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Thermodynamic study of $Cs_3Na(MoO_4)_2$: Determination of the standard enthalpy of formation and standard entropy at 298.15 K

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ABSTRACT

The enthalpy of formation at 298.15 K and low temperature heat capacity of $Cs_3Na(MoO_4)_2$ have been measured for the first time in this work using solution calorimetry and thermal-relaxation calorimetry in the temperature range $T = (1.9–299.6)$ K, respectively. The solution calorimetry measurements, performed in 2 M HNO_3 solution, have yielded an enthalpy equal to $\Delta_r H_m(298.15\ K) = (6.79 \pm 1.72)$ $kJ \cdot mol^{-1}$ for the reaction:

$$3/2Cs_2MoO_4(cr) + 1/2Na_2MoO_4(cr) = Cs_3Na(MoO_4)_2(cr)$$

Combining with the enthalpies of formation of Cs_2MoO_4(cr) and Na_2MoO_4(cr), also determined in this work in 0.1 M CsOH and 0.1 M NaOH solutions, respectively, the standard enthalpy of formation of $Cs_3Na(MoO_4)_2$ at 298.15 K has been determined as $\mathbf{\Delta_f H^o_m}(Cs_3Na(MoO_4)_2, cr, 298.15\ K) = -(2998.5 \pm 3.0)$ $kJ \cdot mol^{-1}$. The heat capacity and entropy values of $Cs_3Na(MoO_4)_2$ at 298.15 K have been derived as $C^o_{p,m}(Cs_3Na(MoO_4)_2, cr, 298.15\ K) = (296.3 \pm 3.3)\ J \cdot K^{-1} \cdot mol^{-1}$ and $S^o_m(Cs_3Na(MoO_4)_2, cr, 298.15\ K) = (467.2 \pm 6.8)\ J \cdot K^{-1} \cdot mol^{-1}$. Combining the newly determined thermodynamic functions, the Gibbs energy of formation of $Cs_3Na(MoO_4)_2$ at 298.15 K has been derived as $\Delta_f G^o_m(Cs_3Na(MoO_4)_2, cr, 298.15K) = -(2784.6 \pm 3.4)\ kJ \cdot mol^{-1}$. Finally, the enthalpies, entropies and Gibbs energies of formation of $Cs_3Na(MoO_4)_2$ from its constituting binary and ternary oxides have been calculated.

1. Introduction

A recent re-investigation of the Na_2MoO_4-Cs_2MoO_4 system has revealed the existence of the double molybdate phase $Cs_3Na(MoO_4)_2$ [1]. Although the Na_2MoO_4-Cs_2MoO_4 pseudo-binary phase diagram has been investigated as early as 1964 [2] by thermal analysis and X-ray diffraction, the presence of this intermediate compound had not been identified to this date. The newly synthesized compound belongs to the class of double molybdate materials $A_nR_m(MoO_4)_2$ (A = alkalis, alkaline-earths, Cu, Tl; R = rare earth elements, Bi, Pb, Zn), which have attracted much interest in recent years because of their interesting properties as phosphor luminescent materials [3,4], solid state lasers [5,6], ferroelastics and ferroelectrics [7–9]. The existence of the $Cs_3Na(MoO_4)_2$ phase is also of relevance for the safety assessment of next generation Sodium cooled Fast Reactors [10]. During irradiation of the $(U_{1-y}Pu_y)O_{2-x}$ nuclear fuel in such reactors, cesium and molybdenum are generated with a high fission yield [11], and subsequently migrate from the centre of the fuel pin towards the pellet rim due to the strong axial temperature gradient (~450 $K \cdot mm^{-1}$). They accumulate in the space between the fuel and cladding in the form of a 150–300 μm layer of cesium orthomolybdate Cs_2MoO_4 [11]. In case of a breach of the stainless steel cladding, although extremely rare under normal operating conditions, the liquid sodium coolant in these reactors would come into contact with the cesium orthomolybdate layer. The aftermath of this reaction is still subject of controversy. Past studies have suggested a substitution of the cesium by sodium to form sodium molybdate and cesium metal which would dissolve in the liquid sodium [12,13]. But the later work by [14] has contradicted this hypothesis, and rather suggested the formation of cesium, sodium and molybdenum oxides. In light of the evidence for the possible formation of the $Cs_3Na(MoO_4)_2$ quaternary phase [1], the mechanism of the interaction between liquid sodium and cesium orthomolybdate needs to be re-visited [10]. To this end, the determination of the thermodynamic properties of $Cs_3Na(MoO_4)_2$ is a necessity.

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In this work we report for the first time the determination of the standard enthalpy of formation and standard entropy of $Cs_3Na(MoO_4)_2$ at 298.15 K using solution calorimetry and low temperature thermal-relaxation calorimetry. The standard enthalpies of formation of Cs_2MoO_4 and Na_2MoO_4 were moreover measured with the same solution calorimeter, and compared to literature data to serve as a benchmark for the present studies. Combining the newly determined thermodynamic functions, the Gibbs energy of formation of $Cs_3Na(MoO_4)_2$ at 298.15 K was derived, as well as the Gibbs energies of formation from the constituting oxides (Table 10).

2. Experimental methods

2.1. Sample preparation

$Cs_3Na(MoO_4)_2$ was synthesized by reaction between accurately weighted quantities of cesium orthomolybdate Cs_2MoO_4 and sodium orthomolybdate (Na_2MoO_4 anhydrous, 99.9% trace metal basis, Sigma–Aldrich). The cesium orthomolybdate starting material was synthesized as described in [15]. The stoichiometric mixture was heated under argon inside a tightly closed stainless steel container at 723 K for 200 h, with intermediate regrinding steps. Because of the molybdates' hygroscopic nature, handling was done exclusively inside the dry atmosphere of an argon-filled glove box. The purity of the sample was examined by X-ray and neutron diffraction [10] at room temperature, Differential Scanning Calorimetry [10], and ICP-MS analysis. No secondary phases were detected by XRD and neutron diffraction. The ICP-MS analysis yielded a cesium to molybdenum ratio of (1.44 ± 0.07[1]) at/at and a sodium to molybdenum ratio of (0.51 ± 0.03[2]), which corresponds to the global composition $Cs_{2.88(\pm0.14)}Na_{1.02(\pm0.06)}(MoO_4)_2$, hence within uncertainties, in good agreement with the stoichiometric formula. In addition, the Differential Scanning Calorimetry measurements performed on this compound, and reported in detail in [10], showed a single peak in the heat flow signal as a function of temperature, corresponding to the melting event. No additional peaks could be assigned to impurities, in good agreement with the X-ray and neutron diffraction data. The sample purity is expected to be better than 99 wt% (Table 1).

2.2. Powder X-ray and neutron diffraction

The X-ray diffraction measurements were carried out at room temperature (295 ± 3[3] K) using a PANalytical X'Pert PRO X-ray diffractometer mounted in the Bragg–Brentano configuration with a Cu anode (0.4 mm × 12 mm line focus, 45 kV, 40 mA). The X-ray scattered intensities were measured with a real time multi strip (RTMS) detector (X'Celerator). The data were collected by step scanning in the angle range $10° \leqslant 2\theta \leqslant 120°$ with a step size of 0.008° (2θ); total measuring time was about 8 h.

Neutron diffraction data were recorded on the beamline PEARL at the Hoger Onderwijs Reactor at TU Delft [16]. The sample was encapsulated in a vanadium container hermetically closed with a rubber o-ring. The data were collected at room temperature (295 ± 3[4] K), at a fixed wavelength ($\lambda = 0.1667$ nm) for 43 h over the range $11° \leqslant 2\theta \leqslant 158°$. Structural analysis was performed by the Rietveld method with the Fullprof2k suite [17].

$Cs_3Na(MoO_4)_2$ crystallizes with a hexagonal structure, in space group $P\overline{3}m1$ ($Z = 1$), belonging to the glaserite type. The refined cell parameters by XRD ($a = 0.634381$[5] and $c = 0.821888$[6] nm (note that the statistically derived s.u:s are underestimated by about one order of magnitude); $\rho = 4.2991$[7] $g\cdot cm^{-3}$) and neutron diffraction ($a = 0.63352$[8] and $c = 0.82068$[9] nm (note that the statistically derived s.u:s are underestimated by about one order of magnitude); $\rho = 4.317$[10] $g\cdot cm^{-3}$) were found in good agreement with the single crystal data of Zolotova et al. ($a = 0.63461$[11] and $c = 0.82209$[12] nm) [1]. The refined lattice parameters using XRD are considered more precise than those derived from the neutron diffraction data. A detailed structural study of this compound can be found in [10] (Fig. 1).

2.3. Solution calorimetry

The enthalpy of dissolution of $Cs_3Na(MoO_4)_2$, Cs_2MoO_4 and Na_2MoO_4 materials were measured using a TA Instruments Precision Solution Calorimeter (semi-adiabatic or isoperibolic calorimeter) and TAM IV thermostat. The calorimetric unit consists of a reaction vessel and stirrer system (motor and gold stirrer holding a glass ampoule). The experiments were performed in a thin-walled 25 mL Pyrex-glass reaction vessel equipped with a thermistor for measuring the temperature rise and a heater for calibration during the measurement and equilibration of the initial baseline in the optimal operating range of the calorimeter before starting the experiment. The samples to be studied were placed inside a 1 mL glass ampoule, which was subsequently sealed using bee wax. The latter operation was performed in the dry atmosphere of the glove box because of the sensitivity of the samples to air and moisture. The solid samples were dissolved into solution (cesium hydroxyde CsOH, sodium hydroxyde NaOH, or nitric acide HNO_3 solutions) by breaking the bottom of the glass ampoule on the sapphire breaking tip mounted at the bottom of the reaction vessel. The heat of breaking is exothermic, with a value below 10 mJ, and can thus be neglected. The temperature during the measurements was maintained in the oil bath with an accuracy of $\pm1\cdot10^{-4}$ K. Electrical calibrations were performed immediately before and after each enthalpy of reaction measurement so as to determine the energy equivalent of the system.

The accuracy of the measurements was verified by measuring the enthalpy of dissolution of potassium chloride (KCl, Sigma–Aldrich, 99.7%) in distilled water. The experimentally determined dissolution enthalpy of KCl(cr) into 1000 H_2O (molality $m = 0.05551\ mol\cdot kg^{-1}$), i.e. $\Delta_{diss}H^o_m(1000H_2O,\ 298.15\ K) = (17.510 \pm 0.024)\ kJ\cdot mol^{-1}$ corresponding to $\Delta_{diss}H^o_m(500H_2O,\ 298.15\ K) = (17.560 \pm 0.024)\ kJ\cdot mol^{-1}$ after correction[13] to $m = 0.111\ mol\cdot kg^{-1}$, was found in very good agreement with the value recommended by

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[1] The uncertainty is an expanded uncertainty $U = k\cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. The coverage factor is $k = 2$.

[2] The uncertainty is an expanded uncertainty $U = k\cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. The coverage factor is $k = 2$.

[3] The quoted uncertainty is a standard uncertainty.

[4] The quoted uncertainty is a standard uncertainty.

[5] Standard uncertainties u are $u(a) = 0.000002$ nm.

[6] Standard uncertainties u are $u(c) = 0.000003$ nm.

[7] Standard uncertainties u are $u(\rho) = 0.0002\ g\cdot cm^{-3}$.

[8] Standard uncertainties u are $u(a) = 0.00003$ nm.

[9] Standard uncertainties u are $u(c) = 0.00005$ nm.

[10] Standard uncertainties u are $u(\rho) = 0.004\ g\cdot cm^{-3}$.

[11] Standard uncertainties u are $u(a) = 0.00002$ nm.

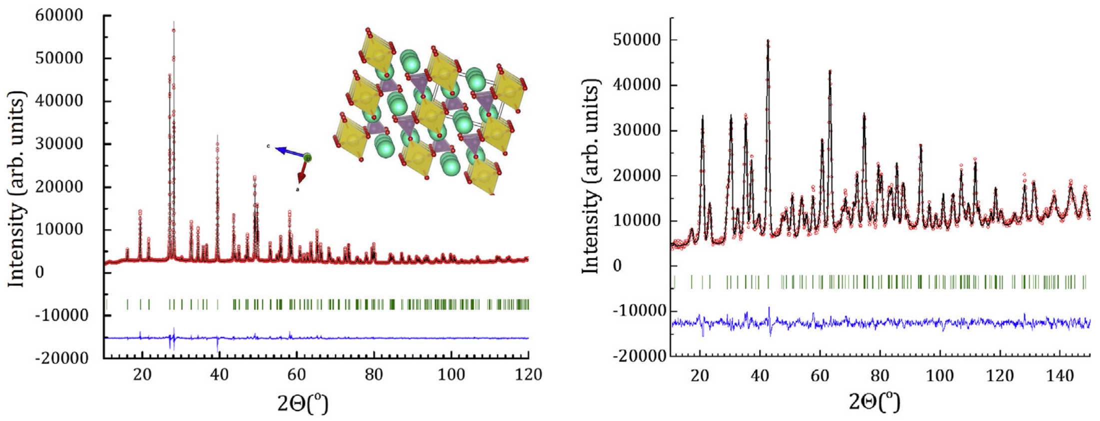
[12] Standard uncertainties u are $u(c) = 0.00003$ nm.

[13] The correction mentioned here was performed as recommended by the NBS in [18]: the measured dissolution enthalpy was corrected to the molality of the certified enthalpy value $m = 0.111\ mol\cdot kg^{-1}$ using the relationship $\Delta H^o(500H_2O, 298.15\ K) = \Delta H(nH_2O,\ 298.15\ K) - \{\Phi_L(nH_2O) - \Phi_L(500H_2O)\}$, where $\Delta H(nH_2O,\ 298.15\ K)$ is the measured dissolution enthalpy corrected to the reference temperature, and the term $\{\Phi_L(nH_2O) - \Phi_L(500H_2O)\}$, derived from Parker's tabulation [19] and listed in [18], corrects the molality to the certified value. The uncertainty on the correction was estimated not to exceed $5\ J\cdot mol^{-1}$ [18].

Table 1
Provenance and purity of the samples used in this study. XRD: X-ray diffraction; ND: neutron diffraction; DSC: Differential Scanning Calorimetry; ICP-MS: Inductively Coupled Plasma-Mass Spectrometry.

Formula	Source	State	Color	Mass fraction purity[a]	Purity analysis method
Na_2MoO_4	Sigma–Aldrich	Powder	White	0.999 ± 0.001	Provided by supplier
MoO_3	Sigma–Aldrich	Powder	Light yellow/green	$\geqslant 0.995 \pm 0.005$	Provided by supplier
Cs_2CO_3	Sigma–Aldrich	Powder	White	$\geqslant 0.99 \pm 0.01$	Provided by supplier
Cs_2MoO_4	Synthesized	Powder	White	0.995 ± 0.005	XRD
$Cs_3Na(MoO_4)_2$	Synthesized	Powder	Light grey	0.99 ± 0.01	XRD/ND/DSC/ICP-MS
CsOH 50%	Alfa Aeser	Solution	Transparent	0.999 ± 0.001	Provided by supplier
NaOH	Sigma–Aldrich	Pellets (anhydrous)	White	$\geqslant 0.98 \pm 0.02$	Provided by supplier
HNO_3 70%	VWR chemicals	Solution	Transparent	0.995 ± 0.005	Provided by supplier

[a] The quoted uncertainties correspond to standard uncertainties.



(a) XRD (b) Neutrons

Fig. 1. Comparison between the observed (Y_{obs}, in red) and calculated (Y_{calc}, in black) (a) X-ray diffraction patterns and (b) neutron diffraction patterns of $Cs_3Na(MoO_4)_2$. $Y_{obs} - Y_{calc}$, in blue, is the difference between the experimental and calculated intensities. The Bragg reflections' angular positions are marked in green. Measurement at λ = Cu-Kα (XRD) and λ = 0.1667 nm (neutrons) [10]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the National Bureau of Standards [18,20], i.e. $\Delta_{diss}H^o_m(500H_2O, 298.15\ K) = (17.584 \pm 0.017)\ kJ{\cdot}mol^{-1}$ for the dissolution of KCl(cr) into 500 H_2O (molality $m = 0.111\ mol{\cdot}kg^{-1}$). The measured value corresponds to an enthalpy at infinite dilution of $\Delta_{diss}H^o_m(\infty H_2O, 298.15\ K) = (17.217 \pm 0.024)\ kJ{\cdot}mol^{-1}$, in very good agreement with the NBS data in [18,20], i.e. $\Delta_{diss}H^o_m(\infty H_2O, 298.15\ K) = (17.241 \pm 0.018)\ kJ{\cdot}mol^{-1}$, and that in [21], i.e. $\Delta_{diss}H^o_m(\infty H_2O, 298.15\ K) = 17.22\ kJ{\cdot}mol^{-1}$. In addition, the enthalpies of formation of Cs_2MoO_4 and Na_2MoO_4 were determined with this instrument in cesium hydroxyde CsOH and sodium hydroxide NaOH solutions as described below, and found in excellent agreement with the literature data [22–26].

2.4. Low temperature heat capacity

Low temperature heat capacity measurements were performed on $m = 13.04$[14] mg of $Cs_3Na(MoO_4)_2$ in the temperature range $T = (1.9–299.6)$ K using a PPMS (Physical Property Measurement System, Quantum Design) instrument at applied magnetic fields $B = 0$ and 9 T. This technique is based on a relaxation method, which was critically assessed by Lashley et al. [27]. The contributions of the sample platform, wires, and grease were deduced by a separate measurement of an addenda curve. Based on the experience acquired on this instrument with standard materials and other compounds [28], the uncertainty was estimated at about 1% from 100 to 300 K, and reaching about 3% at the lowest temperatures [27,28].

3. Results

3.1. Enthalpy of formation of Cs_2MoO_4

To assess the performance of our instrument, the enthalpy of formation of Cs_2MoO_4 was firstly determined in CsOH solution, with a thermochemical cycle very similar to that of O'Hare and Hoekstra [22]. The detail of the reaction scheme used to derive these data is listed in Table 2. Cesium orthomolybdate and molybdenum oxide (MoO_3, 99.5%, Alfa Aesar) were dissolved in 0.1 M and 0.148 M CsOH solutions, respectively. The details of the calorimetric results for the dissolution of both compounds are listed in Table 3. The dissolutions in both cases were instantaneous. Supposing the solutions formed by reactions (1a) and (2a) in Table 2 are identical, one obtains the following enthalpy of reaction $\Delta_r H^o_m = \Delta_r H_2 - \Delta_r H_1 = -(79.30 \pm 1.17)\ kJ{\cdot}mol^{-1}$ for the reaction:

$$MoO_3(cr) + 2CsOH(sln) = Cs_2MoO_4(cr) + H_2O(sln) \qquad (1)$$

The enthalpy of reaction (4a) in Table 2 was derived from the enthalpy of formation of CsOH(aq) reported by Gunn [29], i.e., $\Delta_f H^o_m(CsOH,\ aq,\ 298.15\ K) = -(488.110 \pm 0.042)\ kJ{\cdot}mol^{-1}$, based on the dissolution reaction $Cs(cr) + (n+1)\ H_2O(l) = CsOH(aq){\cdot}nH_2O + 0.5H_2(g)$, and the CODATA value for the enthalpy of formation of $H_2O(l)$, $\Delta_f H^o_m(H_2O,\ l,\ 298.15\ K) = -(285.83 \pm 0.04)\ kJ{\cdot}mol^{-1}$ [30]. The latter value is perfectly consistent with the latest recommended data for the enthalpy of formation of CsOH(cr), i.e. $\Delta_f H^o_m(CsOH,\ cr,\ 298.15\ K) = -(416.2 \pm 0.5)\ kJ{\cdot}mol^{-1}$ [32,33] and the measured dissolution enthalpy of CsOH(cr) in H_2O, i.e. $\Delta_{diss}H^o_\infty(298.15\ K) = -(71.9 \pm 0.4)\ kJ{\cdot}mol^{-1}$ [32,33]. The enthalpy

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[14] Standard uncertainties u are $u(m) = 0.05$ mg.

Table 2
Thermochemical cycle used for the determination of the enthalpy of formation of Cs_2MoO_4. Solution calorimetry measurements were performed at a pressure p = (0.105 ± 0.005[a]) MPa, and in the temperature interval T = (298.15 ± 0.30[a]) K.

	Reaction	$\Delta_rH^o_m$(298.15 K)/kJ·mol^{-1}	Ref.
(1a)	$Cs_2MoO_4(cr) + 4.1665(CsOH{\cdot}555.556H_2O) = Cs_2MoO_4(sln) + 4.1665CsOH(sln) + 2314.724H_2O(sln)$	2.83 ± 0.87[a]	This work
(2a)	$MoO_3(cr) + 6.1665(CsOH{\cdot}375.209H_2O) = Cs_2MoO_4(sln) + 4.1665CsOH(sln) + 2314.724H_2O(sln)$	−76.47 ± 0.78[a]	This work
(3a)	$Mo(cr) + 3/2O_2(g) = MoO_3(cr)$	−745.0 ± 1.0[a]	[23]
(4a)	$2Cs(cr) + 2H_2O(l) = 2CsOH(sln) + H_2(g)$	−404.56 ± 0.12[a]	[29,30]
(5a)	$H_2(g) + 1/2O_2(g) = H_2O(l)$	−285.83 ± 0.04[a]	[30]
(6a)	$H_2O(l) + (sln) = H_2O(sln)$	~0	[31,30]
(7a)	$2Cs(cr) + Mo(cr) + 2O_2(g) = Cs_2MoO_4(cr)$	−1514.69 ± 1.54[a]	This work

[a] The quoted uncertainty corresponds to the standard uncertainty.

Table 3
Calorimetric results for the dissolution of Cs_2MoO_4 (M = 425.757 g·mol^{-1}) in 0.1[a] M CsOH solution, and MoO_3 (M = 143.938 g·mol^{-1}) in 0.148[a] M CsOH at 298.15 K. Solution calorimetry measurements were performed at a pressure p = (0.105 ± 0.005[b]) MPa, and in the temperature interval T = (298.15 ± 0.30[b]) K.

No.	$m(Cs_2MoO_4)$[c]/mg	ΔT[d]/mK	C_p[e]/J·K^{-1}	Q[f]/J	$\Delta_rH^o_m$(298.15 K)[g]/kJ·mol^{-1}
1	255.30	−12.206	113.939	1.39	2.32
2	256.40	−19.498	113.839	2.22	3.69
3	254.70	−18.082	113.971	2.06	3.45
4	255.30	−10.269	110.020	1.13	1.88
No.	$m(MoO_3)$[c]/mg	ΔT[d]/mK	C_p[e]/J·K^{-1}	Q[f]/J	$\Delta_rH^o_m$(298.15 K)[g]/kJ·mol^{-1}
1	86.40	398.727	114.463	−45.64	−76.03
2	86.30	400.601	113.143	−45.33	−75.60
3	86.60	419.006	110.834	−46.44	−77.19
4	86.50	408.332	113.390	−46.30	−77.05

m is the sample weight, ΔT the temperature change caused by the dissolution, C_p the energy equivalent of the calorimeter, Q the amount of heat generated by the dissolution, $\Delta_rH^o_m$(298.15 K) the corresponding molar enthalpy of reaction.

[a] The standard uncertainties u on the molar concentrations are $u(C)$ = 0.002 M.

[b] The quoted uncertainty corresponds to the standard uncertainty.

[c] The standard uncertainties u on the weights are $u(m)$ = 0.10 mg.

[d] The relative standard uncertainties on ΔT are $u_r(\Delta T)$ = 0.2.

[e] The relative standard uncertainties on C_p are $u_r(C_p)$ = 0.2.

[f] The relative standard uncertainties on Q are $u_r(Q)$ = 0.3.

[g] The relative standard uncertainties on $\Delta_rH^o_m$(298.15 K) are $u_r(\Delta_rH^o_m(298.15K))$ = 0.3.

of formation of MoO_3(cr) was taken from the review work by Cordfunke and Konings [23]. Finally, the correction for the relative partial molar enthalpy of water in 0.1 M CsOH solution was considered negligible (Table 2).

The summation of reactions (1a)-(6a) such that $\Delta_rH_{7a} = \Delta_rH_{1a} - \Delta_rH_{2a} + \Delta_rH_{3a} + \Delta_rH_{4a} + \Delta_rH_{5a} - \Delta_rH_{6a}$ yields the standard enthalpy of formation of Cs_2MoO_4 as **$\Delta_fH^o_m$(Cs_2MoO_4, cr, 298.15 K) = −(1514.7 ± 1.5) kJ·mol^{-1}**. The latter value is in excellent agreement with that measured by O'Hare and Hoekstra in 0.2 M CsOH solution (99.41 mL) using a LKB-8700 Precision Calorimeter System [22], and the recommended value in the review work of Cordfunke and Konings [23], i.e., $\Delta_fH^o_m$(Cs_2MoO_4, cr, 298.15 K) = −(1514.5 ± 1.0) kJ·mol^{-1}.

3.2. Enthalpy of formation of Na_2MoO_4

Next, the enthalpy of formation of Na_2MoO_4 was measured in NaOH solution. Using a similar procedure as previously, Na_2MoO_4 and MoO_3 were dissolved in 0.1 M and 0.164 M NaOH solutions, respectively. The dissolutions were again instantaneous. The corresponding reaction scheme is shown in Table 4, and the detail of the calorimetric results are listed in Table 5. The enthalpy of reaction (2) is equal to $\Delta_rH^o_m = \Delta_rH_{2b} - \Delta_rH_{1b} = -(66.47 \pm 0.85)$ kJ·mol^{-1}.

$$MoO_3(cr) + 2NaOH(sln) = Na_2MoO_4(cr) + H_2O(sln) \qquad (2)$$

The enthalpy of reaction (4b) in Table 2 was derived from the enthalpy of formation of NaOH(aq) reported by Gunn [29], i.e.

Table 4
Thermochemical cycle used for the determination of the enthalpy of formation of Na_2MoO_4. Solution calorimetry measurements were performed at a pressure p = (0.105 ± 0.005[a]) MPa, and in the temperature interval T = (298.15 ± 0.30[a]) K.

	Reaction	$\Delta_rH^o_m$(298.15 K)/kJ·mol^{-1}	Ref.
(1b)	$Na_2MoO_4(cr) + 3.149(NaOH{\cdot}555.556H_2O) = Na_2MoO_4(sln) + 3.149NaOH(sln) + 1749.44H_2O(sln)$	−8.81 ± 0.05[a]	This work
(2b)	$MoO_3(cr) + 5.149(NaOH{\cdot}339.569H_2O) = Na_2MoO_4(sln) + 3.149NaOH(sln) + 1749.44H_2O(sln)$	−75.28 ± 0.85[a]	This work
(3b)	$Mo(cr) + 3/2O_2(g) = MoO_3(cr)$	−745.0 ± 1.0[a]	[23]
(4b)	$2Na(cr) + 2H_2O(l) = 2NaOH(sln) + H_2(g)$	−369.23 ± 0.15[a]	[29,30]
(5b)	$H_2(g) + 1/2O_2(g) = H_2O(l)$	−285.83 ± 0.04[a]	[30]
(6b)	$H_2O(l) + (sln) = H_2O(sln)$	~0	[31,30]
(7b)	$2Na(cr) + Mo(cr) + 2O_2(g) = Na_2MoO_4(cr)$	−1466.53 ± 1.32[a]	This work

[a] The quoted uncertainty corresponds to the standard uncertainty.

Table 5

Calorimetric results for the dissolution of Na_2MoO_4 (M = 205.925 g·mol^{-1}) in 0.1[a] M NaOH solution, and MoO_3 (M = 143.938 g·mol^{-1}) in 0.164[a] M NaOH at 298.15 K. Solution calorimetry measurements were performed at a pressure p = (0.105 ± 0.005[b]) MPa, and in the temperature interval T = (298.15 ± 0.30[b]) K.

No.	$m(Na_2MoO_4)$[c]/mg	ΔT[d]/mK	C_p[e]/J·K^{-1}	Q[f]/J	$\Delta_r H^o_m$(298.15 K)[g]/kJ·mol^{-1}
1	163.47	60.906	114.313	−6.96	−8.77
2	163.20	60.998	114.297	−6.97	−8.80
3	163.90	61.643	114.704	−7.07	−8.88
4	163.40	61.693	113.206	−6.98	−8.80
No.	$m(MoO_3)$[c]/mg	ΔT[d]/mK	C_p[e]/J·K^{-1}	Q[f]/J	$\Delta_r H^o_m$(298.15 K)[g]/kJ·mol^{-1}
1	114.17	522.887	114.808	−60.03	−75.68
2	114.50	521.298	114.949	−59.92	−75.33
3	114.40	522.975	115.546	−60.43	−76.03
4	114.10	502.630	116.840	−58.73	−74.08

m is the sample weight, ΔT the temperature change caused by the dissolution, C_p the energy equivalent of the calorimeter, Q the amount of heat generated by the dissolution, $\Delta_r H^o_m$(298.15 K) the corresponding molar enthalpy of reaction.

[a] The standard uncertainties u on the molar concentrations are $u(C)$ = 0.002 M.

[b] The quoted uncertainty corresponds to the standard uncertainty.

[c] The standard uncertainties u on the weights are $u(m)$ = 0.10 mg.

[d] The relative standard uncertainties on ΔT are $u_r(\Delta T)$ = 0.2.

[e] The relative standard uncertainties on C_p are $u_r(C_p)$ = 0.2.

[f] The relative standard uncertainties on Q are $u_r(Q)$ = 0.3.

[g] The relative standard uncertainties on $\Delta_r H^o_m$(298.15 K) are $u_r(\Delta_r H^o_m(298.15K))$ = 0.3.

Table 6

Thermochemical cycle used for the determination of the enthalpy of formation of $Cs_3Na(MoO_4)_2$. Solution calorimetry measurements were performed at a pressure p = (0.105 ± 0.005[a]) MPa, and in the temperature interval T = (298.15 ± 0.30[a]) K.

	Reaction	$\Delta_r H^o_m$(298.15 K)/kJ·mol^{-1}	Ref.
(1c)	$Cs_3Na(MoO_4)_2$(cr) + (sln) = 1/2 Na_2MoO_4(sln) + 3/2 Cs_2MoO_4(sln)	−109.65 ± 1.43[a]	This work
(2c)	1/2 Na_2MoO_4(cr) + (sln) = 1/2 Na_2MoO_4(sln)	−23.41 ± 0.66[a]	This work
(3c)	3/2 Cs_2MoO_4(cr) + 1/2 Na_2MoO_4(sln) = 1/2 Na_2MoO_4(sln) + 3/2 Cs_2MoO_4(sln)	−79.45 ± 0.69[a]	This work
(4c)	Na(cr) + 1/2Mo(cr) + O_2(g) = 1/2 Na_2MoO_4(cr)	−733.3 ± 0.7[a]	This work
(5c)	3/2Cs(cr) + 3/2Mo(cr) + 3O_2(g) = 3/2Cs_2MoO_4(cr)	−2272.0 ± 2.3[a]	This work
(6c)	3Cs(cr) + Na(cr) + 2Mo(cr) + 4O_2(g) = $Cs_3Na(MoO_4)_2$(cr)	−2998.5 ± 3.0[a]	This work

[a] The quoted uncertainty corresponds to the standard uncertainty.

Table 7

Calorimetric results for the dissolution of $Cs_3Na(MoO_4)_2$ (M = 741.597 g·mol^{-1}), Na_2MoO_4 (M = 205.925 g·mol^{-1}) and Cs_2MoO_4 (M = 425.757 g·mol^{-1}) in 2[a] M HNO_3 at 298.15 K. Solution calorimetry measurements were performed at a pressure p = (0.105 ± 0.005[b]) MPa, and in the temperature interval T = (298.15 ± 0.30[b]) K.

No.	$m(Cs_3Na(MoO_4)_2)$[c]/mg	ΔT[d]/mK	C_p[e]/J·K^{-1}	Q[f]/J	$\Delta_r H^o_m$(298.15 K)[g]/kJ·mol^{-1}.
1	18.40	25.163	108.076	−2.72	−109.61
2	18.52	25.174	108.098	−2.72	−108.97
3	18.10	24.312	108.178	−2.63	−107.76
4	18.50	25.741	108.108	−2.78	−111.55
5	18.64	25.680	108.042	−2.77	−110.38
No.	$m(Na_2MoO_4)$[c]/mg	ΔT[d]/mK	C_p[e]/J·K^{-1}	Q[f]/mJ	$\Delta_r H^o_m$(298.15 K)[g]/kJ·mol^{-1}
1	2.70	5.457	107.997	−589.34	−44.95
2	2.66	5.615	108.226	−607.69	−47.04
3	2.77	6.072	107.679	−653.83	−48.61
4	2.60	5.499	108.157	−594.76	−47.11
5	2.75	5.732	108.133	−619.82	−46.41
No.	$m(Cs_2MoO_4)$[c]/mg	ΔT[d]/mK	C_p[e]/J·K^{-1}	Q[f]/J	$\Delta_r H^o_m$(298.15 K)[g]/kJ·mol^{-1}
1	16.90	19.496	107.754	−2.10	−52.92
2	16.45	19.036	107.729	−2.05	−53.08
3	16.70	19.616	107.144	−2.10	−53.58
4	16.00	18.486	107.627	−1.99	−52.94
5	17.06	19.434	107.830	−2.10	−52.30

m is the sample weight, ΔT the temperature change caused by the dissolution, C_p the energy equivalent of the calorimeter, Q the amount of heat generated by the dissolution, $\Delta_r H^o_m$(298.15 K) the corresponding molar enthalpy of reaction.

[a] The standard uncertainties u on the molar concentrations are $u(C)$ = 0.002 M.

[b] The quoted uncertainty corresponds to the standard uncertainty.

[c] The standard uncertainties u on the weights are $u(m)$ = 0.05 mg.

[d] The relative standard uncertainties on ΔT are $u_r(\Delta T)$ = 0.2.

[e] The relative standard uncertainties on C_p are $u_r(C_p)$ = 0.2.

[f] The relative standard uncertainties on Q are $u_r(Q)$ = 0.3.

[g] The relative standard uncertainties on $\Delta_r H^o_m$(298.15 K) are $u_r(\Delta_r H^o_m(298.15K))$ = 0.4.

$\Delta_f H^o_m$(NaOH, aq, 298.15 K) = –(470.445 ± 0.063) kJ·mol^{-1}, and the CODATA value for the enthalpy of formation of H_2O(l). There again the correction for the relative partial molar enthalpy of water in 0.1 M NaOH solution was considered negligible. Combining with the enthalpies of formation of H_2O(l) [30] and MoO_3(cr) [23], the standard enthalpy of formation of Na_2MoO_4 is derived as **$\Delta_f H^o_m$(Na_2MoO_4, cr, 298.15 K) = –(1466.5 ± 1.3) kJ·mol^{-1}**. This value is in excellent agreement with the data of Graham and Kepler [24] obtained in 0.531 M NaOH solution by dissolution of Na_2MoO_4 and MoO_3 compounds, i.e., $\Delta_f H^o_m$(Na_2MoO_4, cr, 298.15 K) = –1466.1 kJ·mol^{-1}. It is also in very good agreement with the data of Tangri [26] derived from the dissolution enthalpy of Na_2MoO_4 in 0.024 M NaOH solution combined with the standard enthalpies of formation of Na^+(aq) and MoO_4^{2-}(aq), i.e., $\Delta_f H^o_m$(Na_2MoO_4, cr, 298.15 K) = –(1465.87 ± 0.98) kJ·mol^{-1}, and the data of the US Bureau of Mines, i.e., $\Delta_f H^o_m$(Na_2MoO_4, cr, 298.15 K) = –(1467.74 ± 1.26) kJ·mol^{-1} [25].

3.3. Enthalpy of formation of $Cs_3Na(MoO_4)_2$

The enthalpy of formation of $Cs_3Na(MoO_4)_2$ was determined in 2 M HNO_3 solution. Surprisingly, this quaternary compound could not be dissolved in a basic solution such as {NaOH + CsOH}. However, the dissolutions of $Cs_3Na(MoO_4)_2$ and the constituting ternary oxides Na_2MoO_4 and Cs_2MoO_4 were complete in nitric acid solution. The thermochemical cycle used in this case is detailed in Table 6 and the calorimetric results in Table 7. The reaction scheme is as follows:

$$Cs_3Na(MoO_4)_2(cr) + (HNO_3sln) = sol.1 \quad (3)$$

$$1/2Na_2MoO_4(cr) + (HNO_3sln) = sol.2 \quad (4)$$

$$3/2Cs_2MoO_4(cr) + sol.2 = sol.3 \quad (5)$$

The amount of sample dissolved was adjusted such that *sol*.1 and *sol*.3 had the same composition. The enthalpy of the reaction of formation from the constituting ternary oxides (6) is equal to $\Delta_r H^o_m = \Delta_r H_{2c} + \Delta_r H_{3c} - \Delta_r H_{1c} = (6.79 \pm 1.72)$ kJ·mol^{-1}.

$$1/2Na_2MoO_4(cr) + 3/2Cs_2MoO_4(cr) = Cs_3Na(MoO_4)_2(cr) \quad (6)$$

Combining with the newly determined standard enthalpies of formation of Cs_2MoO_4(cr) and Na_2MoO_4(cr), the standard enthalpy of formation of $Cs_3Na(MoO_4)_2$(cr) is finally derived as **$\Delta_f H^o_m$($Cs_3Na(MoO_4)_2$, cr, 298.15 K) = –(2998.5 ± 3.0) kJ·mol^{-1}**.

3.4. Low temperature heat capacity of $Cs_3Na(MoO_4)_2$

The low temperature heat capacity data of $Cs_3Na(MoO_4)_2$ measured in the absence of magnetic field in the temperature range *T* = (1.9–299.6) K are shown in Fig. 2a and listed in Table A. 1. The heat capacity of $Cs_3Na(MoO_4)_2$ increases smoothly with temperature, and reaches values that are about 60 J·K^{-1}·mol^{-1} below the classical Dulong-Petit limit ($C_{lat} = 3nR \sim 349$ J·K^{-1}·mol^{-1} for the fourteen atoms in the formula unit) as the temperature approaches 298.15 K. The collected data do not exhibit any anomaly, and the applica-

Table 8
Summary of fitting parameters of the heat capacity of $Cs_3Na(MoO_4)_2$ within the temperature range *T* = (1.9–10.0) K and *T* = (10.0–299.6) K.

Harmonic lattice-model		Debye and Einstein fit	
Temp. range/K	1.9–10.0	Temp. range/K	10.0–299.6
γ/mJ·mol^{-1}·K^{-2}	0	n_D/mol	3.3013
B_3/mJ·mol^{-1}·K^{-4}	3.61	θ_D/K	94.61
B_5/mJ·mol^{-1}·K^{-6}	8.26098·10^{-2}	n_{E1}/mol	3.7437
B_7/mJ·mol^{-1}·K^{-8}	–5.17842·10^{-4}	θ_{E1}/K	146.80
B_9/mJ·mol^{-1}·K^{-10}	4.69597·10^{-7}	n_{E2}/mol	2.3755
		θ_{E2}/K	317.30
		n_{E3}/mol	3.7755
		θ_{E3}/K	586.74
		$n_D + n_{E1} + n_{E2} + n_{E3}$/mol	13.20

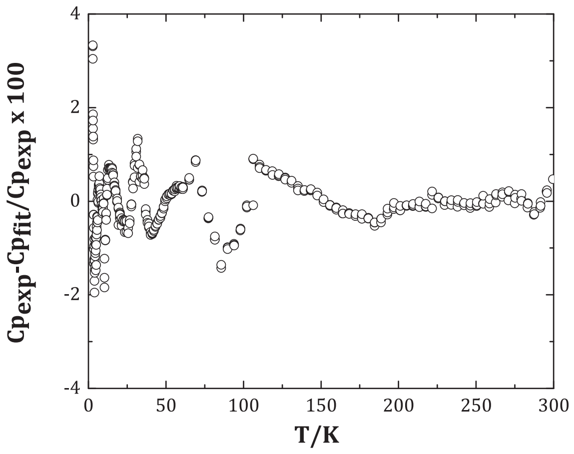
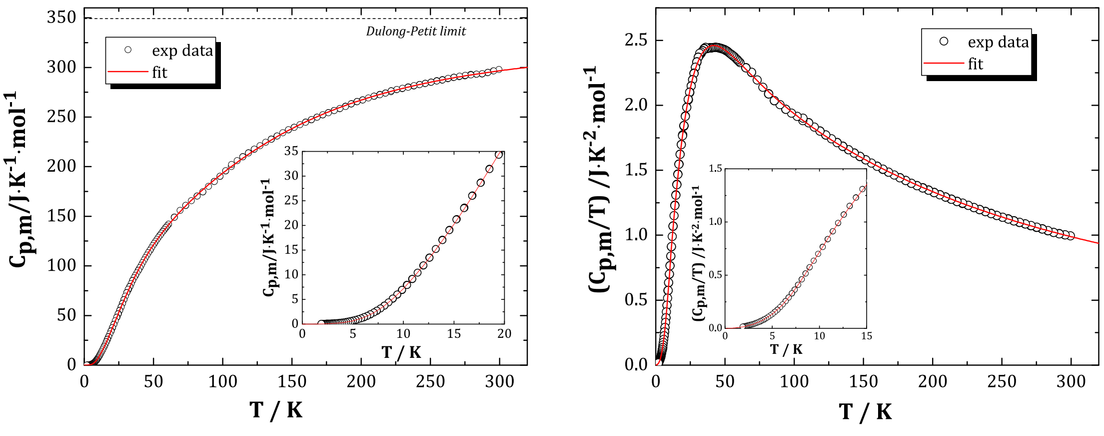


Fig. 3. Deviation of the fitting equations from the experimental data.



(a) $C_{p,m}$ (b) $C_{p,m}$/T

Fig. 2. Heat capacity of $Cs_3Na(MoO_4)_2$ (○) measured in zero magnetic field and fit to the data (red line): (a) $C_{p,m}$ and (b) $C_{p,m}$/T. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 9

Standard thermodynamic functions for $Cs_3Na(MoO_4)_2$ at pressure p = 100 *kPa*. $\phi^o_m(T) = S^o_m(T) - [H^o_m(T) - H^o_m(0)]/T$.[a]

T/K	$C^o_{p,m}(T/K)/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$S^o_m(T/K)/(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$H^o_m(T/K) - H^o_m(0)/(kJ{\cdot}mol^{-1})$	$\phi^o_m(T/K)/(J{\cdot}K^{-1}{\cdot}mol^{-1})$
0	0	0	0	–
0.5	$4.5383{\cdot}10^{-4}$	$1.5398{\cdot}10^{-4}$	$5.8899{\cdot}10^{-8}$	$3.6178{\cdot}10^{-5}$
1	$3.6900{\cdot}10^{-3}$	$1.2300{\cdot}10^{-3}$	$9.2557{\cdot}10^{-7}$	$3.0050{\cdot}10^{-4}$
2	0.03146	0.01094	$1.8500{\cdot}10^{-5}$	$1.6900{\cdot}10^{-3}$
3	0.11642	0.03820	$9.2440{\cdot}10^{-5}$	$7.3900{\cdot}10^{-3}$
4	0.30727	0.09602	$3.0429{\cdot}10^{-4}$	0.019950
5	0.66987	0.20141	$7.9285{\cdot}10^{-4}$	0.042840
6	1.2819	0.37522	$1.7700{\cdot}10^{-3}$	0.080430
7	2.2191	0.64056	$3.5200{\cdot}10^{-3}$	0.13781
8	3.5323	1.0198	$6.3900{\cdot}10^{-3}$	0.22047
9	5.2148	1.5303	0.010770	0.33381
10	7.1622	2.1781	0.016960	0.48244
15	20.251	7.4127	0.083810	1.8255
20	36.350	15.400	0.22463	4.1682
25	53.269	25.325	0.44866	7.3789
30	69.657	36.500	0.75639	11.287
35	84.753	48.389	1.1430	15.732
40	98.318	60.608	1.6013	20.575
45	110.42	72.900	2.1237	25.707
50	121.25	85.105	2.7034	31.037
55	131.03	97.127	3.3344	36.501
60	139.93	108.91	4.0121	42.046
65	148.12	120.44	4.7325	47.635
70	155.73	131.70	5.4923	53.239
75	162.85	142.69	6.2889	58.838
80	169.58	153.42	7.1202	64.416
85	175.97	163.89	7.9842	69.960
90	182.07	174.12	8.8794	75.464
95	187.90	184.13	9.8045	80.921
100	193.49	193.91	10.758	86.327
110	204.01	212.85	12.746	96.974
120	213.72	231.02	14.836	107.39
130	222.65	248.49	17.018	117.58
140	230.86	265.29	19.286	127.53
150	238.37	281.48	21.633	137.26
160	245.23	297.09	24.051	146.76
170	251.48	312.14	26.535	156.05
180	257.18	326.68	29.079	165.13
190	262.36	340.73	31.677	174.01
200	267.08	354.31	34.325	182.68
210	271.37	367.44	37.017	191.17
220	275.28	380.16	39.751	199.47
230	278.85	392.47	42.522	207.60
240	282.10	404.41	45.327	215.55
250	285.08	415.99	48.163	223.34
260	287.80	427.22	51.028	230.96
270	290.30	438.13	53.918	238.44
273.15	291.04	441.51	54.834	240.76
280	292.59	448.73	56.833	245.76
290	294.69	459.04	59.769	252.94
298.15	296.29	467.23	62.178	258.68
300	296.63	469.06	62.726	259.97

[a] The relative combined standard uncertainties in the values of the fitted heat capacities are determined from the experimental and fitted uncertainties to be $u_r(C^o_{p,m}) = 0.031$ for T/K < 15, $u_r(C^o_{p,m}) = 0.026$ for 15 < T/K < 30, $u_r(C^o_{p,m}) = 0.021$ for 30 < T/K < 50, $u_r(C^o_{p,m}) = 0.016$ for 50 < T/K < 100, and $u_r(C^o_{p,m}) = 0.011$ for T/K > 100.

Table 10

Thermodynamic data for $Cs_3Na(MoO_4)_2$ at pressure p = 100 *kPa*. The quoted uncertainties correspond to the standard uncertainties.

Reaction	$\Delta_rH^o_m(298.15\ K)/kJ{\cdot}mol^{-1}$	$\Delta_rS^o_m(298.15\ K)/J{\cdot}K^{-1}{\cdot}mol^{-1}$	$\Delta_rG^o_m(298.15\ K)/kJ{\cdot}mol^{-1}$
$3Cs(cr) + Na(cr) + 2Mo(cr) + 4O_2(g) = Cs_3Na(MoO_4)_2(cr)$	-2998.6 ± 2.9	-717.5 ± 4.7	-2784.7 ± 3.2
$3/2Cs_2O(cr) + 1/2Na_2O(cr) + 2MoO_3(cr) = Cs_3Na(MoO_4)_2(cr)$	-780.6 ± 5.9	53.9 ± 6.8	-796.7 ± 6.3
$3/2Cs_2MoO_4(cr) + 1/2Na_2MoO_4(cr) = Cs_3Na(MoO_4)_2(cr)$	6.8 ± 3.7	15.0 ± 6.3	2.3 ± 4.2

tion of a 9 T magnetic field (not shown) does not affect the results, as expected for such insulating material.

The thermodynamic functions of $Cs_3Na(MoO_4)_2$ were derived at 298.15 K by fitting the experimental data using the OriginPro 2015 software to theoretical functions below T = 10.0 K [34], and a combination of Debye and Einstein heat capacity functions [35–37] from T = (10.0 to 299.6) K. The fitting was done with the Levenbergh Marquardt iteration algorithm, using Origin C type fitting

Table A. 1
Experimental heat capacity data[a] for $Cs_3Na(MoO_4)_2$ measured at p = 1.25 mPa[b] and magnetic field B = 0T. R is the ideal gas constant equal to 8.3144598 $J \cdot K^{-1} \cdot mol^{-1}$.

T/K	$C_{p,m}(T/K)$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$C_{p,m}(T/K)/R$
299.590	297.96	35.84	143.414	234.04	28.15	44.347	108.42	13.04	10.888	9.130	1.098
295.493	296.38	35.65	143.476	234.15	28.16	44.351	108.41	13.04	10.352	7.932	0.9540
295.740	296.52	35.66	143.461	234.10	28.16	43.307	105.90	12.74	10.365	7.928	0.9535
295.741	296.35	35.64	139.289	230.80	27.76	43.308	105.92	12.74	10.370	7.920	0.9526
291.393	294.55	35.43	139.342	230.89	27.77	43.311	105.93	12.74	9.866	6.897	0.8296
291.631	294.96	35.48	139.328	230.83	27.76	42.266	103.32	12.43	9.873	6.904	0.8303
291.643	294.73	35.45	135.171	227.73	27.39	42.262	103.32	12.43	9.877	6.912	0.8313
287.290	293.28	35.27	135.217	227.55	27.37	42.272	103.36	12.43	9.397	5.958	0.7166
287.534	293.37	35.28	135.207	227.63	27.38	41.227	100.72	12.11	9.401	5.965	0.7174
287.529	293.51	35.30	131.042	224.48	27.00	41.222	100.70	12.11	9.403	5.963	0.7172
283.199	292.87	35.22	131.088	224.56	27.01	41.229	100.74	12.12	8.959	5.133	0.6173
283.421	293.20	35.26	131.081	224.46	27.00	40.189	98.10	11.80	8.966	5.142	0.6185
283.424	293.16	35.26	126.921	221.10	26.59	40.181	98.12	11.80	8.971	5.147	0.6191
279.103	292.54	35.18	126.961	221.03	26.58	40.188	98.16	11.81	8.534	4.390	0.5280
279.313	292.87	35.22	126.956	221.10	26.59	39.146	95.57	11.49	8.536	4.393	0.5284
279.317	292.46	35.17	122.800	217.46	26.15	39.143	95.65	11.50	8.539	4.395	0.5285
275.006	291.34	35.04	122.847	217.60	26.17	39.148	95.60	11.50	8.129	3.735	0.4492
275.224	291.73	35.09	122.836	217.53	26.16	38.108	92.94	11.18	8.133	3.736	0.4493
275.213	291.92	35.11	118.672	213.86	25.72	38.100	92.95	11.18	8.137	3.745	0.4505
270.916	290.57	34.95	118.713	213.71	25.70	38.105	92.99	11.18	7.744	3.166	0.3808
271.113	291.14	35.02	118.702	213.71	25.70	37.068	90.29	10.86	7.745	3.167	0.3809
271.117	291.18	35.02	114.549	209.90	25.25	37.059	90.33	10.86	7.748	3.172	0.3815
266.810	289.80	34.85	114.587	209.97	25.25	37.062	90.38	10.87	7.379	2.679	0.3222
267.014	290.12	34.89	114.578	209.93	25.25	36.030	88.09	10.60	7.381	2.680	0.3223
267.018	290.00	34.88	110.436	206.07	24.78	36.014	87.95	10.58	7.386	2.685	0.3229
262.711	288.42	34.69	110.473	205.95	24.77	36.019	88.08	10.59	7.086	2.330	0.2802
262.912	288.99	34.76	110.465	205.99	24.78	34.984	85.28	10.26	7.085	2.323	0.2794
262.909	288.91	34.75	106.303	200.05	24.06	34.968	85.07	10.23	7.086	2.326	0.2797
258.607	287.08	34.53	106.382	202.15	24.31	34.976	85.15	10.24	6.735	1.942	0.2336
258.804	287.62	34.59	106.378	202.12	24.31	33.948	82.14	9.880	6.740	1.947	0.2342
258.790	287.33	34.56	102.177	195.59	23.52	33.922	82.05	9.868	6.745	1.951	0.2347
254.502	286.19	34.42	102.219	195.73	23.54	33.928	82.08	9.872	6.419	1.635	0.1966
254.689	286.72	34.48	102.224	195.69	23.54	32.910	78.95	9.496	6.420	1.632	0.1962
254.670	286.22	34.42	98.051	190.16	22.87	32.888	79.19	9.524	6.425	1.637	0.1968
250.391	284.89	34.26	98.088	190.27	22.88	32.877	79.14	9.518	6.113	1.372	0.1651
250.570	285.18	34.30	98.099	190.25	22.88	31.866	76.00	9.141	6.117	1.368	0.1645
250.556	284.99	34.28	93.936	185.01	22.25	31.856	76.41	9.190	6.120	1.379	0.1658
246.274	283.58	34.11	93.972	184.98	22.25	31.853	76.45	9.194	5.824	1.149	0.1381
246.444	283.93	34.15	93.971	185.00	22.25	30.828	72.96	8.775	5.824	1.153	0.1387
246.434	283.78	34.13	89.822	180.10	21.66	30.824	73.06	8.787	5.827	1.150	0.1383
242.153	282.62	33.99	89.844	180.10	21.66	30.821	73.00	8.780	5.547	0.9656	0.1161
242.322	282.71	34.00	89.846	180.05	21.65	29.804	69.39	8.346	5.548	0.9652	0.1161
242.309	282.56	33.98	85.699	174.36	20.97	29.781	69.53	8.362	5.552	0.9656	0.1161
238.025	281.15	33.81	85.729	174.52	20.99	29.783	69.50	8.359	5.288	0.8124	0.0977
238.191	281.61	33.87	85.736	174.53	20.99	28.771	65.91	7.927	5.287	0.8111	0.0976
238.173	281.48	33.85	81.552	170.23	20.47	28.744	65.91	7.927	5.290	0.8122	0.0977
233.906	280.05	33.68	81.595	170.39	20.49	28.731	65.88	7.923	5.038	0.6825	0.0821
234.059	280.26	33.71	81.593	170.26	20.48	27.730	62.30	7.493	5.036	0.6777	0.0815
234.052	279.98	33.67	77.420	165.56	19.91	27.699	62.20	7.481	5.039	0.6822	0.0821
229.805	278.55	33.50	77.463	165.66	19.92	27.701	62.18	7.478	4.798	0.5738	0.0690
229.958	278.83	33.54	77.463	165.64	19.92	26.689	58.64	7.053	4.798	0.5706	0.0686
229.938	278.83	33.54	73.291	160.79	19.34	26.661	58.58	7.046	4.801	0.5741	0.0691
225.701	277.51	33.38	73.337	160.91	19.35	26.643	58.52	7.038	4.571	0.4842	0.0582
225.839	277.61	33.39	73.338	160.88	19.35	25.647	55.13	6.630	4.570	0.4843	0.0582
225.836	277.63	33.39	69.176	155.82	18.74	25.647	55.06	6.623	4.573	0.4837	0.0582
221.622	275.46	33.13	69.224	155.96	18.76	25.603	54.98	6.612	4.356	0.4080	0.0491
221.738	276.50	33.25	69.226	155.95	18.76	24.600	51.70	6.219	4.352	0.4070	0.0490
221.720	276.29	33.23	65.061	148.90	17.91	24.597	51.57	6.203	4.356	0.4070	0.0490
217.524	274.00	32.96	65.111	149.05	17.93	24.560	51.56	6.201	4.149	0.3444	0.0414
217.652	274.24	32.98	65.108	148.98	17.92	23.561	48.20	5.797	4.146	0.3428	0.0412
217.637	274.09	32.97	60.935	141.89	17.07	23.551	48.05	5.779	4.151	0.3438	0.0413
213.417	272.46	32.77	60.990	142.04	17.08	23.529	48.10	5.785	3.954	0.2897	0.0348
213.537	272.78	32.81	60.995	142.04	17.08	22.516	44.68	5.373	3.951	0.2908	0.0350
213.529	272.45	32.77	60.993	142.05	17.08	22.504	44.62	5.367	3.955	0.2905	0.0349
209.309	270.80	32.57	60.986	141.99	17.08	22.485	44.58	5.361	3.764	0.2474	0.0298
209.430	270.97	32.59	60.986	141.97	17.08	21.471	41.17	4.951	3.764	0.2464	0.0296
209.415	270.89	32.58	59.935	140.19	16.86	21.462	41.07	4.940	3.766	0.2475	0.0298
205.199	269.11	32.37	59.940	140.24	16.87	21.443	41.03	4.935	3.587	0.2106	0.0253
205.306	269.14	32.37	59.951	140.26	16.87	20.424	37.67	4.531	3.586	0.2095	0.0252
205.309	269.17	32.37	58.891	138.44	16.65	20.411	37.62	4.524	3.588	0.2092	0.0252
201.075	267.04	32.12	58.901	138.43	16.65	20.407	37.62	4.525	3.418	0.1794	0.0216
201.196	267.34	32.15	58.912	138.52	16.66	20.366	37.44	4.504	3.415	0.1789	0.0215
201.183	267.09	32.12	57.850	136.58	16.43	20.406	37.58	4.520	3.416	0.1791	0.0215

Table A. 1 (*continued*)

T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$
196.961	265.25	31.90	57.863	136.65	16.43	20.399	37.60	4.522	3.253	0.1537	0.0185
197.072	265.65	31.95	57.868	136.63	16.43	19.465	34.51	4.151	3.251	0.1533	0.0184
197.067	265.39	31.92	56.808	134.78	16.21	19.452	34.46	4.144	3.251	0.1529	0.0184
192.840	263.00	31.63	56.822	134.73	16.20	19.442	34.31	4.126	3.096	0.1310	0.0158
192.949	263.38	31.68	56.827	134.76	16.21	18.529	31.46	3.783	3.094	0.1307	0.0157
192.937	263.15	31.65	55.769	132.80	15.97	18.526	31.46	3.784	3.096	0.1309	0.0157
188.714	260.73	31.36	55.779	132.76	15.97	18.516	31.41	3.777	2.947	0.1119	0.0135
188.822	260.81	31.37	55.788	132.82	15.97	17.663	28.68	3.449	2.948	0.1117	0.0134
188.806	260.58	31.34	54.724	130.82	15.73	17.659	28.65	3.446	2.948	0.1119	0.0135
184.602	258.27	31.06	54.739	130.85	15.74	17.642	28.62	3.442	2.807	0.0967	0.0116
184.695	258.50	31.09	54.743	130.84	15.74	16.844	26.06	3.135	2.805	0.0965	0.0116
184.693	258.48	31.09	53.692	128.76	15.49	16.832	26.03	3.131	2.806	0.0963	0.0116
180.485	256.48	30.85	53.696	128.78	15.49	16.807	25.97	3.123	2.673	0.0840	0.0101
180.585	256.55	30.86	53.705	128.80	15.49	16.052	23.61	2.840	2.671	0.0838	0.0101
180.569	256.58	30.86	52.647	126.76	15.25	16.040	23.57	2.835	2.672	0.0839	0.0101
176.369	254.39	30.60	52.658	126.74	15.24	16.014	23.50	2.827	2.544	0.0727	0.0087
176.466	254.52	30.61	52.666	126.79	15.25	15.290	21.26	2.557	2.543	0.0724	0.0087
176.447	254.26	30.58	51.605	124.69	15.00	15.284	21.26	2.557	2.544	0.0725	0.0087
172.253	252.01	30.31	51.624	124.71	15.00	15.259	21.19	2.548	2.424	0.0628	0.0076
172.340	252.17	30.33	51.623	124.71	15.00	14.565	19.09	2.296	2.421	0.0630	0.0076
172.333	252.16	30.33	50.577	122.51	14.73	14.563	19.08	2.295	2.422	0.0630	0.0076
168.136	249.73	30.04	50.576	122.54	14.74	14.543	19.02	2.288	2.308	0.0546	0.0066
168.218	249.73	30.04	50.589	122.59	14.74	13.876	17.07	2.053	2.307	0.0545	0.0066
168.213	249.77	30.04	49.540	120.31	14.47	13.882	17.08	2.054	2.309	0.0545	0.0066
164.019	247.16	29.73	49.539	120.33	14.47	13.865	17.03	2.048	2.196	0.0461	0.0055
164.093	247.21	29.73	49.549	120.38	14.48	13.215	15.20	1.828	2.195	0.0459	0.0055
164.088	247.38	29.75	48.500	117.94	14.19	13.221	15.21	1.830	2.196	0.0462	0.0056
159.899	244.84	29.45	48.499	117.99	14.19	13.211	15.19	1.828	2.089	0.0393	0.0047
159.976	244.85	29.45	48.507	118.00	14.19	12.580	13.43	1.616	2.086	0.0392	0.0047
159.956	244.75	29.44	47.461	115.61	13.90	12.588	13.48	1.622	2.089	0.0392	0.0047
155.775	242.16	29.13	47.458	115.63	13.91	12.588	13.46	1.619	1.985	0.0342	0.0041
155.843	242.25	29.14	47.469	115.62	13.91	11.978	11.85	1.425	1.984	0.0341	0.0041
155.835	242.26	29.14	46.424	113.23	13.62	11.992	11.87	1.427	1.985	0.0342	0.0041
151.652	239.61	28.82	46.421	113.27	13.62	11.993	11.87	1.428	1.893	0.0299	0.0036
151.721	239.69	28.83	46.430	113.28	13.62	11.412	10.40	1.251	1.890	0.0298	0.0036
151.712	239.54	28.81	45.382	110.86	13.33	11.422	10.42	1.254	1.891	0.0298	0.0036
147.540	236.96	28.50	45.386	110.86	13.33	11.425	10.41	1.253			
147.600	236.91	28.49	45.390	110.88	13.34	10.875	9.101	1.095			
147.579	237.05	28.51	44.345	108.39	13.04	10.885	9.122	1.097			

[a] The standard uncertainties u on the temperature are: $u(T) = 0.01$ K for $1.9 < T/K < 20$, $u(T) = 0.02$ K for $20 < T/K < 100$, $u(T) = 0.05$ K for $100 < T/K < 300$. The relative standard uncertainties on the values of the heat capacities are determined to be $u_r(C_{p,m}) = 0.03$ for $T/K < 15$, $u_r(C_{p,m}) = 0.025$ for $15 < T/K < 30$, $u_r(C_{p,m}) = 0.02$ for $30 < T/K < 50$, $u_r(C_{p,m}) = 0.015$ for $50 < T/K < 100$, and $u_r(C_{p,m}) = 0.01$ for $T/K > 100$.

[b] The standard uncertainty u on the pressure is: $u(p) = 0.01$ *mPa*.

function above $T = 10.0$ K, and simple expression type function below $T = 10.0$ K. The fitted data are shown with solid lines in Figs. 2a and 2b.

At very low temperatures ($T < 10.0$ K), the phonon contribution is well-represented using an harmonic-lattice model [34], as expressed by Eq. (7), where the number of required terms augments with the high temperature limit of the fit:

$$C_{latt} = \sum B_n T^n, \quad where\ n = 3, 5, 7, 9\ldots \tag{7}$$

Four terms were used over the temperature range $T = (1.9–10.0)$ K. The corresponding coefficients are listed in Table 8. The electronic contribution of the conduction electrons at the Fermi surface are represented with a linear term γT [38]. In this case, $Cs_3Na(MoO_4)_2$ being an insulating material, the electronic specific heat is zero.

Above $T = 10.0$ K, the lattice contribution dominates and can be modelled using a combination of Debye and Einstein functions [39], as written in Eq. (8). Such method has been applied successfully in the literature to different classes of inorganic compounds: iron phosphates [40–42], zirconolite [35], calcium titanate [36], dicesium molybdate [43], sodium uranate and neptunate [44]. Three Einstein functions were used in this work to fit the data. Fitting with a single or two Einstein functions was attempted, but could not reproduce accurately the high temperature region. The fitted parameters are listed in Table 8. The sum $(n_D + n_{E1} + n_{E2} + n_{E3})$ is slightly smaller than 14. The deviation of the fitted data from the experimental results remains below about 1.5% over the temperature range $T = (10–299.6)$ K, as shown in Fig. 3.

$$C_{p,m} = n_D D(\theta_D) + n_{E1} E(\theta_{E1}) + n_{E2} E(\theta_{E2}) + n_{E3} E(\theta_{E3}) \tag{8}$$

where $D(\theta_D), E(\theta_{E1}), E(\theta_{E2})$ and $E(\theta_{E3})$ are the Debye and Einstein functions, respectively, as written in Eqs. (9) and (10). θ_D, θ_{E1}, θ_{E2} and θ_{E3} are the characteristic Debye and Einstein temperatures. n_D, n_{E1}, n_{E2} and n_{E3} are adjustable parameters, whose sum $(n_D + n_{E1} + n_{E2} + n_{E3})$ should be approximately equal to the number of atoms in the formula unit (i.e., 14 in this case).

$$D(\theta_D) = 9R\left(\frac{1}{x}\right)^3 \int_0^x \frac{exp(x)x^4}{[exp(x) - 1]^2} \cdot dx, \quad x = \frac{\theta_D}{T} \tag{9}$$

$$E(\theta_E) = 3Rx^2 \frac{exp(x)}{[exp(x) - 1]^2}, \quad x = \frac{\theta_E}{T} \tag{10}$$

where R is the universal gas constant equal to 8.3144598 $J{\cdot}K^{-1}{\cdot}mol^{-1}$.

The heat capacity value at 298.15 K obtained by interpolation is $C^{o}_{p,m}(Cs_3Na(MoO_4)_2, cr, 298.15K) = (296.3 \pm 3.3)$[15] $J{\cdot}K^{-1}{\cdot}mol^{-1}$. The experimental standard entropy at 298.15 K determined by

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[15] The quoted uncertainty corresponds to the standard uncertainty.

Table A. 2

Experimental heat capacity data[a] for $Cs_3Na(MoO_4)_2$ measured at p = 1.25 mPa[b] and magnetic field B = 9T. R is the ideal gas constant equal to 8.3144598 $J{\cdot}K^{-1}{\cdot}mol^{-1}$.

T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$	T/K	$C_{p,m}(T/K)$ $(J{\cdot}K^{-1}{\cdot}mol^{-1})$	$C_{p,m}(T/K)/R$
60.966	141.82	17.06	38.107	92.87	11.17	16.031	23.43	2.818	5.248	0.8492	0.1021
60.954	141.76	17.05	37.071	90.19	10.85	16.016	23.39	2.813	5.247	0.8490	0.1021
60.956	141.79	17.05	37.055	90.23	10.85	15.281	21.15	2.543	5.250	0.8469	0.1019
59.926	139.98	16.84	37.062	90.26	10.86	15.279	21.14	2.543	4.995	0.7161	0.0861
59.923	140.04	16.84	36.034	87.92	10.57	15.260	21.08	2.535	4.994	0.7090	0.0853
59.921	140.06	16.84	36.008	87.87	10.57	14.559	18.98	2.283	4.997	0.7161	0.0861
58.890	138.25	16.63	36.016	87.97	10.58	14.561	19.00	2.285	4.753	0.6007	0.0722
58.887	138.28	16.63	34.990	85.15	10.24	14.542	18.93	2.277	4.752	0.5981	0.0719
58.884	138.26	16.63	34.963	84.99	10.22	13.868	16.98	2.043	4.757	0.6008	0.0723
57.855	136.41	16.41	34.969	85.02	10.23	13.876	16.99	2.044	4.523	0.5063	0.0609
57.850	136.48	16.41	33.956	81.83	9.842	13.860	16.97	2.041	4.522	0.5059	0.0608
57.854	136.47	16.41	33.933	81.93	9.854	13.205	15.13	1.820	4.525	0.5063	0.0609
56.815	134.65	16.19	33.932	81.96	9.857	13.214	15.17	1.825	4.306	0.4284	0.0515
56.809	134.58	16.19	32.909	79.06	9.509	13.209	15.14	1.821	4.306	0.4266	0.0513
56.820	134.59	16.19	32.892	79.04	9.506	12.568	13.38	1.609	4.307	0.4276	0.0514
55.772	132.72	15.96	32.890	79.02	9.503	12.582	13.44	1.617	4.100	0.3609	0.0434
55.775	132.64	15.95	31.865	75.87	9.125	12.583	13.42	1.614	4.099	0.3593	0.0432
55.787	132.70	15.96	31.855	76.34	9.182	11.971	11.82	1.422	4.101	0.3614	0.0435
54.733	130.71	15.72	31.848	76.27	9.174	11.983	11.87	1.427	3.903	0.3056	0.0367
54.734	130.71	15.72	30.830	72.78	8.754	11.985	11.87	1.428	3.900	0.3059	0.0368
54.743	130.77	15.73	30.820	72.91	8.769	11.408	10.41	1.252	3.903	0.3049	0.0367
53.693	128.69	15.48	30.815	72.84	8.761	11.420	10.43	1.254	3.713	0.2589	0.0311
53.697	128.66	15.47	29.799	69.24	8.328	11.421	10.44	1.255	3.711	0.2584	0.0311
53.708	128.75	15.48	29.777	69.38	8.344	10.866	9.117	1.097	3.713	0.2580	0.0310
52.653	126.64	15.23	29.767	69.35	8.341	10.875	9.145	1.100	3.536	0.2212	0.0266
52.659	126.61	15.23	28.761	65.70	7.902	10.879	9.149	1.100	3.533	0.2198	0.0264
52.666	126.66	15.23	28.740	65.70	7.902	10.346	7.973	0.9589	3.536	0.2199	0.0265
51.628	124.56	14.98	28.736	65.67	7.898	10.359	7.965	0.9579	3.364	0.1889	0.0227
51.619	124.59	14.98	27.725	62.05	7.463	10.363	7.967	0.9582	3.363	0.1871	0.0225
51.626	124.60	14.99	27.694	62.01	7.458	9.855	6.945	0.8353	3.364	0.1884	0.0227
50.585	122.42	14.72	27.693	61.99	7.455	9.861	6.960	0.8371	3.199	0.1612	0.0194
50.583	122.43	14.72	26.682	58.47	7.033	9.863	6.962	0.8374	3.198	0.1604	0.0193
50.592	122.51	14.73	26.663	58.40	7.024	9.387	6.021	0.7242	3.199	0.1598	0.0192
49.544	120.22	14.46	26.641	58.35	7.018	9.392	6.022	0.7242	3.044	0.1368	0.0165
49.542	120.23	14.46	25.639	54.94	6.608	9.397	6.026	0.7248	3.041	0.1364	0.0164
49.551	120.24	14.46	25.640	54.99	6.614	8.941	5.195	0.6249	3.042	0.1363	0.0164
48.508	117.84	14.17	25.600	54.79	6.590	8.945	5.193	0.6245	2.895	0.1166	0.0140
48.501	117.90	14.18	24.597	51.49	6.193	8.948	5.199	0.6253	2.894	0.1166	0.0140
48.512	117.90	14.18	24.597	51.49	6.192	8.520	4.457	0.5361	2.893	0.1165	0.0140
47.470	115.50	13.89	24.561	51.39	6.180	8.525	4.464	0.5369	2.755	0.1008	0.0121
47.465	115.53	13.90	23.555	47.95	5.767	8.530	4.468	0.5373	2.753	0.1004	0.0121
47.474	115.54	13.90	23.550	47.76	5.745	8.115	3.808	0.4579	2.754	0.1008	0.0121
46.428	113.09	13.60	23.522	47.88	5.759	8.116	3.807	0.4578	2.621	0.0870	0.0105
46.427	113.19	13.61	22.512	44.48	5.350	8.119	3.812	0.4585	2.619	0.0866	0.0104
46.435	113.17	13.61	22.502	44.46	5.348	7.728	3.239	0.3896	2.620	0.0868	0.0104
45.389	110.73	13.32	22.483	44.39	5.339	7.731	3.242	0.3899	2.495	0.0746	0.0090
45.389	110.77	13.32	21.468	40.95	4.925	7.733	3.248	0.3906	2.492	0.0745	0.0090
45.393	110.78	13.32	21.460	40.86	4.914	7.360	2.751	0.3309	2.493	0.0744	0.0089
44.349	108.29	13.02	21.443	40.86	4.914	7.359	2.747	0.3304	2.375	0.0644	0.0077
44.351	108.32	13.03	20.420	37.49	4.509	7.362	2.750	0.3307	2.372	0.0642	0.0077
44.354	108.32	13.03	20.409	37.45	4.504	7.058	2.389	0.2873	2.373	0.0642	0.0077
43.312	105.79	12.72	20.395	37.37	4.494	7.057	2.388	0.2873	2.260	0.0548	0.0066
43.306	105.80	12.72	20.363	37.26	4.481	7.057	2.387	0.2871	2.257	0.0545	0.0066
43.316	105.84	12.73	20.406	37.44	4.503	6.700	1.996	0.2400	2.257	0.0545	0.0066
42.267	103.21	12.41	20.391	37.40	4.498	6.704	1.996	0.2401	2.148	0.0456	0.0055
42.264	103.21	12.41	19.454	34.31	4.126	6.710	2.001	0.2407	2.146	0.0453	0.0055
42.271	103.25	12.42	19.453	34.30	4.126	6.380	1.684	0.2026	2.147	0.0454	0.0055
41.227	100.62	12.10	19.438	34.26	4.121	6.385	1.688	0.2030	2.043	0.0388	0.0047
41.225	100.62	12.10	18.551	31.37	3.773	6.389	1.688	0.2031	2.040	0.0387	0.0047
41.232	100.61	12.10	18.533	31.23	3.756	6.077	1.420	0.1708	2.040	0.0387	0.0047
40.193	98.02	11.79	18.507	31.23	3.756	6.077	1.425	0.1714	1.942	0.0335	0.0040
40.184	98.04	11.79	17.664	28.54	3.432	6.085	1.425	0.1714	1.939	0.0334	0.0040
40.190	98.05	11.79	17.656	28.50	3.428	5.785	1.191	0.1432	1.939	0.0333	0.0040
39.153	95.40	11.47	17.631	28.43	3.419	5.787	1.198	0.1441	1.848	0.0288	0.0035
39.143	95.49	11.48	16.834	25.91	3.116	5.790	1.194	0.1437	1.847	0.0287	0.0035
39.149	95.48	11.48	16.828	25.91	3.117	5.509	1.004	0.1207	1.846	0.0286	0.0034
38.112	92.79	11.16	16.809	25.76	3.098	5.510	1.001	0.1204			
38.099	92.84	11.17	16.033	23.42	2.817	5.513	1.003	0.1207			

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[a] The standard uncertainties u on the temperature are: $u(T)$ = 0.01 K for 1.9 < T/K < 20, $u(T)$ = 0.02 K for 20 < T/K < 61. The relative standard uncertainties on the values of the heat capacities are determined to be $u_r(C_{p,m})$ = 0.03 for T/K < 15, $u_r(C_{p,m})$ = 0.025 for 15 < T/K < 30, $u_r(C_{p,m})$ = 0.02 for 30 < T/K < 50, $u_r(C_{p,m})$ = 0.015 for 50 < T/K < 61.

[b] The standard uncertainty u on the pressure is: $u(p)$ = 0.01 *mPa*.

numerical integration of $(C_{p,m}/T) = f(T)$ using the aforementioned fitted functions, is $S^{o}_{m}(Cs_3Na(MoO_4)_2, cr, 298.15K) = (467.2 \pm 6.8)^{16}$ J·K^{-1}·mol^{-1}. Standard thermodynamic functions were calculated at selected temperatures between T = (0 and 300) K and are listed in Table 9.

4. Discussion

Combining the newly determined value of the standard entropy with the ones for cesium [45], sodium [45], molybdenum [23], and oxygen [45], the standard entropy of formation of $Cs_3Na(MoO_4)_2$ was derived as $\Delta_f S^{o}_{m}(Cs_3Na(MoO_4)_2, cr, 298.15K) = -(717.5 \pm 5.2^{17})$ J·K^{-1}·mol^{-1}. From the latter value and the measured enthalpy of formation, the Gibbs energy of formation at 298.15 K was determined as $\Delta_f G^{o}_{m}(Cs_3Na(MoO_4)_2, cr, 298.15K) = -(2784.6 \pm 3.4^{18})$ kJ·mol^{-1}.

The entropy, enthalpy and Gibbs energy of formation of $Cs_3Na(MoO_4)_2$ from its constituting oxides were finally derived as listed in Table 10. These data were calculated using the following values for the enthalpies of formation of Cs_2O(cr), Na_2O(cr), MoO_3(cr), Cs_2MoO_4(cr) and Na_2MoO_4(cr), respectively: $-(345.98 \pm 1.17)$ [23], $-(417.98 \pm 4.20)$ [47], $-(745.0 \pm 1.0)$ [23], $-(1514.7 \pm 1.5)$ (this work), $-(1466.5 \pm 1.3)$ (this work) kJ·mol^{-1}. The corresponding standard entropies are: (146.87 ± 0.44) [23], (75.04 ± 0.10) [23], (77.76 ± 1.30) [23], (248.35 ± 0.30) [23], (159.40 ± 1.20) [48] J·K^{-1}·mol^{-1}.

The derived Gibbs energy of formation of $Cs_3Na(MoO_4)_2$ from the constituting binary oxides Cs_2O(cr), Na_2O(cr), and MoO_3(cr) equals $\Delta_f G^{o}_{m,bin.ox.}(298.15K) = -(796.6 \pm 6.3)$ kJ·mol^{-1}. The Gibbs energy of formation from the constituting ternary oxides Cs_2MoO_4(cr) and Na_2MoO_4(cr) is positive at 298.15 K: $\Delta_f G^{o}_{m,ter.ox.}(298.15K) = (2.3 \pm 4.4)$ kJ·mol^{-1}, suggesting $Cs_3Na(MoO_4)_2$ is not stable with respect to Cs_2MoO_4(cr) and Na_2MoO_4(cr) at room temperature. However, the calculation of the Gibbs energy for this reaction in the temperature range T = (298.15–778) K yields^{19} $\Delta_f G^{o}_{m,ter.ox.}(T/K) = (7.141–0.0162\ T)$ kJ·mol^{-1}, which becomes negative above T = 440 K. This result is in accordance with the observations of Zolotova et al. [1], who reported that “according to XRD data, a noticeable interaction between Na_2MoO_4 and Cs_2MoO_4 begins at 250°C” (523 K). It also explains the need for a very long thermal treatment (150 h at 693 K in the work of [1] and 200 h at 723 K in this work) to obtain a complete reaction between the sodium and cesium molybdates.

5. Conclusions

The enthalpies of formation of Cs_2MoO_4, Na_2MoO_4 and $Cs_3Na(MoO_4)_2$ have been measured in this work using solution calorimetry in 0.1 M CsOH, 0.1 M NaOH, and 2 M HNO_3 solutions, respectively. The values derived for Cs_2MoO_4, i.e., $\Delta_f H^{o}_{m}(Cs_2MoO_4$, cr, 298.15 K) = $-(1514.7 \pm 1.5)$ kJ·mol^{-1}, and Na_2MoO_4, i.e., $\Delta_f H^{o}_{m}(Na_2MoO_4$, cr, 298.15 K) = $-(1466.5 \pm 1.3)$ kJ·mol^{-1}, were found in very good agreement with the literature, which gave us good confidence in the accuracy of our measurements. The measurements on a well-characterized sample of the double molybdate $Cs_3Na(MoO_4)_2$ have yielded: $\Delta_f H^{o}_{m}(Cs_3Na(MoO_4)_2$, cr, 298.15 K) = $-(2998.5 \pm 3.0)$ kJ·mol^{-1}. The experimental low temperature heat capacity data of $Cs_3Na(MoO_4)_2$ have been fitted to theoretical functions below 10 K and to a combination of Debye and Einstein functions above this temperature. The derived standard entropy is $S^{o}_{m}(Cs_3Na(MoO_4)_2, cr, 298.15K) = (467.2 \pm 6.8)$ J·K^{-1}·mol^{-1}. Finally, the Gibbs energy of formation of $Cs_3Na(MoO_4)_2$ from its constituting elements and oxides have been derived. The compounds appears to be metastable with respect to Cs_2MoO_4 and Na_2MoO_4 at room temperature. However, the Gibbs energy of the reaction of formation from the constituting ternary oxides becomes negative above T = 440 K. These results concur with the observations of Zolotova et al. [1] and ours regarding the ease of the synthesis reaction.

Appendix A. Appendix

Tables A. 1 A. 2.

References

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[16] The quoted uncertainty corresponds to the standard uncertainty.

[17] The reported uncertainty was calculated as recommended in [46].

[18] The reported uncertainty was calculated as recommended in [46].

[19] The high temperature heat capacity function of Cs_2MoO_4 was taken from [49], while that of Na_2MoO_4 and $Cs_3Na(MoO_4)_2$ were estimated using the Neumann–Kopp role applied to Na_2O [47], MoO_3 [23] and Cs_2MoO_4 [49].

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