# Structural and thermodynamic study of $Cs_3Na(MoO_4)_2$: Margin to the safe operation of sodium cooled fast reactors

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## ARTICLE INFO

## ABSTRACT

Neutron diffraction measurements of the double molybdate $Cs_3Na(MoO_4)_2$ have been performed for the first time in this work and the crystal structure refined using the Rietveld method. The thermal expansion of this trigonal phase, in space group $P\bar{3}m1$, measured using high temperature X-ray diffraction (XRD), remains moderate: $\alpha_a = 31 \cdot 10^{-6} K^{-1}$ and $\alpha_c = 24 \cdot 10^{-6} K^{-1}$ in the temperature range $T = (298–723)$ K. The melting temperature of this compound has been determined at $T_{fus} = (777 \pm 5)$ K using Differential Scanning Calorimetry (DSC). No phase transition was detected, neither by DSC, nor by high temperature XRD or high temperature Raman spectroscopy, which disagrees with the literature data of Zolotova et al. (2016), who reported a reversible phase transition around 663 K. Finally, thermodynamic equilibrium calculations have been performed to assess the probability of formation of $Cs_3Na(MoO_4)_2$ inside the fuel pin of a Sodium cooled Fast Reactor by reaction between the cesium molybdate phase $Cs_2MoO_4$, which forms at the pellet rim at high burnup, the fission product molybdenum (either as metallic or oxide phase), and the liquid sodium coolant in the accidental event of a breach of the stainless steel cladding and sodium ingress in the failed pin.

## 1. Introduction

Double molybdates of the form $A_nR_m(MoO_4)_2$ (A=alkalis, alkaline-earths, Cu, Tl; R=rare earth elements, Bi, Pb, Zn) have been studied extensively in the past few years because of their exciting properties as phosphors luminescent materials [1,2], solid state lasers [3,4], ferroe-lastics and ferroelectrics [5–7]. Phases such as $A_3LiZn_2(MoO_4)_4$ (A = Rb, Cs) and $Cs_3LiCo_2(MoO_4)_4$ have also been reported [8,9], with promising properties as solid-lithium ion conductors [10]. While studying the phase formations in the $Na_2MoO_4$-$Cs_2MoO_4$-$Zn_2MoO_4$ system, and the possible insertion of sodium into the $Cs_6Zn_5(MoO_4)_8$ structure, Zolotova et al. [10] recently reported two new phases, namely $Cs_3Na(MoO_4)_2$ and $Cs_3NaZn_2(MoO_4)_4$. The authors re-investi-gated the poorly known $Na_2MoO_4$-$Cs_2MoO_4$ system, which is of particular interest for the safety assessment of next generation Sodium cooled Fast Reactors (SFRs).

During irradiation of the mixed oxide $(U_{1-y}Pu_y)O_{2-x}$ fuel (MOX) in fast neutrons reactors such as SFRs, the fission products cesium, molybdenum, iodine and tellurium are generated with a high fission yield [11]. Because of the high volatility of the latter products and the strong axial temperature gradient ($\sim 450$ K $\cdot mm^{-1}$ with $\sim 2273$ K in the centre and $\sim 973$ K at the pellet rim) in the fuel pin, they migrate after formation towards the pellet rim, where they accumulate in the space between fuel and cladding. Post-irradiation examinations of fuel pins irradiated in the Phénix reactor [11] have demonstrated the formation of a multi-component phase, the so-called JOG phase (Joint Oxide Gain), whose main constituents are $Cs_2MoO_4$, CsI, $Cs_2Te$, and $Cs_2UO_4$ [12,13].

One of the important safety considerations for the operation of SFRs concerns the risk of a breach of the stainless steel cladding during normal operation or accidental conditions. Although extremely rare, such clad breach can occur due to manufacturing defaults in the cladding material, fuel cladding mechanical or chemical interaction [14], due to blocking of a coolant channel or unexpected change in the neutron flux [15]. A thorough safety assessment of the reactor there-fore requires to consider the aftermath of an accidental ingress of sodium in a failed pin. Past studies have suggested that sodium could substitute cesium in the main component of the JOG phase, namely cesium molybdate, leading to sodium molybdate formation in the gap between fuel and cladding, and reduction of the cesium to cesium

metal: $2Na + Cs_2MoO_4 = 2Cs + Na_2MoO_4$ [16]. This assumption is still subject of controversy, however, and the studies of Tête in 1999 using thermal analysis and scanning electron microscopy suggested no cesium-sodium substitution, but rather the formation of cesium, sodium and molybdenum oxides [15]. The phase relationships in the $Cs_2MoO_4$-$Na_2MoO_4$ system have been investigated by X-ray diffraction and thermal analysis as early as 1964 [17], but it is only very recently that the formation of the quaternary phase $Cs_3Na(MoO_4)_2$ has been established. Given the remaining uncertainties regarding the product of the sodium-cesium molybdate interaction, a comprehensive structural and thermodynamic characterization of the $Cs_3Na(MoO_4)_2$ phase is necessary.

In this work, we report for the first time neutron diffraction measurements at room temperature of $Cs_3Na(MoO_4)_2$, the study of its thermal expansion behaviour and polymorphism using high-temperature X-ray diffraction, Differential Scanning Calorimetry, and high-temperature Raman spectroscopy. Using the thermodynamic functions newly measured in our research group for this compound [18], the probability of the formation of $Cs_3Na(MoO_4)_2$ in the fuel pin by reaction of the sodium coolant with $Cs_2MoO_4$ was finally assessed.

## 2. Experimental methods

### 2.1. Sample preparation

$Cs_3Na(MoO_4)_2$ was synthesized by reaction between accurately weighted quantities of cesium molybdate $Cs_2MoO_4$ and sodium molybdate ($Na_2MoO_4$ anhydrous, 99.9% trace metal basis, Sigma-Aldrich). The cesium molybdate starting material was synthesized as described in [19]. The stoichiometric mixture was heated under argon inside a tightly closed stainless steel container at 723 K for 200 h, with intermediate regrinding steps. Because of the molybdates' hygroscopic nature, handling was done exclusively inside the dry atmosphere of an argon-filled glove box. The purity of the sample was examined by X-ray and neutron diffraction at room temperature, Differential Scanning Calorimetry (DSC), and ICP-MS analysis. No secondary phases were detected by XRD and neutron diffraction. The DSC measurements showed a single peak in the heat flow signal as a function of temperature, corresponding to the melting event, as detailed in Section 3.2. No additional peaks could be assigned to impurities. The ICP-MS analysis yielded a cesium-to-molybdenum ratio of ($1.44 \pm 0.07$[1]) at/at and a sodium to molybdenum ratio of ($0.51 \pm 0.03$[2]), which corresponds to the global composition $Cs_{2.88(\pm 0.14)}Na_{1.02(\pm 0.06)}(MoO_4)_2$, hence within uncertainties, in good agreement with the stoichiometric formula. The sample purity is expected to be better than 99 wt%.

### 2.2. Neutron diffraction

Neutron diffraction data were recorded on the beamline PEARL at the Hoger Onderwijs Reactor at TU Delft [20]. The sample was encapsulated in a vanadium cylindrical container (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) for 30 h over the range $11° \leq 2\theta \leq 158°$. Structural analysis was performed by the Rietveld method with the Fullprof2k suite [21].

### 2.3. Powder X-ray diffraction

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

### 2.4. High temperature X-ray diffraction

The thermal expansion and polymorphism of $Cs_3Na(MoO_4)_2$ were also investigated by high temperature X-ray diffraction using the same diffractometer equipped with an Anton Paar TTK450 chamber. Measurements were conducted under vacuum (0.02 mbar) from room temperature up to 723 K, with 50 K heating steps. The temperature was measured with a Pt100 resistor. Each temperature plateau was maintained for 6 h after a stabilisation time of 30 min.

### 2.5. Differential scanning calorimetry

3D-heat flow DSC measurements were moreover performed up to 853 K using a Setaram Multi HTC module of the 96 Line calorimeter. The sample (96.7 mg) was placed in a nickel liner and encapsulated for the calorimetric measurements in a stainless steel crucible closed with a screwed bolt as described in [22] to avoid vaporization at high temperatures. The measurement program consisted in four successive heating cycles with 5 K·min$^{-1}$ heating rate, and $2 - 5 - 10 - 15$ K·min$^{-1}$ cooling rates. The sensitivity of the corresponding measurement was around 0.443 μV·mW$^{-1}$. The temperatures were monitored throughout the experiments by a series of interconnected S-types thermocouples. The temperature on the heating ramp was calibrated by measuring the melting points of standard materials (Au, Ag, In, Al, Pb, Sn, Zn). The temperature on the cooling ramp was obtained by extrapolation to 0 K·min$^{-1}$ cooling rate. The transition temperatures were derived on the heating ramp as the onset temperature using tangential analysis of the recorded heat flow.

### 2.6. High temperature Raman spectroscopy

High temperature Raman spectra were recorded using a Horiba Jobin-Yvon Aramis spectrometer equipped with a Linkam TS-1500 heating device. The $Cs_3Na(MoO_4)_2$ sample was placed in a platinum crucible and inserted in the furnace. A rate of 10 K/min was applied upon heating and 5 min of stabilisation time were maintained at each temperature plateau before acquisition of the spectrum. The 532 nm line of a Nd-YAG laser was used as excitation wavelength and focused by means of an Olympus BX41, thus delivering about 40 mW at the sample surface. Slits and confocal hole were set to result in a 1 cm$^{-1}$ resolution. For each spectrum, an acquisition time of 3 s was considered with an average of 4 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 greater than 0.997 were systematically obtained.

## 3. Results and discussion

### 3.1. Structural refinement of $Cs_3Na(MoO_4)_2$ from neutron diffraction data

$Cs_3Na(MoO_4)_2$ shows a trigonal structure at room temperature, in space group $P\bar{3}m1$, belonging to the glaserite type, as shown by the recent single crystal studies of Zolotova et al. [10]. The X-ray and neutron diffraction patterns for this compound are shown in Figs. 1 and 2. The refined cell parameters by XRD, $a = 6.34381(2)$ Å

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

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