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Structural and Thermodynamic Investigation of the Perovskite Ba$_2$NaMoO$_{5.5}$

Guilhem Kauric, Enrica Epifano, Philippe M. Martin, Lambert van Eijck, Daniel Bouëxière, Nicolas Clavier, Christine Guéneau,* and Anna L. Smith*

1. INTRODUCTION

Sodium-cooled fast reactors (SFRs) are, in terms of performance and safety, among the most advanced designs for the next generation (Generation IV) of nuclear reactors. SFRs use metallic sodium as a coolant and heat-transfer medium, allowing high power density with low coolant volume fraction. The Mo−O and Mo−Ba distances have been compared to the neutron diffraction data with good agreement. The coefficient of thermal expansion measured in the temperature range of 303−923 K, using high temperature X-ray diffraction (HT-XRD) ($\alpha_V = 55.8 \times 10^{-6}$ K$^{-1}$), has been determined to be $\sim 2$ times higher than that of the barium molybdates BaMoO$_3$ and BaMoO$_4$. Moreover, no phase transition nor melting have been observed, neither by HT-XRD nor Raman spectroscopy nor differential scanning calorimetry, up to 1473 K. Furthermore, the standard enthalpy of formation ($\Delta H^\circ_\text{m}$) for Ba$_2$NaMoO$_{5.5}$(cr) has been determined to be $-2524.75 \pm 4.15$ kJ mol$^{-1}$ at 298.15 K, using solution calorimetry. Finally, the margin for safe operation of sodium-cooled fast reactors (SFRs) has been assessed by calculating the threshold oxygen potential needed, in liquid sodium, to form the quaternary compound, following an interaction between irradiated mixed oxide (U,Pu)O$_2$ fuel and sodium coolant.

During operation and irradiation, fission products such as molybdenum and barium are generated with a high fission yield in the ceramic fuel matrix. Past studies have shown that these elements form oxide precipitates, more specifically BaMoO$_3$ dissolved in the gray phase (Ba$_x$Sr$_{1-x}$)$_2$−(Zr$_{0.1}$U$_{0.9}$)$_4$(RE)$_{10}$O$_{19}$ (RE = rare earths) and/or BaMoO$_3$ depending on temperature, oxygen potential conditions, and burnup. In particular, the recent PHEBUS FPT2 test within the PHEBUS FP Program (which is a study of the degradation of the core and the fission products release in case of an accident) has shown a clear association of Mo and Ba in oxide precipitates at grain boundaries in fuel test sections. In case of a severe accident (an accident where the reactor fuel is damaged with possible melting of the reactor core), the fission product compounds within the fuel pellet would interact with sodium on a large temperature scale (from 900 K to >3000 K). To assess the safety of the reactor, the possible reaction products between sodium and barium−molybdenum fission product phases must be investigated. Structural and thermodynamic investigation of the Ba−Mo−Na−O system is a first step, and it can serve as input for the development of comprehensive thermodynamic models of the multicomponent system Ba−Cs−Na−Mo−Sr−Zr−U−Pu−RE−O, using the CALPHAD methodology.

The quaternary compound Ba$_2$NaMoO$_{5.5}$ was reported by Sabatier et al., who synthesized this compound while attempting to form a layered perovskite. This compound has also been studied for its high oxide-ion conductivity at relatively low temperatures ($\sim 850$ K) by Thangadurai et al., which is a property particularly interesting to develop commercially viable solid oxide fuel cells (SOFCs). Among the...
studied oxygen-deficient double perovskites $\text{Ba}_2\text{BB'O}_{5.5}$ (B = Li, Na; B' = Mo, W, Te), $\text{Ba}_2\text{NaMoO}_5\text{O}_3$ has shown the highest conductivity. However, thermophysical properties and chemical behavior of the aforementioned compound at high temperatures have not been determined to this date. These data are key for the prediction of the behavior of the irradiated fuel and the phase formation in case of an accident in the SFR, as Ba-Mo-O phases are found in the irradiated fuel and are very likely to react with the sodium coolant.

This work reports neutron diffraction and X-ray absorption spectroscopy (XAS) measurements on $\text{Ba}_2\text{NaMoO}_5\text{O}_{5.5}$ at room temperature, which have allowed to assess and refine the atomic oxygen positions and vacancies in the structure precisely. Moreover, the thermal expansion and thermal stability of the compounds were studied using high-temperature X-ray diffraction (HT-XRD), high-temperature Raman spectroscopy, and differential scanning calorimetry (DSC). The standard enthalpy of formation of $\text{Ba}_2\text{NaMoO}_5\text{O}_{5.5}$ at 298.15 K was measured via solution calorimetry. Using these newly determined data, the likelihood of formation of this quaternary compound in the irradiated fuel by reaction between the sodium coolant and $\{\text{BaMoO}_4 + \text{BaO}\}$ or $\{\text{BaMoO}_3 + \text{BaO}\}$ fission product phases was finally assessed.

2. EXPERIMENTAL SECTION

2.1. Synthesis Method. $\text{Ba}_2\text{NaMoO}_5\text{O}_{5.5}$ was synthesized by reaction between barium molybdate ($\text{BaMoO}_4$) and stoichiometric amounts of barium carbonate (BaCO$_3$) (Fluka, >99%) and anhydrous sodium carbonate Na$_2$CO$_3$ (Sigma–Aldrich, >99.5%). The stoichiometric mixture was heated under oxygen flow at 973 K for 60 h with intermediate regrinding steps. Samples were analyzed by X-ray and neutron diffraction at room temperature.

The starting reagent BaMoO$_4$ was synthesized by grinding barium carbonate BaCO$_3$ (Fluka, >99%) and molybdenum trioxide MoO$_3$ (Alfa Aesar, >99.5%) together in stoichiometric ratio and heating under dry oxygen at 1073 K for 45 h with intermediate regrinding steps. Samples were analyzed by X-ray and neutron diffraction at room temperature (see Figure S1 in the Supporting Information).

$\text{Na}_2\text{Mo}_2\text{O}_7$ was synthesized for solution calorimetry purposes by heating a stoichiometric mixture of anhydrous Na$_2$CO$_3$ (Sigma–Aldrich, >99.5%) and Na$_2$MoO$_4$ (Sigma–Aldrich, 99.5%) under dry oxygen at 773 K for 60 h with intermedialy regrinding. The sample then was checked by XRD and DSC measurements (see Figures S2 and S3 in the Supporting Information).

In every analysis, no secondary phase was observed. Therefore, the purity of every compound is expected to be better than 99.5%.

2.2. Neutron Diffraction. Neutron data were collected at the Hoge Onderwijs Reactor at TU Delft at the PEARL beamline. The sample was encapsulated under an argon atmosphere in a cylindrical vanadium can (50 mm high, 6 mm inner diameter) closed with a Viton O-ring. The data were collected at room temperature, at a fixed wavelength $\lambda = 1.667$ Å and $\lambda = 1.333$ Å for 12 h over a range of 11.9° $\leq$ 2$\theta$ $\leq$ 158°. The Rietveld method implemented in the Fullprof2k suite was used for the structural analysis.

2.3. Powder X-ray Diffraction. X-ray diffraction (XRD) data at room temperature were collected using a PANalytical X’Pert PRO X-ray diffractometer mounted in the Bragg–Brentano configuration with a Cu anode ($\text{Cu}\ K_\alpha$, $\lambda = 1.541$ Å, $\text{Cu}\ K_\beta$, $\lambda = 1.544$ Å) (0.4 mm × 12 mm line focus, 45 kV, 40 mA) and a real-time multi strip (RTMS) detector (X’Celerator). Diffraction patterns were obtained by step scanning in step sizes of 0.008° (20) in the angle range of 10° $\leq$ 2$\theta$ $\leq$ 120° with an integration time of 7.18 h. The Rietveld method implemented in the Fullprof2k suite was used for the structural analysis.

2.4. High-Temperature X-ray Diffraction (HT-XRD). The thermal expansion of $\text{Ba}_2\text{NaMoO}_5\text{O}_{5.5}$ was investigated by HT-XRD using a Bruker Model D8 X-ray diffractometer mounted with a curved Ge monochromator (111), a copper X-ray tube (40 kV, 40 mA), a Linx Eye position-sensitive detector, and equipped with an Anton Paar HTK 2000 chamber. Measurements were conducted in a 600 mbar helium atmosphere from room temperature up to 1223 K, with 100 K heating steps. The temperature, measured with a thermocouple, was previously calibrated using the thermal expansion data of MgO. The uncertainty on the temperature is estimated to be 20 K at 1223 K.

2.5. X-ray Absorption Spectroscopy (XAS). XAS data were collected at the BM26A-DUBBLE beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). For the XAS measurements, ~20 mg of powdered samples were mixed with boron nitride (BN), pressed into pellets and encapsulated in Kapton foils. The aforementioned operations were performed inside an argon-filled glovebox, where oxygen and water levels were kept below 1 ppm. The storage ring operating conditions were 6.0 GeV and 170–200 mA. A double crystal monochromator mounted with a Si(111) crystal coupled to collimating and focusing Pt coated mirrors was used. Rejection of higher harmonics was achieved by three Si mirrors at an angle of 2 mrad, relative to the incident beam.

XANES and EXAFS spectra were collected at room temperature, in transmission mode at the Mo K-edge. A step size of 1 eV was used in the edge region. The energy of the edge absorption threshold position ($E_0$) was taken at the inflection point of the spectrum by using the first node of the second derivative. The position of the prepeak in the edge was selected from the first node of the first derivative. Several acquisitions were performed on the same sample and averaged to improve the signal-to-noise ratio. Before averaging the scans, each spectrum was aligned using the XANES spectrum of a metallic molybdenum reference foil measured before and after the sample under investigation. The ATHENA software was used to normalize the spectra and extract the EXAFS signal from the raw data.

The EXAFS data were collected in this work, up to 15 Å$^{-1}$, and were Fourier-transformed using the Hanning window over the k-range of 3.5–13.5 Å$^{-1}$ ($dk = 1$). Curve fitting was performed based on the standard EXAFS equation using the ARTEMIS software in $k$, $k^2$, and $k$-space. Phases and amplitudes for the interatomic scattering paths were calculated with the ab initio code FEFF8.40.20 The shift in the threshold energy ($\Delta E_0$) was varied as a global parameter. The amplitude factor $S_0^2$ was fixed for all paths to 0.9. The coordination numbers, Debye–Waller factors, and interatomic distances parameters, i.e., $N$, $\sigma$ and $R$, respectively, were allowed to vary for each shell.

2.6. High-Temperature Raman Spectroscopy. High-temperature Raman spectra were recorded using a Horiba Jobin-Yvon Aramis spectrometer equipped with a Linkam T5-1500 heating device. The $\text{Ba}_2\text{NaMoO}_5\text{O}_{5.5}$ sample was placed in a platinum crucible and inserted in the furnace. A rate of 10 K min$^{-1}$ was applied upon heating, and 5 min of stabilization time was maintained at each temperature plateau before acquisition of the spectra. The 632.8 nm line of a He–Ne laser was used as the excitation wavelength and focused by means of an Olympus BX41 (magnification factor of 50×), thus delivering ~10 mW at the sample surface. Slits and a confocal hole were set to result in a resolution of 1 cm$^{-1}$. For each spectrum, an acquisition time of 4 s was considered with an average of four scans. Before analysis, the apparatus was calibrated with a silicon wafer, using the first-order Si line at 520.7 cm$^{-1}$. Band component analysis of the different spectra was performed with the Jandel Peakfit software, using pseudo-Voigt functions with the minimum number of components. Correlation coefficients of >0.997 were systematically obtained.

2.7. Differential Scanning Calorimetry. Three-dimensional (3D)-heat-flow DSC measurements were performed from 303 K up to 953 K for $\text{Ba}_2\text{MoO}_4$ and up to 1473 K for $\text{Ba}_2\text{NaMoO}_5\text{O}_{5.5}$ using a Setaram Multi HTC module of the 96 Line calorimeter. The sample (80.7 mg for $\text{Ba}_2\text{MoO}_4$ and 80.3 mg for $\text{Ba}_2\text{NaMoO}_5\text{O}_{5.5}$) was placed in an alumina liner and encapsulated for the calorimetric measurements inside a stainless steel crucible that was closed with a screwed bolt to avoid vaporization at high temperatures. The measurement was done as follows: four successive heating cycles with a heating rate of 5 K min$^{-1}$, and cooling rates of 5, 8, 10, and 12 K min$^{-1}$. The temperature was monitored by a series of interconnected S-types.
thermocouples, and corrected on the heating ramp using a temperature calibration equation obtained from the measurement of standard materials (In, Pb, Sn, Zn, Al, Ag, Au) of well-known melting temperatures. The transition temperatures were derived on the heating ramp as the onset temperatures, using tangential analysis of the recorded heat flow.

2.8. Solution Calorimetry. The enthalpies of dissolution of Ba2NaMoO5.5, BaO, and Na2Mo2O7 in 2 M nitric acid solution were measured using a TA Instruments Precision Solution calorimeter (semidiabetic or isoperibolic calorimeter) and a TAM IV thermostat. The calorimetric unit consists of a reaction vessel and stirrer holding a glass ampule. The experiments were performed in a thin-walled 100 mL Pyrex-glass reaction vessel equipped with a thermostor 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 under study (BaO, Na2Mo2O7, Ba2NaMoO5.5) were placed inside a 1 mL glass ampule, which was sealed with bee wax. The latter operation was performed in the dry atmosphere of an argon-filled glovebox, because of the sensitivity of the samples to air and moisture. The solid samples were dissolved into a solution of 2 M HNO3 by breaking the bottom of the glass ampule on the sapphire breaking tip mounted at the bottom of the reaction vessel. The heat produced when breaking the ampule is exothermic, with a value below 10 mJ, and can thus be neglected (measured values are more than 1 J greater than 10 mJ). 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 to determine the equivalent energy 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(aq) into 1000 H2O (molality m = 0.05551 mol kg−1), i.e., ΔH°m(1000H2O, 298.15 K) = (17.467 ± 0.011) kJ mol−1 corresponds to ΔH°m(500H2O, 298.15 K) = (17.517 ± 0.011) kJ mol−1 after correction to m = 0.111 mol kg−1. The correction mentioned here was performed as recommended by the NBS.22 The measured dissolution enthalpy was corrected to the moality of the certified enthalpy value m = 0.111 mol kg−1, using the relationship ΔH°(500H2O, 298.15 K) = ΔH°(mH2O, 298.15 K) − (ΦL(mH2O) − ΦL(500H2O)). ΔH°(mH2O, 298.15 K) is the measured dissolution enthalpy corrected to the reference temperature, and the term (ΦL(mH2O) − ΦL(500H2O)), derived from Parker’s tabulation23 and listed by NBS,24 corrects the molality to the certified value. The uncertainty on the correction was estimated not to exceed 5 J mol−1.22,24 The measured value corresponds to an enthalpy at infinite dilution of ∆H°m(∞H2O, 298.15 K) = (17.174 ± 0.011) kJ mol−1, in good agreement with the NBS data,22,24 i.e., ∆H°m(∞H2O, 298.15 K) = (17.241 ± 0.018) kJ mol−1, and that in ref 25, i.e., ∆H°m(∞H2O, 298.15 K) = (17.22 ± 0.01) kJ mol−1.

3. RESULTS AND DISCUSSION

3.1. Refinement of the Ba2NaMoO5.5 Structure Using X-ray and Neutron Diffraction. Ba2NaMoO5.5 crystallizes at room temperature with a cubic perovskite structure in space group Fm3m (No. 225).13 The collected X-ray and neutron diffraction patterns are reported in Figures 1 and 2. The refined cell parameter obtained from the Rietveld refinement of the XRD data, a = 8.3156(4) Å, is consistent with the value reported by Thangarudai et al.14 (a = 8.319(3) Å). The neutron diffraction data (a = 8.305(1) Å at λ = 1.667 Å and a = 8.303(1) Å at λ = 1.33 Å) are consistent with the XRD results, as seen in Table 1. The atomic positions obtained after the Rietveld refinement of the neutron diffraction data are reported in Table 2 (data at λ = 1.667 Å) and Table S1 in the Supporting Information (data at λ = 1.33 Å). The results obtained from the two neutron diffraction measurements are similar. The measurement at λ = 1.33 Å gives extra information on peaks at high angles (Figure S4 in the Supporting Information). However, the resolution of the peaks is decreasing.26 Ba2NaMoO5.5 shows a perovskite-type structure with infinite chains of alternating corner-sharing MoO6 and NaO6 regular octahedra, along the a-, b-, and c-axes, as shown in Figure 3. These regular octahedra have distances of 2.220(2) Å for Na–O bonds and 1.933(2) Å for Mo–O bonds. Moreover, the presence of oxygen vacancies is assessed by the refinement of the occupancy factor on the 24e site of the oxygen. The refined occupancy, i.e., 0.91(1), yields a chemical composition corresponding to S.5. S. Ba atoms are located in the center of a cube formed by the alternating NaO6/MoO6 octahedra, as illustrated in Figure 3, in 12 coordination, with Ba–O distances of 2.940(1) Å and Mo–Ba and Na–Ba distances of 3.569(1) Å. The thermal displacement factors B0 for the Na atom in both refinements of
Table 1. Profile Parameters of Ba$_2$NaMoO$_{5.5}$ Obtained with the Different Diffraction Methods$^a$

| parameter                      | XRD | neutron |
|--------------------------------|-----|---------|
| chemical formula               | Ba$_2$NaMoO$_{5.5}$ | Ba$_2$NaMoO$_{4.4}$ |
| formula weight (g mol$^{-1}$)  | 481.6 | 481.6 |
| temperature (K)                | $(293 \pm 3)$ | $(293 \pm 3)$ |
| wavelength, $\lambda$ (Å)     | 1.541/1.544 | 1.667 | 1.33 |
| crystal system                 | cubic | cubic |
| space group                    | $Pm\bar{3}m$ (No. 225) | $Pm\bar{3}m$ (No. 225) |
| $a$ (Å)                        | 8.3156(4) | 8.305(1) | 8.303(1) |
| cell volume, $V$ (Å$^3$)       | 575.01(8) | 572.9(3) | 572.3(2) |
| $Z$                            | 4    | 4      |
| $d$-space range (Å)            | 0.89–8.84 | 0.78–8.35 | 0.78–8.35 |
| $\chi^2$                      | 6.59 | 3.85 | 2.74 |
| $R_p$                          | 18.4 | 10.1 | 9.77 |
| $R_{wp}$                       | 13.3 | 5.14 | 5.9 |

“Definition of $R$-factors hereafter: $\chi^2 = \sum w_o(y_o - y_a)^2/(N - P)$, where $N$ is the number of observations and $P$ the number of parameters used in the refinement, $w_o$ the weights of the observations, $y_o$ the calculated counts, and $y_a$ the observed counts at the $k$-step. $R_p$ is the profile factor: $R_p = \sum(y_o - y_a)/\sum y_o$. $R_{wp}$ is the weighted profile factor: $R_{wp} = \sum w_o(y_o - y_a)^2/\sum w_o y_o^2$.

Table 2. Refined Atomic Positions, Isotropic Thermal Displacement Factor ($B_o$) and Occupancy in the Ba$_2$NaMoO$_{5.5}$ Compound (Noted as Occ. in the Table) Derived from the Neutron Refinement at $\lambda = 1.667$ Å$^a$

| atom | oxidation state | Wyckoff | $x$  | $y$  | $z$  | $B_o$(Å$^2$) | Occ. |
|------|-----------------|---------|------|------|------|-------------|------|
| Ba   | $+2$            | 8c      | 0.25 | 0.25 | 0.25 | 1.34(3)     | 1    |
| Na   | $+1$            | 4a      | 0    | 0    | 0    | 0.80(8)     | 1    |
| Mo   | $+6$            | 4b      | 0.5  | 0.5  | 0.5  | 1.34(3)     | 1    |
| O    | $-2$            | 24e     | 0.2673(2) | 0   | 0   | 1.98(2) | 0.91(1) |

“Background obtained by linear interpolation between operator-selected points in the pattern with refinable heights.

3.2. X-ray Absorption Spectroscopy. X-ray Absorption Near-Edge Structure Analysis. The XANES spectrum of Ba$_2$NaMoO$_{5.5}$ collected at the Mo K-edge, are reported in Figure 4, together with that of Mo$^0$ metal, Mo$^{VI}$, and Mo$^{V}$ reference materials.

The energy position of the inflection points are listed in Table 3. The $E_0$ value for Ba$_2$NaMoO$_{5.5}$ is similar to that of MoO$_3$, confirming the oxidation state $+VI$ of molybdenum in this material. This result was expected, given that the synthesis reaction consisted in the stoichiometric reaction between hexavalent BaMoO$_{4.0}$, BaCO$_3$, and Na$_2$CO$_3$ starting materials under oxygen flow. The Ba$_2$NaMoO$_{5.5}$ starting material was itself prepared from hexavalent MoO$_3$ and BaCO$_3$ materials. A shift of $E_0$ to higher energies is also observed with increasing oxidation state, as expected. In addition, the spectrum of Ba$_2$NaMoO$_{5.5}$ shows a prepeak at ~2000 eV, which is observed as a shoulder, because of the core hole broadening. This prepeak comes from to the hybridization of O(2p) with Mo(4d) and Mo(5p) and thus corresponds to 1s(Mo) → 5p + 4d(Mo) transition.

EXAFS Analysis. The Mo K-edge fitted and experimental EXAFS data are reported hereafter (see Figure 5). The path corresponding to the six Na atoms surrounding the Mo were not taken into account for the fitting, because their intensity is too weak.

Table 3. Energy Position of the Inflection Points for the Reference Materials and Ba$_2$NaMoO$_{5.5}$

| Compound                  | $E_0^n$(eV) |
|---------------------------|-------------|
| Ba$_2$NaMoO$_{5.5}$       | 20015.2     |
| Mo$^{VI}$                 | 20015.7     |
| Mo$^{V}$                  | 20012.0     |
| Mo$^0$                    | 20000.0     |

“The standard uncertainties $\sigma$ on the energy position of the inflection points are $\sigma(E_0) = 1$ eV.

Figure 3. Sketch of the structure of Ba$_2$NaMoO$_{5.5}$. The octahedrons around the Mo and Na atoms are represented in purple and yellow, respectively. Ba atoms are represented in green, and O atoms are shown in red.

Figure 4. XANES spectra of the Ba$_2$NaMoO$_{5.5}$ compound obtained at the Mo K-edge and comparison with spectra of Mo$^0$, Mo$^{VI}$, and Mo$^{V}$ used as a reference.
The number of O (5.6(2)) and Ba (8) atoms in the first and second coordination shells around Mo determined with EXAFS are consistent with the theoretical formula and the neutron diffraction data (5.46(6)). The Mo–Ba distances obtained by EXAFS and neutron diffraction measurements, reported in Table 4, are in good agreement within uncertainties. As for the O atoms, the Mo–O bond lengths derived by EXAFS are slightly lower than those obtained by neutron diffraction for the first sphere. Based on the amplitude of the Mo–O–Mo–O path in the EXAFS signal calculated by FEFF (35%, compared to 37% for the Mo–Ba path), a multisattering path (designed hereafter with an asterisk (*)), involving two O atoms of the first coordination shell, was added for the fitting to reproduce the experimental data satisfactorily. However, to minimize the refined parameter of the oxygen coordination shell does not introduce a non-linear term), neither in the O shell nor the Ba shell to reproduce the EXAFS measurements. To check the consistency with the theoretical formula and the neutron value. Hence, this is consistent with the hypothesis of a tilting of the octahedra in the structure of Ba2NaMoO5.5.

Finally, possible anharmonicity effects were considered. However, during the fitting of the EXAFS data, it was not necessary to introduce any anharmonicity parameter (cumulant term), neither in the O shell nor the Ba shell to reproduce the experimental data. Thus, the oxygen vacancy observed in the oxygen coordination shell does not introduce a non-Gaussian distribution of the Mo–O distances.

3.3. High-Temperature Behavior. The assessment of the thermal expansion behavior of Ba2NaMoO5.5 is key for the safety analysis of an accidental scenario in a SFR to determine the effect on the swelling of the fuel due to the formation of a quaternary compound. The evolution of the cell parameters, as a function of temperature, was determined by Rietveld refinement of the HT-XRD data (see Figure S2 in the Supporting Information). No change was observed between the XRD patterns obtained up to the maximum temperature of T = 1223 K. Only a shift to lower 2θ values was observed following the expansion of the unit cell. The relative thermal expansion of the unit lattice parameters is reported in Figure 6 between room temperature and T = 1223 K. The mean relative linear thermal expansion coefficient, \( \frac{d_\ell}{l_0} \), where \( l = (abc)^{1/3} \) and \( l_0 = (a_0b_0c_0)^{1/3} \) is the reference length at 303 K, can be expressed as a polynomial function of the temperature T(K) (see eq 1):

\[
\frac{d_\ell}{l_0} = -3.69 \times 10^{-3} + 1.0047 \times 10^{-5}T + 6.74121 \times 10^{-9}T^2
\]

The plots of relative expansion, \( \frac{l - l_0}{l_0} = f(T) \), for the compounds Ba2NaMoO5.5, BaMoO4, and BaMoO3 are shown hereafter (see Figure 6):

The mean relative linear thermal expansion of the quaternary compound is ~2 times higher than that of the two barium molybdates BaMoO4 and BaMoO3 which are thermodynamically stable under certain operating conditions. The average volumetric thermal expansion of BaMoO4 and BaMoO3 are equal to \( \alpha_v = 26.6 \times 10^{-6} \) K\(^{-1}\) and 28.4 \( \times 10^{-6} \) K\(^{-1}\) respectively.
\[\text{K}^{-1}\] in the temperature ranges of 298–1273 K and 298–873 K, respectively.\(^{31,32}\) In comparison to these values, the average volumetric thermal expansion of Ba\(_2\)NaMoO\(_5.5\) is \(\sim 2\) times higher: \(55.8 \times 10^{-6} \text{K}^{-1}\) in the temperature range of 303–1223 K. This distinct property of the quaternary compound can be related to the local structure properties. In particular, when comparing the structure of Ba\(_2\)NaMoO\(_5.5\) with that of BaMoO\(_3\), which is also a cubic perovskite, one can note that the local structural arrangement is similar, but also that the introduction of Na atoms into the three-dimensional (3D) network is responsible for the observed high-temperature behavior. In BaMoO\(_3\), Mo atoms are octahedrally coordinated and form a 3D structure of corner-sharing MoO\(_6\) octahedra. The Ba atoms are found between the chains in 12-fold cuboctahedral coordination. The continuous 3D lattice of strong Mo–O bonds ensures the structure’s rigidity and constrains the expansion of the weaker Ba–O bonds. The quaternary Ba\(_2\)NaMoO\(_5.5\) shows the same 3D arrangement, except that half of the MoO\(_6\) octahedra are replaced by NaO\(_6\) octahedra. The Mo\(_{VI}\)–O bonds, alternating with much weaker NaI–O bonds, result in a much stronger thermal expansion. The Ba–O bond length in Ba\(_2\)NaMoO\(_5.5\) is also higher than in BaMoO\(_3\), as observed by neutron diffraction (2.940(1) Å in this work vs 2.857 Å, as reported by Nassif et al.\(^{33}\)), which indicates weaker Ba–O bonds in the quaternary compound. This property, together with the less-restraining octahedral network, explains a significantly higher swelling. Therefore, an increased swelling of the irradiated fuel is to be expected, in the case of the formation of this quaternary phase, following the interaction with the sodium coolant.

**3.4. High-Temperature Raman Spectroscopy.** Five sets of bands associated with the internal modes of vibration of the MoO\(_6\) units are observed in the Ba\(_2\)NaMoO\(_5.5\) Raman spectrum at room temperature (Figure 7), which are consistent with the data reported for MeMoO\(_4\) (Me = Ba, Ca, Pb, Sr\(^{34–36}\)) and for Cs\(_2\)Na(MoO\(_4\))\(_2\).\(^{37}\)

Liegeois-Duyckaerts and Tarte\(^{34}\) studied A\(_2\)B\(_{3}\)Al\(_{VI}\)O\(_8\) (A = Ba, Pb, Sr; B = Ba, Sr, Ca, Cd, Zn, Cu, Co, Ni, Mg) ordered perovskites with Raman spectroscopy. In the different spectra obtained, they attributed the highest-frequency band with a strong intensity \((\nu_1 \approx 891 \text{ cm}^{-1})\) to the totally symmetric stretching of the MoO\(_6\) octahedron in the internal modes approximation. The vibrations between 780 cm\(^{-1}\) and 850 cm\(^{-1}\) (\(\nu_3\)) are associated with the antisymmetric stretching of the MoO\(_6\) octahedron. In this range of frequencies, a wide feature is also observed due to the defects of the octahedron, which partly break the symmetry.\(^{38}\) This is consistent with the neutron diffraction and EXAFS results (oxygen vacancies and tilting of the angles of the Mo–O–Mo–O bond). The peaks obtained at \(\sim 300\) and 380 cm\(^{-1}\) are associated with the antisymmetric (\(\nu_4\)) and the symmetric (\(\nu_2\)) bending modes. The external modes at low frequencies (50 to 110 cm\(^{-1}\)) are associated with the translation of the Na\(^+\) cation.\(^{34,39,40}\)

No noticeable change in the spectrum is seen between room temperature and 993 K, as observed in Figure 8, except for a slight widening of the peaks and shift in the wavenumber due to anharmonic effects appearing with increasing temperature.\(^{41}\) Moreover, the bands position shift with temperature follows a linear function, as reported in Table 5, as well as Figure S5 in the Supporting Information. These results are consistent with the HT-XRD data, which also do not reveal any phase transition nor melting up to 1223 K. Moreover, a DSC measurement performed in this work up to 1473 K also did not show any phase transition nor melting of the compound. Hence, the quaternary Ba\(_2\)NaMoO\(_5.5\) compound is determined to be stable up to at least 1473 K.

**Figure 6.** Relative thermal expansion of Ba\(_2\)NaMoO\(_5.5\) compared to BaMoO\(_3\)\(^{31}\) and BaMoO\(_3\).\(^{32}\)

**Figure 7.** Raman spectrum of Ba\(_2\)NaMoO\(_5.5\) obtained at 298 K.

**Figure 8.** Variation of the Raman spectrum of Ba\(_2\)NaMoO\(_5.5\) versus temperature.
-reported which is relatively close to the present data measured in a Ba2NaMoO5.5, BaO, and Na2Mo2O7 in nitric acid were, in all cases, instantaneous and complete. The calorimetric results of the three compounds dissolution are reported in Table 6.

To ensure that sol. 1 and sol 3 had the same final composition, a specific amount of sample was dissolved into solution. The detail of the calorimetric measurements is reported in Table 7. The enthalpy of dissolution of BaO in a 1 M HCl solution was measured in the work of Fitzgibbon et al.42 They reported \( \Delta H_m^o \) (298.15 K) = \( -(273.17 \pm 0.96) \) kJ mol\(^{-1}\), which is relatively close to the present data measured in a solution of 2 M HNO\(_3\), i.e., \( -(284.19 \pm 0.17) \) kJ mol\(^{-1}\). To the best of our knowledge, there have not been measurements of the dissolution of Na2MoO2; in acidic solution reported in the literature.

3.5 Solution calorimetry measurement of the standard enthalpy of formation. The standard enthalpy of formation of Ba2NaMoO5.5 at 298.15 K was obtained in 2 M HNO3 solution (99.5%) using the thermodynamic cycle detailed in Table 6. The dissolutions of Ba2NaMoO5.5, BaO, and Na2Mo2O7 in nitric acid were, in all cases, instantaneous and complete. The calorimetric results of the three compounds dissolution are reported in Table 6.

Considering that the sodium is quasi-pure, with very little oxygen dissolved (typically 3 wppm under normal operation conditions), the partial Gibbs energy of sodium \( \Delta G_{Na}^o \) was considered to be zero. Therefore, the equilibrium oxygen potential for the different reactions can be expressed as

\[
\Delta G_{O_2}^o(T) = RT \ln \left( \frac{P_{O_2}}{P^0} \right) 
\]

\[
= 4[\Delta G_{m}^o(Ba_2NaMoO_{5.5}, s, T) - \Delta G_{m}^o(BaMoO_4, s, T) - \Delta G_{m}^o(BaO, s, T)] 
\]

3.5. Solution Calorimetry Measurement of the Standard Enthalpy of Formation. The standard enthalpy of formation of Ba2NaMoO5.5 at 298.15 K was obtained in 2 M HNO3 solution (VWR Chemicals, 99.5%) using the thermodynamic cycle detailed in Table 6. The dissolutions of Ba2NaMoO5.5, BaO, and Na2Mo2O7 in nitric acid were, in all cases, instantaneous and complete. The calorimetric results of the three compounds dissolution are reported in Table 6.

\[
\Delta H_{m}^o = \Delta H_{m}^o + \Delta H_{m}^o - \Delta H_{m}^o = -306.24 \pm 0.65 \text{ kJ mol}^{-1}\]

\[
\frac{1}{2} \text{Na}_2\text{Mo}_2\text{O}_7(cr) + 2\text{BaO}(cr) = \text{Ba}_2\text{NaMoO}_{5.5}(cr)\]

The enthalpy of dissolution of BaO in a 1 M HCl solution has been measured in the work of Fitzgibbon et al. They reported \( \Delta H_m^o \) (298.15 K) = \( -(273.17 \pm 0.96) \) kJ mol\(^{-1}\), which is relatively close to the present data measured in a solution of 2 M HNO3, i.e., \( -(284.19 \pm 0.17) \) kJ mol\(^{-1}\). To the best of our knowledge, there have not been measurements of the dissolution of Na2MoO2; in acidic solution reported in the literature.

Combining with the standard enthalpy of formation of BaO(cr), and Na2Mo2O7(cr), the standard enthalpy of formation of Ba2NaMoO5.5 is finally derived as \( \Delta H_m^o = -(2524.75 \pm 4.15) \) kJ mol\(^{-1}\).

\[
\Delta G_{O_2}^o(T) = RT \ln \left( \frac{P_{O_2}}{P^0} \right) 
\]

\[
= \frac{4}{3}[\Delta G_{m}^o(Ba_2NaMoO_{5.5}, s, T) - \Delta G_{m}^o(MoO_2, s, T) - 2\Delta G_{m}^o(BaO, s, T)] 
\]

3.6. Margin to the Safe Operation of SFRs. In a severe accident scenario, the BaMoO3 dissolved in the gray phase, BaMoO4, and BaO phases formed during irradiation could interact with the liquid sodium at different stages of a severe accident and form the Ba2NaMoO5.5 compound. Several equilibrium reactions could be envisaged:

\[
\text{BaMoO}_3 + \text{BaO} + \text{Na}(l) + \frac{3}{4} \text{O}_2 \rightarrow \text{Ba}_2\text{NaMoO}_{5.5} \quad (1a) 
\]

\[
2\text{BaO} + \text{Na}(l) + \text{MoO}_3 + \frac{1}{4} \text{O}_2 \rightarrow \text{Ba}_2\text{NaMoO}_{5.5} \quad (2) 
\]

\[
2\text{BaO} + \text{Na}(l) + \text{MoO}_3 + \frac{3}{4} \text{O}_2 \rightarrow \text{Ba}_2\text{NaMoO}_{5.5} \quad (3) 
\]

\[
2\text{BaO} + \text{Na}(l) + \text{MoO}_3 + \frac{7}{4} \text{O}_2 \rightarrow \text{Ba}_2\text{NaMoO}_{5.5} \quad (4) 
\]

\[
2\text{BaO} + \text{Na}(l) + \text{MoO}_3 + \frac{11}{4} \text{O}_2 \rightarrow \text{Ba}_2\text{NaMoO}_{5.5} \quad (4) 
\]

Table 6. Reaction Cycle

| cycle | reaction | \( \Delta H_m^o \) (298.15 K) \( \text{kJ mol}^{-1}\) | uncertainty \( \text{kJ mol}^{-1}\) | reference |
|-------|----------|----------------------------------|-----------------|----------|
| (1)   | \( \text{Ba}_2\text{NaMoO}_{5.5}(s) + x\text{HNO}_3 = \text{sol. 1} \) | \( -276.68 \) | 0.55 | this work |
| (2a)  | \( x\text{BaO(s) + xHNO}_3 = \text{sol. 2} \) | \( -568.38 \) | 0.34 | this work |
| (2b)  | \( \frac{1}{3}\text{Na}_2\text{Mo}_2\text{O}_7(s) + \text{sol. 2 = sol. 3} \) | \( -14.55 \) | 0.09 | this work |
| (3)   | \( \text{Ba}(s) + \frac{1}{3}\text{O}_2(g) = \text{BaO(s)} \) | \( -548.00 \) | 2.00 | 42 |
| (4)   | \( 2\text{Na}(s) + 2\text{Mo}(s) + \frac{7}{4}\text{O}_2(g) = \text{Na}_2\text{MoO}_3(s) \) | \( -2245.02 \) | 1.81 | 43 |
| (5)   | \( 2\text{Ba}(s) + \text{Na}(s) + \text{Mo}(s) + \frac{11}{4}\text{O}_2(g) = \text{Ba}_2\text{NaMoO}_{5.5}(s) \) | \( -2524.75 \) | 4.15 | this work |

\( \Delta H_m^o \) and \( \Delta G_{O_2}^o \) were calculated at the pressure of \( p = 0.105 \pm 0.005 \text{ MPa} \), and in the temperature interval of \( T = 298.15 \pm 0.30 \text{ K} \). The uncertainties correspond to the standard ones.
When entering the reactor core, and an average of 823 K reported by Noden with the Gibbs energy of liquid sodium. Combining the oxygen solubility equation in sodium reported in eqs 1, 2, 3, 4, and 5), the threshold oxygen potential can increase, and therefore the oxygen potential can be derived for each reaction was subsequently combined. The expected temperature of the sodium coolant is ~680 K when entering the reactor core, and 823 K as an average above the core, and will increase during an accident. Therefore, the possible formation of Ba$_2$NaMoO$_{5.5}$ was studied in this work up to the maximum temperature to which it is known to be stable (1473 K).

Using the thermodynamic functions listed in Tables S3 and S4 in the Supporting Information for the different compounds reported in eqs 1, 2, 3, 4, and 5), the threshold oxygen potential of formation of Ba$_2$NaMoO$_{5.5}$ was derived for the different reactions. They are listed in Table 8. The standard entropy at 298.15 K of the quaternary phase, and its heat capacity at high temperature were still unknown and were estimated in this work with a simple additive rule (entropy) and the Neumann–Kopp rule (heat capacity) applied to Ba$_2$NaMoO$_{5.5}$, BaMoO$_4$, BaMoO$_3$, BaO, MoO$_3$, and MoO$_2$, respectively. T is the temperature and R the universal gas constant.

The expected temperature of the sodium coolant is ~680 K when entering the reactor core, and 823 K as an average above the core, and will increase during an accident. Therefore, the possible formation of Ba$_2$NaMoO$_{5.5}$ was studied in this work up to the maximum temperature to which it is known to be stable (1473 K).

Using the thermodynamic functions listed in Tables S3 and S4 in the Supporting Information for the different compounds reported in eqs 1, 2, 3, 4, and 5), the threshold oxygen potential of formation of Ba$_2$NaMoO$_{5.5}$ was derived for the different reactions. They are listed in Table 8. The standard entropy at 298.15 K of the quaternary phase, and its heat capacity at high temperature were still unknown and were estimated in this work with a simple additive rule (entropy) and the Neumann–Kopp rule (heat capacity) applied to Ba$_2$NaMoO$_{5.5}$, BaMoO$_4$, and MoO$_3$. The threshold derived for each reaction was subsequently compared to the concentration levels of oxygen dissolved in liquid sodium. Combining the oxygen solubility equation in sodium reported by Noden with the Gibbs energy of formation of Na$_2$O, the oxygen potential limit in sodium is given by

\[
\Delta G^\circ_{\text{eq}}(T/K) = -735691.3 + (33.232 + 38.287 \log C_0) T \text{ J mol}^{-1}
\]

where $C_0$ is the dissolved concentration in liquid sodium.

Figure 9 shows the oxygen potential thresholds of formation of Ba$_2$NaMoO$_{5.5}$, considering all of the reactions (reactions 1–5). Under normal operation, the oxygen level in sodium is expected to be ~3 wppm.44 Therefore, at the beginning of the accident, all of the reactions would be possible, except for reaction 5 with metallic molybdenum. However, during an accident, the oxygen potential can increase, and therefore the reaction with metallic molybdenum (reaction 5) could be expected. Note that the oxygen potential threshold for the other four mechanisms is lower than that for the formation of the trisodium uranate (Na$_3$UO$_4$), which is the phase predicted to form in case of interaction between sodium and hyperstoichiometric uranium dioxide.

The most favorable reaction is that with BaO and MoO$_3$, which form at high burnup. Nevertheless, the barium molybdate compounds BaMoO$_4$ and BaMoO$_3$ could also

| No. | mass of the sample, $m$ (mg) | temperature change, $\Delta T$ (mK) | energy equivalent of the calorimeter, $C_P$ (J K$^{-1}$) | $Q_r$ (kJ) | molar enthalpy of reaction, $\Delta H^r_m$ (298.15 K) (kJ mol$^{-1}$) |
|-----|----------------------------|------------------------------------|-----------------------------------------------|----------|--------------------------------------------------|
| 1   | 16.0                       | 409.511                            | 3.257                                          | -1.334   | 29.17                                            |
| 2   | 15.9                       | 411.617                            | 3.157                                          | -1.299   | 28.40                                            |
| 3   | 16.0                       | 411.108                            | 3.226                                          | -1.326   | 28.99                                            |
| 4   | 16.0                       | 409.800                            | 3.263                                          | -1.337   | 29.24                                            |
| 5   | 15.9                       | 410.749                            | 3.189                                          | -1.31    | 28.82                                            |

$^a$Solution calorimetry measurements were performed at a pressure of $p = 0.105 \pm 0.005$ MPa, and in the temperature interval of $T = 298.15 \pm 0.30$ K. (For pressure and temperature, the reported uncertainty is the standard uncertainty.) $^b$The uncertainty on $u$ on the weights are $u(m) = 0.1$ mg. $^c$Temperature change associated with the dissolution. The reported uncertainty on $\Delta T$ is $u(\Delta T) = 0.2$. $^d$The reported uncertainty on $C_P$ is $u(C_P) = 0.002$. $^e$The reported uncertainty on $\Delta H^r_m$ (298.15 K) are $u(\Delta H^r_m(298.15 \text{ K})) = 0.4$.

\[
\Delta G^\circ_{\text{eq}}(T) = RT \ln \left( \frac{P_O}{P^0} \right)
\]

\[
\Delta G^\circ_{\text{eq}}(T) = A + BT
\]

\[
\Delta G^\circ_{\text{eq}}(T) = -735691.3 + (33.232 + 38.287 \log C_0) T \text{ J mol}^{-1}
\]
react both with BaO and liquid sodium to form Ba$_2$NaMoO$_{5.5}$. Therefore, from a thermodynamic point of view, the quaternary compound Ba$_2$NaMoO$_{5.5}$ could be formed under accidental conditions.

4. CONCLUSIONS

A detailed study of the crystal structure of the quaternary perovskite phase Ba$_2$NaMoO$_{5.5}$ is reported in this work by combining neutron diffraction, Raman spectroscopy, and EXAFS data. The hexavalent molybdenum valence state has also been confirmed from XANES spectroscopy measurements at the Mo K-edge. HT-XRD measurements performed in the temperature range of 303–1223 K have allowed us to derive the volumetric thermal expansion coefficient as $\alpha_{\text{vol}} = 55.8 \times 10^{-6}$ K$^{-1}$, which is ~2 times higher than that of the ternary barium molybdate compounds BaMoO$_3$ and BaMoO$_4$ formed in the irradiated fuel under certain conditions. The high thermal expansion was explained in relation with the local structural arrangement. No phase transition was observed, neither in the HT-XRD, Raman spectroscopy, nor DSC measurements, showing that this quaternary perovskite phase is stable up to at least 1473 K. Moreover, the enthalpy of formation was derived from solution calorimetry measurements as $\Delta H_{f}^{\circ}$(Ba$_2$NaMoO$_{5.5}$, cr, 298.15 K) = $-(2524.75 \pm 4.15)$ kJ mol$^{-1}$. The oxygen potential thresholds for the formation of the quaternary compound were finally derived considering different reaction mechanisms between liquid sodium and fission products phases in irradiated U$_{1-x}$PuO$_2$ fuel. It was found that, in cases where barium oxide would be present together with MoO$_2$, MoO$_3$, BaMoO$_3$, or BaMoO$_4$, the contact with liquid sodium would lead to the formation of Ba$_2$NaMoO$_{5.5}$; hence, the thermodynamic and thermophysical properties of this phase are important for the SFR safety analysis. However, BaMoO$_3$ is not found as a pure compound in the irradiated fuel but in solution in the gray phase (Ba,Cs,Sr)(Zr,U,Pu,Mo,RE)O$_3$ (RE = rare earths). Therefore, it would be highly interesting and relevant to extend this study to the entire phases formed in the "gray phase", with the end goal to develop a full thermodynamic assessment of the Na-Ba-Cs-Na-Mo-Sr-U-Pu-RE-O system using the CALPHAD method. The present results will be used as input for the assessment of the Ba-Mo-Na-O system, as part of a wider research program in our group dedicated to the development of a Na-U-Pu-O-FPs database (where FPs = fission products).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00210.

This XRD and neutron diffraction crystallographic files in CIF format of Ba$_2$NaMoO$_{5.5}$; XRD patterns of the BaMoO$_4$ and Na$_2$MoO$_3$; DSC heat flow curve of the Na$_2$MoO$_3$; neutron diffraction pattern at $\lambda = 1.33$ Å and atomic positions after refinement of Ba$_2$NaMoO$_{5.5}$ lattice parameters evolution of Ba$_2$NaMoO$_{5.5}$ as a function of the temperature; evolution of the Raman band position of Ba$_2$NaMoO$_{5.5}$ as a function of the temperature; thermodynamic data used in the thermodynamic equilibrium calculations. (PDF)

AUTHOR INFORMATION

Corresponding Authors

Anna L. Smith — Faculty of Applied Sciences, Radiation Science & Technology Department, Delft University of Technology, 2629 Delft, The Netherlands; orcid.org/0000-0002-0355-5859; Email: a.l.smith@tudelft.nl

Christine Guéneau — DEN-Service de la Corrosion et du Comportement des Matériaux dans leur Environnement (SCCMC), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France; Email: christine.gueneau@cea.fr

Authors

Guilhem Kauric — DEN-Service de la Corrosion et du Comportement des Matériaux dans leur Environnement (SCCMC), CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

Enrica Epifano — Faculty of Applied Sciences, Radiation Science & Technology Department, Delft University of Technology, 2629 Delft, The Netherlands

Philippe M. Martin — CEADEN, DMRC, Univ. Montpellier, Marcoule, France

Lambert van Eijck — Faculty of Applied Sciences, Radiation Science & Technology Department, Delft University of Technology, 2629 Delft, The Netherlands

Daniel Bouxsière — European Commission, Joint Research Center, D-76125 Karlsruhe, Germany

Nicolas Clavier — CEA, CNRS, ENSCM, ICMS, Univ Montpellier, Bagnols-sur-Ceze, France

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00210

Notes

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ADDITIONAL NOTE

Four icl path details: Mo(c) → O(1) (180°) → Mo(c) 0° → O(2) 180° → Mo(c)).

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