The Third Law Entropy of Strontium Molybdates

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The heat capacities, \( C_{pm} \), for SrMoO$_4$ at 200-300 K were measured by the relaxation method. The third law entropy, \( S_m \), and the Debye temperatures, \( \theta_D \), were determined from the measured \( C_{pm} \). The obtained thermodynamic properties were: \( S_m(SrMoO_4(cr), 298.15 \, K) / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 136.56 \pm 1.37; \theta_D(SrMoO_4(cr))/K = 373 \pm 6 \). Such thermodynamic properties can be used for evaluating the hierarchy for formation of the yellow phase related-substances in the nuclear waste glasses. [doi:10.2320/matertrans.M2014470]

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1. Introduction

The radio-active components in the nuclear fuel wastes from operated nuclear reactors for generation of electric power have been immobilized predominantly in an alkali borosilicate glass matrix. The nuclear fuel wastes are processed in three steps: (1) They are dissolved in a concentrated aqueous of nitric acid; (2) uranium and plutonium are separated by extraction from the aqueous solution; (3) the remaining liquid after uranium and plutonium are removed is high-level waste, containing used fuel in the form of fission products and minor actinides (Np, Am, Cm) as well as structural materials from the nuclear fuel cell. It is conditioned by calcining and incorporation of the dry material into borosilicate glass.1-7) The waste glass is generally planned to be enclosed in an artificial barrier composed of steel, cement and bentonite, and to be disposed by burying it 300 m underground. However, direct contact between high level nuclear waste glasses and ground water is assumed to be unavoidable due to collapse of such an artificial barrier over thousands of years and unpredictable natural disasters such as the earth’s crustal movements.

Molybdenum is generated as fission product from uranium in the operating nuclear reactor. It is a harmful element as it forms hygroscopic crystals called yellow phase in the borosilicate nuclear waste glass. The host crystal of the yellow phase is A$_2$MoO$_4$ (A: alkaline metals)3-5,7) and CaMoO$_4$5-7) depending on the composition and process for the waste glass.3-7) There is immiscibility in alkali silicate3) and alkali borosilicate glasses.9) Molybdenum oxide in the borosilicate glass expands the compositional range and elevates the temperature of immiscibility,1-5,7,10) this means that it is precipitating in the sodium- and boron-rich region of the glass matrix.11) Hyatt et al.3) clarified that molybdenum forms predominantly the tetrahedral MoO$_4^{2-}$ species in the glass which is not immobilized within the polymeric borosilicate network, instead is likely to be located in extra-framework cavities, together with network modifier cations such as Na$^+$ and Ca$^{2+}$. Therefore, the yellow phase appears to be crystallized as the equilibrium phase resulting from the reaction among MoO$_4^{2-}$ species and cations such as Na$^+$ and Ca$^{2+}$.1-3,6) In order to understand the phase stability of the yellow phases, the thermodynamic properties should be inevitably necessary.

Strontium is the element as fission products and its molybdate SrMoO$_4$ is the end member of the yellow phase. Shukla et al.10) measured the standard enthalpy, \( \Delta_H^{m}_m \), at 298.15 K of SrMoO$_4$ by solution calorimetry. However, its third law entropy, \( S_m \), has not yet been measured. In the present study \( S_m \) at 298.15 K was determined by measuring their heat capacities, \( C_{pm} \), at 200-300 K by the relaxation method11-13) Because a small amount (5-30 mg) of a sample is enough to measure \( C_{pm} \), these methods14-16) can change the sample temperature rapidly. The standard Gibbs energy of formation, \( \Delta_G^{m}_m \), of SrMoO$_4$ at 298.15 K was derived by combining the obtained \( S_m \) with the \( \Delta_H^{m}_m \) by Shukula.10) The hierarchy of the crystallization among such an end-member of the yellow phase, SrMoO$_4$ and transition metal molybdates, NiMoO$_4$ and Zr$_2$MoO$_8$ resulting from components for the nuclear fuel cell constituents was discussed on the basis of their \( \Delta_G^{m}_m \) data.

2. Experimental

2.1 Starting materials

Commercial powder of SrMoO$_4$ (99.9%, Johnson Matthey Co, UK) was used as the starting materials. Each powder was pressed in a steel die with 1.2 MPa to form powder compacts (φ10 × 5 mm). The powder compacts were sintered by heating up to 1073 K with 10 K·min$^{-1}$ held for 2 h. The X-ray diffraction (XRD) patterns confirmed that the sintered bodies are composed of the mono-phase. The samples were submitted to the \( C_{pm} \) measurement.

2.2 Low temperature \( C_{pm} \)

The heat capacities for SrMoO$_4$ were measured in the temperature range 200-300 K by using a relaxation method instrument (model PPMS, Quantum Design, San Diego, CA).11-13) The samples were attached on a sample platform made from alumina with grease (ASTM standard N-grease). The fine heater wire and thermal relaxation wire are attached to the sample platform. Both wires were made from a gold-based alloy. The sum of the heat capacities of the sample and…

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sample platform, \( C_{p,m}^{\text{sample+platform}} \), was given from the thermal relaxation through the wire.

\[
C_{p,m}^{\text{sample+platform}} \frac{dT}{dt} = K_w(T - T_0) + P(t) \tag{1}
\]

Where \( K_w \) is the thermal conductance of the wire, \( T \) and \( T_0 \) are the temperature of the sample and the thermal bath, respectively, and \( P(t) \) is the power applied by the heater. For each measurement, initially the heat capacity of the platform coated with a grease, \( C_{p,m}^{\text{platform}} \), was measured, and then the sum of the heat capacity of the sample and platform, \( C_{p,m}^{\text{sample+platform}} \), was measured. The sample heat capacity, \( C_{p,m}^{\text{sample}} \), was determined by subtracting \( C_{p,m}^{\text{platform}} \) from \( C_{p,m}^{\text{sample+platform}} \). Two samples (\( \pm 2.5 \times 2.5 \times 1 \text{ mm} \)) were prepared by polishing the sintered bodies. Three series measurements were carried out for each sample. The average of the six series, i.e. sum of each three series was adopted as the result. The uncertainty of the measured \( C_{p,m}^{\text{sample}} \) values of six series were evaluated on the basis of the Guide to the Expression of Uncertainty in Measurement.\(^{(17,18)} \)

The measured \( C_{p,m}^{\text{sample}} \) values were evaluated by the recent Debye-Einstein-Schottky formula\(^{(19-22)} \)

\[
C_{p,m}^{\text{sample}} = 3R \left\{ mD \left( \frac{\Theta_D}{T} \right) + nE \left( \frac{\Theta_E}{T} \right) \right\} + X_1 \cdot R \left\{ nS \left( \frac{\Theta_S}{T} \right) \right\} \\
+ (1 - X_1) \cdot \left( A_1T + A_2T^2 \right) \\
+ X_2 \cdot \left( B_1T + B_2T^2 \right) \tag{2}
\]

where \( R \) is gas constant (\( \approx 8.3145 \ [\text{J K}^{-1} \text{mol}^{-1}] \)), \( T \) is absolute temperature, \( X_1 \) and \( X_2 \) are parameters defined from the following switch function\(^{(20)} \)

\[
X_1 = 0.5 \times \{ 1 - \tan h(\alpha T - 200) \} \tag{3}
\]

\[
X_2 = 0.5 \times \{ 1 - \tan h(\beta T - 20) \} \tag{4}
\]

that the parameter \( X_1 \) switches\(^{(20)} \) the second term: \( R \left\{ nS \left( \frac{\Theta_S}{T} \right) \right\} \) off and third term: \( (A_1T + A_2T^2) \) on with a sharpness controlled by \( \alpha \) at 200 K as well as the parameter \( X_2 \) switches fourth term: \( (B_1T + B_2T^2) \) off with a sharpness controlled by \( \beta \) at 20 K. \( \Theta_D \), \( \Theta_E \) and \( \Theta_S \) are the Debye, Einstein and Schottky temperatures, being used for adjustable parameters. \( m, n \), and \( n_S \) are adjustable parameters. Sum of \( m \) and \( n \) should be closed to the number of atoms in the chemical formula of SrMoO\(_4\), that is, six. \( A_1 \) and \( A_2 \) as well as \( B_1 \) and \( B_2 \) are adjustable parameters to fit difference between \( C_{p,m}^{\text{sample}} \) and isochoric heat capacity, \( C_{v,m}^{\text{sample}} \), as well as to fit electronic terms.\(^{(17,18)} \) \( D(\Theta_D/T) \) and \( E(\Theta_E/T) \) are the Debye and Einstein functions, respectively, defined as eqs. (5) and (6), respectively.\(^{(23,24)} \)

\[
D(\frac{\Theta_D}{T}) = \frac{12}{(\Theta_D/T)^3} \int_0^{\Theta_D/T} x^3 \frac{e^x - 1}{e^x - e^{\Theta_D/T}} dx - 3 \frac{\Theta_D}{e^{\Theta_D/T} - 1} \tag{5}
\]

\[
E(\frac{\Theta_E}{T}) = \left( \frac{\Theta_E}{T} \right)^2 \exp(\frac{\Theta_E}{T}) \tag{6}
\]

\( S(\frac{\Theta_S}{T}) \) is a tw-level Schottky function\(^{(21)} \) with the degeneracies of both levels set equal to one, defined as eq. (7).

\[
S \left( \frac{\Theta_S}{T} \right) = \left( \frac{\Theta_S}{T} \right)^2 \frac{1}{2 \cos h \left( \frac{\Theta_S}{2T} \right)} \tag{7}
\]

The Debye heat capacity, \( C_{V,m}^{\text{Debye}} \), and the Einstein heat capacity, \( C_{V,m}^{\text{Einstein}} \), are defined as eqs. (8) and (9), respectively.\(^{(23,24)} \)

\[
C_{V,m}^{\text{Debye}} = 3R \times D \left( \frac{\Theta_D}{T} \right) \tag{8}
\]

\[
C_{V,m}^{\text{Einstein}} = 3R \times E \left( \frac{\Theta_E}{T} \right) \tag{9}
\]

Kelly and King\(^{(23)} \) developed a method to estimate \( C_{p,m}^{\text{sample}} \) below 50 K from \( C_{p,m}^{\text{sample}} \) measured about 50 K by combining \( D(\Theta_D/T) \) and \( E(\Theta_E/T) \). However, for reproducing the experimental data measured from very low to high temperatures, the evaluation by the recent formula given by eq. (2) is inevitably necessary.\(^{(19-22)} \)

At very low temperatures, \( C_{V,m} \) can be approximately expressed as eq. (10) due to that almost phonons occupy near ground states,\(^{(25)} \) where \( n \) is the number of atoms in the formula unit.

\[
C_{V,m} = n \frac{12\pi^4 R}{5} \left( \frac{T}{\Theta_D} \right)^3 \tag{10}
\]

Consequently at low temperatures \( \Theta_D \) should independent of \( T \):

\[
\Theta_D = \frac{12\pi^4}{5} n^{1/3} \left( \frac{C_{V,m}}{R} \right)^{-1/3} \tag{11}
\]

Since \( C_{V,m} \) and \( C_{p,m}^{\text{sample}} \) are very similar at very low temperatures,\(^{(26)} \) \( \Theta_D \) was determined from the values of \( C_{p,m}^{\text{sample}} \) and \( T \) which satisfied the relationship by eq. (11).

Their third law entropy, \( S_m^{\text{SrMoO}_4} \), at 298.15 K is defined as eq. (12).

\[
S_m^{\text{SrMoO}_4}(298.15 \text{ K}) = \int_0^{298.15} \frac{C_{p,m}^{\text{SrMoO}_4}}{T} dT \tag{12}
\]

\( C_{p,m}^{\text{SrMoO}_4} \)'s below 2 K were negligibly small. Therefore, \( S_m^{\text{SrMoO}_4} \) were determined from the Debye-Einstein-Schottky function fitted to \( C_{p,m}^{\text{sample}} \)'s over 2 K in the present study.

The entropy of formation, \( \Delta S_m^{\text{SrMoO}_4} \), of SrMoO\(_4\) at 298.15 K defined as

\[
\Delta S_m^{\text{SrMoO}_4}(298.15 \text{ K}) = \int_0^{298.15} \frac{C_{p,m}^{\text{SrMoO}_4}}{T} dT - \int_0^{298.15} \frac{C_{p,m}^{\text{Sr}}}{T} dT \\
- \int_0^{298.15} \frac{C_{p,m}^{\text{Mo}}}{T} dT - 2 \times \int_0^{298.15} \frac{C_{p,m}^{\text{O}}}{T} dT \tag{13}
\]

where the \( S_m\)'s values for the elements were referred from the related data book for Sr(cr),\(^{(27)} \) O\(_2\)(g)\(^{(28)} \) and Mo(cr).\(^{(28)} \)

Enthalpy change as a function of temperature from 298 K, \( H_m^{\text{SrMoO}_4} - H_m^{\text{SrMoO}_4} \), was given by

\[
H_m^{\text{SrMoO}_4} - H_m^{\text{SrMoO}_4} = \int_{298.15}^{T} \frac{C_{p,m}^{\text{SrMoO}_4}}{T} dT \tag{14}
\]
In our previous study, and the reference ones were found to be less than 0.7 was observed up to 4.888 K (23.894 K²). Equation (11) can for SrMoO₄. The linear relationship between (Zn₃⁻¹) and NiO⁻³ were measured and compared with the standard data. About 300 K, vibration. About 300 K, (\theta_D) was adopted as the final Debye temperature: \theta_D = 373 ± 6 K. The error of \theta_D was estimated that the error of C_p,m's at very low temperatures are assumed to be 5%.

3. Results and Discussion

Figure 1 shows the measured C_p,m values for SrMoO₄ at 200-300 K. They were found to be closed to zero as a function of temperature, following the thermodynamic third law. Over 20 K, it increased rapidly due to active lattice vibration. About 300 K, C_p,m were found to follow Neumann Kopp's rule.

Tables 1 and 2 shows the measured C_p,m values for SrMoO₄ and the error budget table. The uncertainties of the present measurements, \sigma(C_p,m), were evaluated as percent of twice of \sigma(C_p,m) against C_p,m to obtain 95% reliability on the basis of GUM. The biases between the measured values and the reference ones were found to be less than 0.7% over 100 K and 1.7% at 50 K. The present statistical \sigma(C_p,m) indicating from 0.24 to 0.79% appears to be correlated with such biases from the standard reference data.

Figure 2 shows the relationship between (C_p,m/T) and T² for SrMoO₄. The linear relationship between (C_p,m/T) and T² was observed up to 4.888 K (23.894 K²). Equation (11) can be re-written as eq. (11'), meaning that \theta_D can be calculated at very low temperatures at which \theta_D is in proportion to T²:

$$\frac{C_{p,m}}{T} = \frac{12\pi^4 R}{5} \theta_D^{-3} T^2$$

\(T\) | \(C_{p,m}\) [J K⁻¹ mol⁻¹] | \(C_{p,m}\) [J K⁻¹ mol⁻¹] | \(C_{p,m}\) [J K⁻¹ mol⁻¹]
---|---|---|---
2.01 | 0.002 | 67.24 | 38.20 | 186.49 | 93.56
2.27 | 0.003 | 71.72 | 41.47 | 190.96 | 94.81
2.52 | 0.004 | 76.18 | 44.63 | 195.43 | 95.88
2.77 | 0.005 | 80.63 | 47.61 | 199.90 | 97.05
3.02 | 0.006 | 84.66 | 50.20 | 204.36 | 98.20
3.23 | 0.007 | 89.14 | 52.96 | 208.82 | 99.35
3.44 | 0.009 | 93.61 | 55.75 | 213.31 | 100.54
3.65 | 0.011 | 98.09 | 58.29 | 217.31 | 101.47
3.86 | 0.013 | 102.55 | 60.78 | 221.77 | 102.57
4.06 | 0.015 | 107.01 | 63.14 | 226.23 | 103.48
4.27 | 0.017 | 111.47 | 65.53 | 230.69 | 104.28
4.48 | 0.020 | 115.94 | 67.74 | 235.16 | 105.30
4.68 | 0.023 | 120.41 | 69.8 | 239.63 | 106.12
4.89 | 0.027 | 124.88 | 71.78 | 244.10 | 107.24
7.56 | 0.101 | 129.80 | 73.63 | 248.56 | 107.95
10.00 | 0.247 | 133.36 | 75.33 | 253.16 | 108.67
14.99 | 0.970 | 137.83 | 77.25 | 257.52 | 109.38
21.27 | 3.078 | 142.30 | 79.23 | 261.50 | 110.41
26.31 | 5.776 | 146.76 | 81.93 | 265.96 | 111.25
31.35 | 9.244 | 151.23 | 84.52 | 270.42 | 111.77
36.37 | 13.0 | 155.70 | 87.44 | 274.88 | 112.91
40.41 | 16.48 | 160.16 | 88.52 | 279.34 | 113.52
44.88 | 20.30 | 164.62 | 89.53 | 283.81 | 114.45
49.36 | 24.05 | 169.09 | 89.53 | 288.28 | 115.03
53.83 | 27.72 | 173.11 | 89.53 | 292.74 | 115.77
58.29 | 31.33 | 177.57 | 89.53 | 297.19 | 116.09
62.76 | 34.79 | 182.03 | 89.53 | 301.70 | 117.08

Table 2 The standard deviations, \sigma(C_p,m), of the six times measured heat capacities and the uncertainty, \sigma(C_p,m), of the C_p,m data for SrMoO₄ in the present study.

\(T\) [K] | \(\sigma(C_p,m)\) [J K⁻¹ mol⁻¹] | \(\sigma(C_p,m)*\) [%]
---|---|---
53.83 | 0.11 | 0.79
102.55 | 0.15 | 0.49
151.23 | 0.21 | 0.51
204.35 | 0.12 | 0.37
253.02 | 0.29 | 0.54
297.19 | 0.41 | 0.71

\(\sigma(C_p,m)* = 2\sigma(C_p,m)/C_p,m \times 100\%\).
Debye-Einstein-Schottky function reproduce well the experimental $C_p,m$'s. For SrMoO$_4$, not only Debye and Einstein functions but also the Schottky function was necessary to reproduce the experimental $C_p,m$ data, being similar to SiO$_2$ molecular sieve.$^{21}$

The third law entropy, $S_m^0$, at 298.15 K were determined from integral of the present Debye-Einstein-Schottky function as

$$S_m^0(\text{SrMoO}_4\text{(cr)}, 298.15 \text{ K}) = 136.56 \pm 1.37 \text{ [J K}^{-1} \text{ mol}^{-1}]$$

The integral uncertainty, $\sigma_{int}$, to $S_m^0$ was unknown. Judging from the $\sigma_c(\text{C}_p,m)$ data evaluated as 0.24–0.79% as shown in Table 2, the uncertainty of the third law entropy, $\sigma_c(S_m^0)$, was assumed to be 1% in the present study.

The standard entropy of formation, $\Delta_f S_m^0$, was determined based on the elements: Strontium(cr) ($= 55.700 \pm 0.210$ [JK$^{-1}$mol$^{-1}$]$^{22}$); Oxygen(g) ($= 205.152 \pm 0.005$ [JK$^{-1}$mol$^{-1}$]$^{22}$); Molybdenum(cr) ($= 28.605$ [JK$^{-1}$mol$^{-1}$]$^{28}$),

$$\Delta_f S_m^0(\text{SrMoO}_4\text{(cr), 298.15 K}) = -358.05 \pm 1.39 \text{ [J K}^{-1} \text{ mol}^{-1}]$$

Table 3 summarized the thermodynamic functions as a function of temperature for SrMoO$_4$.

Shukla $et al.$ determined the enthalpies of formation, $\Delta_f H_m^0$, at 298.15 K of SrMoO$_4$ by the solution calorimetry as $-1543.8 \pm 3.6$ [kJ mol$^{-1}$]. Combining $\Delta_f H_m^0$ by Shukla $et al.$ with the $\Delta_f S_m^0$ obtained in the present study, the standard Gibbs energies of formation, $\Delta_f G_m^0$, at 298.15 K was determined as

$$\Delta_f G_m^0(\text{SrMoO}_4\text{(cr), 298.15 K}) = -1437.05 \pm 3.60 \text{ [kJ mol}^{-1}]$$

Hierarchy of crystallization in the nuclear fuel waste glasses was discussed on the basis of the $\Delta_f G_m^0$ of SrMoO$_4$ as well as the related transition metal molybdates, NiMoO$_4$, and Zr$_2$MoO$_6$. Ni is element for the heat resistant alloys for the nuclear fuel cell constituents. Zr is main component of the nuclear fuel cell.

Their hierarchy can be evaluated from the standard Gibbs energies of reaction, $\Delta_r G_m^0$, of eqs. (20) and (21).

![Graph](image)

**Fig. 2** $C_p,m^{-1}$ vs. $T^2$ for SrMoO$_4$ at very low temperature range.
concluded to be hardly depressed by the addition of the transition metal molybdates such as NiMoO$_4$ and ZrMo$_2$O$_8$ from view of equilibrium theory. Therefore, during waste glass making, enough cooling rate to immobilize the ionic species for the yellow phase in glass structure as quasi-equilibrium state should be kept for depressing crystallization of the yellow phase.

4. Conclusion

The heat capacities, $C_p,m$, for SrMoO$_4$ at 200-300 K were measured by the relaxation method. The third law entropy, $S_m$, and the Debye temperatures, $\Theta_D$, were determined from the measured $C_p,m$. The standard Gibbs energy of formation, $\Delta G_m$, was determined by combining the present $S_m$ with the reference datum of the standard enthalpy of formation, $\Delta H_m^\circ$. The obtained thermodynamic properties were: $S_m$(SrMoO$_4$(cr), 298.15 K)/J K$^{-1}$ mol$^{-1}$ = 136.56 ± 1.37; $\Delta H_m^\circ$(SrMoO$_4$(cr), 298.15 K) = −358.05 ± 1.38; $\Theta_D$(SrMoO$_4$(cr))/K = 373 ± 6; $\Delta G_m$(SrMoO$_4$(cr), 298.15 K)/kJ mol$^{-1}$ = −1437.05 ± 3.62. Hierarchy of crystallization in the nuclear fuel waste glasses was discussed on the basis of the $\Delta G_m$ of SrMoO$_4$ as well as the related transition metal molybdates, NiMoO$_4$, and Zr$_2$MoO$_8$. The end-member of the yellow phase SrMoO$_4$ was more stable than the transition metal molybdates NiMoO$_4$ and Zr$_2$MoO$_8$. Therefore, during waste glass making, enough cooling rate to immobilize the ionic species for the yellow phase in glass structure as quasi-equilibrium state should be kept for depressing crystallization of the yellow phase.

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