The low temperature heat capacity of Li₂Mo₀.₀₅W₀.₉₅O₄

A E Musikhin *, ¹, M A Bespyatov ¹, T M Kuzin ¹, V D Grigorieva ¹, V N Shlegel ¹

¹ Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia

* E-mail: musikhin@niic.nsc.ru

Abstract. The heat capacity of a lithium tungstate single crystal doped by 5% molybdenum Li₂Mo₀.₀₅W₀.₉₅O₄ in the range of 78.₅–3₀₂.₈ K was measured by the adiabatic method. No anomalous behavior of heat capacity was found. The heat capacity function was obtained in the range of 0–3₀₃ K by extrapolating to zero temperature and fitting experimental points. Thermodynamic functions of entropy, enthalpy increment and Gibbs free energy at 2₉₈.₁₅ K were calculated using the obtained data.

1. Introduction

Lithium molybdate and lithium tungstate are promising materials for various practical applications. They possess luminescent and scintillation properties [1–4]. Such properties allow their use as optical elements of various equipment, including as cryogenic phonon-scintillation detectors for the search of neutrinoless double beta decay [5–7]. Numerous studies of Li₂MoO₄, including its structural, optical, scintillation, and thermodynamic characteristics, are presented in the literature. Li₂MoO₄ crystals of sufficient size to make bolometers for 0ν2β-decay searching experiments have been grown by the low thermal gradient Czochralski technique [6]. However, the isostructural compound, Li₂WO₄, has not yet been fully investigated. Until recently, it was assumed that Li₂WO₄ could not be grown by the Czochralski method due to the presence of a high-temperature phase transition. Therefore, a series of works on growing Li₂WO₄ doped with molybdenum [5,8,9], which showed the possibility of obtaining crystals with molybdenum content from 15 to 2.₅%. Currently, the low-temperature heat capacity of lithium molybdate has been studied [10]. Also, high-temperature Li₂Mo₀.₆₆W₁₋₉₄O₄ heat capacity data obtained by DSC method [9] and enthalpy measurements of Li₂WO₄ and Li₂MoO₄ above 4₀₀ K [11] are given in the literature. But the low-temperature heat capacity data for Li₂Mo₀.₆₆W₁₋₉₄O₄ and Li₂WO₄ is absent. This paper shows for the first time the results of the low-temperature heat capacity study of lithium tungstate doped with molybdenum.

2. Experimental

2.1. Sample

We needed a high quality sample with constant structure throughout the crystal with a molybdenum inclusion value that makes a significant contribution to the heat capacity. This will allow further analysis of the heat capacity of the studied compound in comparison with Li₂WO₄ and Li₂MoO₄ in order to identify any features or patterns associated with molybdenum doping. At the same time, this contribution of molybdenum does not give difficulty in growing a single crystal of homogeneous structure [8]. The Li₂Mo₀.₀₅W₀.₉₅O₄ single crystal was grown by the low thermal gradient Czochralski technique.
technique [12]. Deeply purified WO₃ and MoO₃ [13], and commercial high purity Li₂CO₃ were used as the initial reagents. As a result, a transparent single crystal without optical defects was obtained. The crystal structure belongs to the structural type of phenacite, space group R3. According to the results of quantitative chemical analysis, the sample purity is not less than 99.99%.

2.2. Measurement of heat capacity

A vacuum adiabatic calorimeter assembled at the NIIC SB RAS [14] was used to measure the heat capacity. The obtained data reliability is confirmed by heat capacity measurements of a standard substance (benzoic acid), characterizing the uncertainty of setup calibration. The deviation from standard data [15] in the temperature range from 80 to 300 K is 0.15%. The calorimetric ampoule temperature is measured with a platinum resistance thermometer; the standard temperature uncertainty corresponds to 0.01 K. A dismountable nickel calorimetric ampoule was filled by a set of Li₂Mo₀.₀⁵W₀.₉⁵O₄ crystals with a typical size of about 5 mm in diameter and vacuumed at room temperature. The mass of the sample was 18.471 g. Then, to improve the heat exchange, the calorimetric ampoule was filled with a small amount of gaseous helium (p = 1.0 kPa) and sealed. The molar mass used to represent the heat capacity corresponds to the chemical formula and is equal to 257.33 g mol⁻¹. The heat capacity was measured at 52 points in the range of 78.5–302.8 K. The results are shown in Figure 1. Analysis of the experimental data did not reveal any anomalies in the behavior of the heat capacity.

![Figure 1. The experimental molar heat capacity of Li₂Mo₀.₀⁵W₀.₉⁵O₄.](image)

3. Results and discussion

3.1. Extrapolation to zero temperature

To calculate integral thermodynamic functions of entropy, enthalpy and others it is necessary to have information about the heat capacity from 0 to 78 K. As a rule, to describe the lattice component of the heat capacity near 0 K we use the Debye T³ law [16], Debye function [16] or a combination of Debye and Einstein functions [17,18]. In our case, the experimental heat capacity is known at higher temperatures, so other approximations must be used. In this work, we used an equation describing the heat capacity of solids over a wide range of temperatures [19,20], which can be used when extrapolating experimental data on heat capacity to zero temperature:

\[
\frac{C_V(T)}{3Rn} = C(T) = \left( (aT)^{-\alpha \beta} + 1 \right)^{-\frac{1}{\alpha}},
\]

where α and β are dimensionless parameters which can be determined from the experiment; R is the universal gas constant; n is the number of atoms in a molecular formula. The parameter a characterizes the tangent of the slope of the function in the linearized Y(T) coordinates:
\[ Y(T) = (C^{-\alpha} - 1)^{-\frac{1}{\beta}} = aT. \] (2)

This equation well describes the lattice heat capacity in the entire temperature region for simple compounds whose phonon density of states can be represented in the single-peak approximation. In our case, the density of states of the isostructural Li$_2$MoO$_4$ compound (and \( g(\omega) \) of the studied compound, respectively) has a complex three-peak form [21]. Therefore, the applicability of the method to the Li$_2$MoO$_4$ data was preliminarily evaluated. It was found that within the equation (1) the heat capacity from zero to high temperatures is not described satisfactorily; it is necessary to select three temperature intervals, which when described independently give good results. The intervals roughly correspond to temperature intervals: below 30–40 K; from 30–40 to 75–95 K; and from 75–95 to 270–280 K. Given the small values of the heat capacity in the range below 30 K, equation (1) can be used to extrapolate experimental data to zero temperatures. The corresponding uncertainty of heat capacity will give a small contribution to the thermodynamic functions at standard temperature.

A description of the experimental points for Li$_2$MoO$_4$ and extrapolation to zero for Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ in the range of 0–95 K was made. The found parameters correspond to the minimum of the sum of squared deviations in the linearized coordinates (2); they are given in Table 1. It should be noted that the parameters \( \alpha \) and \( \beta \) for isostructural compounds should be close, as we observe (Table 1). This confirms that the Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ heat capacity description below 78 K is correct. The results are shown in Figure 2. The relative standard uncertainty of the Li$_2$MoO$_4$ heat capacity description is 0.6 at \( T \leq 22 \) K; 0.05 at 22 K < \( T \leq 63 \) K and 0.0029 at 63 K < \( T \leq 95 \) K. Based on these data, an estimate of the uncertainty in the calculation of the thermodynamic functions for Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ will be made.

**Table 1.** Coefficients \( \alpha, \beta \) and \( a \) of equation (1) that give the best description of the experimental data in the interval from \( T_1 \) to \( T_2 \), and the corresponding standard \( \sigma \) and relative standard \( \sigma_r \) deviations.

| Parameter | Li$_2$MoO$_4$ | Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ | Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ |
|-----------|---------------|-------------------------------|-------------------------------|
| \( \alpha \) | 0.689 | 0.671 | 1.628 |
| \( \beta \) | 1.90 | 1.90 | 1.29 |
| \( a \) | 8.13·10$^{-3}$ | 8.45·10$^{-3}$ | 4.26·10$^{-3}$ |
| \( T_1 \) | 20.4 K | 78.5 K | 78.5 K |
| \( T_2 \) | 94.9 K | 94.8 K | 271.3 K |
| \( \sigma(C_p) \) | 0.4 (0.12*) | 0.03 | 0.10 |
| \( \sigma_r(C_p) \) | 0.05 (0.0028*) | 0.0007 | 0.0015 |

* for an interval of 78.7–94.9 K.

**Figure 2.** The heat capacity of Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ (blue) and Li$_2$MoO$_4$ (magenta) in \( Y(T) \) (left) and \( C_p(T) \) (right) coordinates: circles – experimental dots, lines – calculated function.
3.2. Experimental heat capacity description

Smoothing of the experimental data of Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ was done in two ways. The first one is a description within the Equation (1). The best result was obtained in the temperature range of 78.5–271.3 K with the parameters given in Table 1; the relative standard uncertainty is 0.0015. Above 271.3 K, the experimental points systematically deviate, which may be due to a significant anharmonic contribution (Figure 3).

Figure 3. The molar heat capacity of Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ (left) and relative deviation of the experimental values from the calculated functions (right).

As a result, equation (1) did not describe all points of the experimental curve, so we used the second method. This is a description within a combination of Einstein models [17,22]:

$$\frac{C_p(T)}{3Rn} = C(T) = \sum_{i=1}^{n} A_i C_{E,i}(T),$$  \hspace{1cm} (3)

where $n$ is the parameter determining the number of used terms (from 1 to 4); $A_i$ is the scale factor (the sum of $A_i$ must equal one or be slightly greater); $C_{E,i}(T)$ is the Einstein heat capacity calculated by the formula:

$$C_{E}(T) = \left(\frac{\theta_{E}}{T}\right)^2 \cdot \frac{e^{-\theta_{E}/T}}{\left(e^{-\theta_{E}/T} - 1\right)^2},$$  \hspace{1cm} (4)

where $\theta_{E}$ is the characteristic Einstein temperature. The best result was obtained in the range of 78.5–302.8 K with the parameters given in Table 2; the relative standard uncertainty is 0.0009.

Table 2. Coefficients $n$, $A_i$ and $\theta_{E,i}$ of equation (3) that give the best description of the Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$ experimental data in the interval from $T_1$ to $T_2$, and the corresponding standard $\sigma$ and relative standard $\sigma_r$ deviations.

| Parameter | Value  |
|-----------|--------|
| $n$       | 3      |
| $A_1$     | 0.3200 |
| $\theta_{E,1}$ | 179.7 K |
| $A_2$     | 0.5118 |
| $\theta_{E,2}$ | 571.0 K |
| $A_3$     | 0.2882 |
| $\theta_{E,3}$ | 1379 K |
| $T_1$     | 78.5 K |
| $T_2$     | 302.8 K |
| $\sigma(C_p)$ | 0.09  |
| $\sigma_r(C_p)$ | 0.0009 |
The second way gave a description in the entire experimental region and a smaller standard deviation of the experimental points (Figure 3). Therefore, we consider the description of the heat capacity by equation (3) as a smoothed experimental curve from 81 to 303 K. The result is shown in Figure 3. It should be noted that the description within the equation (3) can be used to extrapolate the heat capacity in some small region of high temperatures.

3.3. Thermodynamic functions
The results of extrapolation heat capacity to zero by equation (1) in the range of 0–81 K and description of experimental points by equation (3) in the range of 81–303 K were used as smoothed dependence of $\text{Li}_2\text{Mo}_{0.05}\text{W}_{0.95}\text{O}_4$ heat capacity $C_{p,m}(T)$. This dependence was used to calculate the thermodynamic functions: entropy $\Delta^0S_{p,m}$, enthalpy increment $\Delta^0H_m$ and Gibbs free energy $\Delta^0G_m$.

Their values under standard conditions ($T = 298.15$ K, $p = 0.1$ MPa) were as follows:

$C_{p,m}^o = 131.4 \pm 0.3$ J mol$^{-1}$ K$^{-1}$,
$\Delta^0_{298.15}S_{p,m}^o = 138 \pm 3$ J mol$^{-1}$ K$^{-1}$,
$\Delta^0_{298.15}H_m = 21.79 \pm 0.11$ kJ mol$^{-1}$,
$\Delta^0_{298.15}G_m = -19.4 \pm 0.7$ kJ mol$^{-1}$ K$^{-1}$.

An expanded combined uncertainty (confidence interval of 95%) of thermodynamic function values, which is due to the scatter of experimental points, the uncertainty in the calibration of the experimental setup, and the uncertainty in the method of extrapolating the heat capacity to zero temperatures, is given.

3.4. Discussion
In the literature there are experimental data [9] obtained by the DSC method in the range of 193–370 K. They are given together with the adiabatic data in Figure 3. It can be seen that they lie lower than our data by 1.2–2.7% at 193–303 K, respectively.

4. Conclusions
The heat capacity of $\text{Li}_2\text{Mo}_{0.05}\text{W}_{0.95}\text{O}_4$ single crystal in the range of 78.5–302.8 K was measured by adiabatic method for the first time. The heat capacity was extrapolated to zero temperature. The uncertainty of the obtained results was evaluated. The thermodynamic functions under standard conditions are calculated. Comparison with the high-temperature data available in the literature and the data for the isostructural compound $\text{Li}_2\text{MoO}_4$ is made.

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