Thermodynamic properties of single crystals based on lithium tungstate by reaction and DSC calorimetry

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Abstract. For the first time, single crystals of undoped lithium tungstate and lithium tungstate doped by 1.25% molybdenum were grown by the low-temperature-gradient Czochralski technique. The standard formation enthalpies, lattices enthalpies, stabilization energies, and the heat capacity were determined in the temperature range of 320-997 K. The lattice enthalpy dependence on Mo content was constructed.

1. Introduction

Molybdates and tungstates of the first and second groups are promising materials for high-energy physics and new energetics [1-5]. In particular, to search for rare events, such as double neutrinoless beta decay, elastic coherent neutrino scattering, single crystals in lithium molybdate - lithium tungstate system with isotopes $^{100}$Mo, $^{186}$W are widely used. The hypothesis of double neutrinoless beta decay existence was proposed in 1938. However, there is still no experimental confirmation of this hypothesis. In this regard, materials scientists all over the world are faced with the task of growing scintillation single crystals with improved functional characteristics, in particular, with high light output. One of the problems that existed in Li$_2$MoO$_4$-Li$_2$WO$_4$ system until now was the impossibility to grow single crystals of lithium tungstate with low molybdenum doping.

In the present study, single crystals of Li$_2$WO$_4$ and Li$_2$W$_{1.0-0.0125}$Mo$_{0.0125}$O$_4$ were grown for the first time by the low-temperature-gradient Czochralski technique, and their thermodynamic studies were carried out by reaction and differential scanning calorimetry.

2. Experimental

The single crystals of undoped lithium tungstate and lithium tungstate doped by 1.25% molybdenum were grown by the low-temperature-gradient Czochralski technique according to the technology described in detail in paper [6]. The single crystals were grown from deeply purified precursors (Li$_2$CO$_3$, MoO$_3$, WO$_3$). Lithium carbonate (purity > 0.9999), tungsten oxide (purity > 0.9998), molybdenum oxide (purity > 0.9998) were used for growing. The chemical reaction to grow single crystals of Li$_2$WO$_4$ and Li$_2$W$_{1.0-0.0125}$Mo$_{0.0125}$O$_4$ proceeded in a platinum crucible.

For growing Li$_2$W$_{1.0-0.0125}$Mo$_{0.0125}$O$_4$ single crystal, a stoichiometric mixture of starting reagents was placed in a platinum crucible and heated up to 725°C at a rate of 60°C/h, and calcined for 5 h until complete homogenization. The single crystal of Li$_2$W$_{1.0-0.0125}$Mo$_{0.0125}$O$_4$ is presented in figure 1.
To grow Li$_2$WO$_4$ single crystal, precursors were annealing at 400°C for 10 h for solid-state synthesis. After the solid-state reaction, the temperature was increased up to 760°C. Growth parameters were set in analogy with Li$_2$MoO$_4$ growth process parameters [4] as these crystals possess similar structure and crystallization features, the growth rate was 0.5 mm/h, rotation velocity - 5 rev/min. Obtained crystals were transparent, slightly yellowish in bulk volume. The single crystal of Li$_2$WO$_4$ is presented in figure 2.

X-ray, chemical, energy dispersive, and mass spectrometric analyzes were used to characterize single crystals of Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ and Li$_2$WO$_4$. As shown by analysis results, the grown single crystals were individual phases, did not contain impurity phases, had phenakite structure, space group R-3.

The standard formation enthalpies for Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ and Li$_2$WO$_4$ single crystals were determined using an automated solution calorimeter. The detailed design of the calorimeter and experimental procedure were described in papers [3, 7]. To determine the standard formation enthalpies, a thermochemical cycle was designed in such a way that dissolution enthalpies of lithium carbonate, molybdenum oxide, and potassium tungstate were compared with dissolution enthalpies of single crystals. The dissolution was carried out at a temperature of 298.15 K in the aqueous solution of 0.40162 mol kg$^{-1}$ KOH. Further, using obtained experimental data and literature values, the standard formation enthalpies of Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ and Li$_2$WO$_4$ single crystals were calculated. Based on measured standard formation enthalpies, the lattice enthalpies, as well as stabilization energies were calculated.

To determine the heat capacity and find out the existence of phase transitions in Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ single crystal, differential scanning calorimetry was used. The measurements were carried out by DSC 404 F1 Pegasus calorimeter in the temperature range of 320-997 K. The measurement principle and procedure were described in detail in papers [8-9].

3. Results and discussion
Based on dissolution enthalpies of Li$_2$CO$_3$, MoO$_3$, Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$, and Li$_2$WO$_4$ single crystals measured in our research, using literature values, the standard formation enthalpies of Li$_2$WO$_4$ and Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ single crystals were calculated. The standard formation enthalpies of Li$_2$CO$_3$, MoO$_3$, H$_2$O, KOH, K$_2$WO$_4$, and ions (K$^+$, CO$_3^{2-}$) were required to calculate the standard formation
enthalpies of Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ and Li$_2$WO$_4$ single crystals. The values were taken from the reference book [10]. In addition, the dissolution enthalpy of K$_2$WO$_4$ in the aqueous solution of 0.40162 mol kg$^{-1}$ KOH was required. The value was taken from paper [11]. The standard formation enthalpies of Li$_2$WO$_4$ and Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ single crystals obtained in this research were as follows: $\Delta_{f}H^0$(Li$_2$WO$_4$, 298.15 K) = $-1601.1 \pm 2.7$ kJ mol$^{-1}$; $\Delta_{f}H^0$(Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$, 298.15 K) = $-1602.3 \pm 1.9$ kJ mol$^{-1}$. The standard formation enthalpy of ceramic lithium tungstate was determined in paper [10]. Comparison of standard formation enthalpy of Li$_2$WO$_4$ single crystal with that for ceramic lithium tungstate showed that both values were in good agreement.

Further, based on measured standard formation enthalpies of Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ and Li$_2$WO$_4$ single crystals, the lattice enthalpies were calculated. Lattice enthalpies were calculated using Born-Haber cycle and were as follows: $\Delta_{lat}H^0$(Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$, 298.15 K) = $-26150$ kJ mol$^{-1}$; $\Delta_{lat}H^0$(Li$_2$WO$_4$, 298.15 K) = $-26120$ kJ mol$^{-1}$. The formation enthalpies of lithium, molybdenum, tungsten, and oxygen ions were taken from the reference book [10]. Besides, the stabilization energies were calculated as following values: $\Delta_{ox}H^0$(Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$, 298.15 K) = $-162.9 \pm 2.1$ kJ mol$^{-1}$; $\Delta_{ox}H^0$(Li$_2$WO$_4$, 298.15 K) = $-160.5 \pm 2.8$ kJ mol$^{-1}$.

Earlier, we measured the standard formation enthalpies of lithium tungstate single crystals doped by molybdenum, the general formula is Li$_2$W$_{1-x}$Mo$_x$O$_4$, $x = 0.15; 0.1; 0.05; 0.025$. Based on obtained standard formation enthalpies, the lattice enthalpies were calculated for these single crystals. Using these data and lattice enthalpies for Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ and Li$_2$WO$_4$ single crystals obtained in this research, we plotted lattice enthalpy depending on molybdenum content ($x$). The dependence is presented in figure 3.

**Figure 3.** Dependence of lattice enthalpy of Li$_2$W$_{1-x}$Mo$_x$O$_4$ on $x$ (Mo content).

As is seen, the relationship is linear. The linearity of dependence can be explained based on the Kapustinsky formula for lattice energy for compounds with low doping. For compounds with low doping, the lattice energy is a linear function of doping degree, namely, Mo content in our case, which was confirmed by us experimentally.

To measure the heat capacity of Li$_2$W$_{1-0.0125}$Mo$_{0.0125}$O$_4$ single crystal, differential scanning calorimetry was used. The sample was placed in a platinum crucible with a corundum insert and platinum lid. To improve the contact with the crucible, the sample 5 mm in diameter and 1.5 mm thick was cut from the single crystal. Three thermal cycles were carried out. Within uncertainty, the results of the heat capacity measurements for the second and third cycles were in good agreement. The results
of the first cycle differed from those of the second and third cycles, which were related to annealing of the sample and removal of absorbed compounds.

Before each thermal cycle, the working volume of the calorimeter was evacuated up to a vacuum of about 1 Pa and washed several times with argon, whose purity was 99.992 vol. %. Sapphire weighing 85.30 mg was used as a calibration sample. The mass was weighed using AND GH-252 electronic balance with an error of no more than 0.3 mg and was 102.10 mg for Li$_2$W$_{1-x}$Mo$_x$O$_4$. The measurements were carried out at a heating rate of 6 K/min in a flowing argon atmosphere (20 ml/min). The measurement error for this setup was estimated at 2-3%, which was confirmed by experiments with samples of high-purity platinum and sapphire. The temperature dependence of the heat capacity for the third cycle is presented in figure 4.

![Figure 4](image_url)

Figure 4. Temperature dependence of the heat capacity for Li$_2$W$_{1-x}$Mo$_x$O$_4$ single crystal.

As is seen, the temperature dependence of the heat capacity did not have any anomalies. So, there were no phase transitions for Li$_2$W$_{1-x}$Mo$_x$O$_4$ single crystal in the temperature range of 320-997 K, which made this single crystal promising for application. The temperature dependence of the heat capacity of third heating was well described by cubic equation: $C_p,m(T) (\text{J mol}^{-1} \text{K}^{-1}) = 45.569 + 0.402T - 4.491 \cdot 10^{-4}T^2 + 1.8616 \cdot 10^{-7}T^3$.

4. Conclusion

Single crystals of Li$_2$WO$_4$ and Li$_2$W$_{1-x}$Mo$_x$O$_4$ were grown by the low-temperature-gradient Czochralski technique with weight control. The standard formation enthalpies for grown single crystals were measured by reaction calorimetry. The obtained experimental data were used to calculate the lattice enthalpies and stabilization energies. The dependence of the lattice enthalpy on molybdenum content for Li$_2$W$_{1-x}$Mo$_x$O$_4$ single crystals was constructed. It was shown that dependence was linear. The DSC calorimetry was used to measure the heat capacity of Li$_2$W$_{1-x}$Mo$_x$O$_4$ single crystal in the temperature range of 320-997 K. It was shown that there were no phase transitions in the temperature range of 320-997 K for Li$_2$W$_{1-x}$Mo$_x$O$_4$ single crystal. The temperature dependence of the heat capacity of third heating for investigated single crystal was well described by a cubic polynomial.

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