Heat capacity of lithium tungstate single crystal by DSC calorimetry data in the temperature range of 319-997 K

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Abstract. The heat capacity of lithium tungstate single crystal (Li₂WO₄) was measured for the first time in the temperature range of 319-997 K. The experiments were carried out by DSC calorimetry. The Li₂WO₄ single crystal was first grown by low-temperature-gradient Czochralski technique with weight control. The temperature dependence of Li₂WO₄ heat capacity in the temperature range 319-997 K was monotonic. According to results of our studies, there were no phase transitions in Li₂WO₄ in the investigated temperature range.

1. Introduction

Single crystals and ceramics based on lithium tungstate are promising materials for high energy physics, sensors for various purposes, new energetics, etc. [1–3]. In particular, they can be applied to study rare events. The study of elastic coherent scattering of neutrinos on nuclei using single crystals of molybdates and tungstates allows one to create miniature sensors for monitoring the zone of nuclear detectors, new faster methods of transmitting information, etc. The use of perfect single crystals of molybdates and tungstates for these purposes will allow performing experiments with kilograms, not tons. One of the problems in material science of lithium tungstates replaced by molybdenum was the growth of Li₂WO₄ with low molybdenum content. Information on the growing pure single crystal of lithium tungstate is contradictory [1, 4–5].

The aim of this research is to measure the heat capacity of lithium tungstate single crystal in the temperature range of 319–997 K and to reveal the presence or absence of phase transitions.

2. Experimental

Lithium tungstate single crystal was grown by the low-temperature-gradient Czochralski technique (LTG Cz) with weight control using technology described in paper [6]. This modification of Czochralski technique for growing crystals from melt, developed at NIIC SB RAS (Novosibirsk, Russia), is characterized by temperature gradients below 1°C/cm, which are two orders of magnitude lower than in conventional Czochralski technique. Due to low temperature gradients the thermoelastic stresses in growing crystals are significantly reduced that allows obtaining large-size crystals with incongruent melting type, cleavage and other propensities to structure disruption during growth and cooling. Another advantage of LTG Cz is the absence of local overheatings, thus, volatilization of melt components is suppressed, preventing the loss of initial materials and non-stoichiometry of the melt.
Charge for crystal growth was made by stoichiometric mixing of Li$_2$CO$_3$ (LLC “Redmet”, 20-2 TS 6-09-4757-84, 99.99%) and WO$_3$ powders. Li$_2$CO$_3$ and WO$_3$ were additionally purified and annealed at 400°C for 10 h for solid state synthesis. Annealing was carried out in the same platinum crucible and furnace of the puller where growth processes were realized. No additional impurities could be injected in the growth charge in such a way. After solid-state synthesis temperature was increased up to 760°C and kept for 4 h for complete homogenization of the melt. First crystal growth was realized on platinum seed holder, introduced through pipe socket of the lid into the melt in the crucible, to obtain Li$_2$WO$_4$ polycrystals. The oriented crystal seeds were cut out from obtained polycrystals for the following crystal growth. The growth parameters were set by analogy with the Li$_2$MoO$_4$ growth parameters as these crystals possess similar structure and crystallization features; the growth rate was 0.5 mm/h, and the rotation velocity was 5 rev/min. The obtained crystals were transparent, slightly yellowish in bulk volume, had a diameter of 25 mm and a length of 50 mm. Li$_2$WO$_4$ single crystal didn’t exhibit tendency to structure disruption during cooling, though we did observe cracking along cleavage planes under mechanical pressure. Li$_2$WO$_4$ single crystal is presented in figure 1.

![Figure 1. Single crystal of Li$_2$WO$_4$.](image)

The characterization of Li$_2$WO$_4$ single crystal was carried out by X-ray phase analysis. The single crystal had phenakite structure and space group R-3.

The heat capacity of lithium tungstate single crystal is measured by differential scanning calorimetry. The operation principle of differential scanning calorimeters is to measure the temperature difference between the crucible, where the investigated and standard samples are placed in turn, and the empty crucible. This resulting temperature difference, multiplied by the calibration factor determined during the pre-calibration process, is the gauge of heat flux absorbed or emitted by investigated sample during its heating or cooling. A DSC 404 F1 Pegasus calorimeter manufactured by NETZSCH company is applied for measurements. The DSC 404 F1 calorimeter is designed to accurately determine the heat capacity of high quality materials at high temperatures. Due to design of heating system, the baseline stability and high reproducibility are achieved. The Proteus software under Windows is used in DSC 404 F1. Proteus software includes everything to perform measurements and process the data.

For optimizing the baseline, a micrometer adjustment system is integrated into the measurement part. This adjustment system allows placing the sensor at the optimum central position in the furnace. This guarantees a stable and reproducible baseline without any major adjustment efforts.

For the calibration of temperature, enthalpy and specific heat capacity in the high temperature range, multiple sets containing different calibration materials are available for various crucible materials. The calibration materials are selected and prepared for measurement in accordance with the recommendations of the corresponding standards.

3. Results and discussion
Platinum crucibles with platinum lids were used to measure the heat capacity of Li$_2$WO$_4$ single crystal. Platinum crucibles were supplied by corundum inserts. Sapphire (weight 85.28 mg), the heat capacity of which is well known, was used as calibration sample. The heating and cooling rates of sample were chosen in such a way to provide precise measurements of the heat capacity. The heating and cooling
rate was 6 K/min. The measurements were carried out in an argon flow (20 ml/min). Detailed information on measurement procedure is presented in papers [7-9]. The argon purity was 99.992 vol. %. The sample mass was weighed on AND GH-252 electronic balance with uncertainty of no more than 0.3 mg and was 113.58 mg. Three thermal cycles for Li₂WO₄ single crystal were carried out. Before carrying out each thermal cycle, the working volume of the calorimeter was evacuated up to 1 Pa and washed several times with argon. To carry out measurements, the special sample was prepared as cylinder with sizes ∅ 5 x 1.5 mm². The measurement uncertainty of calorimeter was estimated to be 2-3%, which was confirmed by experiments with high purity platinum and sapphire.

The data obtained in the second and third cycles are in a good agreement with each other. The results for the first heating are different. This is due to the fact that the sample is annealed during the first heating. In this case, stress relief and removal of adsorbed compounds from the surface occur. The mass of Li₂WO₄ single crystal after the first heating decreases by 0.25% and is 113.30 mg. After the second and third heating, the mass of sample does not change. The data on heat capacity of Li₂WO₄ single crystal based on results of third heating are presented in figure 2.

![Figure 2](image_url)

**Figure 2.** Heat capacity of Li₂WO₄ single crystal from temperature.

As can be seen, the temperature dependence of the heat capacity of lithium tungstate single crystal is monotonic. This means that according to our experiments, there are no phase transitions in the temperature range of 320–997 K.

Temperature data on the heat capacity of third heating for lithium tungstate single crystal are entered and approximated using APROC program, included in software package for Databank of Electronic Technique Materials Properties (DB ETMP). The experimental data are well approximated by cubic polynomial (J/K mol): $C_p = 60.437 + 0.33238 T - 3.4002 \times 10^{-4} T^2 + 1.4171 \times 10^{-7} T^3$.

The deviation of smoothed heat capacity values from experimental values is no more than 1%.

The heat capacity of lithium tungstate single crystal is entered in DB ETMP. Then, on the basis of DB ETMP programs, using the spline function approximation, the thermodynamic functions are calculated for lithium tungstate single crystal in the temperature range of 319–997 K: $H(T) - H(298.15)$, $S(T) - S(298.15)$. The programs for calculations are described in detail in papers [10, 11].
In paper [12], the enthalpies of ceramic lithium tungstate were determined by the drop method in an ice calorimeter. Enthalpy values were smoothed as polynomials by the least squares method. The heat capacity was derived from enthalpy curves.

Let us compare the heat capacity measured for Li$_2$WO$_4$ single crystal with heat capacity of ceramic lithium tungstate, measured by the drop calorimetry [12]. Figure 3 shows values of the heat capacity measured in our research and in paper [12].

![Figure 3. Lithium tungstate heat capacity of our research and paper [12].](image)

As can be seen from figure 3, the results of both research works are in a good agreement within 1%, which is at the level of measurement uncertainty of both methods. This good agreement evidences the reliability of data obtained by DSC method in our research and by the drop calorimetry method in paper [12].

Data on phase transitions for lithium tungstate are contradictory. Here is some information about phase transitions for Li$_2$WO$_4$ compound. In paper [13] it is reported that at room temperature, ceramic Li$_2$WO$_4$ having a phenakite structure is thermodynamically unstable, however, the phase transition is very slow and takes more than one month. Paper [14] reports about phase transition in ceramic Li$_2$WO$_4$, proceeding at temperature 640°C according to the data of differential thermal analysis. However, only one heating was performed, and this effect could be due to the sample annealing. Further research is needed to understand whether lithium tungstate is thermodynamically stable or metastable.

**Conclusions**

In our research, the heat capacity of lithium tungstate single crystal has been measured for the first time by differential scanning calorimetry in the temperature range of 320–997 K. The temperature dependence of the heat capacity of lithium tungstate single crystal is monotonic. According to our experiments, there are no phase transitions in lithium tungstate in the temperature range of 320–997 K. The data obtained on heat capacity of lithium tungstate single crystal are in a good agreement with data on heat capacity of ceramic lithium tungstate, measured earlier by the drop calorimetry.
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