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Structural and thermodynamic study of dicesium molybdate $Cs_2Mo_2O_7$: Implications for fast neutron reactors

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ABSTRACT

The structure of α-$Cs_2Mo_2O_7$ (monoclinic in space group $P2_1/c$), which can form during irradiation in fast breeder reactors in the space between nuclear fuel and cladding, has been refined in this work at room temperature from neutron diffraction data. Furthermore, the compounds' thermal expansion and polymorphism have been investigated using high temperature X-ray diffraction combined with high temperature Raman spectroscopy. A phase transition has been observed at $T_{tr}(\alpha \rightarrow \beta) = (621.9 \pm 0.8)$ K using Differential Scanning Calorimetry, and the structure of the β-$Cs_2Mo_2O_7$ phase, orthorhombic in space group $Pbcm$, has been solved ab initio from the high temperature X-ray diffraction data. Furthermore, the low temperature heat capacity of α-$Cs_2Mo_2O_7$ has been measured in the temperature range $T = (1.9–313.2)$ K using a Quantum Design PPMS (Physical Property Measurement System) calorimeter. The heat capacity and entropy values at $T = 298.15$ K have been derived as $C^{o}_{p,m}(Cs_2Mo_2O_7, cr, 298.15\ \mathrm{K}) = (211.9 \pm 2.1)\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $S^{o}_{m}(Cs_2Mo_2O_7, cr, 298.15\ \mathrm{K}) = (317.4 \pm 4.3)\ \mathrm{J\ K^{-1}\ mol^{-1}}$. When combined with the enthalpy of formation reported in the literature, these data yield standard entropy and Gibbs energy of formation as $\Delta_f S^{o}_{m}(Cs_2Mo_2O_7, cr, 298.15\ \mathrm{K}) = -(628.2 \pm 4.4)\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $\Delta_f G^{o}_{m}(Cs_2Mo_2O_7, cr, 298.15\ \mathrm{K}) = -(2115.1 \pm 2.5)\ \mathrm{kJ\ mol^{-1}}$. Finally, the cesium partial pressure expected in the gap between fuel and cladding following the disproportionation reaction $2Cs_2MoO_4 = Cs_2Mo_2O_7 + 2Cs(g) + 1/2\ O_2(g)$ has been calculated from the newly determined thermodynamic functions.

1. Introduction

The fission products cesium, iodine, tellurium and molybdenum are generated with a high fission yield during irradiation of the mixed oxide (MOX) fuel in fast breeder reactors [1]. They subsequently migrate from the center of the fuel pin (~2273 K) towards the pellet edge due to the strong temperature gradient (~450 K mm^{-1}), and accumulate in the space between the fuel and the cladding (~973 K) as shown by the post-irradiation examinations of the Phénix fuel pins [1], forming a multi-component phase, the so-called JOG phase (Joint Oxide Gain). Cesium orthomolybdate Cs_2MoO_4 is suggested as one of the major components of the JOG [2–5]. As such, extensive structural, thermodynamic and thermophysical studies have been reported in the literature for this compound. Cs_2MoO_4 shows an orthorhombic structure at room temperature in space group $Pnma$ [6,7], and transforms to an hexagonal phase in space group $P6_3/mmc$ [7] at $T_{tr} = (841.3 \pm 0.4)$ K [3]. Its thermal expansion was found to be high and increasing substantially with temperature [8,7], while its thermal conductivity measured up to the melting point $T_{fus} = (1229.5 \pm 0.2)$ K [3] appeared to be one order of magnitude lower than the fuel [8,9]. The compounds thermodynamic properties and vaporization behaviour were reported in the studies of [2,3,10]. The mass spectrometric studies of Johnson [10] suggested that Cs_2MoO_4 actually decomposed into cesium dimolybdate $Cs_2Mo_2O_7$ and gaseous Cs_2O at high temperatures. The latter product decomposes to Cs(g) and O_2(g) rapidly, which corresponds to the following reaction:

$$2Cs_2MoO_4(cr) = Cs_2Mo_2O_7(cr) + 2Cs(g) + 1/2O_2(g) \tag{1}$$

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The formation of Cs(g) from the disproportionation reaction of cesium orthomolybdate Cs_2MoO_4 is hence to be expected at the periphery of the fuel pin considering the high temperatures and oxygen potential conditions at this location. A thorough knowledge of the structural and thermodynamic properties of the cesium dimolybdate $Cs_2Mo_2O_7$ is hence critical to assess the Gibbs energy of this reaction, and therefore the driving force for the release of radioactive material (source term) such as ^{135}Cs and ^{137}Cs into the coolant in case of a clad breach.

In this work neutron diffraction measurements at room temperature of both phases Cs_2MoO_4 and $Cs_2Mo_2O_7$ are reported for the first time. The thermal expansion behaviour and polymorphism of $Cs_2Mo_2O_7$ have been investigated using high temperature X-ray diffraction (XRD) combined with high temperature Raman spectroscopy. The occurrence of a phase transition has been revealed, and the structure of the high temperature phase has been solved for the first time. In addition, the temperature of the $\alpha \rightarrow \beta$ transition has been determined from simultaneous TG-DSC and DSC data. Finally, the low-temperature heat capacity of α-$Cs_2Mo_2O_7$ has been measured in the temperature range $T = (1.9–313.2\ \text{K})$ using thermal relaxation calorimetry, and the heat capacity and standard entropy values have been derived at 298.15 K. From those data, the expected partial pressures of cesium at the periphery of the fuel pin of a fast breeder reactor have been estimated.

2. Experimental methods

2.1. Sample preparation and characterization

$Cs_2Mo_2O_7$ was synthesized under argon flow by reaction between accurately weighted quantities of cesium orthomolybdate Cs_2MoO_4 and molybdenum oxide (MoO_3, 99.5%, Alfa Aesar). The cesium orthomolybdate starting material was synthesized as described in [7]. The stoichiometric mixture was heated at 823 K for 16 h in an alumina boat, above the melting temperature of $Cs_2Mo_2O_7$, followed by regrinding and thermal treatment at 623 K for 16 h. The purity of the sample was examined by X-ray and neutron diffraction at room temperature. No secondary phases were detected, and 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 [11]. 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 43 h over the range $11° \leq 2\theta \leq 158°$. Structural analysis was performed by the Rietveld method with the Fullprof2k suite [12].

2.3. Room temperature X-ray diffraction

The 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 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 $Cs_2Mo_2O_7$ 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 683 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. 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 $Cs_2Mo_2O_7$ 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 2 s was considered with an average of 6 scans. Before analysis, the apparatus was calibrated with a silicon wafer, using the first-order Si line at 520.7 cm^{-1}.

2.6. Calorimetry

Simultaneous TG-DSC (Thermogravimetry-Differential Scanning Calorimetry) measurements were performed on $Cs_2Mo_2O_7$ (308.7 mg) using a Setaram 96 Line calorimeter in 450 μL alumina crucibles up to 700 K. The sample was heated under argon flow with a flow rate of 30 ml min^{-1} in four successive cycles with 10 K min^{-1} heating rates and 2–5–10–20 K min^{-1} cooling rates. The sensitivity of the corresponding measurement was around 0.215 μV mW^{-1}.

3D-heat flow DSC measurements were moreover performed up to 813 K (above the melting temperature) using a Setaram Multi HTC module of the 96 Line calorimeter. The sample (155.6 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 [13] to avoid vaporization at high temperatures. The measurement program consisted in four successive heating cycles with 2 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 and melting temperatures were derived on the heating ramp as the onset temperature using tangential analysis of the recorded heat flow.

2.7. Low temperature heat capacity

Low temperature heat capacity measurements were performed on 30.95(5) mg of $Cs_2Mo_2O_7$ material in the temperature range $T = (1.9–313.2)$ K using a PPMS (Physical Property Measurement System, Quantum Design) instrument at applied magnetic fields B=0 and 14 T. This technique is based on a relaxation method, which was critically assessed by Lashley et al. [14]. The contributions of the sample platform, wires, and grease were deduced by a separate measurement of an addenda curve. Based on the experience acquired on this instrument with standard materials and other compounds, the uncertainty was estimated at about 1% from 100 to 300 K, and reaching about 3% at the lowest temperatures [14].

3. Results and discussion

3.1. Structural refinement of Cs_2MoO_4 and $Cs_2Mo_2O_7$ from neutron diffraction data

Cs_2MoO_4 shows an orthorhombic symmetry at room temperature