High-temperature behavior of dicesium molybdate Cs_2MoO_4: Implications for fast neutron reactors

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A B S T R A C T

Dicesium molybdate (Cs_2MoO_4)'s thermal expansion and crystal structure have been investigated herein by high temperature X ray diffraction in conjunction with Raman spectroscopy. This first crystal-chemical insight at high temperature is aimed at predicting the thermostructural and thermomechanical behavior of this oxide formed by the accumulation of Cs and Mo fission products at the periphery of nuclear fuel rods in sodium-cooled fast reactors. Within the temperature range of the fuel's rim, Cs_2MoO_4 becomes hexagonal $P6_3/mmc$, with disordered MoO_4 tetrahedra and 2D distribution of Cs–O bonds that makes thermal axial expansion both large ($50 \leq \alpha_l \leq 70 \ 10^{-6} \,^{\circ}C^{-1}$, 500–800 °C) and highly anisotropic ($\alpha_c - \alpha_a = 67 \times 10^{-6} \,^{\circ}C^{-1}$, hexagonal form). The difference with the fuel's expansion coefficient is of potential concern with respect to the cohesion of the Cs_2MoO_4 surface film and the possible release of cesium radionuclides in accidental situations.

1. Introduction

Cesium and molybdenum rank among the most abundant solid fission products. They each represent about 10 mass% of the total fission-product inventory, depending on the fuel initial composition, burn-up and type of reactor [1]. In UOX (UO_2) and $(U,Pu)O_2$ nuclear fuels, strongly electropositive Cs readily oxidizes, and so does Mo if the oxygen potential is high enough [2]. In the fuel pins of pressurized water reactors, where temperature ranges from 400 °C (in periphery) to 1050 °C (core), these two elements generally form solid solutions or intergranular phases, whereas in fast breeder reactor (FBR) fuels, where the core temperature is much higher ($\sim$2000 °C) and the temperature gradient very steep (450 °C mm^{-1}), the Cs_2O and MoO_3 oxides evaporate and diffuse towards the coolest part of the fuel rod, in the pellet-cladding gap ($\sim$700 °C). In agreement with their antagonistic natures, respectively basic and acidic, these oxides are prone to react with each other, so that as soon as 1973, O'Hare and Hoekstra predicted the formation of Cs_2MoO_4 [3]. Indeed, post-irradiation analyses of the Phénix experimental FBR pins evidenced high concentrations of Cs

and Mo [4] at the periphery of the pellets, whose oxides turned out to be the main components of the 150–200 µm-thick neo-formed solid that fills the oxide-clad gap at high burnup, but their chemical form was not identified.

Hoekstra's Cs_2MoO_4–MoO_3 phase diagram [5], considered as the most reliable one, reveals six compounds with formulae $Cs_2Mo_nO_{3n+1}$ ($n=1$–5 and 7), whose structural and thermodynamic properties have been reported [6]. Among these cesium molybdates, Cs_2MoO_4 appears as the most stable under the thermodynamic and chemical conditions of a FBR pin's surface [6,7]. Furthermore, it is the only one that occurs as a solid in the considered temperature range, owing to its higher melting point (956 °C) compared to the other cesium molybdates [5].

At room temperature, Cs_2MoO_4 [8] exhibits the same orthorhombic (space group $Pnma$) crystal structure as Cs_2SO_4 [9], Cs_2CrO_4 [10] and most other $M_2^IX^{VI}O_4$ compounds with $M=$K, Rb and $X=$S, Cr, Mo. This form will be termed as o-Cs_2MoO_4 in the following discussion. Several past studies have endeavored exploring its properties at high temperatures [11,12]. Thermal conductivity, measured up to the melting point, was found to be of one order of magnitude lower than that of the fuel itself [12,13]. However, the knowledge of the other properties remains precarious above 600 °C, that is, in the range corresponding to the FBR fuel's surface. For instance, thermal expansion was measured along the three crystallographic axes, but only up to 500 °C [12]. Besides, a transition to a hexagonal form (h-Cs_2MoO_4) [14] was

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reported at 568 °C [11], but the crystal structure and the dilatometric behavior of this phase remain unknown. Yet the latter property appears as a key parameter for two main reasons:

- The thermal evolution of the mechanical stress sustained by the clad at high burnup, when surface Cs_2MoO_4 entirely fills the gap.
- The risks of decohesion at the interface in case of overheating if the difference between the coefficients of thermal expansion of fuel and Cs_2MoO_4 is high.

In fact, these two issues would determine the possible release of cesium radioisotopes ^{135}Cs and ^{137}Cs into the primary cooling circuit in case of an accidental clad breach. So, as a first milestone prior to further studies that will deal with the Cs_2MoO_4-fuel system, the present work is dedicated to the investigation of the crystal structure, Raman spectra and thermal expansion of Cs_2MoO_4 in the temperature range corresponding to the FBR fuel's surface.

2. Experimental
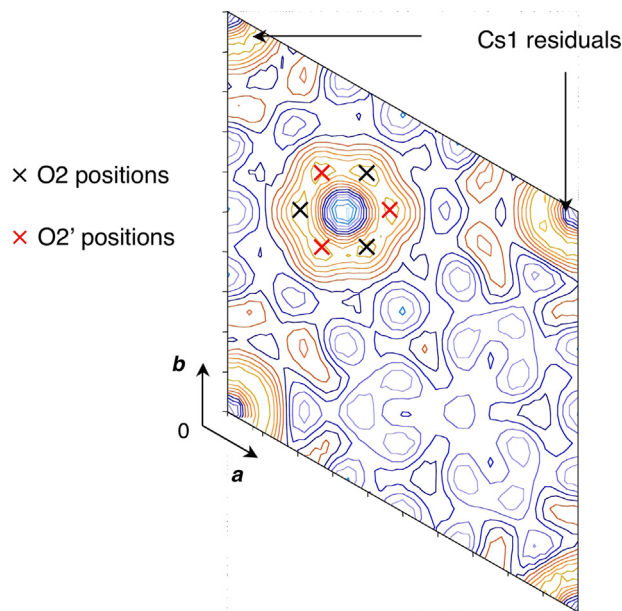
Cs_2MoO_4 was synthesized by solid-state reaction from dried MoO_3 (Sigma-Aldrich, purity $\geq 99.5\%$) and Cs_2CO_3 (Sigma-Aldrich, $\geq 99\%$). After grinding in a mortar, the powder mixture was heated at 200 °C, regrinded and annealed at 700 °C for 12 h. No secondary phases could be detected by X ray diffraction (XRD) and the white product appeared to be of a satisfactory purity (Bragg peaks of unidentified spurious phases were $< 1\%$ in intensity). Because of its high sensitivity to moisture, the product was kept under P_2O_5-dried air. During XRD measurements at room temperature, the sample was protected from moisture by an air-tight 50 μm-thick beryllium foil. Diffracted intensities were correspondingly corrected for the absorption due to the foil.
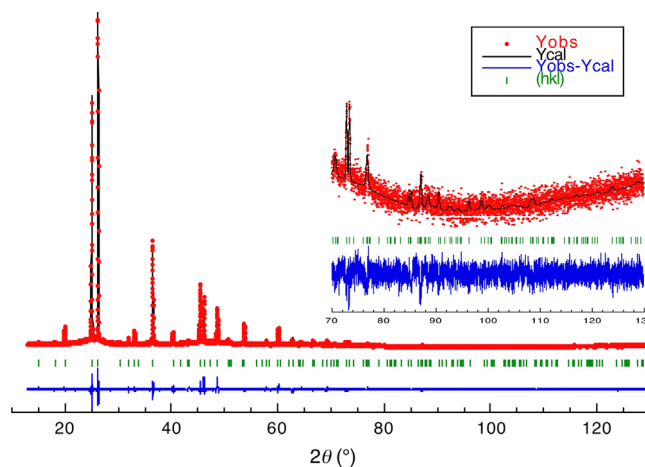
X ray diffraction experiments at high temperature (HTXRD) were carried out using a Panalytical X'Pert Pro (Bragg–Brentano) apparatus fitted with an Anton-Parr furnace. Acquisition conditions are summarized in Table 1. The determination of the cell parameters, atomic coordinates and thermal factors was performed by Rietveld analysis using the Fullprof suite [15]. Below the o–h transition, the orthorhombic $Pnma$ structural data set [8] was taken as a starting model. At higher temperatures, the structure was solved on the basis of the hexagonal cell [14]. The reflection conditions (hhl, $l=2n$) suggested either $P6_3mc$ or $P6_3/mmc$ as the most probable space groups. Considering the former one, the cesium atoms were localized by Patterson synthesis, and then the molybdenum and oxygen atoms were inferred from the Fourier maps. According to the latter, apical oxygen O2 (ideally forming a c-directed Mo–O_2 bond) is de-localized on 6 positions that form a ring about 1.7 Å in diameter centered at the three-fold axis (Fig. 1). This led us to split this atom into 2 different groups of positions, namely O2 and O2′. All the atomic

Fig. 1. Fourier-difference map showing the 6-site annular distribution of oxygens O2/O2′ at $z=0.45$.

Fig. 2. Rietveld plot for h-Cs_2MoO_4 at 675 °C, with experimental (red dots), calculated (black line), residual (blue) intensities and Bragg positions (green bars). Inset: $\times 17$ magnification of intensities in the high angles domain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

positions eventually appeared to be fully compatible with $P6_3/mmc$ because of a [001] upside-down disorder of the MoO_4 tetrahedra. Due to the low electron density of oxygen and the limited number of intense diffraction peaks, soft constraints had to be applied on the Mo–O distances in the final refinement, consistently with the high covalency of these bonds. Atoms O2 and O2′ were also constrained to be on the same circle centered at the three-fold axis. This measure was made necessary by the very low occupancy factor of these sites (1/12). The refinement parameters are gathered in Table 1; the Rietveld plot is presented in Fig. 2. More details concerning the structure resolution can be found in the Supplementary material section.

High temperature Raman spectra were recorded using a Horiba Jobin-Yvon Aramis spectrometer equipped with a Linkam TS-1500 heating device. Samples were placed in a platinum crucible without any prior preparation and inserted in the furnace. The 532 nm line of a Nd-YAG laser was used as excitation wavelength and

Table 1
Main acquisition, refinement and lattice data for h-Cs_2MoO_4.

Apparatus	Panalytical X'Pert Pro
Anode, monochromator	$CuK\alpha_1$ (40 kV, 45 mA), Ge (111)
Scan range, step, time	$8.00° \leq 2\theta \leq 130.00°$, 0.013°, 8 h
Temperature (°C)	675
Measured reflections	151
Intensity/profile parameters	13/10 (split pseudo-Voigt)
Reliability factors	$R_P=0.052$; $R_{WP}=0.068$; $R_{Bragg}=0.046$; $\chi^2=2.1$
System, space group	hexagonal, $P6_3/mmc$ (194)
Cell parameters, volume	$a=6.840(1)$ Å; $c=8.977(2)$ Å; $V=363.7(2)$ Å^3
Formula per cell/calc. density	2/3.89