Features of thermodynamic properties of single crystals on the basis of lithium tungstate: «thermodynamics – structure – functional characteristics» correlations

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Abstract. On the basis of obtained experimental data, the features of thermodynamic properties for lithium tungstate single crystals doped by molybdenum have been revealed. Correlations between enthalpies and structural parameters have been found. The relation between lattice energies and scintillation characteristics has been revealed.

1. Introduction

Single crystals on the basis of alkali metal molybdates and tungstates are promising materials for optics, magnetic and moisture sensors, searching of rare events, in particular, coherent interactions between neutrinos and nucleons and double neutrinoless beta decay [1-5]. The existence of rare events is contradictory. In addition, it is believed that neutrinos rarely interact with matter and often tons of compounds are required for studying the rare events. Therefore, at present a lot of investigations are being carried out to find and grow new scintillation single crystals, which allow, in particular, reducing weight of compounds for research. Materials applied to search for rare events should have a set of required properties, such as high radio-purity, an absence of phase transitions, etc.

Earlier [4, 5], we grew single crystals of lithium molybdate and lithium tungstate doped by 15% and 10% molybdenum, and their thermodynamic investigations were carried out. The standard formation enthalpies, enthalpies and lattice energies, stabilization energies were determined for above single crystals.

2. Experimental

Here, for the first time we grew single crystal of lithium tungstate doped by molybdenum with composition of Li₂W₀.⁰⁵Mo₀.⁰⁵O₄, carried out its thermodynamic investigations and also performed the systematic consideration of thermodynamic properties for Li₂W₁⁺ₓMoₓO₄ compounds (x = 1; 0.15; 0.1; 0.05). The regularities of changes in properties depending on tolerance factors have been revealed, and correlations of lattice energy with scintillation characteristics have been found.

In order to grow perfect single crystal (lithium tungstate doped by 5% molybdenum) we used the following precursors: Li₂CO₃ (purity > 0.999), MoO₃ (purity > 0.999), WO₃ (purity > 0.999).

Here, it is necessary to mentions that these single crystals are applied not only to study thermodynamic properties, but also to search for rare events (double neutrinoless beta decay, coherent neutrino scattering on nuclei) in underground laboratories. The study of rare processes requires high...
purity of single crystals. In particular, it is necessary to have low background radiation. Therefore, deep purification of tungsten and molybdenum oxides was carried out before growing. The purification of tungsten and molybdenum oxides was described in papers [6–7]. The purification process aims at reducing impurities level that are harmful to study processes associated with rare events.

The batch of lithium tungstate doped by molybdenum was obtained from homogeneous thoroughly mixed mixture due to solid-phase synthesis, in which chemical reaction occurred due to diffusion mass transfer between grains of solid reagents. The growth device [8] was designed to grow single crystals up to 1300 K, using low-temperature-gradient Czochralski technique (LTG Cz) in air or in controlled non-aggressive atmosphere. Automatic weight control allowed one to grow single crystal with predefined size.

The reaction took place in platinum crucible. A stoichiometric mixture of starting reagents (LiCO3, WO3 and MoO3) was placed in a crucible. Next, the mixture was heated up to 1000 K with the rate of 60 K h⁻¹ and maintained for 5 h until the melt was completely homogenized.

The single crystal was transparent and did not contain any inclusions. Characterization was carried out by X-ray powder diffraction, differential thermal analyzes. Shimadzu XRD - 7000 diffractometer was used to perform X-ray powder analysis. Mass spectrometric analysis was used to study the amount of impurities. Energy dispersive fluorescence analysis was used to determine the content of molybdenum and tungsten. The grown single crystal was an individual phase, did not contain any impurity phases and had phenacite structure (space group R3).

Thermodynamic characteristics of grown single crystal were determined by two methods. Reaction calorimetry was used to determine the solution enthalpy of the grown single crystal at standard temperature of 298.15 K. Differential scanning calorimetry was used to determine the heat capacity of single crystal and to clarify the existence of phase transitions. An automated solution calorimeter with isothermal jacket developed at Nikolaev Institute of Inorganic Chemistry SB RAS and procedure to perform solution experiments were described in detail in [4, 5]. An aqueous solution of potassium hydroxide (0.40162 mol kg⁻¹) was used as solvent. The calorimeter was tested by dissolving the standard compound, namely potassium chloride. Uncertainty of the calorimeter was about 0.1%.

The combined device was used to determine the heat capacity, which allows obtaining heat capacity and thermal conductivity coefficients. The device included DSC 404 F1 Pegasus differential scanning calorimeter (NETSCH Company). The calorimeter served to determine heat capacity at the level of 1-3% with appropriate calibration [9-10]. All measurements were carried out in platinum crucibles with corundum inserts and platinum lids. The presence of covers reduced temperature gradients. The measurements were carried out in high purity argon.

3. Results and discussion

On the basis of measured solution enthalpies of grown crystal, lithium carbonate, molybdenum oxide, and potassium tungstate, the enthalpy of the following reaction was calculated: Li2W0.95Mo0.05O4 (s) + 2 K⁺ (sol) + CO3²⁻ (sol) + 0.05 H2O = Li2CO3 (s) + 0.05 MoO3 (s) + 0.1 KOH (sol) + 0.95 K2WO4 (s). The enthalpy of above reaction was equal to: ΔHº = −7.60 ± 1.85 kJ mol⁻¹.

Further, using reference values for standard formation enthalpies of lithium carbonate, molybdenum oxide, potassium hydroxide, potassium tungstate, water, potassium ion and carbonate ion, the standard formation enthalpy of lithium tungstate doped by molybdenum was calculated as follows: ΔHº(Li2(W0.95Mo0.05)O4) = −1599.2 ± 2.4 kJ mol⁻¹.

Earlier, in papers [4, 5] we measured the standard formation enthalpies of lithium molybdate single crystal and single crystals of lithium tungstate doped by 10-15% molybdenum. The grown single crystals of lithium tungstate doped with molybdenum are spinels. One of structural parameters that determine spinel stability is the tolerance factor. Here, we calculate the tolerance factor for lithium molybdate, lithium tungstate doped by 15, 10 and 5% molybdenum and build the dependence of standard formation enthalpy for single crystals on tolerance factor. The dependence is presented in figure 1.
Figure 1. Dependence of formation enthalpy for Li$_2$W$_{1-x}$Mo$_x$O$_4$ on tolerance factor.

As can be seen, the standard formation enthalpies increase in absolute values with increasing of tolerance factor. The obtained dependence serves to predict standard formation enthalpies for compounds with uninvestigated tolerance factors.

Next, we calculate the lattice energy for grown Li$_2$W$_{0.95}$Mo$_{0.05}$O$_4$ single crystal. The Born-Haber cycle is used for calculation. The calculated lattice energy is: $\Delta_{\text{lat}}E(\text{Li}_2\text{W}_{0.95}\text{Mo}_{0.05}\text{O}_4) = 26260 \text{ kJ mol}^{-1}$. We also systematically consider the lattice energy for investigated Li$_2$W$_{0.95}$Mo$_{0.05}$O$_4$ single crystal and for earlier studied Li$_2$W$_{1-x}$Mo$_x$O$_4$ ($x = 1; 0.15; 0.1$) single crystals. The lattice energies are shown to increase in raw Li$_2$W$_{0.95}$Mo$_{0.05}$O$_4$ − Li$_2$W$_{0.9}$Mo$_{0.1}$O$_4$ − Li$_2$W$_{0.85}$Mo$_{0.15}$O$_4$ − Li$_2$MoO$_4$ and are within the range of 26260 kJ mol$^{-1}$ − 28970 kJ mol$^{-1}$.

Then, formation enthalpy from simple oxides for grown single crystal is calculated. The standard formation enthalpy measured in this work and standard formation enthalpies of simple oxides, namely Li$_2$O, WO$_3$ and MoO$_3$, are required for calculations. Values for simple oxides are taken from reference book [11]. The formation enthalpy is: $\Delta_{\text{ox}}H^0(\text{Li}_2\text{W}_{0.95}\text{Mo}_{0.05}\text{O}_4, 298.15 \text{ K}) = -163.5 \pm 2.6 \text{ kJ mol}^{-1}$. On the basis of data calculated here and data of our earlier papers [4, 5], we construct the dependence of formation enthalpy from oxides on tolerance factor as the following equation: $\Delta_{\text{ox}}H^0 = -2803.8 + 2731.8 \cdot t$.

Further, correlations are found between lattice energy and luminescence energy in Li$_2$WO$_4$ − Li$_2$MoO$_4$ system on the basis of our experimental data and literature data [12]. The luminescence energy is shown to decrease with increasing lattice energy. The correlations are important for practice. It is known that the lattice energy can be calculated using Kapustinsky formula or Born-Haber cycle, to predict the direction of changing luminescence energy.
The heat capacity of grown Li<sub>2</sub>W<sub>0.95</sub>Mo<sub>0.05</sub>O<sub>4</sub> single crystal is measured by differential scanning calorimetry in the temperature range of 303–915 K. The purpose of heat capacity measurements is to find out the question of existence or absence of phase transitions for the grown single crystal. The composition of this single crystal (Li<sub>2</sub>W<sub>0.95</sub>Mo<sub>0.05</sub>O<sub>4</sub>) is close to lithium tungstate. The problem of growing pure lithium tungstate by Czochralski method has not been resolved yet, as it is stated in papers [13-14], due to the existence of phase transitions in Li<sub>2</sub>WO<sub>4</sub>. Cylinder of 5 × 1.5 mm size was cut from grown single crystal to measure heat capacity. The weight of Li<sub>2</sub>W<sub>0.95</sub>Mo<sub>0.05</sub>O<sub>4</sub> single crystal was 107.99 mg. Sapphire weighing 85.26 mg was used as standard material. The temperature dependence of heat capacity is shown in figure 2.

![Figure 2](image.png)

**Figure 2.** Heat capacity of Li<sub>2</sub>W<sub>0.95</sub>Mo<sub>0.05</sub>O<sub>4</sub> on temperature.

As can be seen, heat capacity has no anomalies in investigated temperature range. The fact that there are no anomalies provides perspectives for growing single crystals with lower molybdenum content, in particular, pure lithium tungstate. Li<sub>2</sub>WO<sub>4</sub> has not been grown by Czochralski technique yet.

**Conclusion**

A single crystal of Li<sub>2</sub>W<sub>0.95</sub>Mo<sub>0.05</sub>O<sub>4</sub> has been grown by the low-temperature-gradient Czochralski technique for the first time. The standard formation enthalpy, formation enthalpy from simple oxides and lattice energy have been determined on the basis of experimental data obtained by solution calorimetry. Correlations have been found between standard formation enthalpies in Li<sub>2</sub>WO<sub>4</sub> – Li<sub>2</sub>MoO<sub>4</sub> system and tolerance factor, as well as between lattice energies and luminescence energies. The heat capacity of Li<sub>2</sub>W<sub>0.95</sub>Mo<sub>0.05</sub>O<sub>4</sub> has been measured in the temperature range of 303–915 K. No anomalies have been found in investigated temperature range.
Acknowledgments
The research was supported by the Russian Science Foundation (project 19-19-00095).

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