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Report of the Double-Molybdate Phase Cs₂Ba(MoO₄)₂ with a Palmierite Structure and Its Thermodynamic Characterization

Anna L. Smith,* Nathan de Zoete, Maikel Rutten, Lambert van Eijck, Jean-Christophe Griveau, and Eric Colineau

ABSTRACT: The existence of a novel double-molybdate phase with a palmierite-type structure, Cs₂Ba(MoO₄)₂, is revealed in this work, and its structural properties at room temperature have been characterized in detail using X-ray and neutron diffraction measurements. In addition, its thermal stability and thermal expansion are investigated in the temperature range 298−673 K using high-temperature X-ray diffraction, leading to the volumetric thermal expansion coefficient α_v ≈ 43.0 × 10⁻⁶ K⁻¹. The compound’s standard enthalpy of formation at 298.15 K has been obtained using solution calorimetry, which yielded Δ_H°(Cs₂Ba(MoO₄)₂, cr, 298.15 K) = −3066.6 ± 3.1 kJ·mol⁻¹, and its standard entropy at 298.15 K has been derived from low-temperature (2.1−294.3 K) thermal-relaxation calorimetry as S_m°(Cs₂Ba(MoO₄)₂, cr, 298.15 K) = 381.2 ± 11.8 J·K⁻¹·mol⁻¹.

1. INTRODUCTION

A significant interest exists for molybdate materials because of their appealing optical and electronic properties for the fields of photoluminescence,¹,² ionic conductivity,³⁴ ferroelastic and ferroelectric behavior,⁵⁶ and laser materials activated by lanthanide ions.⁷⁸ A novel double molybdate with the palmierite structure that is isostructural with K₂Pb(SO₄)₂,⁹ i.e. trigonal in space group R₃m, is reported in this work. Cs₂Ba(MoO₄)₂ was found to form by the reaction between barium molybdate (BaMoO₄) and cesium molybdate (Cs₅MoO₄) at high temperatures. Our prime interest at the moment of the study was the investigation of the solubility of cesium in barium molybdate, a fission product phase expected to form at high burnup in the current generation of light water reactors (LWRs) and next-generation fast neutron reactors fueled with a ceramic (U,Pu)O₂ type of fuel.

Among the numerous fission products formed during irradiation of uranium dioxide and mixed uranium–plutonium oxide fuel, cesium, barium, and molybdenum are of primary importance. Cesium is classified as volatile together with iodine and tellurium and constitutes a concern for the public, as the radioactive isotopes ¹³⁵Cs and ¹³⁷Cs represent a radiological health hazard in a severe accident (SA) scenario with release to the environment. Barium belongs to the so-called semivolatile species, meaning that its release kinetics from the fuel matrix depend on the redox conditions of the surrounding environment.¹⁰ Their exact speciation in irradiated fuel is rather intricate, although it is of paramount importance for SA analysis, where the temperature and oxygen potential can vary widely.

Cesium is generated with a high yield and is present in irradiated fuel in various forms. It is mostly present as gaseous Cs and in association with other fission products in the form of Cs₂ZrO₄, Cs₂Te, and CsI at low oxygen potentials¹¹−¹³ (below about ~400 kJ·mol⁻¹ at 1273 K according to a study by Imoto¹¹). The CsI fraction remains constant irrespective of the oxygen potential, while at higher oxygen potentials (above ~370 kJ·mol⁻¹) cesium orthomolybdate (Cs₅MoO₄) becomes the dominant phase, the other phases becoming unstable.¹¹−¹³ The formation of Cs₅MoO₄ in fast neutron reactors in the so-called “joint oxyde gaine” (JOG) layer (~150−300 μm thickness) between the cladding and fuel above ~7−8% FIMA (fission per initial metal atom) has been documented quite extensively.¹⁴−¹⁶ Cs₅MoO₄ is the major constituting phase of the JOG, but other chemical elements are also found in its heterogeneous structure, notably Te, I, Zr, and Ba and the cladding components Fe and Cr.¹⁶ The exact chemical composition of the JOG and mechanisms of its formation are still largely unknown, however, despite the clear importance for

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the assessment of the fuel behavior in fast neutron reactors. Cs2MoO4 is known to have a lower thermal conductivity in comparison to the fuel (about 1 order of magnitude lower)21,22 and a high thermal expansion,23 which is detrimental to the fuel properties.

Barium, because of its large ionic radius, shows a very limited solubility in the (U,Pu)O2 fuel matrix24 and, rather, tends to form oxide precipitates. Barrachin et al.25 recently observed in fuel text sections of the PHEBUS FPT2 test the association of barium and molybdenum at grain boundaries in the form of oxide precipitates. The thermochemical calculations by Imoto,11 Cordfunke and Konings,13 and Kurosaki et al.,26 post-irradiation examinations (PIE) by Kleykamp,24 and experimental studies by Paschoal et al.27 and Murourama et al.28 show that, at low oxygen potentials, the so-called gray phase, a perovskite compound of composition (Ba1−x−ySrxCy)(Zr1−x−yMo1−yREy)O3 (RE = rare earth only present at high potentials),11,13,26,28 the formation of the latter potential (−1 and Ba(Mo,U)O4 (94.9% Mo, 5.1% U) at a high oxygen potential (−1, RE = rare earth only present at high burnup) is formed with a limited solubility of BaMoO4,27 while the scheelite-type Ba(Mo1−yUy)O2 is the dominant phase at high oxygen potentials.13,14,26,28 The formation of the latter phase should be even more noticeable in fast neutron reactors, which reach higher burnup levels. According to the calculations of Kurosaki et al.26 for (U0.8Pu0.2O2) fuel at 100 GWd/t burnup under fast reactor circumstances, the formation of Ba(Zr,Mo,U)O3 (38.6% Zr, 2.5% Mo, 58.9% U) should occur at 1273 K for an oxygen potential of around −500 to −400 kJ mol−1 and Ba(Mo,U)O4 (94.9% Mo, 5.1% U) at a high oxygen potential (−300 to −200 kJ mol−1).

Finally, molybdenum is present in metallic form, along with ruthenium, rhodium, palladium, and technetium, forming the so-called “white inclusions” at low oxygen potential, and forms higher valence state compounds (Mo2O7 gray phase, Mo3O8 scheelite, Cs2MoO4, etc.) with an increase in oxygen potential.27,28 The Mo/MoO2 redox couple plays a key role in SA analysis, as it acts as an oxygen potential buffer, which determines the chemical state of other fission products such as cesium, barium, and strontium and therefore their release behavior.10,11,24

Because the chemistry of cesium in irradiated fuel is of paramount importance to assess the driving force for its release into the environment, studies of its chemical speciation are a necessity. The solubility of cesium in the gray phase is reported to be low, but much less is known about its solubility in the scheelrite structure Ba(U,Mo)O4 formed at high oxygen potentials. With the aim of improving the evaluation of the source term in severe accident codes, a study of the solubility of cesium in barium molybdate (BaMoO4) was thus carried out in our research group in the framework of the TCOFF project (thermodynamic characterization of fuel debris and fission products based on a scenario analysis of severe accident progression at the Fukushima-Daiichi nuclear power station).29 The identification of the novel double molybdate Cs2Ba(MoO4)2 is reported in this work, and a detailed characterization of the structure using X-ray and neutron diffraction is given. The thermal stability and thermal expansion of Cs2Ba(MoO4)2 up to 673 K are estimated using high-temperature X-ray diffraction. Finally, the standard enthalpy of formation and standard entropy at 298.15 K are determined using solution calorimetry and thermal relaxation calorimetry, respectively.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation. Barium molybdate (BaMoO4) was synthesized by a solid-state reaction between barium carbonate (BaCO3; >99%, Fluka) and molybdenum oxide (MoO3; 99.95%, Sigma-Aldrich), with heating in air at 1023 K twice for 12 h with an intermediate regrounding step. Cesium orthomolybdate (Cs2MoO4) was synthesized by a reaction between stoichiometric amounts of cesium carbonate (Cs2CO3; 99.99%, Alfa Aesar) and molybdenum oxide (MoO3; 99.95%, Sigma-Aldrich) as described in ref 23. Cs2Ba(MoO4)2 was subsequently obtained by a reaction between barium molybdate and cesium molybdate mixed in a stoichiometric ratio with heating in an alumina boat under an oxygen flow for 62 h at 1023 K with intermediate regrounding steps. Handling of the samples was done in an argon-filled glovebox, with a dry atmosphere (H2O and O2 contents <5 ppm), because of the known hygroscopic nature of the Cs2MoO4 precursor. Mixing of the precursors was done using a Retsch MM400 ball mill, with milling times ranging between 30 and 100 min.

The purity of the sample was examined by X-ray diffraction (XRD) and neutron diffraction (ND) at room temperature. The collected patterns did not reveal any secondary phases, and the sample’s purity is thus expected to be better than 99.9%.

2.2. Powder X-ray Diffraction (XRD). A PANanalytical 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) and a real-time multistrip (RTMS) detector (X’Celerator) was used for the collection of X-ray diffraction patterns at room temperature. The samples were measured inside a sealed sample holder, with a Kapton foil cover, maintaining the dry argon atmosphere of the glovebox. A typical diffractogram was obtained in about 8 h, by step scanning in the angle range 10° ≤ 2θ ≤ 120° with a step size of 0.008° (2θ). The Rietveld method as implemented in the FullProf suite30 was used for the structural analysis.

2.3. High-Temperature X-ray Diffraction (HT XRD). High-temperature X-ray diffraction measurements were performed from room temperature up to 673 K (the maximum temperature that can be reached with our equipment) using the same diffractometer as above equipped with an Anton Paar TTK450 chamber to assess the thermal expansion and polymorphism of Cs2Ba(MoO4)2. The data were collected at vacuum (0.02 mbar). The temperature was monitored with a Pt100 resistor. A typical isothermal measurement was performed in 6 h after 30 min of stabilization time at the measurement temperature.

2.4. Neutron Diffraction (ND). Neutron diffraction data were recorded at room temperature at the PEARL beamline at the Hoger Onderwijs Reactor at TU Delft.31 The sample of Cs2Ba(MoO4)2 (2.4 g) was encapsulated in a vanadium cylindrical container (50 mm high, 6 mm inner diameter) closed with a Viton O-ring in the dry argon atmosphere of the glovebox. The data were collected at a fixed wavelength (λ = 1.667 Å) for 20 h over the range 10° ≤ 2θ ≤ 160°. The Rietveld method as implemented in the FullProf suite30 was used for the structural analysis.

2.5. Solution Calorimetry. The dissolution enthalpies of Cs2Ba(MoO4)2, BaMoO4, and Cs2MoO4 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 25 mL Pyrex glass reaction vessel and stirrer system (motor and gold stirrer holding a glass ampule). The temperature changes during the experiment were monitored with a thermistor, while a heater was used 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 were encapsulated inside a 1 mL glass ampule sealed using beeswax. The latter operation was performed in the dry atmosphere of an argon-filled glovebox because of the hygroscopic nature of Cs2MoO4. The solid samples were dissolved in 2 M nitric acid HNO3 solution (molality m = 1.57 mol kg−1) by breaking the bottom of the glass ampule 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 ±1 × 10⁻⁴ 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 enthalpy of dissolution of potassium chloride (KCl; Sigma-Aldrich, 99.7%) into 1000H₂O (distilled water) (molality m = 0.05551 mol kg⁻¹) was first measured to check the instrument accuracy, which yielded Δ_<sub>diss</sub>ₜₜₜ(H₂O, 298.15 K) = 17.510 ± 0.024 kJ mol⁻¹. This corresponds to a dissolution enthalpy in 500 H₂O equal to Δ_<sub>diss</sub>ₜₜₜ(500H₂O, 298.15 K) = 17.560 ± 0.024 kJ mol⁻¹ after correction, as recommended by the National Bureau of Standards (NBS)₃₂,₇₇ to m = 0.111 mol kg⁻¹, which is in very good agreement with the value recommended by the NBS:₃₅,₅₄ i.e., Δ_<sub>diss</sub>ₜₜₜ(500H₂O, 298.15 K) = 17.584 ± 0.017 kJ mol⁻¹. The measured value corresponds to an enthalpy at infinite dilution of Δ_<sub>diss</sub>ₜₜₜ(H₂O, 298.15 K) = 17.217 ± 0.024 kJ mol⁻¹, in very good agreement with the NBS data in refs 32 and 34, i.e. Δ_<sub>diss</sub>ₜₜₜ(H₂O, 298.15 K) = 17.241 ± 0.018 kJ mol⁻¹ and that in ref 35, i.e. Δ_<sub>diss</sub>ₜₜₜ(H₂O, 298.15 K) = 17.22 kJ mol⁻¹. In addition, the enthalpies of formation of Cs₂MoO₄ and Na₂MoO₄ were determined with this instrument in cesium hydroxide (CsOH) and sodium hydroxide (NaOH) solutions as described in a previous work and were found to be in excellent agreement with the literature data, which gives us confidence in the reliability of the measurements. The uncertainties on the dissolution enthalpies are reported hereafter as uncertainties on the dissolution enthalpies are reported hereafter as

![Graph](https://dx.doi.org/10.1021/acs.inorgchem.0c01469)

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural Characterization of the Double Molybdate Cs₅Ba(MoO₄)₂

During an investigation of the possible solubility of cesium in barium molybdate by mixing BaMoO₄ and Cs₂MoO₄ in various stoichiometric ratios (BaMoO₄:Cs₂MoO₄ = 1 – x:x) and heating at 1023 K under an oxygen flow for 24 h, a novel phase, not reported to this date in the literature, was identified in the collected X-ray diffraction patterns. The quaternary compound Cs₅Ba(MoO₄)₂ was found to form as a single phase when BaMoO₄ and Cs₂MoO₄ were mixed in a 1:1 ratio and mixed together with barium molybdate for x < 0.5 and with cesium molybdate for x > 0.5. The results of this study and our conclusions on the solubility of cesium in BaMoO₄ are described in detail in ref 45. A slight decrease in the lattice parameter of the scheelite phase was observed with increasing Cs content, which could suggest the formation of a Ba₁₋ₓCsₓMoO₄₋ₓ/₂ solid solution with a limited cesium solubility. Further investigations using techniques sensitive to the oxygen environment (neutron diffraction, extended X-ray absorption fine structure spectroscopy) and molybdenum valence state (X-ray absorption near edge structure spectroscopy) would be required to ascertain this hypothesis. In any case, the major finding of this work is the acknowledgment of the possible formation of the double molybdate Cs₅Ba(MoO₄)₂ under reactor conditions and the consequences this could have on the irradiated fuel behavior.

The obtained quaternary phase was found to be isotypic with the palmierite mineral K₃Pb(SO₄)₂₆, i.e. trigonal in space group R₃m, and isostructural with K₃Ba(MoO₄)₂₆ and Rb₂Ba(MoO₄)₂₆. The X-ray and neutron diffraction patterns are shown in parts a and b of Figures 1, respectively.

![XRD data](https://dx.doi.org/10.1021/acs.inorgchem.0c01469)

**Figure 1.** Experimental (Y₁obs in red) and calculated (Y₁calc in black) XRD and ND patterns of Cs₅Ba(MoO₄)₂. The difference between calculated and experimental intensities Y₁obs – Y₁calc is shown in blue. The angular positions of Bragg reflections are shown in green. Measurement at (a) λ = 1.667 Å.
The refined cell parameters obtained from the XRD and ND data are given in Table 1. The atomic positions and bond lengths obtained from the Rietveld refinement of the ND data are given in Tables 2 and 3, respectively. The calculated and measured diffraction intensities showed good agreement for both the XRD and ND data, which gives us confidence in the structural model adopted.

Cs$_2$Ba(MoO$_4$)$_2$ is made of layers in the $ab$ plane of corner-sharing BaO$_6$ octahedra and MoO$_4$ tetrahedra alternating with bilayers of CsO$_{10}$ decahedra sharing faces with the BaO$_6$ octahedra and edges plus corners with the MoO$_4$ tetrahedra (Figure 2). The MoO$_4$ tetrahedra are slightly distorted with one Mo–O$_{2}$ distance at 1.728(6) Å and three distances at 1.751(2) Å, while the BaO$_6$ octahedra have only one Ba–O$_{1}$ distance at 2.781(2) Å but a significant degree of angle distortion. The cesium decahedra are very distorted with distances varying between 2.872(7) and 3.278(2) Å.

The bond distances are moreover compared in the Table 3 with the distances reported for the isostructural K$_2$Ba(MoO$_4$)$_2$, Rb$_2$Ba(MoO$_4$)$_2$, and Rb$_2$Ba(WO$_4$)$_2$ compounds. One sees very clearly a trend of increasing alkali–oxygen bond distances in the 10-fold-coordinated AO$_{10}$ polyhedra when the ionic radius of the alkali cation (K, Rb, and Cs, respectively, in coordination [X], according to the tabulated data of Shannon$^{49}$). The situation in K$_2$Ba(MoO$_4$)$_2$ is very similar to that in Cs$_2$Ba(MoO$_4$)$_2$, but the angular distortion is much less.

To conclude this section on the structural characterization of Cs$_2$Ba(MoO$_4$)$_2$, the unit cell volume is compared with those reported for a series of isostructural compounds A$_2$Ba(MoO$_4$)$_2$, with various transition-metal cations (M = Cr, Mo, W, Mn, V) and A alkali or alkaline-earth cations (A = K, Rb, Cs, Sr, Ba) (see Figures 3a,b). One sees a very clear linear increasing trend of the unit cell volume with increasing size of the A cation (Figure 3a). Three distinct trends are visible, with almost parallel slopes. The first group includes Cs$_2$Ba(MoO$_4$)$_2$ together with Rb$_2$Ba(MoO$_4$)$_2$ and K$_2$Ba(MoO$_4$)$_2$, and Rb$_2$Ba(WO$_4$)$_2$, Rb$_2$Ba(CrO$_4$)$_2$ and K$_2$Ba(CrO$_4$)$_2$ form a separate group due to the much smaller ionic radius of hexavalent Cr in 4-fold coordination (0.26 Å) in comparison to hexavalent Mo (0.41 Å) and W (0.42 Å). Interestingly, the third class of compounds (Sr$_2$Ba(CrO$_4$)$_2$, Sr$_2$Ba(VO$_4$)$_2$, Ba$_3$(MoO$_4$)$_2$, Ba$_3$(CrO$_4$)$_2$ and Ba$_3$(VO$_4$)$_2$), where A is now an alkaline earth (A = Sr, Ba) and the transition metal (M = V, Cr, Mn) is pentavalent, shows the same linear trend with an almost identical slope. The same classification appears on plotting the unit cell volume versus the normalized difference in ionic radius between the A cation and the M transition metal (Figure 3b). The slope is positive and very similar between the different groups.

Finally, it is interesting to look at the relationship between the $a$ and $c$ lattice parameters in the palmierite structure.

### Table 1. Refined Profile Parameters of Cs$_2$Ba(MoO$_4$)$_2$ from the XRD and ND Data

<table>
<thead>
<tr>
<th>chemical formula</th>
<th>Cs$_2$Ba(MoO$_4$)$_2$</th>
<th>723.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>cristal syst</td>
<td>trigonal</td>
<td>R3m</td>
</tr>
<tr>
<td>Z</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>wavelength $\lambda$ (Å)</td>
<td>1.541/1.544</td>
<td>1.667</td>
</tr>
<tr>
<td>$a = b$ (Å)</td>
<td>6.18381(3)$^a$</td>
<td>6.1757(2)$^a$</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>23.0759(2)$^a$</td>
<td>23.0452(9)$^a$</td>
</tr>
<tr>
<td>cell volume $V$ (Å$^3$)</td>
<td>764.191(8)</td>
<td>761.18(4)</td>
</tr>
<tr>
<td>$d'$-space range (Å)</td>
<td>0.89–8.83</td>
<td>0.78–8.35</td>
</tr>
</tbody>
</table>

“The standard uncertainties obtained from the refinement are underestimated by about 1 order of magnitude.

### Table 2. Refined Atomic Positions in Cs$_2$Ba(MoO$_4$)$_2$ Derived from the ND Refinement$^a$

<table>
<thead>
<tr>
<th>atom</th>
<th>oxid state</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>−2</td>
<td>18b</td>
<td>0.48877(15)</td>
<td>0.51123(15)</td>
<td>0.24536(9)</td>
<td>2.99(5)</td>
</tr>
<tr>
<td>Cs</td>
<td>+1</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.19794(19)</td>
</tr>
<tr>
<td>O2</td>
<td>−2</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.32255(16)</td>
</tr>
<tr>
<td>Mo</td>
<td>+6</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.39754(14)</td>
</tr>
<tr>
<td>Ba</td>
<td>+2</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.4(1)</td>
</tr>
</tbody>
</table>

$^a$ $R_p = 10.0$, $R_w = 10.5$, $R_{wp} = 2.83$, $\chi^2 = 13.7$. Individual B parameters: O1, $B_{11} = 1.96(5)$; $B_{12} = 1.96(5)$, $B_{33} = 5.1(1)$, $B_{13} = 1.24(6)$, $B_{23} = 0.40(3)$, $B_{22} = -0.40(3)$; Cs, $B_{11} = 1.9(1)$, $B_{12} = 1.9(1)$, $B_{33} = 1.6(2)$, $B_{13} = 0.9(6)$; O2, $B_{11} = 9.5(3)$, $B_{22} = 9.5(3)$, $B_{13} = 1.0(2)$, $B_{23} = 4.8(2)$; Mo, $B_{11} = 1.21(8)$, $B_{22} = 1.21(8)$, $B_{33} = 1.4(1)$, $B_{13} = 0.60(4)$; Ba, $B_{11} = 3.2(2)$, $B_{22} = 3.2(2)$, $B_{33} = 0.9(3)$, $B_{13} = 1.6(1)$. 

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are compressed axially along the unit cell parameters, i.e. ($c$). The evolution of the relative thermal expansions of the cell parameters derived from a Rietveld refinement of the XRD patterns at each measurement temperature are given in Table 2. Temperature.

The thermal expansion of Cs$_2$Ba(MoO$_4$)$_2$ is assessed up to 673 K using high-temperature X-ray diffraction. No polymorphic transition was detected. The unit cell parameters derived from a Rietveld refinement of the XRD patterns at each measurement temperature are given in Table 4. The evolution of the relative thermal expansions of the $a$ and $c$ unit cell parameters, i.e. ($a - a_0$)/$a_0$ and ($c - c_0$)/$c_0$ (where $a_0$ and $c_0$ are the reference lengths at room temperature), is shown in Figure 4. The expansion is higher along the $a$ and $b$ directions, where MoO$_4$ tetrahedra alternate with BaO$_6$ octahedra via corner sharing, and is more limited along the $c$ direction, where bilayers of CsO$_{10}$ dodecahedra make the linkages between the previous layers. The volumetric thermal expansion is equal to $\alpha V = 0.01010 \pm 0.00004 \, \text{K}^{-1}$, as assessed as a polynomial function of the temperature $T(K)$

$$\frac{dV}{V} = -6.94 \times 10^{-3} + 2.16789 \times 10^{-5}T + 5.38893 \times 10^{-9}T^2$$

where $l_0 = (a_0b_0c_0)^{1/3}$ is the reference length at room temperature.

The relative thermal expansion is found between those reported in the literature for Cs$_2$MoO$_4$ and BaMoO$_4$ (shown as dotted lines in Figure 4).

### 3.3. Standard Enthalpy of Formation Determination

The enthalpy of formation of Cs$_2$Ba(MoO$_4$)$_2$ was measured using the thermochemical cycle detailed in Table 5 in a solution of 2 M HNO$_3$. The corresponding reaction scheme is

$$\text{Cs}_2\text{Ba(MoO}_4\text{)}_2(\text{cr}) + \text{HNO}_3(\text{sln}) = \text{Cs}_2\text{MoO}_4(\text{sln}) + \text{BaMoO}_4(\text{sln})$$

$$\Delta_{\text{f}298}^\circ H = -5.38893 \times 10^{-9}T^2$$

$$\Delta_{\text{f}298}^\circ H = 0.01010 \pm 0.00004 \, \text{K}^{-1}$$

and is extended here to a larger set of compounds. As the ionic radius of the metal $M$ cation increases, the MO$_4$ tetrahedra expand, thus producing an increase in the $a$ parameter. At the same time, the AO$_{10}$ sites are compressed axially along the $c$ direction (the axial $A$–$O$1 ($\times 3$) and $A$–$O$2 bonds along $c$ shorten) and expand equatorially in the $ab$ plane (the six $A$–$O$2 bonds lengthen) (see Figure 2), resulting in a decrease in the $c$ lattice parameter. If Cs$_2$Ba(WO$_4$)$_2$ and Cs$_2$Ba(CrO$_4$)$_2$ exist as stable phases (their existences have not been reported to this date in the literature), their lattice parameters should fall on a parallel trend.

### 3.2. Assessment of the Thermal Expansion with Temperature

The thermal expansion of Cs$_2$Ba(MoO$_4$)$_2$ was assessed up to 673 K using high-temperature X-ray diffraction. No polymorphic transition was detected. The unit cell parameters derived from a Rietveld refinement of the XRD patterns at each measurement temperature are given in Table 4. The evolution of the relative thermal expansions of the $a$ and $c$ unit cell parameters, i.e. ($a - a_0$)/$a_0$ and ($c - c_0$)/$c_0$ (where $a_0$ and $c_0$ are the reference lengths at room temperature), is shown in Figure 4. The expansion is higher along the $a$ and $b$ directions, where MoO$_4$ tetrahedra alternate with BaO$_6$ octahedra via corner sharing, and is more limited along the $c$ direction, where bilayers of CsO$_{10}$ dodecahedra make the linkages between the previous layers. The volumetric thermal expansion is equal to $\alpha V = 0.01010 \pm 0.00004 \, \text{K}^{-1}$, as assessed as a polynomial function of the temperature $T(K)$

$$\frac{dV}{V} = -6.94 \times 10^{-3} + 2.16789 \times 10^{-5}T + 5.38893 \times 10^{-9}T^2$$

where $l_0 = (a_0b_0c_0)^{1/3}$ is the reference length at room temperature.

The relative thermal expansion is found between those reported in the literature for Cs$_2$MoO$_4$ and BaMoO$_4$ (shown as dotted lines in Figure 4).

### 3.3. Standard Enthalpy of Formation Determination

The enthalpy of formation of Cs$_2$Ba(MoO$_4$)$_2$ was measured using the thermochemical cycle detailed in Table 5 in a solution of 2 M HNO$_3$. The corresponding reaction scheme is

$$\text{Cs}_2\text{Ba(MoO}_4\text{)}_2(\text{cr}) + \text{HNO}_3(\text{sln}) = \text{Cs}_2\text{MoO}_4(\text{sln}) + \text{BaMoO}_4(\text{sln})$$

$$\Delta_{\text{f}298}^\circ H = 0.01010 \pm 0.00004 \, \text{K}^{-1}$$

and is extended here to a larger set of compounds. As the ionic radius of the metal $M$ cation increases, the MO$_4$ tetrahedra expand, thus producing an increase in the $a$ parameter. At the same time, the AO$_{10}$ sites are compressed axially along the $c$ direction (the axial $A$–$O$1 ($\times 3$) and $A$–$O$2 bonds along $c$ shorten) and expand equatorially in the $ab$ plane (the six $A$–$O$2 bonds lengthen) (see Figure 2), resulting in a decrease in the $c$ lattice parameter. If Cs$_2$Ba(WO$_4$)$_2$ and Cs$_2$Ba(CrO$_4$)$_2$ exist as stable phases (their existences have not been reported to this date in the literature), their lattice parameters should fall on a parallel trend.

### 3.2. Assessment of the Thermal Expansion with Temperature

The thermal expansion of Cs$_2$Ba(MoO$_4$)$_2$ was assessed up to 673 K using high-temperature X-ray diffraction. No polymorphic transition was detected. The unit cell parameters derived from a Rietveld refinement of the XRD patterns at each measurement temperature are given in Table 4. The evolution of the relative thermal expansions of the $a$ and $c$ unit cell parameters, i.e. ($a - a_0$)/$a_0$ and ($c - c_0$)/$c_0$ (where $a_0$ and $c_0$ are the reference lengths at room temperature), is shown in Figure 4. The expansion is higher along the $a$ and $b$ directions, where MoO$_4$ tetrahedra alternate with BaO$_6$ octahedra via corner sharing, and is more limited along the $c$ direction, where bilayers of CsO$_{10}$ dodecahedra make the linkages between the previous layers. The volumetric thermal expansion is equal to $\alpha V = 0.01010 \pm 0.00004 \, \text{K}^{-1}$, as assessed as a polynomial function of the temperature $T(K)$

$$\frac{dV}{V} = -6.94 \times 10^{-3} + 2.16789 \times 10^{-5}T + 5.38893 \times 10^{-9}T^2$$

where $l_0 = (a_0b_0c_0)^{1/3}$ is the reference length at room temperature.

The relative thermal expansion is found between those reported in the literature for Cs$_2$MoO$_4$ and BaMoO$_4$ (shown as dotted lines in Figure 4).

### 3.3. Standard Enthalpy of Formation Determination

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$$\text{Cs}_2\text{Ba(MoO}_4\text{)}_2(\text{cr}) + \text{HNO}_3(\text{sln}) = \text{Cs}_2\text{MoO}_4(\text{sln}) + \text{BaMoO}_4(\text{sln})$$

$$\Delta_{\text{f}298}^\circ H = 0.01010 \pm 0.00004 \, \text{K}^{-1}$$
The dissolutions of Cs₂Ba(MoO₄)₂, BaMoO₄, and Cs₂MoO₄ in the nitric acid solutions were in all cases instantaneous. The details of all calorimetric results are given in Table 6.

By adjusting the amount of dissolved samples such that sol.1 (with associated dissolution enthalpy $\Delta_{sln}H_1$) and sol.3 (with associated dissolution enthalpy $\Delta_{sln}H_3$) had the same final composition, one can express the enthalpy of the reaction of formation from the constituting ternary oxides (eq 5) as

$$\Delta_{r}H^\circ_m = \Delta_{sln}H_2 + \Delta_{sln}H_3 - \Delta_{sln}H_1 = -5.14 \pm 2.71 \text{ kJ mol}^{-1}.$$  

$$\text{BaMoO}_4(\text{cr}) + \text{Cs}_2\text{MoO}_4(\text{cr}) = \text{Cs}_2\text{Ba(MoO}_4)_2(\text{cr})$$  

Figure 3. Evolution of the unit cell volume of $A_2\text{Ba(MO}_4)_2$ with $A = \text{K, Rb, Cs, Sr, Ba}$ and $M = \text{Cr, Mo, W, Mn, V}$ as a function of the (a) ionic radius of the $A$ cation in 10-fold coordination and (b) difference in ionic radii between the $A$ cation and the $M$ transition-metal element. (c) Relationship between the $a$ and $c$ lattice parameters in several classes of $A_2\text{Ba(MO}_4)_2$ compounds.

Table 4. Refined Unit Cell Parameters and Unit Cell Volume as a Function of Temperature

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>6.184(2)</td>
<td>23.081(8)</td>
<td>764.4(4)</td>
</tr>
<tr>
<td>373</td>
<td>6.196(2)</td>
<td>23.106(8)</td>
<td>768.1(4)</td>
</tr>
<tr>
<td>473</td>
<td>6.203(2)</td>
<td>23.124(9)</td>
<td>770.6(5)</td>
</tr>
<tr>
<td>573</td>
<td>6.212(3)</td>
<td>23.14(1)</td>
<td>773.4(6)</td>
</tr>
<tr>
<td>673</td>
<td>6.224(2)</td>
<td>23.169(8)</td>
<td>777.3(5)</td>
</tr>
</tbody>
</table>

Figure 4. Relative linear thermal expansion of Cs₂Ba(MoO₄)₂ along the crystallographic axes. Also shown (as dotted line) are the results of Wallez et al.²³ and Sahu et al.⁵⁴ for the mean relative linear expansions $dl/l_0$ of Cs₂MoO₄ and BaMoO₄, respectively.


### Table 5. Thermochemical Cycle Used to Determine the Standard Enthalpy of Formation of Cs₂Ba(MoO₄)₂:

<table>
<thead>
<tr>
<th>entry</th>
<th>reaction</th>
<th>$\Delta H_m$ (298.15 K) (kJ mol⁻¹)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Cs}_2\text{Ba(MoO}_4\text{)}_2$ (cr) + (sln) = $\text{BaMoO}_4$ (sln) + $\text{Cs}_2\text{MoO}_4$ (sln)</td>
<td>$-87.55 \pm 1.48^b$</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>$\text{BaMoO}_4$ (cr) + (sln) = $\text{BaMoO}_4$ (sln)</td>
<td>$-34.37 \pm 0.34^b$</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Cs}_2\text{MoO}_4$ (cr) + $\text{BaMoO}_4$ (sln) = $\text{BaMoO}_4$ (sln) + $\text{Cs}_2\text{MoO}_4$ (sln)</td>
<td>$-58.32 \pm 2.24^b$</td>
<td>this work</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Ba}(cr) + \text{Mo}(cr) + 2\text{O}_2(g) = \text{BaMoO}_4(cr)$</td>
<td>$-1547.23 \pm 1.22$</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>$2\text{Cs}(cr) + \text{Mo}(cr) + 2\text{O}_2(g) = \text{Cs}_2\text{MoO}_4(cr)$</td>
<td>$-1514.25 \pm 0.72^c$</td>
<td>36–38, 55</td>
</tr>
<tr>
<td>6</td>
<td>$2\text{Cs}(cr) + \text{Ba}(cr) + 2\text{Mo}(cr) + 4\text{O}_2(g) = \text{Cs}_2\text{Ba(MoO}_4\text{)}_2$ (cr)</td>
<td>$-3066.6 \pm 3.1$</td>
<td>this work</td>
</tr>
</tbody>
</table>

"Measurements were performed in the temperature interval $T = 298.15 \pm 0.30$ K. The enthalpy of formation of $\text{Cs}_2\text{Ba(MoO}_4\text{)}_2$ was calculated using the relation $\Delta H_m^{\circ}(6) = \Delta H_m^{\circ}(2) + \Delta H_m^{\circ}(3) - \Delta H_m^{\circ}(1) + \Delta H_m^{\circ}(4) + \Delta H_m^{\circ}(5)$. Expanded uncertainty $U$ with a coverage factor $k = 2$, corresponding to a 95% confidence interval. The selected value is the average of the data reported in refs 36–38 and 55.

### Table 6. Measured Dissolution Enthalpies at 298.15 K for $\text{Cs}_2\text{Ba(MoO}_4\text{)}_2$ (cr) ($M = 723.042$ g mol⁻¹), $\text{BaMoO}_4$ ($M = 297.276$ g mol⁻¹), and $\text{Cs}_2\text{MoO}_4$ ($M = 425.766$ g mol⁻¹) in 2 M HNO₃:

<table>
<thead>
<tr>
<th>entry</th>
<th>$m(\text{Cs}_2\text{Ba(MoO}_4\text{)}_2)$ (mg)</th>
<th>$\Delta T$ (mK)</th>
<th>$C_p$ (J K⁻¹)</th>
<th>$Q$ (J)</th>
<th>$\Delta H_m^{\circ}$ (298.15 K) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>71.81</td>
<td>79.932</td>
<td>109.888</td>
<td>-8.78</td>
<td>-88.44</td>
</tr>
<tr>
<td>2</td>
<td>73.17</td>
<td>80.361</td>
<td>110.123</td>
<td>-8.85</td>
<td>-87.45</td>
</tr>
<tr>
<td>3</td>
<td>72.25</td>
<td>78.965</td>
<td>110.271</td>
<td>-8.71</td>
<td>-87.14</td>
</tr>
<tr>
<td>4</td>
<td>72.30</td>
<td>78.639</td>
<td>110.118</td>
<td>-8.66</td>
<td>-86.60</td>
</tr>
<tr>
<td>5</td>
<td>72.25</td>
<td>79.972</td>
<td>110.112</td>
<td>-8.81</td>
<td>-88.12</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>entry</th>
<th>$m(\text{BaMoO}_4)$ (mg)</th>
<th>$\Delta T$ (mK)</th>
<th>$C_p$ (J K⁻¹)</th>
<th>$Q$ (J)</th>
<th>$\Delta H_m^{\circ}$ (298.15 K) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.43</td>
<td>44.682</td>
<td>110.166</td>
<td>-4922.44</td>
<td>-34.49</td>
</tr>
<tr>
<td>2</td>
<td>42.39</td>
<td>44.656</td>
<td>110.382</td>
<td>-4929.22</td>
<td>-34.57</td>
</tr>
<tr>
<td>3</td>
<td>42.55</td>
<td>44.454</td>
<td>110.255</td>
<td>-4901.28</td>
<td>-34.24</td>
</tr>
<tr>
<td>4</td>
<td>42.35</td>
<td>44.474</td>
<td>110.194</td>
<td>-4900.77</td>
<td>-34.40</td>
</tr>
<tr>
<td>5</td>
<td>42.62</td>
<td>44.455</td>
<td>110.160</td>
<td>-4697.16</td>
<td>-34.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>entry</th>
<th>$m(\text{Cs}_2\text{MoO}_4)$ (mg)</th>
<th>$\Delta T$ (mK)</th>
<th>$C_p$ (J K⁻¹)</th>
<th>$Q$ (J)</th>
<th>$\Delta H_m^{\circ}$ (298.15 K) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.64</td>
<td>37.353</td>
<td>109.520</td>
<td>-4.09</td>
<td>-58.76</td>
</tr>
<tr>
<td>2</td>
<td>29.82</td>
<td>37.021</td>
<td>109.544</td>
<td>-4.06</td>
<td>-57.90</td>
</tr>
<tr>
<td>3</td>
<td>29.74</td>
<td>38.171</td>
<td>109.738</td>
<td>-4.19</td>
<td>-59.97</td>
</tr>
<tr>
<td>4</td>
<td>29.67</td>
<td>36.234</td>
<td>109.555</td>
<td>-3.97</td>
<td>-56.96</td>
</tr>
<tr>
<td>5</td>
<td>29.65</td>
<td>36.895</td>
<td>109.481</td>
<td>-4.04</td>
<td>-58.00</td>
</tr>
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</table>

"The measurements were performed in the temperature range $T = 298.15 \pm 0.30$ K. Definitions: $m$, sample weight; $\Delta T$, temperature change caused by the dissolution; $C_p$, energy equivalent of the calorimeter; $Q$, amount of heat generated by the dissolution; $\Delta H_m^{\circ}(298.15$ K), molar enthalpy of the reaction.

![Figure 5. Heat capacity of Cs₂Ba(MoO₄)₂ (O) and fit to the data (red line): (a) $C_{p,m}$ (b) $C_{p,m}/T$.](https://dx.doi.org/10.1021/acs.inorgchem.0c01469)

When the aforementioned enthalpy of reaction is combined with the enthalpies of formation of $\text{Cs}_2\text{MoO}_4$ (cr) and $\text{BaMoO}_4$ (cr), the standard enthalpy of formation of Cs₂Ba(MoO₄)₂(cr), finally derived as $\Delta H_m^{\circ}(\text{Cs}_2\text{Ba(MoO}_4\text{)}_2, \text{cr}, 298.15$ K), $-3066.6 \pm 3.1$ kJ mol⁻¹. The selected value for the enthalpy of formation of Cs₂MoO₄(cr) is the average of the data reported by O’Hare and Hoekstra 37 and revised by Cordfunke and Konings 38 (−1514.5 ± 1.0 kJ mol⁻¹), the data...
Benigni et al. (high temperature limit of the material).

Generally, the number of required terms increases with the temperature. The low-temperature heat capacity data collected in the temperature range 2.1–294.3 K are shown in Figure 5a and given in Table S1 in the Supporting Information. The heat capacity and standard entropy at 298.15 K of BaCs2(MoO4)2 were obtained by fitting the experimental data to the other. The fitting equations from the experimental data are shown with solid lines in Figure 5. A slight scatter in the experimental data is seen around 270–300 K related to a vitreous transition of the thermal grease around 300 K, which is unfortunately not reproducible from one experiment to the other. The fitted heat capacity function increases smoothly in this temperature region and follows a reasonable trend.

A harmonic-lattice model was used in the low-temperature region to represent the phonon contribution, as given by eq 6. Generally, the number of required terms increases with the high temperature limit of the fit:

$$C_{\text{latt}} = \sum B_{n} T^{n} \quad n = 3, 5, 7, 9, ... \tag{6}$$

The fitting coefficients are given in Table 7. The electronic contribution of the conduction electrons at the Fermi surface are expressed with the linear term $\gamma T$. It was found to be equal to zero in this case, as expected for such an insulating material.

In the high-temperature region, the contribution from lattice vibrations prevails, which is modeled herein using a combination of Debye and Einstein functions, as expressed in eq 7.

$$C_{\text{ph,m}} = n_{D} D(\theta_{D}) + n_{E1} E(\theta_{E1}) + n_{E2} E(\theta_{E2}) + n_{E3} E(\theta_{E3}) \tag{7}$$

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 8 and 9. $\theta_{D}$, $\theta_{E1}$, $\theta_{E2}$ and $\theta_{E3}$ 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 come close to the number of atoms in the formula unit:

$$D(\theta_{D}) = 9R \left( \frac{T}{\theta_{D}} \right)^{3} \int_{0}^{\theta_{D}/T} \frac{e^{x} x^{3}}{[e^{x} - 1]^{2}} \, dx \tag{8}$$

$$E(\theta_{E}) = 3Rx^{2} \frac{e^{x}}{[e^{x} - 1]} \, x = \frac{\theta_{E}}{T} \tag{9}$$

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

This method has been used in the literature for various inorganic materials: the iron phosphates Fe(PO3)$_{3}$, Fe$_{2}$P$_{2}$O$_{7}$, FePO$_{4}$, Fe$_{3}$(P$_{2}$O$_{7}$)$_{2}$, Fe$_{3}$PO$_{4}$ and Fe$_{3}$(P$_{2}$O$_{7}$)$_{3}$, zirconolite CaZrTi$_{2}$O$_{7}$, calcium titanate CaTiO$_{3}$, dicesium molybdate Cs$_{2}$Mo$_{2}$O$_{7}$, the mixed cesium sodium molybdate Cs$_{3}$Na$_{3}$(MoO$_{4}$)$_{3}$, sodium uranate Na$_{4}$UO$_{5}$ and sodium neptunate Na$_{4}$NpO$_{5}$, and potassium uranate K$_{2}$UO$_{4}$ and potassium neptunate K$_{2}$NpO$_{4}$. Three Einstein functions were used in combination with a Debye function. The fitted parameters are given in Table 7. The deviation of the fitted data from the experimental results is below 0.4% above ~10 K (see Figure 6). The sum $n_{D} + n_{E1} + n_{E2} + n_{E3}$ is equal to 14.2 and is hence a reasonable trend.

![Figure 6. Deviation of the fitting equations from the experimental data.](https://dx.doi.org/10.1021/acs.inorgchem.0c01469)

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Table 7. Fitting Parameters of the Heat Capacity of Cs$_{3}$Ba(MoO$_{4}$)$_{2}$ within the Temperature Intervals $T = 2.1$–16.9 K and $T = 14.4$–294.3 K

<table>
<thead>
<tr>
<th>Harmonic Lattice Model</th>
<th>Debye and Einstein Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp range (K)</td>
<td>2.1–16.9</td>
</tr>
<tr>
<td>$\gamma$ (mJ mol$^{-1}$ K$^{-2}$)</td>
<td>0</td>
</tr>
<tr>
<td>$B_{1}$ (mJ mol$^{-1}$ K$^{-4}$)</td>
<td>1.48</td>
</tr>
<tr>
<td>$B_{2}$ (mJ mol$^{-1}$ K$^{-6}$)</td>
<td>$2.91387 \times 10^{-5}$</td>
</tr>
<tr>
<td>$B_{3}$ (mJ mol$^{-1}$ K$^{-8}$)</td>
<td>$-6.40657 \times 10^{-6}$</td>
</tr>
<tr>
<td>$n_{0}$ (mol)</td>
<td>4.3802</td>
</tr>
<tr>
<td>$n_{D}$ (mol)</td>
<td>166.36</td>
</tr>
<tr>
<td>$n_{E1}$ (mol)</td>
<td>3.0006</td>
</tr>
<tr>
<td>$n_{E2}$ (mol)</td>
<td>243.08</td>
</tr>
<tr>
<td>$n_{E3}$ (mol)</td>
<td>3.7308</td>
</tr>
<tr>
<td>$\theta_{D}$ (K)</td>
<td>456.77</td>
</tr>
<tr>
<td>$\theta_{E1}$ (K)</td>
<td>3.0908</td>
</tr>
<tr>
<td>$\theta_{E2}$ (K)</td>
<td>873.98</td>
</tr>
<tr>
<td>$\theta_{E3}$ (K)</td>
<td>14.2</td>
</tr>
</tbody>
</table>

Reported by Smith et al. (–1514.69 ± 1.54 kJ mol$^{-1}$) and by Benigni et al. (–1513.56 ± 1.11 kJ mol$^{-1}$). The enthalpy of formation of BaMoO$_{4}$ was taken from the critical review of Gamsjäger and Morishita, on the basis of the data measured by O’Hare and Shukla et al.
Cs$_2$Ba(MoO$_4$)$_2$ is not stable at room temperature and rather reported herein, would mean that the quaternary phase lower standard entropy at 298.15 K in comparison to that ruled out on the basis of the collected XRD and ND data. The presence of a secondary (impurity) phase can also be considered but discarded on the basis of the occurrence of a structural disorder in the material by, for instance, mutual substitution of the Cs and Ba cations (anti-site mixing) that would contribute to an excess entropic contribution was considered but discarded on the basis of the collected neutron diffraction data as outlined in section 3.1.

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The derived Gibbs energy of formation of Cs$_2$Ba(MoO$_4$)$_2$ from the constituting ternary oxides Cs$_2$MoO$_4$(cr) and BaMoO$_4$(cr) is slightly positive at 298.15 K: $\Delta G_{\text{m,ter.ox.}}^\circ$(298.15 K) = 0.8 ± 4.9 kJ mol$^{-1}$, suggesting that Cs$_2$Ba(MoO$_4$)$_2$ is not stable with respect to Cs$_2$MoO$_4$(cr) and BaMoO$_4$(cr) at room temperature.

Interestingly, a similar result was obtained for Cs$_2$Na(MoO$_4$)$_2$ formed by a stoichiometric reaction between Cs$_2$MoO$_4$ and Na$_2$MoO$_4$ as reported by Smith et al. The Gibbs energy of formation from the constituting ternary oxides was found to be slightly positive at 298.15 K: i.e., 2.3 ± 4.4 kJ mol$^{-1}$.

### 4. CONCLUSIONS

With the aim of improving the assessment of the source term in severe accident codes, the solubility of cesium in BaMoO$_4$ was investigated by our research group, which suggested a very limited solubility but revealed instead the formation of the quaternary phase Cs$_2$Ba(MoO$_4$)$_2$ by the reaction between BaMoO$_4$ and Cs$_2$MoO$_4$ at high temperature. This novel double molybdate adopts a palmierite type of structure, as evidenced from post-XRD characterizations. The compound’s thermal expansion was evaluated between room temperature and 673 K, which yielded a volumetric thermal expansion coefficient equal to $\alpha_V \approx 43.0 \times 10^{-6}$ K$^{-1}$. Its standard enthalpy of formation was assessed using solution calorimetry as $\Delta H_{\text{m,ter.ox.}}^\circ$(298.15 K) = −3066.6 ± 3.1 kJ mol$^{-1}$, and its standard entropy was derived from low-temperature thermal relaxation calorimetry as $S_{\text{m,ter.ox.}}^\circ$(298.15 K) = 381.2 ± 11.8 J K$^{-1}$ mol$^{-1}$.

These findings could be of interest for the field of photoluminescent materials and have implications for the safety assessment of irradiated fuel behavior. The existence of this phase is particularly relevant for the fuel chemistry in fast neutron reactors, where higher burnup and oxygen potentials are reached. Because Cs$_2$MoO$_4$ is largely dominant in the JOG between the fuel and cladding and the presence of barium has also been identified in this layer, one could imagine a possible formation of Cs$_2$Ba(MoO$_4$)$_2$ in localized areas. To test this
hypothesis, a complete thermodynamic assessment of the Cs–Ba–Mo–O system using the CALPHAD methodology would be required, allowing the performance of thermodynamic equilibrium calculations under various oxygen potential and temperature conditions. The thermodynamic data collected herein, i.e. standard enthalpy of formation and standard entropy, can serve as inputs for the development of such a thermodynamic model of the complex multi-element JOG system.

**REFERENCES**


**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01469.

Experimental heat capacity data of Cs₂Ba(MO₄)₃ and standard thermodynamic functions from 0 to 300 K (PDF).

**Accession Codes**

CCDC 2004804 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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(73) Guillaumont, R.; Fanghanel, T.; Fuger, J.; Grenthe, I.; Neck, V.; Palmer, D. A.; Rand, M. H. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium; Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium & technetium; OECD Nuclear Energy Agency: Data Bank, 2003.


(77) The measured dissolution enthalpy was corrected to the molality of the certified enthalpy value \( m = 0.111 \text{ mol kg}^{-1} \) using the relationship \( 
\Delta H^\circ(500\text{H}_2\text{O}, 298.15 \text{ K}) = \Delta H(n\text{H}_2\text{O}, 298.15 \text{ K}) - (\Phi(n\text{H}_2\text{O}) - \Phi(500\text{H}_2\text{O})) \), where \( \Delta H(n\text{H}_2\text{O}, 298.15 \text{ K}) \) is the measured dissolution enthalpy corrected to the reference temperature and the term \( (\Phi(n\text{H}_2\text{O}) - \Phi(500\text{H}_2\text{O})) \), derived from Parker’s tabulation in ref 33 and listed in ref 32, corrects the molality to the certified value. The uncertainty on the correction was estimated not to exceed 5 J mol\(^{-1}\). 32

(78) Average value of refs 36, 37, and 55.