Investigation of the Cs₂(Mo,Te)O₄ Solid Solution and Implications on the Joint Oxyde-Gaine System in Fast Neutron Reactors

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ABSTRACT: The formation of a thin layer, the so-called Joint Oxyde-Gaine (JOG), between the (U,Pu)O₂ fuel pellets and the cladding has been observed in fast neutron reactors, due to the accumulation of volatile fission products. Cs₂MoO₄ is known to be one of the major components of the JOG, but other elements are also present, in particular tellurium and palladium. In this work, an investigation of the structural and thermodynamic properties of Cs₂TeO₄ and Cs₂MoO₄−xTeₓO₄ solid solution is reported. The existence of a complete solubility between Cs₂MoO₄ and Cs₂TeO₄ is demonstrated, combining X-ray diffraction (XRD), neutron diffraction (ND), and X-ray absorption spectroscopy (XAS) results. High-temperature XRD measurements were moreover performed on Cs₂TeO₄, which revealed the existence of a α−β phase transition around 712 K. Thermal expansion coefficients were also obtained from these data. Finally, phase equilibria points in the Cs₂MoO₄−Cs₂TeO₄ pseudobinary phase diagram were collected using differential scanning calorimetry and used to develop a thermodynamic model for this system using a regular solution formalism.

1. INTRODUCTION

The Generation IV International Forum is currently investigating innovative nuclear reactor designs which should lead to improved safety, sustainability, and efficiency. Among the considered designs, fast neutron reactors (FNRs), such as the sodium-cooled and lead-cooled reactors, are very promising as they would allow achieving higher thermal efficiencies than currently used Light-Water Reactors (LWRs), by operating at higher temperatures. Mixed uranium–plutonium oxide (or MOX) pellets, enclosed inside a stainless steel cladding, are currently the preferred choice for the fuel in these reactors. The behavior of these materials in FNR conditions is currently under investigation. Various irradiation tests and post-irradiation examinations of MOX fuels in FNR prototypes have shown a specific behavior not previously observed in the light-water reactor fuels. In particular, the formation of an oxide fission products layer (up to a few hundred micrometers in thickness) between the fuel and the cladding, named “Joint Oxyde-Gaine” or JOG (the French term for the oxide-cladding joint), has been observed. This layer is formed by volatile and semi-volatile fission product elements, mainly cesium, molybdenum, iodine, tellurium, and palladium, that migrate from the center of the fuel pellet (T ≃ 2300 K) toward the edge, due to the strong radial thermal gradient (∼450 K mm⁻¹), and accumulate between the fuel and the cladding, where the temperature is lower (T ≃ 973 K). Knowing the thermal and mechanical properties of this layer is crucial for the safety assessment of the reactor. The irradiated fuel-cladding interaction needs to be well understood and controlled to prevent the release of radioactive elements from the fuel into the main circuit. The formation of the JOG layer could induce mechanical stresses on the cladding or drops in thermal conductivity, leading to creation of hot spots and local melting, and to an acceleration of the cladding corrosion. All these effects could cause a failure of the cladding integrity, and for this reason, the JOG needs to be investigated and accounted for in Fuel Performance Codes.

The JOG is a complex, multi-element system, including Cs−Mo−Te−Pd−Ba−I−U−O chemical elements stable in the forms of Cs₂MoO₄, CsI, Cs₂Te, etc. The main crystalline phase in the JOG is Cs₂MoO₄, according to post-irradiation examinations (PIE) and thermochemical calculations. The thermodynamic properties of this phase and the phase equilibria in the Cs−Mo−O system are relatively well known. However, a thorough knowledge of the JOG thermodynamic behavior requires also the investigation of the other subsystems, for which data are still missing, as for
instance the Cs–Te–O system, which presents several ternary compounds. Loopstra and Goubitz identified the crystallographic structures of three cesium tellurites, namely, Cs₂Te₂O₅, Cs₂Te₃O₆, and Cs₂Te₄O₉, as well as a mixed valence state compound of chemical formula Cs₂TeO₄. The crystallographic structure of the cesium tellurate, Cs₂TeO₄, was identified by Weller et al. The only available phase diagram data refer to a differential scanning calorimetry (DSC) study of the TeO₂−Cs₂TeO₃ pseudo-binary system, while the available thermodynamic data are limited to the enthalpies of formation of Cs₂TeO₄, Cs₂Te₂O₅, Cs₂Te₃O₆, and Cs₂Te₄O₉. Further studies are hence necessary in order to completely determine the Cs–Te–O phase equilibria and the possible effects on the JG system.

This work focuses on the Cs₂TeO₄ compound and the Cs₂(Mo,Te)O₄ solid solution. The Cs₂TeO₄ phase is of particular interest for the JG as it is iso-structural with Cs₂MoO₄. The existence of a complete Cs₂(Mo,Te)O₄ solid solution is shown herein. The structural properties of Cs₂TeO₄ and mixed compounds are investigated by combining X-ray diffraction (XRD), neutron diffraction (ND), and X-ray absorption spectroscopy (XAS) measurements. The polymorphism of Cs₂TeO₄ is investigated using high-temperature (HT) XRD, and the coefficients of thermal expansion are assessed from the measured data. Differential scanning calorimetry (DSC) is used to investigate phase equilibria in the Cs₂MoO₄−Cs₂TeO₄ system, in particular to determine phase transition temperatures and associated enthalpies. Finally, a thermodynamic model of the Cs₂MoO₄−Cs₂TeO₄ system is reported using a regular solution formalism, based on the collected experimental data.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation. Cs₂Moₓ₋ₓTe₄O₈ samples were synthesized by reaction between Cs₂MoO₄ and Cs₂TeO₄ powders. Stoichiometric mixtures with x = Te/(Te + Mo) = 5, 10, 20, 40, 50, 60, 80, and 90 at. % were placed in alumina boats and heated under oxygen flow at 873 K, for a total duration of ~50 h. One intermediate reglazing step has been performed, inside an argon-filled glovebox, to ensure a complete reaction between the two end-members. The Cs₂MoO₄ precursor was prepared starting from Cs₂CO₃ (Alpha Aesar, 99.999%) and MoO₃ (Alpha Aesar, 99.95%), according to the procedure described in ref 20. The obtained powder was white/light yellow. The Cs₂TeO₄ precursor was prepared by solid-state reaction between Cs₂CO₃ and TeO₂ (Alpha Aesar, 99.999%) at 873 K in oxygen flow (O₂ ≥ 99.5%, rest Ar and N₂, H₂O < 1500 ppm) for ~60 h. The powder exhibited a light gray color. Immediately after the synthesis, the samples were transferred in an argon-filled glovebox, with dry atmosphere, where the H₂O and O₂ contents were kept below 5 ppm. The handling of the samples was always done inside this glovebox, because of the hygroscopic nature of the synthesized materials.

2.2. X-Ray Powder Diffraction (XRD). Room-temperature X-ray diffraction measurements were carried out 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 powdered samples were placed in a sealed sample holder, with a kapton foil cover, to maintain the dry argon atmosphere during the XRD measurement. The data were collected by step scanning in the range 10° ≤ 2θ ≤ 120°, with a step size of 0.008° (2θ); one single scan was performed, for a total measuring time of about 8 h. Structural analysis was performed by the Rietveld method with the FullProf Suite. The displacement of the sample surface with respect to the goniometer was refined and compared to that of a gold powder standard, which was measured using the same sample holder. In all the cases, comparable displacements were obtained from the refinement.

2.3. High-temperature X-ray Powder Diffraction (HT-XRD). High-temperature XRD experiments were carried out from 298 to 1073 K in a Bragg–Brentano mode on a Panalytical X’Pert Pro diffractometer equipped with an Anton Parr furnace, using the Cu–Kα radiation (Ge (111) monochromator). Measurements were performed under a silica gel-dried air flow. Each pattern was recorded by scanning the 16–80° 2θ range, with a step size of 0.013°, and using a 1 h 40 min counting time. The data were treated by Rietveld analysis using the FullProf Suite in order to refine the lattice and structure parameters. Irregular peak shapes were observed and attention was paid to their origin. Lattice distortions were considered, but finally ruled out, and the irregular peak shapes were attributed to the small amount of powder, which only covered part of the holder’s surface. These imperfections were eventually corrected by introducing a secondary ”fictional” phase in the refinement, and a geometric intensity correction for incomplete illumination was applied. The two phases (in a 95:5 ratio according to the refinements) were given the same set of atomic coordinates but independent cell edges. As the thermal evolution was found to be similar for the two phases, the computation of the thermal expansion was made on the parameters of the main one.

Due to strong differences in electron densities between oxygen and the heavy Cs and Te cations, soft constraints were applied to the Te–O bond lengths. Likewise, a single B₀ (isotropic atomic displacement) value was used for all the oxygen atoms, whereas independent anisotropic factors were refined for the cations.

2.4. Neutron Diffraction (ND). Neutron diffraction (ND) data were recorded at the PEARL beamline at the Hoger Onderwijs Reactor at TU Delft. The sample was encapsulated in a cylindrical, vanadium can (50 mm high, 6 mm inner diameter) closed with a Viton O-ring. This preparation step was performed inside the glovebox, under dry argon atmosphere. The data were collected at room temperature, at a fixed wavelength (λ = 1.667 Å) over the range 11° < 2θ < 158°. The “instrumental background” (including the contribution from the sample can) was subtracted from the recorded data. Structural analysis was performed by the Rietveld method with the FullProf Suite.

2.5. X-ray Absorption Spectroscopy (XAS). X-ray absorption spectroscopy (XAS) measurements were performed at the BM26A-DUBBLE beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Samples for XAS measurements were prepared inside an argon-filled glovebox. Powdered samples were mixed with boron nitride, pressed in pellets of 5 mm diameter, and encapsulated in kapton foil. The mass of the investigated compounds, ranging from 15 to 50 mg, was optimized in order to correspond to 1–2 absorption lengths. The storage ring operating conditions at the ESRF were 6.0 GeV and 170–200 mA. A Si(111) crystal monochromator was used to select the energy, and calibration was performed using metallic molybdenum (Eₘ₋ₐₓ = 29200 eV) as standard materials for the Mo and Te (Eₘ₋ₐₓ = 31814 eV) K-edge, respectively.

The XAS data were collected at room temperature in transmission mode. XANES spectra were recorded at first, with a step size of 1 eV and a counting time of 3 s per step. This corresponds to an acquisition time of about 20 min per spectrum. For each compound/edge, at least four scans were collected and at least two different spots of the samples were probed. No modifications were observed among these scans. This indicates that changes of the chemical state due to the beam interaction are unlikely, unless these occurred very quickly, within the first few seconds/minutes of the measurement.

Subsequently, EXAFS spectra were collected at the Mo K-edge, with a counting time increasing with energy, from 3 (XANES part) up to 9 s per step. Between four and ten spectra were acquired for each sample, depending on the quality of the data. XANES (X-ray absorption near edge structure spectra) were normalized using the ATHENA software, adopting linear functions.
for pre-edge and post-edge fitting. The absorption edges were identified as the first zero-crossing of the second derivatives.

EXAFS (extended X-ray absorption fine structure) oscillations were also extracted with the ATHENA software24 and Fourier-transformed using a Hanning window (3.5–14 Å⁻¹, dk = 2 Å⁻¹). Interatomic scattering path phases and amplitudes were calculated with the FEFF 8.40 ab initio code.24 Fitting of the EXAFS data was performed simultaneously in k, k², and k⁴ using the ARTEMIS software.25 During the fit, the amplitude prefactor S₀ was initially set at 0.95, while the shift in the threshold energy ΔE₀, the interatomic distances, the Debye–Waller factors, and the coordination numbers were optimized. Once the fit reached a sufficient goodness-of-fit, the S₀ value was also fitted. The variations from the initial value were negligible. Similar ΔE₀ values were obtained for all the Mo K-edge spectra, between 0.5 and 0.8 eV.

2.6. Differential Scanning Calorimetry (DSC). The phase transition, congruent melting (for Cs₂MoO₄ and Cs₂TeO₄) and solidus temperatures of Cs₂Moₓ₋₁TeₐO₄ solid solutions were determined by 3D-heat flux DSC measurements using a Setaram Multi HTC module of the 96 Line calorimeter. The samples were heated inside an alumina crucible under oxygen flow. The temperature was monitored throughout the experiments by a series of interconnected S-type thermocouples. The temperature on the heating ramp (10 K min⁻¹) was calibrated and corrected for the effect of the heating rate by measuring the melting points of standard high purity metals (In, Sn, Pb, Al, Ag, Au) at 2–4–6–8–10–12 K min⁻¹. The calibration procedure was performed as recommended by Höne et al.25 and Gatta et al.26 The transition, congruent melting temperature of Cs₂MoO₄ (respectively, Cs₂TeO₄) and solidus temperatures of Cs₂Moₓ₋₁TeₐO₄ solid solutions were derived on the heating ramp as the onset temperature using tangential analysis of the recorded heat flow. The uncertainty on the measured temperatures is estimated to be ±5 K for the Cs₂MoO₄ and Cs₂TeO₄ end-members and ±10 K for the transitions of the solid solutions.

The enthalpies of transition between the low-temperature orthorhombic structure and the high-temperature hexagonal structure of Cs₂Moₓ₋₁TeₐO₄ solid solutions were moreover determined by placing a reference material of well-known fusion enthalpy (Al and Na₂MoO₄ in this work) in the reference crucible and measuring both the sample and reference materials in the same cycle, under argon flow when using the Al reference and under oxygen flow when using the Na₂MoO₄ reference. This configuration allows to calculate for each individual measurement cycle the detector sensitivity equal to

\[ s_{\text{ref}} = \frac{M_{\text{ref}}A_{\text{ref}}}{m_{\text{ref}}\Delta H_{\text{ref}}(T_{\text{ref}})} \]  

(1)

where \( s_{\text{ref}} \) is the detector sensitivity in \( \mu \text{V mW}^{-1} \), \( M_{\text{ref}} \) the molar mass in g mol⁻¹, \( m_{\text{ref}} \) the weight of the reference in mg, \( A_{\text{ref}} \) the peak area corresponding to the transition event in \( \mu \text{V s} \), and \( \Delta H_{\text{ref}}(T_{\text{ref}}) \) the enthalpy of transition of the reference material in J mol⁻¹.

The detector sensitivity is assumed to remain the same at the temperature of the transition event of the sample, which is a reasonable approximation for two events sufficiently close to each other.

3. RESULTS

3.1. Lattice Parameters Determination of the Cs₂Moₓ₋₁TeₐO₄ Solid Solution. Cs₂MoO₄ and Cs₂TeO₄ show, at room temperature, the same orthorhombic structure, with space group \( Pmnn \), n.62 (noted “a” or “p” in this work). The XRD patterns acquired (at room temperature) on the (Cs₂MoO₄-Cs₂TeO₄) mixtures with \( x = \text{Te}/(\text{Te} + \text{Mo}) = (0.05, 0.10, 0.20, 0.40, 0.60, 0.80, \text{and} 0.90) \) exhibited one single phase, indicating the existence of a complete solid solution for the entire composition range. The lattice parameters were obtained by Rietveld refinements of the XRD patterns, and the results are shown in Figure 1, as a function of the \( \text{Te}/(\text{Te} + \text{Mo}) \) ratio.

For each lattice parameter (\( a, b, c \)), a linear variation is observed, indicating the validity of Vegard’s law for this solid solution. The general lattice parameter \( y \) of the Cs₂Moₓ₋₁TeₐO₄ solid solution, at room temperature, can be expressed as a function of the tellurium content \( x \) as

\[ y = y_0 + mx \]  

(2)

The \( y_0 \) and \( m \) values were obtained by fitting the XRD lattice parameters, and the values are reported in Table 1.

![Graph showing variation of lattice parameters with Te/(Te+Mo) content](image)

**Table 1. Fitting Parameters Assuming Vegard’s Law: \( y = y_0 + mx \)**

| \( x \) | \( y_0 \) (Å) | \( m \) (Å) | \( R^2 \) |
|-----|----------|----------|-------|
| 0.00 | 11.590 ± 0.002 | 0.127 ± 0.003 | 0.996 |
| 0.10 | 6.552 ± 0.002 | 0.135 ± 0.004 | 0.995 |
| 0.20 | 8.500 ± 0.001 | 0.013 ± 0.001 | 0.960 |

Obtained \( m \) values are about ten times larger for the \( a \) and \( b \) axes than for the \( c \) axis, indicating that the substitution of Mo with Te causes an anisotropic expansion of the lattice. The deep examination of the \( \alpha \)-Cs₂MoO₄ crystal structure by Waller et al.20 revealed that the cell edges in the (001) basal plane are ruled by an array of short, strong bonds; on the contrary, the connections between these planes, along the \( c \) axis, depend on long, loose Cs–O bonds. This is consistent with what is observed here for the solid solution, i.e., the substitution of Mo⁶⁺ (ionic radius = 0.41 Å⁻¹) with Te⁶⁺ (ionic radius = 0.48 Å⁻¹) would cause the cell edges in the (001) basal plane to expand more than along the \( c \) axis.
radius = 0.43 Å\(^2\)) results in a marked increase of the parameters in the basal plane \((ab)\), whereas the length of the third edge \((c)\), which is less dependent on the \(\text{Mo}^{6+}/\text{Te}^{6+}−\text{O}\) bond lengths, undergoes a lesser increase.

3.2. Neutron Diffraction Measurements on \(\text{Cs}_2\text{TeO}_4\) and \(\text{Cs}_2\text{Te}_0.5\text{Mo}_0.5\text{O}_4\). Neutron diffraction data were collected on pure \(\text{Cs}_2\text{TeO}_4\) and on the \(\text{Cs}_2\text{Te}_0.5\text{Mo}_0.5\text{O}_4\) solid solution. As already shown by XRD, both these materials exhibit an orthorhombic structure at room temperature, with the space group \(\text{Pcmn}, \text{n}^\circ62\). The neutron diffraction pattern and the relative fit of \(\text{Cs}_2\text{TeO}_4\) is shown in Figure 2 (very similar to the green marks represent the Bragg reflections. Measurement at \(\lambda = 1.667\) Å. The background was taken as linear interpolation between the operator-selected points in the pattern with re

duction data were collected at \(10186\)° for \(\text{Cs}_2\text{TeO}_4\) and \(\text{Cs}_2\text{Mo}_0.5\text{Te}_0.5\text{O}_4\). The high-resolution neutron diffraction data are consistent with those previously obtained by XRD, even if slightly lower. This difference is not surprising since the lattice parameters obtained from neutron diffraction data are generally less accurate than those from XRD. Moreover, comparing the values to those previously obtained from neutron diffraction on \(\text{Cs}_2\text{Mo}_4\) \(a = 11.5623(8)\) Å, \(b = 6.5406(4)\) Å, \(c = 8.4906(5)\) Å\(^2\)), it can be noticed that the lattice parameters of the \(\text{Cs}_2\text{Te}_0.5\text{Mo}_0.5\text{O}_4\) solid solution are almost exactly equal to the average values of the two end-members. This confirms again the validity of Vegard’s law.

The atomic positions, as obtained from the neutron data refinement, are reported in Table 3. The \(\text{Cs}_2\text{Mo}_1−\text{Te}_4\text{O}_4\) structure, shown in Figure 3, consists of isolated and slightly distorted \(\text{Te}_4\text{O}_4\) (respectively, \(\text{Mo}_4\text{O}_4\)) tetrahedra linked by \(\text{Cs}^+\) cations in 9- and 10-fold coordination.

3.3. Valence State Determination by XANES. X-ray absorption near-edge structure (XANES) spectra were collected at the Mo K-edge on pure \(\text{Cs}_2\text{Mo}_4\) and \(\text{Cs}_2\text{Mo}_0.5\text{Te}_0.5\text{O}_4\) solid solutions with \(x = 0.05, 0.10, 0.50,\) and 0.80. The results are shown in Figure 4a and are compared to standard materials, namely, metallic \(\text{Mo}, \text{Mo}^{5+}\), and \(\text{Mo}^{6+}\). Similarities, XANES data were collected at the Te K-edge for \(\text{Cs}_2\text{Te}_4\) and the mixed compounds with \(x = 0.50\) and 0.80 (for the lower Te concentration, the absorption at the Te K-edge was too low); these spectra, shown in Figure 4b, are compared to those of \(\text{Te}^{5+}\) and \(\text{Cs}_2\text{Te}^{10+}\). We remark here that, to the best of our knowledge, this is the first time that XANES data are reported on \(\text{Cs}_2\text{Te}_4\text{O}_4\). The XR

Figure 2. Experimental (red dots) and calculated (black line) neutron diffraction pattern of \(\text{Cs}_2\text{TeO}_4\). The difference is indicated in blue and the green marks represent the Bragg reflections. Measurement at \(\lambda = 1.667\) Å. The background was taken as linear interpolation between the operator-selected points in the pattern with re

duction patterns for \(\text{Cs}_2\text{TeO}_4\) and \(\text{Cs}_2\text{Te}_0.5\text{Mo}_0.5\text{O}_4\) from the ND Data

results are obtained for \(\text{Cs}_2\text{Te}_0.5\text{Mo}_0.5\text{O}_4\) as shown in Figure S1). The refined lattice parameters are \(a = 11.698(2)\) Å, \(b = 6.675(1)\) Å, and \(c = 8.4906(1)\) Å, for \(\text{Cs}_2\text{TeO}_4\) and are \(a = 11.631(2)\) Å, \(b = 6.5406(4)\) Å, \(c = 8.3890(5)\) Å\(^2\)), it can be noticed that the lattice parameters of the \(\text{Cs}_2\text{Te}_0.5\text{Mo}_0.5\text{O}_4\) solid solution are almost exactly equal to the average values of the two end-members. This confirms again the validity of Vegard’s law.

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The absorption edges, defined as the inflection points of the absorption spectra (hence obtained as the zero of the second derivative), are summarized in Table 4.

In general, a clear shift of the absorption edge is observed with increasing oxidation state of the element. For the Mo K-edge, \(\text{Cs}_2\text{Mo}_4\) and the \(\text{Cs}_2\text{Mo}_0.5\text{Te}_0.5\text{O}_4\) solid solutions have absorption edges around 20015 eV, clearly higher than metallic \(\text{Mo} (20000 eV)\) and \(\text{Mo}^{5+} (20012 eV)\), and in line with the \(\text{Mo}^{6+}\) standard (20016 eV). Moreover, similarly to \(\text{Mo}^{6+}\) (but even more evident), all the \(\text{Cs}_2\text{Mo}_0.5−\text{Te}_4\text{O}_4\) samples present a marked pre-edge feature (for these spectra presenting a pre-edge, the \(E_0\) has been taken on the second, main edge). This is characteristic of short, highly covalent \(\text{Mo}−\text{O}\) bonds in tetrahedral geometry, which enhance 4d-5p mixing in Mo through their hybridization with \(\text{O}(2p)\).29−32 It can be confirmed that molybdenum is hexavalent and in tetrahedral \(\text{MoO}_4\) units in all the \(\text{Cs}_2\text{Mo}_0.5−\text{Te}_4\text{O}_4\) solid solutions. Indeed, the pre-edge intensity is even more marked in the solid solutions than in \(\text{MoO}_4\), suggesting a stronger covalency and shorter \(\text{Mo}−\text{O}\) bonds. In fact, the transition is dipole forbidden for a regular octahedra but appears in \(\text{MoO}_4\) as a shoulder due to the distortion of the \(\text{MoO}_4\) octahedra in that compound. Its intensity is related to the degree of octahedral distortion.

For the Te K-edge, there was no Te\(^{VI}\) standard available. However, because of the electroneutrality, tellurium is expected to be in the oxidation state +VI in the investigated materials. In support of this hypothesis, both \(\text{Cs}_2\text{Mo}_0.5−\text{Te}_4\text{O}_4\) and \(\text{Cs}_2\text{Mo}_0.5−\text{Te}_4\text{O}_4\) have an absorption energy equal (within the uncertainty limit) to that of pure \(\text{Cs}_2\text{Te}_4\text{O}_4 (31821 eV)\) and the values are more than 1 eV higher than those of \(\text{Te}^{5+}\) and
Table 3. Refined Atomic Positions in Cs$_2$TeO$_4$ and Cs$_2$Mo$_{0.5}$Te$_{0.5}$O$_4$\textsuperscript{a,b}

| atom   | ox. state | Wyckoff | x     | y     | z     | occ. | $R_{\text{eq}}$ (Å$^2$) |
|--------|-----------|----------|-------|-------|-------|------|-------------------------|
| Cs1    | +1        | 4c       | 0.4145(9) | 0.25 | 0.6714(8) | 1 | 3.3(2) |
| Cs2    | +1        | 4c       | -0.2849(7) | 0.25 | -0.0055(9) | 1 | 2.9(3) |
| Te     | +6        | 4c       | 0.4200(9) | 0.25 | 0.2213(7) | 1 | 2.3(2) |
| O1     | -2        | 4c       | 0.425(2) | 0.25 | 0.0109(7) | 1 | 5.7(3) |
| O2     | -2        | 4c       | 0.5639(8) | 0.25 | 0.302(1) | 1 | 3.7(3) |
| O3     | -2        | 8d       | 0.3475(7) | 0.0289(9) | 0.2921(9) | 1 | 4.7(2) |

\textsuperscript{a}Pcnn setting of the space group n.\textsuperscript{b} Anisotropic atomic displacement factors are reported in the Supporting Information.

Figure 3. Sketch of the Cs$_2$TeO$_4$ crystal structure. Cs atoms are represented in green, Te/Mo in blue, and oxygen atoms in red.

Cs$_2$Te$^{IV}$O$_4$. We believe that the present measurements can serve as reference standards for future studies on tellurium-containing materials.

3.4. Local Structure Studies by EXAFS. The experimental EXAFS data and the relative Fourier transform (FT) collected at the Mo K-edge on Cs$_2$MoO$_4$ and Cs$_2$Mo$_{0.5}$Te$_{0.5}$O$_4$ with $x = 0.05$, 0.10, 0.50, and 0.80, are shown in Figure 5 (open symbols). All the data show a very similar shape. The FT of the data exhibit a first, very intense peak at $R + \Delta R \cong 1.4$ Å, as well as a low intensity peak around 3.6 Å (see also Figure 6).

The crystallographic structure obtained from neutron diffraction (Figure 3) was used as the input to fit the EXAFS data. The Mo (or Te) atom is in the center of a tetrahedron. According to the neutron diffraction refinement, this tetrahedron is not regular and three slightly different Mo–O distances are present. For example, for pure Cs$_2$MoO$_4$, Mo–O$_1$ = 1.76 Å, Mo–O$_2$ = 1.80 Å, and Mo–O$_3$ = 1.77 Å, the latter with a multiplicity equal to 2. These three neighboring shells are very close and difficult to differentiate by EXAFS. Indeed, the distance resolution $\Delta R$ is equal to $\pi/2\Delta k$, where $\Delta k$ is the range of the data in the k-space. In our case, for the data collected at the Mo K-edge, $\Delta R = 0.11$ Å. Therefore, it is not possible to differentiate the three Mo–O distances and the EXAFS data were fitted using only one single oxygen coordination shell, formed of four atoms. Besides the four oxygen in tetrahedral coordination, the next Mo neighbor is a Cs atom, at a distance of 3.78 Å (for Cs$_2$MoO$_4$), followed by a neighbor shell composed of three Cs atoms at a distance $\sim$3.89 Å. Again, these two distances are hardly distinguishable by EXAFS, because of the weak amplitude of these contributions. This is particularly true for these further shells, since the contribution to EXAFS is rapidly dumped with increasing distance. For this reason, the four Cs atoms were included in a single shell for the fit. Finally, a multiple O–Mo–O diffusion path, within the MoO$_4$ tetrahedron and corresponding to an additional distance around 3.5 Å, was also included in the EXAFS model. For the latter, no supplementary fit parameters were introduced since the number of atoms, the distance, and the $\sigma^2$ factor were related to the values used in the Mo–O single scattering path. The inclusion of this multiple scattering path is essential because it creates destructive interference with the Mo–Cs path in the EXAFS spectrum. This interference is one of the reasons of the low intensity of the second peak (around 3.6 Å), together with the high values of the Mo–Cs distance and the Debye–Waller factor of this path (see Table S1 in the Supporting Information). More details on the interference between the paths are also provided in the Supporting Information. The contribution of the three paths to the EXAFS fit is shown in Figure 6 for Cs$_2$MoO$_4$ (similar results are obtained for the other compositions).

A generally good agreement between the fits and the experimental data was obtained for all the compositions, as shown in Figure 5 (experimental data shown with open symbols, fits shown with solid lines). The fitted coordination number and the $\sigma^2$ factors for the two neighboring shells, which are provided in the Supporting Information Table S1, are consistent with the adopted structural model. The obtained Mo–O and Mo–Cs bond distances, for each composition, are reported in Table 5 and are compared to the average distances obtained from neutron diffraction (for $x = 0.05$, 0.10, and 0.80, the distances were estimated by interpolation). The EXAFS Mo–O distance, equal to 1.78(Å), is shorter than the average
The interatomic distances obtained from ND and EXAFS are generally in good agreement, within the experimental uncertainties. However, while the Mo−Cs distances obtained by EXAFS increase with the Te content, in accordance with the neutron data, the EXAFS Mo−O distance is constant throughout all the compositions. According to the neutron diffraction data, a small but detectable increase of the M−O (M = Mo1−xTex) distance should also be observed, i.e., a difference of ~0.03 Å between Cs2MoO4 and Cs2Mo0.20Te0.80O4. However, while the neutron diffraction data provide averaged data for the shared site between Te and Mo, the EXAFS gives information specific to the local environment around Mo. The XRD and neutron diffraction data reveal an expansion of the unit cell with the Te addition (consistent with the increase of the Mo−Cs distance), but the

Mo−O bond length in MoO3, equal to 1.86(1) Å,33,34 confirming the previous hypothesis based on the pre-edge intensity of the XANES.

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Mo−O bond length in MoO3, equal to 1.86(1) Å,33,34 confirming the previous hypothesis based on the pre-edge intensity of the XANES.
To contrary is to be expected by analogy with the results on model reported by Weller et al., an isotype of Cs₂SO₄, the room-temperature orthorhombic structure between 713 and 723 K (Figure 7). As already peaks was observed on heating, contrary form noted for the experiment. Hence, only the XANES data are exploited in this work.

EXAFS data show that the localized, strongly covalent Mo−O bond is unaffected by the tellurium presence. The Mo−O distance is the same in all the solid solutions, despite the large range of compositions investigated. This means that the Te−O distance must be responsible for the variation in the average distances obtained by neutron diffraction in the shared Te/Mo tetrahedra. The Te K-edge (>31 keV) is at the limit of the energy range that can be probed at the BM26A beamline, with the configuration adopted for the experiment. Hence, only the Te XANES data are exploited in this work.

### 3.5. Thermal Expansion and Phase Transition in Cs₂TeO₄

With Cs₂TeO₄ being isostructural with Cs₂MoO₄ at room temperature, the existence of a phase transition from the Pcmn orthorhombic structure (α form noted o-Cs₂TeO₄) to a hexagonal phase (β form noted h-Cs₂TeO₄) at high temperature is to be expected by analogy on the Cs₂MoO₄. To confirm this hypothesis, high-temperature X-ray diffraction measurements were performed in this work on Cs₂TeO₄ from 298 to 1073 K (Figure 7) in dry air.

A sudden disappearance of some of the weak diffraction peaks was observed on heating, confirming a change in crystal structure between 713 and 723 K (Figure 7). As already discussed, below the transition point, the o-Cs₂TeO₄ structure corresponds to the room-temperature orthorhombic Pcmn model reported by Weller et al., an isotype of Cs₂SO₄, Cs₂CrO₄, and Cs₂MoO₄. Beyond 723 K, the structure becomes hexagonal (h-Cs₂TeO₄), following the usual tran-
consistent with the $P6_3/mmc$ supergroup owing to the location of the cations very close to the special positions at $z = 0, 1/4,$ and $3/4$, as well as the $[0 0 \pm 1]$ disorder of the TeO$_4$ tetrahedron. The same symmetry was observed in $h$-Cs$_2$MoO$_4$, but in the tellurate, the apical O$_2$ atom seems to split onto three sites around the axial position (see the Fourier map in the Supporting Information Figure S3) instead of six in the molybdate. Conceivably, the whole TeO$_4$ tetrahedron undergoes this double (upside-down and tilt) disorder; hence, the very high values of the atomic displacement parameter of the oxygen atoms.

The relative linear thermal expansion plots $\left(\frac{h - h_0}{h_0}\right) = f(T)$, where $h = (a, b, c, l)$, $h_0 = (a_0, b_0, c_0, l_0)$, and $l_0 = (a_0b_0c_0)^{1/3}$ are the reference lengths at room temperature (Figure 9a), are very similar to those reported for Cs$_2$MoO$_4$ showing anisotropic thermal expansion behavior. Here also the phase transition goes together with a pronounced break in the cell volume and the $c$-parameter (both $+1.3\%$), while the cell surface in the (001) plane evolves continuously. Indeed, the transition corresponds to the sudden alignment of the Cs$_2$ atoms along the 6-fold axis, but the phenomenon is preceded by a continuous shift, which accelerates between 573 and 623 K, as shown in Figure 9b, resulting in the increased slope of the $c$ linear expansion. As established previously for Cs$_2$MoO$_4$, both the high global expansion, high atomic displacement factors, and orientation disorder of the TeO$_4$ tetrahedron result from the very weak Cs–O bonds.

The relative linear thermal expansion follows a polynomial evolution as a function of temperature $T(K)$:

- in the orthorhombic domain:

$$\frac{dl}{l_0} = -(6.8 \pm 3.6) \times 10^{-3} + (1.2 \pm 1.0) \times 10^{-5}T + (3.7 \pm 1.5) \times 10^{-8}T^2$$ (3)

- in the hexagonal domain:

$$\frac{dl}{l_0} = -(1.011 \pm 0.001) \times 10^{-2} + (5.7 \pm 0.1) \times 10^{-5}T$$ (4)

It is worth noting that the relative linear thermal expansion of Cs$_2$TeO$_4$ is even higher than that of Cs$_2$MoO$_4$, up to 29\% at the maximum temperature reached (1073 K).

3.6. Transition Temperatures and Transition Enthalpy Determinations. The existence of a phase transition in Cs$_2$TeO$_4$, as evidenced from the X-ray diffraction experiments, was moreover confirmed by differential scanning calorimetry. A clear thermal event was detected in the heat flow curve at $T_{tr}(Cs_2TeO_4) = (712 \pm 5) K$, before the congruent melting event observed at $T_{fus}(Cs_2TeO_4) = (1187 \pm 5) K$ (Figure 10).

The measured solid solution compositions also showed a similar phase transition, with a transition temperature decreasing progressively when increasing the Te/(Te + Mo) content (see Table 8 and Figures 12 and 13). The transition enthalpies of the $\alpha$ to $\beta$ phase transition in Cs$_2$Mo$_{1-x}$Te$_x$O$_4$ solid solutions ($x = 0, 0.2, 0.5, 1$) (from the orthorhombic to the hexagonal structure) were furthermore determined in this work by measuring the solid solution compositions together with a reference material of well-known transition enthalpy. This configuration allows us to derive for each individual measurement cycle the detector sensitivity,
which is assumed to remain the same at the temperatures of
the transition events of the sample and reference. Typical
curves of the record heat flow signal are shown in Figures S4
and S5. Note that the opposite directions for the sample and
reference (endothermic) events are due to the different
positioning in the reference and sample crucibles, respectively.
Aluminum was chosen as the reference material, since it
shows a melting temperature close to the sample transition
event without overlapping, and it has a well-known melting
enthalpy equal to 10.711 kJ mol\(^{-1}\) at \(T_{\text{fus}} = 933.5 \text{ K}\).\(^{40}\) It
appeared, however, that a correction factor had to be applied
to the sensitivity factor to match the reported enthalpy of
transition of \(\text{Cs}_2\text{MoO}_4\) as recommended in the review of
Cordfunke and Konings,\(^ {41}\) i.e., \((4.6 \pm 0.1) \text{ kJ mol}^{-1}\).\(^ {41}\) The
necessity for this correction factor is believed to be related to
the very different thermal properties (heat capacity and
thermal conductivity) of the oxide and metallic materials.
The same correction factor was applied to the other
compositions \((x = 0.2, 0.5, 1)\). The reliability of the method
was moreover checked by measuring the transition enthalpy of
\(\text{Cs}_2\text{Mo0.5Te0.5O}_4\) against an oxide reference material, namely,
\(\text{Na}_2\text{MoO}_4\). The transition enthalpy was calculated against the
\(\alpha\) to \(\beta\) phase transition in \(\text{Na}_2\text{MoO}_4\) (from a cubic \(Fd\bar{3}m\) to an
orthorhombic structure \(^{42}\) Note: Bottelberghs and van Buren\(^ {42}\)
suggested \(Pbn2_1\) as the most probable space group, but a
complete structure determination is lacking),\(^{42}\) whose tran-
sition enthalpy is equal to \((22.61 \pm 0.5) \text{ kJ mol}^{-1}\) as reported
by Sugawara et al.\(^ {43}\) In this case, the sample and reference
materials should have comparable thermal properties, and no
correction factor was applied. The derived transition enthalpy
for \(\text{Cs}_2\text{Mo0.5Te0.5O}_4\) using the \(\text{Na}_2\text{MoO}_4\) reference was found
equal to \((2.79 \pm 0.30) \text{ kJ mol}^{-1}\), in very good agreement
within the uncertainty with the value derived with the Al
reference, i.e., \((2.94 \pm 0.05) \text{ kJ mol}^{-1}\), which gives us good

### Table 7. Transition Enthalpy Data Collected by DSC at Atmospheric Pressure\(^a\)

| \(m\) (sample) (mg) | \(m\) (ref) (mg) | \(T\) (°C) | \(\Delta H_m\) (kJ mol\(^{-1}\)) | \(\Delta S_m\) (J K\(^{-1}\) mol\(^{-1}\)) | \(\Delta C_p\) (J K\(^{-1}\) mol\(^{-1}\)) | \(\Delta H_m\) (kJ mol\(^{-1}\)) |
|----------------------|------------------|----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| \(\text{Cs}_2\text{MoO}_4\) versus \(\text{Al}\) reference | | | | | | | |
| 78.24 | 19.0 | 10.711 | 2980.62 | 0.3952 | 422.59 | 5.06 |
| 89.17 | 19.0 | 10.711 | 3105.49 | 0.4117 | 448.89 | 4.53 |
| 93.82 | 19.0 | 10.711 | 3004.55 | 0.3983 | 424.89 | 4.21 |
| **average** | | | | | | | | \((4.60 \pm 0.43)\) |
| \(\text{Cs}_2\text{Mo0.5Te0.5O}_4\) versus \(\text{Al}\) reference | | | | | | | |
| 93.06 | 18.9 | 10.711 | 2093.46 | 0.3209 | 272.80 | 3.95 |
| 120.39 | 18.9 | 10.711 | 2300.50 | 0.3526 | 364.51 | 3.71 |
| 96.46 | 18.9 | 10.711 | 2173.24 | 0.3311 | 249.02 | 3.35 |
| **average** | | | | | | | | \((3.83 \pm 0.17)\) |
| \(\text{Cs}_2\text{Mo0.5Te0.5O}_4\) versus \(\text{Na}_2\text{MoO}_4\) reference | | | | | | | |
| 71.84 | 19.0 | 10.711 | 2984.98 | 0.4551 | 217.47 | 2.94 |
| 114.74 | 19.0 | 10.711 | 3002.77 | 0.4578 | 354.79 | 2.98 |
| 85.16 | 19.0 | 10.711 | 3005.72 | 0.4583 | 255.59 | 2.89 |
| **average** | | | | | | | | \((2.94 \pm 0.05)\) |
| \(\text{Cs}_2\text{TeO}_4\) versus \(\text{Al}\) reference | | | | | | | |
| 94.5 | 47.4 | 22.61 | 3157.26 | 0.6073 | 335.52 | 2.58 |
| 147.63 | 47.8 | 22.61 | 3179.2 | 0.6056 | 608.00 | 3.00 |
| **average** | | | | | | | | \((2.79 \pm 0.30)\) |
| \(\text{Cs}_2\text{TeO}_4\) versus \(\text{Na}_2\text{MoO}_4\) reference | | | | | | | |
| 90.65 | 12.2 | 10.711 | 1953.57 | 0.4594 | 243.40 | 2.67 |
| 92.89 | 12.2 | 10.711 | 1958.93 | 0.4651 | 239.35 | 2.53 |
| 97.17 | 12.2 | 10.711 | 1887.68 | 0.4482 | 267.19 | 2.81 |
| **average** | | | | | | | | \((2.67 \pm 0.14)\) |

\(^a\) The quoted uncertainties correspond to the standard deviations.

progressive decrease in the transition enthalpy value is observed when the tellurium content increases. The transition
enthalpy for the \(\text{Cs}_2\text{TeO}_4\) end-member was found as \((2.67 \pm 0.14) \text{ kJ mol}^{-1}\).

### 3.7. Solidus and Liquidus Equilibria in the \(\text{Cs}_2\text{MoO}_4\)–
\(\text{Cs}_2\text{TeO}_4\) Phase Diagram.

In addition to the phase transition

\[\Delta T_H = \text{heat capacity} \times \Delta T\]

which is a function of composition. The dotted line only serves as a guide for the eye.

![Graph showing the evolution of the transition enthalpy as a function of composition.](image-url)
Gibbs energy of mixing into consideration. Equilibria can be well-represented only when taking the excess deviation from ideal behavior. This means that the phase system does not behave ideally but rather shows a negative measured experimental solidus points, it is clear that the field between the solidus and liquidus curves varies slightly. When comparing the case of an ideal behavior (solidus and liquidus equilibria in dotted lines) in Figure 14 with the measured experimental solidus points, it is clear that the system does not behave ideally but rather shows a negative deviation from ideal behavior. This means that the phase equilibria can be well-represented only when taking the excess Gibbs energy of mixing into consideration.

A regular solution model was used in this work to optimize the Cs$_2$MoO$_4$–Cs$_2$TeO$_4$ phase diagram based on the collected equilibria points. The latter model, the entropy of mixing is assumed to be ideal and the excess Gibbs energy of mixing is given solely by an enthalpic term equal to

$$\Delta_{\text{mix}}^{\text{exc}} G_m^\alpha = \Omega x_{\text{Cs}_2\text{MoO}_4} x_{\text{Cs}_2\text{TeO}_4}$$

where $\Omega$ corresponds to the regular solution constant (also called interaction coefficient) assumed to be independent of temperature, and $x_{\text{Cs}_2\text{MoO}_4}$ and $x_{\text{Cs}_2\text{TeO}_4}$ are the molar fractions of the Cs$_2$MoO$_4$ and Cs$_2$TeO$_4$ end-members, respectively.

Three interaction parameters were optimized in this work, i.e., two for the solid solutions $\alpha$-Cs$_2$Mo$_{1-x}$Te$_x$O$_4$ and $\beta$-Cs$_2$Mo$_{1-x}$Te$_x$O$_4$ and one for the liquid solution:

$$\Delta_{\text{mix}}^{\text{exc}} G_m^\alpha (\alpha) / J \cdot K^{-1} \cdot mol^{-1} = 2300 x_{\text{Cs}_2\text{MoO}_4} x_{\text{Cs}_2\text{TeO}_4}$$

$$\Delta_{\text{mix}}^{\text{exc}} G_m^\alpha (\beta) / J \cdot K^{-1} \cdot mol^{-1} = 2000 x_{\text{Cs}_2\text{MoO}_4} x_{\text{Cs}_2\text{TeO}_4}$$

$$\Delta_{\text{mix}}^{\text{exc}} G_m(\text{liquid}) / J \cdot K^{-1} \cdot mol^{-1} = 1000 x_{\text{Cs}_2\text{MoO}_4} x_{\text{Cs}_2\text{TeO}_4}$$

The optimization was done by a “trial-and-error method” using the FactSage software based on the measured enthalpies of transitions for Cs$_2$MoO$_4$ and Cs$_2$TeO$_4$ and the collected phase equilibrium data (onset temperatures for the phase transitions in the solid solution and solidus points). The computed phase diagram is shown in Figures 12, 13, and 14. The agreement with the experimental data is good within the experimental uncertainties. Because very little is known on the thermodynamic properties of Cs$_2$TeO$_4$ (only the enthalpy of formation has been reported by Cordfunke et al.15), a number of assumptions had to be made for the expressions of the Gibbs energy of the Cs$_2$TeO$_4$ end-member. The selected thermodynamic data for the thermodynamic model are listed in detail in the Supporting Information Section 3, together with a justification for the choice of the thermodynamic functions for this end-member composition. The present model offers a first basis for thermodynamic equilibrium calculations in the Cs$_2$MoO$_4$–Cs$_2$TeO$_4$ system. Nevertheless, for a comprehensive assessment of the JOG system and JOG chemistry, a complete CALPHAD assessment of the Cs–Te–Mo–O system would be necessary, in

| composition | $T_{\text{m-x}}$ (K) | $T_{\text{fus}}$ (K) | $T_{\text{solidus}}$ (K) |
|-------------|----------------------|---------------------|------------------------|
| Cs$_2$MoO$_4$ | (839 ± 5) | (1226 ± 5) | |
| Cs$_2$Mo$_{0.5}$Te$_{0.5}$O$_4$ | (826 ± 5) | (1215 ± 10) | |
| Cs$_2$Mo$_{0.6}$Te$_{0.4}$O$_4$ | (804 ± 5) | (1214 ± 10) | |
| Cs$_2$Mo$_{0.8}$Te$_{0.2}$O$_4$ | (785 ± 5) | (1198 ± 10) | |
| Cs$_2$Mo$_{0.4}$Te$_{0.6}$O$_4$ | (770 ± 5) | (1199 ± 10) | |
| Cs$_2$Mo$_{0.2}$Te$_{0.8}$O$_4$ | (760 ± 5) | (1196 ± 10) | |
| Cs$_2$Mo$_{0.1}$Te$_{0.9}$O$_4$ | (730 ± 5) | (1194 ± 10) | |
| Cs$_2$TeO$_4$ | (726 ± 5) | (1182 ± 10) | |

“See Figures 12, 13, and 14.
particular to account for the effects of changes in oxygen potential with burn-up.

4. CONCLUSIONS AND IMPLICATIONS FOR THE SAFETY ASSESSMENT OF THE FUEL BEHAVIOR IN FNR

In this work, new structural, thermodynamic, and phase diagram data on the Cs–Te–O and Cs–Mo–Te–O systems have been provided. In particular, this study focused on the Cs₂TeO₄ compound as it is, at room temperature, isostructural with Cs₂MoO₄, the major component of the JOG.

The existence of the Cs₂Moₓ₋ₓTeₓO₄ solid solution over the complete composition range 0 < x < 1 is reported for the first time. Combining room-temperature XRD, ND, and XAS, it has been shown that the solid solution obeys Vegard’s law, i.e., a linear expansion of the lattice is observed by increasing the tellurium content. However, EXAFS data on the Mo K-edge have shown that the short, highly covalent Mo–O bonds are not influenced by the tellurium addition, and hence, the oxygen tetrahedral environment around Mo remains unchanged in the solid solution.

High-temperature XRD analysis was performed on Cs₂TeO₄ in order to obtain the coefficients of thermal expansion of this compound. These measurements highlighted also the presence of an α → β phase transition at about 712 K, with a structural change from orthorhombic to hexagonal, equivalent to that exhibited by Cs₂MoO₄ at higher temperature (839 ± 5 K). This transition was also confirmed by DSC experiments, which were performed on various compositions of the Cs₂Moₓ₋ₓTeₓO₄ solid solution. These measurements allowed us to determine the variation of the α → β phase transition temperature with the tellurium content, as well as the enthalpy change associated with this transition. In addition, the congruent melting point of Cs₂TeO₄ and the solidus temperatures of the Cs₂Moₓ₋ₓTeₓO₄ solid solutions were obtained. Thanks to these new phase diagram equilibria points, a first thermodynamic modeling assessment of the Cs₂MoO₄–Cs₂TeO₄ system is proposed.

The data reported in this work represent a step forward for the comprehension of the thermodynamic and thermal properties of the multi-element JOG system. Even if further studies are still necessary, some preliminary considerations can already be made on the Cs–Mo–Te–O sub-system, based on the results of this study. Typically, one of the major concerns in FNRs is the chemical interaction between the oxide pellet and the cladding material, which can have an impact on the mechanical behavior of the fuel element. For that reason, it is important to evaluate the chemical and the mechanical interaction between the JOG and the clad (stainless steel).

As shown in this work, the dissolution of tellurium in Cs₂MoO₄ causes a lattice expansion of this phase. This expansion could increase the mechanical stress sustained by the cladding and hence have deleterious effects on its integrity. However, it must be noticed that the available irradiation tests and associated post-irradiation examinations did not highlight failure of the cladding in the presence of the JOG;²⁻⁸ on the contrary, some of the results seem to indicate a beneficial effect of the JOG formation on the fuel-clad mechanical interaction.³ This could be due to a much higher visco-elasticity of the JOG phases compared to the fuel. Further investigations are needed on this point.

Thermal expansion properties are also essential to assess JOG-cladding and JOG-fuel interactions during the thermal cycles. The thermal expansion behavior of Cs₂MoO₄ was investigated by Wallez et al.²⁰ Concerns rise from the anisotropic thermal expansion of the high-temperature hexagonal phase, which can induce microcracks during the cycles, and from the difference between the thermal expansions of Cs₂MoO₄ and the fuel. The volume increase due to the α → β phase transition and the thermal expansion measured for pure Cs₂TeO₄ are very similar to those reported for Cs₂MoO₄, but shifted to lower temperatures. Therefore, the dilution of Te needs to be taken into account to assess the JOG-fuel interaction during thermal transients.

Finally, one of the most important properties for the safety of a nuclear reactor is the melting temperature of the fuel. As shown herein, the increase of Te content in the Cs₂Moₓ₋ₓTeₓO₄ solid solution induces a regular decrease of the melting temperature, with a maximum difference of almost 130 K between the end-members. It is hence essential to take into account the possible dilution of tellurium into Cs₂MoO₄ under high oxygen potential conditions in order to determine the safety margin of operation of fast neutron reactors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01307.

Neutron diffraction pattern of Cs₂Moₓ₋ₓTeₓO₄ and Rietveld refinement of the data; anisotropic atomic displacement factors data; EXAFS data fitted at the Mo K-edge; Fourier difference map of β-Cs₂TeO₄; heat flow curves for Cs₂TeO₄ and Cs₂Moₓ₋ₓTeₓO₄; and details on the regular solution model of the Cs₂MoO₄–Cs₂TeO₄ system (PDF)

X-ray crystallographic files in CIF format (ZIP)

Accession Codes

CCDC 2000544–2000545 contain 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.
Inorganic Chemistry

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has received funding from the Euratom research and training programme 2014–2018 through the INSFYRE (Investigations Supporting MOX Fuel Licensing in ESNI Prototype Reactors) project under grant agreement no. 754329. The authors are thankful to G. Kauric and S. Mastromarino for their participation to the experiments at the ESRF.

REFERENCES

(1) Buckthorpe, D. In Structural Materials for Generation IV Nuclear Reactors; Yvon, P., Ed.; Woodhead Publishing: 2017.
(2) Tourasse, M.; Boidron, M.; Pasquet, B. Fission product behaviour in phenix fuel pins at high burnup. J. Nucl. Mater. 1992, 188, 49–57.
(3) Maeda, K.; Tanaka, K.; Asaga, T.; Furuya, H. Distributions of volatile fission products in or near the fuel-cladding gap of the FBR reactor fuel. J. Nucl. Mater. 2005, 344, 274–280.
(4) Uwaba, T.; Ito, M.; Mizuno, T.; Katsuyma, K.; Makena, B. J.; Wootan, D. W.; Carmack, J. Irradiation performance of fast reactor MOX fuel pins with ferritic/martensitic cladding irradiated to high burnup. J. Nucl. Mater. 2011, 412, 294–300.
(5) Teague, M.; Gorman, B.; King, J.; Porter, D.; Hayes, S. Microstructural characterization of high burn-up mixed oxide fast reactor fuel. J. Nucl. Mater. 2013, 441, 267–273.
(6) Parrish, R.; Winston, A.; Harp, J.; Atikalivye, A. TEM characterization of high burnup fast-reactor MOX fuel. J. Nucl. Mater. 2019, 527, 151794.
(7) Samuelsson, K.; Dumas, J.-C.; Sundman, B.; Lamontagne, J.; Guéneau, C. Simulation of the chemical state of high burn-up (U,Pu)O2 fuel in fast reactors based on thermodynamic calculations. J. Nucl. Mater. 2020, 532, 151969.
(8) Cappia, F.; Miller, B. D.; Aguilar, J. A.; He, L.; Murray, D. J.; Frickey, B. J.; Stanek, J. D.; Harp, J. M. Electron microscopy characterization of fast reactor MOX Oxide-Gaine (JOB). J. Nucl. Mater. 2020, 531, 151964.
(9) Dumas, J.-C. Etude des conditions de formation du Joint-Oxyde-Gaine dans les combustibles oxydes mixtes des reacteurs a neutrons rapides, observations et proposition dun modele de comportement des produits de fission volatils. Ph.D. Thesis, Institut National Polytechnique de Grenoble: Grenoble, France, 1995.
(10) Konings, R. J. M.; Cordfunke, E. H. P. The thermophysical properties of cesium molybdate, Cs2M9, from 298.15 to 1500 K. Thermochim. Acta 1988, 124, 157–162.
(11) Thi, T. N. P. Caractérisation et modélisation du comportement thermodynamique du combustible RNR-Na sous irradiation. Ph.D. Thesis, Ecole Doctorale Physique et Sciences de la Matière (Aix-Marseille University), 2014.
(12) Hoekstra, H. R. The Cs2MoO4-MoO3 system. Inorg. Nucl. Chem. Lett. 1973, 9, 1291–1301.
(13) Cordfunke, E. H. P.; Konings, R. J. M. Thermochimical data for reactor materials and fission products: The ECN database. J. Phase Equilib. 1993, 14, 457–464.
(14) Thermodynamics of Advanced Fuels, International Database (TAF-ID); www.oeed-nea.org/science/taf-id/ (accessed 2020).
(15) Loopstra, B. O.; Goubitz, K. The structures of four caesium tellurates. Acta Crystallogr., Sect. C. Cryst. Struct. Commun. 1986, 42, 520–523.
(16) Sirtanov, T.; Li, J.; Statcl, K. J.; Macaluso, R. T.; Sleight, A. W.; Subramanian, M. A. Cs2TeO4−α: Novel Mixed-Valence Tellurium Oxides with Framework-Deficient Pyrochlore-Related Structure. Inorg. Chem. 2011, 50, 8494–8501.
(17) Weller, M. T.; Pack, M. J.; Binsted, N.; Dann, S. E. The structure of cesium tellurite (VI) by combined EXAFS and powder X-ray diffraction. J. Alloys Compd. 1999, 282, 76–78.
(18) Cordfunke, E. H. P.; Smitt-Groen, V. M. A DSC study of the phase diagram of the system TeO2-Cs2TeO3. Thermochim. Acta 1984, 80, 181–183.
(19) Cordfunke, E. H. P.; Ouweijtjes, W.; Prins, G. Standard enthalpies of formation of tellurium compounds III. Cs2TeO4, Cs2Te2O5, and Cs2TeO4 and Cs2TeO6. J. Chem. Thermodyn. 1988, 20, 569–573.
(20) Wallez, G.; Raison, P. E.; Smith, A. L.; Clavier, N.; Dacheux, N. High-temperature behavior of dicesium molybdate Cs2M9O4: Implications for fast neutron reactors. J. Solid State Chem. 2014, 215, 225–230.
(21) Rodriguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. Phys. B 1993, 192, 55–69.
(22) van Eijck, L.; Cussen, L. D.; Sykora, G. J.; Schooneveld, E. M.; Rhodes, N. J.; van Well, A. A.; Pappas, C. Design and performance of a novel neutron powder diffractometer: PEARL at TU Delft. J. Appl. Crystalllogr. 2016, 49, 1398–1401.
(23) Borsboom, M.; Bras, W.; Cerraj, I.; Detollenaere, D.; Glatra Van Loon, D.; Goedtkindt, P.; Konijnenburg, M.; Lassing, P.; Levine, Y. K.; Munneke, B.; Oversluizen, M.; Van Tol, R.; Vlieg, E. The Dutch-Belgian beamline at the ESRF. J. Synchrotron Radiat. 1998, 5, 518–520.
(24) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption microscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12, 537–541.
(25) Höhne, G. W. H.; Cammenga, H.; K.; Eysel, W.; Gmelin, E.; Hemminger, W. The temperature calibration of scanning calorimeters. Thermochim. Acta 1990, 160, 1–12.
(26) Della Gatta, G.; Richardson, M. J.; Sarge, S. M.; Stolen, S. Standards, calibration, and guidelines in microcalorimetry. Part 2.
Calibration standards for differential scanning calorimetry (IUPAC Technical Report). Pure Appl. Chem. 2006, 78, 1455−1476.

(27) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. 1976, 32, 751−767.

(28) Smith, A. L.; Kauric, G.; van Eijck, L.; Goubitz, K.; Wallez, G.; Griveau, J.-C.; Colineau, E.; Clavier, N.; Konings, R. J. M. Structural and thermodynamic study of dicesium molybdate Cs2Mo2O7: Implications for fast neutron reactors. J. Solid State Chem. 2017, 253, 89−102.

(29) Aritani, H.; Tanaka, T.; Funabiki, T.; Yoshida, S.; Kudo, M.; Hasegawa, S. Structure of Mo-Mg Binary Oxides in Oxidized/Reduced States Studied by X-ray Absorption Spectroscopy at the Mo K-Edge and Mg K-Edge. J. Phys. Chem. 1996, 100, 5440−5446.

(30) Rocca, F.; Kuzmin, A.; Mustarelli, P.; Tomasi, C.; Magistris, A. XANES and EXAFS at Mo K-edge in (AgI)1-x(Ag2MoO4)x glasses and crystals. Solid State Ionics 1999, 121, 189−192.

(31) Kuzmin, A.; Purans, J. Dehydration of the molybdenum trioxide hydrates MoO3.nH2O: in situ x-ray absorption spectroscopy study at the Mo K edge. J. Phys.: Condens. Matter 2000, 12, 1959−1970.

(32) Lima, F. A.; Bjornsson, R.; Weyhermüller, T.; Chandrasekaran, P.; Glaztze, P.; Neese, F.; DeBeer, S. High-resolution molybdenum K-edge X-ray absorption spectroscopy analyzed with time-dependent density functional theory. Phys. Chem. Chem. Phys. 2013, 15, 20911−20920.

(33) Andersson, G.; Magneli, A.; Sillén, L. G.; Rottenberg, M. On the crystal structure of molybdenum trioxide. Acta Chem. Scand. 1950, 4, 793−797.

(34) Sitepu, H. Texture and structural refinement using neutron diffraction data from molybdate (MoO4) and calcite (CaCO3) powders and a Ni-rich Ni50.7Ti49.30 alloy. Powder Diffr. 2009, 24, 315−326.

(35) Weller, M. T.; Pack, M. J.; Binsted, N.; Dann, S. E. The structure of cesium tellurate (VI) by combined EXAFS and powder X-ray diffraction. J. Alloys Compd. 1999, 282, 76−78.

(36) Ogg, A. The crystal structure of the isomorphous sulfates of potassium, ammonium, rubidium, and cesium. Philos. Mag. 1928, 5, 354−371.

(37) Miller, J. J. The crystal structure of cesium chromate Cs2CrO4. Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem. 1938, 99, 32−37.

(38) Gonschorek, W.; Hahn, T. Die Kristallstruktur des Caesiummolybdats, Cs2MoO4. Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem. 1973, 138, 167−176.

(39) Cordfunke, E.; Vlaanderen, P. The structure of cesium tellurate (VI) by combined EXAFS and powder X-ray diffraction. NIST-JANAF Thermochemical Tables, monograph 9, 4th ed.; American Chemical Society, American Institute of Physics, National Bureau of Standards: New York, 1998.

(41) Cordfunke, E. H. P.; Konings, R. J. M. Thermochemical Data for Reactor Materials and Fission Products; Elsevier Science Publishers B.V.: 1990.

(42) Bottelberghs, P.H.; van Buren, F.R. Phase Relations, Dopant Effects, Structure, and High Electrical Conductivity in the Na3WO4−Na2MoO4 System. J. Solid State Chem. 1975, 13, 182−191.

(43) Sugawara, T.; Jin, K. Enthalpy and heat capacity of Na2MoO4 and CaMoO4. Thermochim. Acta 2018, 669, 185−193.

(44) Stolen, S.; Grande, T.; Allan, N. L. Chemical Thermodynamics of Materials: Macroscopic and Microscopic Aspects; John Wiley & Sons, Ltd: 2004.

(45) Hildebrand, J. H. Solubility. XII. Regular solutions. J. Am. Chem. Soc. 1929, 51, 66.

(46) Pelton, A.; Thompson, W. Phase Diagrams. Prog. Solid State Chem. 1975, 10, 119−155.

(47) Cordfunke, E. H. P.; Cluistra, R.; Van Miltenburg, J. C. The thermodynamic properties of six compounds in (tellurium+oxygen+hydrogen) from 10 to 1000 K. J. Chem. Thermodyn. 1985, 17, 1079–1089.

https://dx.doi.org/10.1021/acs.inorgchem.0c01307
Inorg. Chem. 2020, 59, 10172−10184