Thermodynamics of single crystals of lithium tungstate with low molybdenum content: heat capacities, enthalpies and lattice energies

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Abstract. The thermodynamic properties (enthalpy, heat capacity) of lithium tungstate single crystals with low molybdenum content were measured by reaction and differential scanning calorimetry. An equation for lattice energies in Li₂WO₄-Li₂MoO₄ system on compositions was established. No anomalies connected with phase transitions for lithium tungstate doped with 15% molybdenum were found up to 960 K. An equation to describe heat capacity was proposed.

1. Introduction
At present, single crystals in lithium molybdate – lithium tungstate system are among the most promising materials to search double neutrinoless beta decay and to study elastic coherent neutrino scattering on atomic nuclei [1-6]. The Li₂MoO₄ single crystal, which, among other things, is applied in CUPID project, has a number of advantages. So, it has high radiopurity and contains an extremely low concentration of long-lived isotopes, which complicate registration of the studied processes.

Lithium tungstate is a promising material to study coherent neutrino scattering. Such investigations will contribute to the development of new physics outside the Standard Model. The problem is that it is impossible to grow pure lithium tungstate by Czochralski technique. This is due to fact that according to paper [6] there is “spinel-phenacite” polymorph phase transition in lithium tungstate. For this reason, as it was reported in literature [5], low mass fraction of molybdenum (x is about 0.08) is required to grow single crystals of doped lithium tungstate (Li₂W₁₋ₓMoₓO₄).

2. Experimental
In our paper we grew single crystals of lithium tungstate with low molybdenum content (2.5%) and studied its thermodynamic properties for the first time. The composition of grown single crystal was Li₂W₀.₉₇₅Mo₀.₀₂₅O₄. The low-temperature-gradient Czochralski technique with automatic weight control (LTG CZ) developed at Nikolaev Institute of Inorganic Chemistry SB RAS [7] was applied to grow single crystal of Li₂W₀.₉₇₅Mo₀.₀₂₅O₄. The method was successfully applied for growing high-quality scintillation single crystals, for example, Bi₃Ge₃O₁₂ (BGO).

A lithium tungstate single crystal doped by 2.5% molybdenum was grown from highly pure precursors: lithium carbonate (Li₂CO₃, purity > 0.999), tungsten oxide (VI) (WO₃, purity > 0.999), and molybdenum oxide (VI) (MoO₃, purity > 0.999). The identification carried out by X-ray phase analysis
demonstrated that single crystal was an individual phase, had phenacite structure and did not contain any impurity phases (space group R3). The single crystal was transparent and did not have any inclusions.

The single crystal with composition of Li$_2$W$_{0.85}$Mo$_{0.15}$O$_4$, needed to investigate heat capacity, was grown by the same way.

Thermodynamic properties of obtained Li$_2$W$_{0.975}$Mo$_{0.025}$O$_4$ single crystal were studied by reaction calorimetry [8-10]. There are two methods of reaction calorimetry to determine the formation enthalpies of mixed oxides: (i) high-temperature reaction calorimetry in melts of borate glasses or sodium molybdates; (ii) reaction calorimetry at room temperature in solutions of acids or hydroxides. In accordance with our papers [3-4], reaction calorimetry at room temperature in aqueous solution of potassium hydroxide demonstrated more precise results in determining thermochemical characteristics of lithium molybdates-tungstates. Therefore, in the research we used reaction (solution) calorimetry at room temperature to determine solution enthalpy, standard formation enthalpy and lattice energy of grown single crystal of Li$_2$W$_{0.975}$Mo$_{0.025}$O$_4$.

Detailed information about calorimeter and procedure to perform calorimetric experiments was presented in papers [10-11]. To determine solution enthalpy, the initial sample of single crystal (about 200 mg) was placed in a glass ampoule, and then the ampoule was placed in solution calorimeter. The ampoule was broken after reaching the regular thermal regime. Thermometer placed in calorimeter recorded the temperature rise. The heat of reaction was calculated after the calibration experiment. An aqueous solution of potassium hydroxide with concentration of 0.40162 mol kg$^{-1}$ was used to dissolve the obtained single crystal and precursors.

3. Results and discussion

The solution enthalpy obtained for Li$_2$W$_{0.975}$Mo$_{0.025}$O$_4$ single crystal was measured in the above solution calorimeter at temperature $T = 298.15$ K. Six parallel experiments were performed and the average value of solution enthalpy was calculated as follows: $\Delta_{\text{sol}}H^\circ$(Li$_2$W$_{0.975}$Mo$_{0.025}$O$_4$, 298.15 K) = $-31.37 \pm 0.54$ kJ mol$^{-1}$. An uncertainty was calculated for 95% confidence interval using Student coefficient.

To determine the standard formation enthalpy, it was necessary to construct thermochemical cycle in such a way that solution enthalpy of obtained single crystal (Li$_2$W$_{0.975}$Mo$_{0.025}$O$_4$) was compared with solution enthalpies of compounds, containing lithium, tungsten and molybdenum oxides. The lithium carbonate, molybdenum oxide and potassium tungstate were used for this purpose.

The experimentally determined solution enthalpy of lithium carbonate in aqueous solution of 0.40162 mol kg$^{-1}$ KOH was: $\Delta_{\text{sol}}H^\circ$(Li$_2$CO$_3$, 298.15 K) = $-16.88 \pm 0.64$ kJ mol$^{-1}$. Five parallel experiments were carried out. Uncertainty was calculated for 95% confidence interval.

Experimentally determined solution enthalpy of molybdenum oxide in aqueous solution of 0.40162 mol kg$^{-1}$ KOH was: $\Delta_{\text{sol}}H^\circ$(MoO$_3$, 298.15 K) = $-80.09 \pm 0.66$ kJ mol$^{-1}$. Seven parallel experiments were carried out. Uncertainty was calculated for 95% confidence interval.

Solution enthalpy of potassium tungstate was taken from paper [12] and was as follows: $\Delta_{\text{sol}}H^\circ$(K$_2$WO$_4$, 298.15 K) = $-1.6 \pm 0.7$ kJ mol$^{-1}$.

Experimental data obtained and literature values for H$_2$O, K$^+$, CO$_3^{2-}$, KOH, K$_2$WO$_4$ [13] allowed calculating the standard formation enthalpy for grown single crystal as the following value: $\Delta f^\circ$(Li$_2$W$_{0.975}$Mo$_{0.025}$O$_4$, 298.15 K) = $-1599.8 \pm 3.0$ kJ mol$^{-1}$. Then, we compared our value with standard formation enthalpies of Li$_2$MoO$_4$ single crystal determined in our paper [3] ($\Delta f^\circ$(Li$_2$MoO$_4$, 298.15 K) = $-1521.9 \pm 1.9$ kJ mol$^{-1}$) and standard formation enthalpy for Li$_2$WO$_4$ ($\Delta f^\circ$(Li$_2$WO$_4$, 298.15 K) = $-1603.7 \pm 2.0$ kJ mol$^{-1}$) taken from reference book [13]. As can be seen, our value was within the range of standard formation enthalpies for lithium molybdate – lithium tungstate, which indicates the correctness of our experiments.

After that, we calculated the lattice energy for grown Li$_2$W$_{0.975}$Mo$_{0.025}$O$_4$ single crystal, using Born-Haber cycle. For this, we needed the standard formation enthalpy (determined in this research) and formation enthalpies of the following gaseous ions: Li$^+$ ($\Delta f^\circ$(Li$^+$, 298.15 K) = 679.5 kJ mol$^{-1}$); O$^{2-}$

\[ \text{Li}_2\text{W}_{0.85}\text{Mo}_{0.15}\text{O}_4 \]
(\Delta H^\circ(\text{O}^2-, 298.15 \text{ K}) = 905.8 \text{ kJ mol}^{-1}); \text{ Mo}^{6+} (\Delta H^\circ(\text{Mo}^{6+}, 298.15 \text{ K}) = 22463.9 \text{ mol}^{-1}); \text{ W}^{6+} (\Delta H^\circ(\text{W}^{6+}, 298.15 \text{ K}) = 19533.8 \text{ kJ mol}^{-1}). \text{ Values were taken from the reference book [13].}

The calculated lattice energy was as follows: \(\Delta\text{lat}E(\text{Li}_2\text{MoO}_4, 298.15 \text{ K}) = 28970 \text{ kJ mol}^{-1}\). Earlier, we calculated lattice energies for lithium molybdate, lithium tungstate and mixed lithium tungstate-molybdates with 10 and 15% molybdenum. Calculated lattice energies were: \(\Delta\text{lat}E(\text{Li}_2\text{WO}_4, 298.15 \text{ K}) = 26190 \text{ kJ mol}^{-1}\). As can be seen, the lattice energy decreased in a row \(\text{Li}_2\text{MoO}_4 - \text{Li}_2\text{WO}_4\). The constructed dependence of lattice energy on tungsten content was monotonic, which allowed one to predict lattice energies for uninvestigated compositions in \(\text{Li}_2\text{WO}_4 - \text{Li}_2\text{MoO}_4\) system. The dependence equation was presented as follows: \(\Delta\text{lat}E = 28970 - 2.8511 \cdot 10^3 (1-x) \text{ (kJ mol}^{-1}\).

As it was previously noted, the compound should not have had solid-phase transitions at temperatures below melting temperature to grow perfect single crystals. Here, we studied the existence of phase transitions for lithium tungstate doped by 15% molybdenum. No one has investigated the presence of phase transitions in this compound. We began to study phase transitions with this composition, and then we will study phase transitions of lithium tungstate with lower molybdenum content.

To obtain information about the existence of phase transitions in \(\text{Li}_2\text{W}_{0.85}\text{Mo}_{0.15}\text{O}_4\) single crystals, we measured temperature dependence of heat capacity in the temperature range of 320–965 K. Temperature dependence of heat capacity was shown in figure 1. Heat capacity was measured by comparative method using differential scanning calorimeter (DSC 404 F1) [14-16]. Calorimetric experiments were carried out as follows [16]. The heat flux from an empty crucible and a crucible with a sample were measured. In addition, heat flux of empty crucible and that with sapphire, the heat capacity of which is known with high accuracy, were measured. Based on experimental measurements, heat capacity of the investigated single crystal \(\text{Li}_2\text{W}_{0.85}\text{Mo}_{0.15}\text{O}_4\) was calculated on the basis of three heating-cooling cycles.

![Figure 1. Temperature dependence of heat capacity for lithium tungstate doped by 15% molybdenum.](image-url)
All heating and cooling temperature dependences obtained for the sample were reproduced within experimental uncertainty estimated at 2–3%. It was confirmed by experiments with high-purity platinum and sapphire. The heating and cooling rate was 6 K min\(^{-1}\) and was chosen because the most precise measurements were obtained under such conditions. All the measurements were carried out in high-purity inert gas (argon, purity of 99.992 vol. %). The sample weight was 73.46 mg. The sapphire weight was 63.44 mg.

As can be seen, there were no any anomalies connected with phase transitions. The heat capacity was well described by cubic polynomial: 

\[ C_p = 76.37 + 0.2528 T - 2.23 \times 10^{-4} T^2 + 8.508 \times 10^{-8} T^3 \]  

(J K\(^{-1}\) mol\(^{-1}\)). The absence of phase transitions for Li\(_2\)W\(_{0.85}\)Mo\(_{0.15}\)O\(_4\) single crystal is very important for practical application and gives the perspective to grow pure lithium tungstate.

Conclusions
Experimental data on thermodynamic properties of lithium tungstate single crystal with low molybdenum content (2.5 and 15%) have been obtained.

The equation of lattice energy dependence on tungsten content for compounds in Li\(_2\)WO\(_4\)–Li\(_2\)MoO\(_4\) system has been presented. An equation has been presented for temperature dependence of heat capacity for Li\(_2\)W\(_{1-x}\)Mo\(_x\)O\(_4\) (x = 0.15).

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