Crystal growth and thermodynamic properties of lithium tungstate doped by 4% molybdenum

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For the first time, single crystal of $Li_2W_{0.96}Mo_{0.04}O_4$ has been grown by low-temperature-gradient Czochralski technique. The thermodynamic characteristics (standard formation enthalpy and lattice enthalpy) that are necessary to improve the growth technology have been studied by solution calorimetry. For $Li_2W_{1-x}Mo_xO_4$ single crystals, correlations of lattice enthalpies and standard formation enthalpies with tolerance factor were found.

$Li_2W_{0.96}Mo_{0.04}O_4$

Keywords: lithium tungstate, molybdenum, crystal growth, formation enthalpy, lattice enthalpy, thermodynamics–structure correlation.

Mixed oxides based on transition metals, in particular, molybdates and tungstates of first and second groups, are promising materials for optoelectronics, biomedicine, microelectronics, environment exploration, studying rare events, such as neutrinoless double beta decay, elastic coherent scattering of neutrinos by nuclei, *etc*.[1–6] Inasmuch as rare events are very sensitive to environment, extremly high requirements are imposed on single crystals. This entails the need to develop unique technologies for growing high-quality single crystals. Molybdates and tungstates are also prospective as ionic conductors to create environmental technologies.

To improve functional characteristics of above classes of materials, detailed physicochemical, in particular, thermodynamic study is required. At present, apart from our publications, there is no information in literature about single crystals in Li_2MoO_4–Li_2WO_4 system with molybdenum content below 8%. The reason is that for a long time it was considered impossible to grow a single crystal of pure lithium tungstate (Li_2WO_4) since it had been revealed earlier[7] that phase transitions of the compound occured at high temperatures, which resulted in crystal cracking. Therefore, molybdenum oxide was always added to grow single crystals based on lithium tungstate.[8–10] We have been able to refute this statement and grew a series of single crystals with molybdenum content below 8%, in particular, pure lithium tungstate.[3,11,12]

Here, single crystal of lithium tungstate with molybdenum content of 4% was grown for the first time by low-temperature-gradient Czochralski technique,[†] its thermodynamic properties were studied and correlations between thermodynamics and structural aspects were examined. Solution calorimetry was applied to determine thermodynamic characteristics of $Li_2W_{0.96}Mo_{0.04}O_4$ single crystal.[13–16] The composition containing lithium tungstate with molybdenum content of 4% was chosen for the following reasons. We recently[11,12] explored other compositions of $Li_2W_{1-x}Mo_xO_4$ single crystals. As noted above, it is important to have single crystals of lithium tungstate doped

by low content of molybdenum. Therefore, to build detailed thermodynamics–structure dependence we decided to increase the number of studied compositions in $Li_2W_{1-x}Mo_xO_4$ single crystals and add composition with 4% molybdenum to previously studied compositions with 5% and 2.5% molybdenum. Furthermore, we changed the $Li_2W_{0.96}Mo_{0.04}O_4$ single crystal growth technology compared with previously used technologies in order to check whether growth technology affects the thermodynamic properties. The grown $Li_2W_{0.96}Mo_{0.04}O_4$ single crystal is presented in Figure 1.

Characterization of $Li_2W_{0.96}Mo_{0.04}O_4$ single crystal has been performed by X-ray powder diffraction and chemical analysis. X-ray diffraction pattern is presented in Figure 2.

We measured solution enthalpies of lithium carbonate, molybdenum oxide and lithium tungstate single crystal with 4% molybdenum content in 0.40162 mol kg^{-1} KOH and obtained the following values: $\Delta_{sol}H$ (Li_2CO_3) = -16.88 ± 0.64 kJ mol^{-1} ($n = 6$), $\Delta_{sol}H$ (MoO_3) = -80.09 ± 0.66 kJ mol^{-1} ($n = 8$) and $\Delta_{sol}H$ ($Li_2W_{0.96}Mo_{0.04}O_4$) = -31.02 ± 0.42 kJ mol^{-1} ($n = 6$). Each value was calculated from 6–8 parallel experiments (n). Uncertainties were calculated for 95% confidence interval using Student's coefficient. The value of the dissolution enthalpy of potassium tungstate in 0.40162 mol kg^{-1} KOH, which was necessary to

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Figure 1 Grown single crystal of lithium tungstate doped by 4% molybdenum.

develop the thermochemical cycle, was determined in publication[17] as $\Delta_{sol}H$(K$_2$WO$_4$) = −1.6 ± 0.7 kJ mol^{-1}.

On the basis of the obtained experimental data and literature data for H$_2$O, K$_2$WO$_4$, K$^+$ (water solution), CO$_3^{2-}$ (water solution), KOH (water solution), MoO$_3$, WO$_3$, Li$_2$CO$_3$ and Li$_2$O given in the reference book,[18] we calculated the standard formation enthalpy for lithium tungstate doped by 4% of molybdenum. The standard formation enthalpy of doped lithium tungstate we calculated was Δ_fH (Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$) = −1599.0 ± 2.8 kJ mol^{-1}.

The next step would be to develop 'predictive' thermodynamics, its basics were created by Glasser.[19] That is, we would build dependences of thermodynamic properties on structural parameters, which allowed us to determine thermodynamic properties of uninvestigated compounds.

One of the parameters that characterize the structure of studied compounds is the tolerance factor. The lithium tungstates doped by molybdenum, crystallize in phenakite structure. The tolerance factor for phenakite (AB$_2$X$_4$) is calculated as follows:

$$t = \frac{r_A + r_X}{0.87\,(r_B + r_X)},$$

where r_A, r_B, and r_X are ion radii of the elements in formula AB$_2$X$_4$. Herein, A is Mo or W, B is Li and X is O.

To calculate the tolerance factor we used the values of ion radii given in publication[20] considering their coordination for
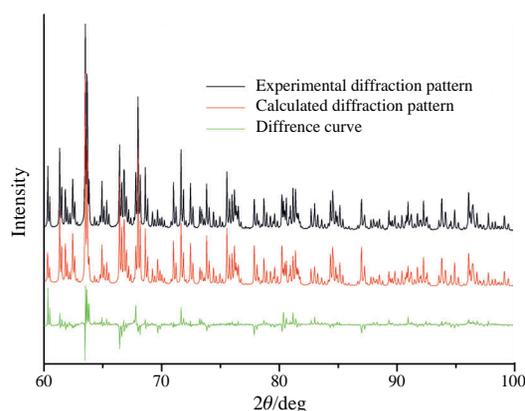

Figure 2 X-ray diffraction pattern for single crystal of Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$.

The single crystal was characterized by X-ray powder diffraction. XRD analysis of the sample was performed on Bruker D8 Advance diffractometer (CuK-alpha radiation, linear LYNXEYE XE-T detector, 5–100° 2θ range, 0.02° 2θ step, 1 s per step). The sample was slightly ground with hexane in an agate mortar; the resulting suspension was deposited on the polished side of a standard plastic sample holder and a smooth thin layer formed after drying. Indexing of the diffraction patterns was carried out using data for compounds reported in the PDF.[22] The unit cell parameters were refined by the Topas Academic v.6 software.[23] The peak profiles were described by the pseudo-Voigt function in the range of 2θ = 60–100°.

According to XRD data, the sample was isostructural to rhombohedral Li$_2$WO$_4$ (PDF #010-76-7883). Experimental peaks were slightly shifted to the smaller angles, so the unit cell parameters (UCP) should be larger than those of pure Li$_2$WO$_4$.[24] Rietveld refinement was
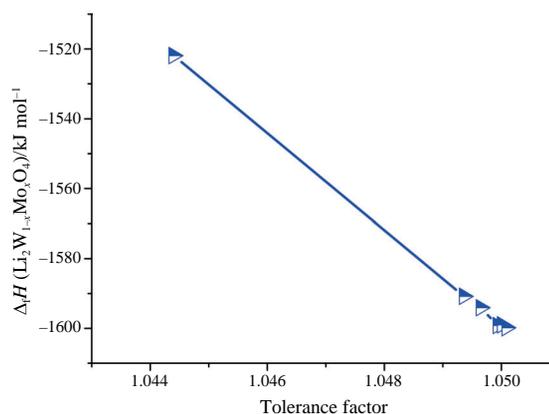

Figure 3 Dependence of standard formation enthalpies for Li$_2$W$_{1-x}$Mo$_x$O$_4$ on the tolerance factor.

phenakite structure. Then, we would construct the dependence of standard formation enthalpies for Li$_2$W$_{1-x}$Mo$_x$O$_4$ (x = 1, 0.15, 0.1, 0.05, 0.04 and 0.025) (see Figure 3). Data for Li$_2$MoO$_4$ and lithium tungstate doped by 15, 10, 5 and 2.5% molybdenum were obtained in our earlier works.[2,8,9,16]

The above dependence is close to linear, which makes it possible to foresee the standard formation enthalpies for unexplored compositions.

As is known, lattice enthalpy is one of the basic thermodynamic characteristics that allows one to predict the stability of the compound and direction of change in its stability. Based on standard formation enthalpy we calculated the lattice enthalpy for Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$ using the Born–Haber cycle. Detailed information on the construction of Born–Haber cycle for similar compounds was reported recently in our publication.[16]

Thus, calculated lattice enthalpy value was $\Delta_{lat}H$ (Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$) = −26230 kJ mol^{-1}.

Furthermore, using this value and data on lattice enthalpies for Li$_2$MoO$_4$ and lithium tungstate doped by 15, 10, 5 and 2.5% molybdenum presented in our earlier papers[3,11,12] we have plotted the dependence of lattice enthalpy for Li$_2$W$_{1-x}$Mo$_x$O$_4$ on the tolerance factor, which is depicted in Figure 4.

As can be seen from Figure 4, obtained dependence of lattice enthalpy for Li$_2$W$_{1-x}$Mo$_x$O$_4$ single crystals on tolerance factor is close to linear. Let us try to validate the linearity of this function.

As is known, the lattice energy (a value of lattice enthalpy with the opposite sign) can be determined by Kapustinsky's formula:

$$U = 1070.9 \, \frac{m\, Z_c\, Z_a}{r_c + r_a}, \qquad (1)$$

where U is the lattice energy, Z_c is number of elementary charges of cation, Z_a is number of elementary charges of anion, r_c and r_a are radii of cation and anion and m is number of ions in the empirical formula.

performed up to R_p = 5.97%, R_{wp} = 8.89%. Lattice parameters for Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$ were: a = 14.366(3) Å, c = 9.607(2) Å, V = 1717 Å^3. Values for Li$_2$WO$_4$ known from literature data were slightly smaller: a = 14.361 Å, c = 9.602 Å, V = 1715 Å^3. The single crystal of Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$ was analyzed by atomic absorption method in air–acetylene flame using Perkin Elmer atomic absorption spectrometer. The standard uncertainty was 0.1–0.7%. The results of the chemical analysis of Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$ single crystal allowed us to conclude that single crystal had the following composition: Li$_{1.998\pm0.003}$W$_{0.962\pm0.002}$Mo$_{0.039\pm0.001}$O$_4$.

Impurity concentrations in Li$_2$W$_{0.96}$Mo$_{0.04}$O$_4$ were obtained by atomic emission spectral analysis using iCAP-6500 spectrometer. The performed analysis has shown the high radiation purity of the crystal. Thus, K content was 91 ppb, Ra content was 54 ppb, Th content was 45 ppt and U content was 8 ppt.
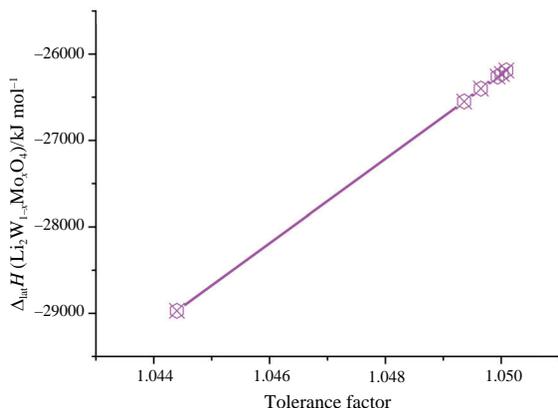
Figure 4 Dependence of lattice enthalpy for $Li_2W_{1-x}Mo_xO_4$ on the tolerance factor.

Note that for single crystals of general formula $Li_2W_{1-x}Mo_xO_4$ the molybdenum content is low. Hence, for low x, one can extend Kapustinsky's formula using a first-order Taylor's expansion to obtain the modified equation:

$$U = A + B x\, r_{Mo}, \qquad (2)$$

where A and B are constants, x is content of Mo in $Li_2W_{1-x}Mo_xO_4$ and r_{Mo} is the radius of molybdenum.

Therefore, it has been experimentally confirmed (see Figure 4) that for low molybdenum-doped lithium tungstate the dependence of lattice energy (lattice enthalpy) is a linear function of molybdenum content. The equation we have derived allows one to calculate lattice energy (lattice enthalpy) for unexplored $Li_2W_{1-x}Mo_xO_4$ compounds with low molybdenum doping.

Since lattice enthalpy and standard formation enthalpy are connected *via* formation enthalpies of ions included in the compound (*i.e.*, lithium, tungsten, molybdenum and oxygen ions), we can derive the equation for standard formation enthalpy of $Li_2W_{1-x}Mo_xO_4$ for low x as follows:

$$\Delta H_f = M + B x\, r_{Mo} - x\, \Delta H_f(Mo^{6+}) - (1-x)\, \Delta H_f(W^{6+}), \qquad (3)$$

where M, B are constants, x is Mo content in $Li_2W_{1-x}Mo_xO_4$, r_{Mo} is radius of molybdenum, ΔH_f is standard formation enthalpy of $Li_2W_{1-x}Mo_xO_4$, $\Delta H_f(Mo^{6+})$ is standard formation enthalpy of Mo^{6+} ion and $\Delta H_f(W^{6+})$ is a standard formation enthalpy of W^{6+} ion.

This equation enables to calculate standard formation enthalpies for $Li_2W_{1-x}Mo_xO_4$ compounds with unexplored content of molybdenum and tungstane.

Further, it was interesting to find the stabilization energy of obtained $Li_2W_{0.96}Mo_{0.04}O_4$ single crystal. The stabilization energy is the difference between standard formation enthalpy of the compound and standard formation enthalpies of simple oxides. Based on the standard formation enthalpy for $Li_2W_{0.96}Mo_{0.04}O_4$ obtained by us and standard formation enthalpies of simple oxides (Li_2O, WO_3 and MoO_3) taken from the reference book,[18] we calculated the value of stabilization energy as $\Delta_{ox}H\,(Li_2W_{0.96}Mo_{0.04}O_4) = -162.3 \pm 2.8$ kJ mol^{-1}.

Thus, for the first time, single crystal of composition $Li_2W_{0.96}Mo_{0.04}O_4$ was grown by low-temperature-gradient Czochralski technique from precursors (Li_2CO_3, MoO_3 and WO_3) with a high degree of purification. It was shown that single crystal possessed high radiation purity. The standard formation enthalpy of $Li_2W_{0.96}Mo_{0.04}O_4$ single crystal, lattice enthalpy and stabilization energy were determined using solution calorimetry. Correlations of standard formation enthalpies and lattice enthalpies for $Li_2W_{1-x}Mo_xO_4$ single crystals with tolerance factors were found. A linear function of standard formation enthalpies and lattice enthalpies on the tolerance factor was obtained and justified.

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