701	4.1002
45	40.933	19.139	0.61260	5.5252
50	48.968	23.863	0.83715	7.1199
60	66.465	34.310	1.4128	10.763
70	85.450	45.966	2.1714	14.946
80	105.42	58.671	3.1251	19.608
90	126.09	72.275	4.2821	24.696
100	147.28	86.653	5.6486	30.167
110	168.83	101.70	7.2289	35.981
120	190.53	117.32	9.0258	42.105
130	212.14	133.43	11.039	48.507
140	233.42	149.93	13.267	55.160
150	254.14	166.74	15.706	62.037
160	274.13	183.79	18.348	69.113
170	293.26	200.98	21.185	76.363
180	311.44	218.27	24.210	83.767
190	328.64	235.57	27.411	91.301
200	344.82	252.84	30.779	98.946
210	360.01	270.04	34.304	106.68
220	374.21	287.12	37.976	114.50
230	387.48	304.05	41.785	122.37

240	399.86	320.80	45.723	130.29
250	411.39	337.36	49.780	138.24
260	422.13	353.71	53.948	146.22
270	432.14	369.83	58.220	154.20
273.15	435.14	374.86	59.586	156.72
280	441.45	385.72	62.588	162.19
290	450.13	401.36	67.047	170.17
298.15	456.76	413.93	70.743	176.66
300	458.22	416.76	71.589	178.13
305	462.05	424.37	73.890	182.10

Table 8. Standard thermodynamic functions of $\text{Ba}_{1.17}\text{Rb}_{0.19}\text{Al}_{2.46}\text{Ti}_{5.53}\text{O}_{16}$ (Rb-hollandite) from 0 K – 300 K. $\varphi_{\text{m}}^{\circ} = \Delta_o^T S_{\text{m}}^{\circ} - \Delta_o^T H_{\text{m}}^{\circ}/T$. $M = 763.98 \text{ g}\cdot\text{mol}^{-1}$.

T / K	$C_{p,\text{m}}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_o^T S_{\text{m}}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta_o^T H_{\text{m}}^{\circ} / \text{kJ}\cdot\text{mol}^{-1}$	$\varphi_{\text{m}}^{\circ} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0	0	0	0	0
1	8.278×10^{-4}	5.357×10^{-4}	3.046×10^{-7}	2.311×10^{-4}
2	4.160×10^{-3}	1.928×10^{-3}	2.497×10^{-6}	6.791×10^{-4}
3	0.01199	4.917×10^{-3}	1.013×10^{-5}	1.540×10^{-3}
4	0.02585	0.01010	2.848×10^{-5}	2.981×10^{-3}
5	0.04790	0.01806	6.453×10^{-5}	5.148×10^{-3}
6	0.08273	0.02962	1.285×10^{-4}	8.205×10^{-3}
7	0.13939	0.04627	2.372×10^{-4}	0.01238
8	0.23048	0.07039	4.189×10^{-4}	0.01803
9	0.37225	0.10512	7.151×10^{-4}	0.02566
10	0.58248	0.15456	1.186×10^{-3}	0.03594
15	2.9268	0.75844	9.023×10^{-3}	0.15694
20	7.3394	2.1625	0.03395	0.46484
25	13.084	4.4002	0.08463	1.0151
30	19.499	7.3451	0.16588	1.8159
35	26.447	10.865	0.28048	2.8509
40	34.028	14.887	0.43153	4.0990
45	41.602	19.330	0.62048	5.5411
50	49.542	24.120	0.84816	7.1567
60	66.827	34.651	1.4284	10.844
70	85.883	46.364	2.1907	15.069
80	106.18	59.146	3.1502	19.769
90	127.19	72.860	4.3166	24.898
100	148.55	87.364	5.6951	30.413
110	170.06	102.53	7.2881	36.276
120	191.51	118.25	9.0961	42.448
130	212.76	134.42	11.118	48.898
140	233.62	150.95	13.350	55.596
150	253.97	167.77	15.788	62.512
160	273.65	184.79	18.427	69.621
170	292.58	201.95	21.259	76.900
180	310.67	219.19	24.276	84.326
190	327.87	236.45	27.469	91.879
200	344.17	253.69	30.830	99.539
210	359.55	270.86	34.350	107.29
220	374.03	287.92	38.018	115.11
230	387.63	304.85	41.827	122.99

240	400.39	321.62	45.768	130.92
250	412.34	338.21	49.832	138.88
260	423.53	354.60	54.012	146.86
270	433.99	370.79	58.301	154.86
273.15	437.15	375.84	59.673	157.38
280	443.78	386.75	62.690	162.86
290	452.93	402.48	67.174	170.85
298.15	459.96	415.13	70.894	177.35
300	461.50	417.98	71.747	178.83
305	465.57	425.65	74.064	182.81

Table 9. Standard thermodynamic functions of $\text{Ba}_{1.18}\text{Cs}_{0.21}\text{Al}_{2.44}\text{Ti}_{5.53}\text{O}_{16}$ (Cs-hollandite) from 0 K – 300 K. $\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_o^T H_m^\circ / T$. $M = 776.49 \text{ g}\cdot\text{mol}^{-1}$.

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	1.250×10^{-3}	1.017×10^{-3}	5.376×10^{-7}	4.792×10^{-4}
2	4.533×10^{-3}	2.722×10^{-3}	3.181×10^{-6}	1.132×10^{-3}
3	0.01164	5.748×10^{-3}	1.088×10^{-5}	2.122×10^{-3}
4	0.02428	0.01067	2.830×10^{-5}	3.598×10^{-3}
5	0.04489	0.01812	6.207×10^{-5}	5.710×10^{-3}
6	0.07820	0.02901	1.223×10^{-4}	8.629×10^{-3}
7	0.13286	0.04482	2.255×10^{-4}	0.01260
8	0.22222	0.06792	3.995×10^{-4}	0.01798
9	0.36451	0.10170	6.877×10^{-4}	0.02529
10	0.57668	0.15041	1.152×10^{-3}	0.03522
15	2.9406	0.75552	9.007×10^{-3}	0.15506
20	7.3426	2.1636	0.03401	0.46327
25	13.002	4.3943	0.08452	1.0137
30	19.281	7.3126	0.16502	1.8118
35	26.120	10.789	0.27824	2.8398
40	33.703	14.767	0.42759	4.0770
45	41.275	19.170	0.61490	5.5060
50	49.239	23.927	0.84100	7.1074
60	66.598	34.410	1.4186	10.767
70	85.722	46.092	2.1789	14.965
80	106.10	58.858	3.1372	19.643
90	127.28	72.572	4.3036	24.754
100	148.94	87.100	5.6844	30.256
110	170.86	102.32	7.2833	36.111
120	192.84	118.13	9.1018	42.284
130	214.68	134.43	11.140	48.742
140	236.17	151.13	13.394	55.457
150	257.14	168.14	15.861	62.401
160	277.43	185.39	18.535	69.548
170	296.92	202.80	21.407	76.873
180	315.54	220.30	24.470	84.355
190	333.21	237.84	27.715	91.972
200	349.93	255.36	31.131	99.703
210	365.68	272.82	34.710	107.53
220	380.48	290.17	38.442	115.44
230	394.37	307.40	42.317	123.41

240	407.37	324.46	46.326	131.43
250	419.53	341.34	50.461	139.49
260	430.90	358.02	54.714	147.58
270	441.52	374.48	59.077	155.68
273.15	444.72	379.62	60.473	158.23
280	451.44	390.72	63.542	163.78
290	460.71	406.72	68.104	171.88
298.15	467.81	419.59	71.888	178.48
300	469.37	422.49	72.754	179.98
305	473.49	430.28	75.112	184.02

Table 10 Thermodynamic parameters for hollandites: $\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Al}_{2.38}\text{Ti}_{5.59}\text{O}_{16}$, $\text{Ba}_{1.17}\text{Rb}_{0.19}\text{Al}_{2.46}\text{Ti}_{5.53}\text{O}_{16}$ and $\text{Ba}_{1.18}\text{Cs}_{0.21}\text{Al}_{2.44}\text{Ti}_{5.53}\text{O}_{16}$ at $T = 298.15$ K.

Hollandite	S° ^a /(J · K ⁻¹ mol ⁻¹)	$\Delta_f H^\circ_{\text{ox}}$ ^b /(kJ · mol ⁻¹)	$\Delta_f S^\circ_{\text{ox}}$ ^c / (J · K ⁻¹ mol ⁻¹)	$\Delta_f G^\circ_{\text{ox}}$ ^d /(kJ · mol ⁻¹)	$\Delta_f H^\circ_{\text{el}}$ ^b /(kJ · mol ⁻¹)	$\Delta_f S^\circ_{\text{el}}$ ^e /(J · K ⁻¹ mol ⁻¹)	$\Delta_f G^\circ_{\text{el}}$ ^f /(kJ · mol ⁻¹)
Sr-hollandite	413.93±8.28	-199.5±11.1	-15.50±8.35	-194.9±11.4	-8154.5±12.3	-1542.66±8.36	-7694.6±12.5
Rb-hollandite	415.13±8.30	-205.1±12.6	-33.78±8.40	-195.0±12.8	-8160.0±13.7	-1552.81±8.38	-7697.0±13.9
Cs-hollandite	419.59±8.39	-212.0±12.6	-36.52±8.46	-201.1±12.8	-8159.7±13.7	-1551.72±8.47	-7697.1±13.9

^a S° : Standard entropy of hollandites. The uncertainty at a 95 percent level of confidence is 2 % for S° .

^b $\Delta_f H^\circ_{\text{ox}}$: Enthalpy of formation from oxides, $\Delta_f H^\circ_{\text{el}}$: enthalpy of formation from elements or standard enthalpy of formation. Data are from previous work [11] and the uncertainty is two standard deviation of the mean. The uncertainty at a 95 percent level of confidence is about 5% for $\Delta_f H^\circ_{\text{ox}}$ and 0.2% for $\Delta_f H^\circ_{\text{el}}$.

^c $\Delta_f S^\circ_{\text{ox}}$: Entropy of formation from constituent oxides calculated by $\Delta_f S^\circ_{\text{ox}} = S^\circ(\text{hollandite}) - \sum S^\circ(\text{oxides})$.

^d $\Delta_f G^\circ_{\text{ox}}$: Gibbs energy of formation from oxides calculated by $\Delta_f G^\circ_{\text{ox}} = \Delta_f H^\circ_{\text{ox}} - T\Delta_f S^\circ_{\text{ox}}$. The uncertainty with a 95 percent level of confidence is 6% for $\Delta_f G^\circ_{\text{ox}}$.

^e $\Delta_f S^\circ_{\text{el}}$: Entropy of formation from elements calculated by $\Delta_f S^\circ_{\text{el}} = S^\circ(\text{hollandite}) - \sum S^\circ(\text{elements})$.

^f $\Delta_f G^\circ_{\text{el}}$: Gibbs energy of formation from elements calculated by $\Delta_f G^\circ_{\text{el}} = \Delta_f H^\circ_{\text{el}} - T\Delta_f S^\circ_{\text{el}}$. The uncertainty at a 95 percent level of confidence is 0.2% for $\Delta_f G^\circ_{\text{el}}$.

Table 11 Standard entropy of constituent oxides at 298.15 K.

Oxides	$S^\circ_{298.15}$ / (J · K ⁻¹ mol ⁻¹)
BaO	72.07 ± 0.38 ^a
Al ₂ O ₃	50.92 ± 0.10 ^a
TiO ₂	50.29 ± 0.17 ^a
SrO	55.52 ± 0.42 ^a
Rb ₂ O	125.52 ± 4.18 ^b
Cs ₂ O	146.87 ± 0.44 ^a

^a Robie and Hemingway (1995) [30]

^b Gurvich (1982) [31]

Table 12 Standard entropy of elements at 298.15K.

Elements	$S^\circ_{298.15}/(\text{J} \cdot \text{K}^{-1} \text{mol}^{-1})$
Ba	$62.42 \pm 0.84^{\text{a}}$
Al	$28.35 \pm 0.08^{\text{a}}$
Ti	$30.63 \pm 0.08^{\text{a}}$
Sr	$55.40 \pm 0.17^{\text{a}}$
Rb	$76.78 \pm 0.30^{\text{a}}$
Cs	$85.23 \pm 0.40^{\text{a}}$
O ₂	$205.15 \pm 0.04^{\text{a}}$

^a Robie and Hemingway (1995) [30]

Figure 1. Experimental heat capacity and fitted curves from 0 K to 300 K of: (a) $\text{Ba}_{1.14}\text{Sr}_{0.10}\text{Ti}_{5.59}\text{Al}_{2.38}\text{O}_{16}$, (b) $\text{Ba}_{1.26}\text{Rb}_{0.22}\text{Ti}_{5.38}\text{Al}_{2.59}\text{O}_{16}$ and (c) $\text{Ba}_{1.13}\text{Cs}_{0.21}\text{Ti}_{5.52}\text{Al}_{2.48}\text{O}_{16}$. Insets show the data below 10 K.