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Thermodynamic characteristics of sodium ditungstate single crystal

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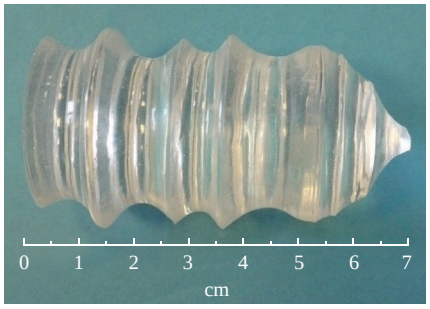
The single crystal of $Na_2W_2O_7$ has been grown by the low-temperature-gradient Czochralski technique. The thermodynamic properties (standard enthalpy of formation, lattice enthalpy and stabilization energy), the knowledge of which is necessary to improve the growth technology, have been measured using reaction calorimetry. It has been shown that in the $Na_2W_2O_7$–$Na_2Mo_2O_7$ series, the luminescence wavelength increases from 540 to 650 nm, respectively, along with a change in the lattice enthalpy from −49030 to −54730 kJ mol^{-1}.



Keywords: Czochralski technique, sodium ditungstate, single crystal, solution calorimetry, enthalpy of formation.

Single crystals of alkali metal molybdates and tungstates are promising materials for optoelectronics and photonics, as well as for studying rare events and searching for dark matter.[1–10] The advantages of these materials over others are rather low synthesis temperatures, congruent melting and the possibility of achieving high radiation purity. The latter is very important for studying rare events, since rare events are very sensitive to the surrounding background. In this regard, experiments on rare events are carried out deep underground.

Lithium molybdate is one of the promising crystals widely used to create bolometers.[11–13] However, it has significant drawbacks, such as hygroscopicity and low light output. Therefore, one of the actual tasks for the mentioned applications is the search for single crystals that are non-hygroscopic and have a higher light output. It seems that one of the promising single crystals for these purposes can be sodium molybdates and tungstates.

To improve the technology of growing single crystals, to search for the direction of change in physicochemical, in particular, thermodynamic properties with a change in composition, as well as to search for various kinds of correlations, a detailed physicochemical, in particular, thermodynamic study is necessary for the systems on the basis of which single crystals are grown.

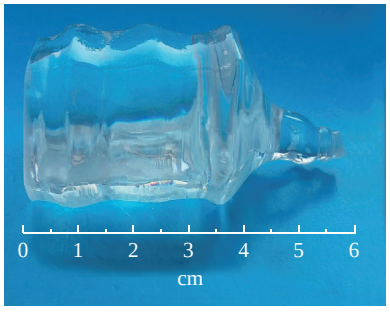


Figure 1 Photograph of a grown single crystal of sodium ditungstate.

In this work, a single crystal of sodium ditungstate was grown by the low-temperature-gradient Czochralski technique.† The characterization of a single crystal was carried out and the basic thermodynamic characteristics of a single crystal, such as the standard enthalpy of formation, lattice enthalpy and stabilization energy, were determined. Solution calorimetry was chosen to determine the standard enthalpy of formation of sodium ditungstate. The technique and procedure for measuring the enthalpies of dissolution with a solution calorimeter were described in detail in previous articles.[14–17] The single crystal growth procedure was described in detail previously.[18–20] A photograph of the grown $Na_2W_2O_7$ single crystal is shown in Figure 1.

The characterization of the $Na_2W_2O_7$ single crystal was performed by powder X-ray diffraction (XRD) and chemical analysis.‡ The XRD pattern is presented in Figure 2.

In order to determine the standard enthalpy of formation of a $Na_2W_2O_7$ single crystal, the thermodynamic cycle was constructed in such a way that the enthalpy of dissolution of sodium ditungstate

† The $Na_2W_2O_7$ single crystal was grown by the low-temperature-gradient Czochralski technique from the melt. The synthesis of the compound was carried out directly in a growth device from the initial components: Na_2CO_3 (Nikolaev Institute of Inorganic Chemistry SB RAS) and WO_3 (Nikolaev Institute of Inorganic Chemistry SB RAS). A stoichiometric mixture of initial components was placed in a platinum crucible. The crucible was placed in three-zone furnace with a resistive heater. The compounds were mixed, heated to 450 °C at a rate of 30 °C h^{-1} and kept at this temperature for 5 h. After that, the temperature was elevated to 20 °C above the melting point at a rate of 70 °C h^{-1} and kept at this temperature for 3 h for melt homogenization. The product was annealed at 750 °C for 12 h to yield a charge for growing. Large $Na_2W_2O_7$ single crystals were grown along [001].

‡ The single crystal was characterized by powder XRD performed on a Shimadzu XRD-7000 diffractometer with CuKα radiation. According to XRD data, the sample is orthorhombic, space group *Cmca*, a = 7.216(1), b = 11.899(1) and c = 14.716(3) Å, Z = 8, and its structure contains both tetrahedral WO_4 and octahedral WO_6 groups.

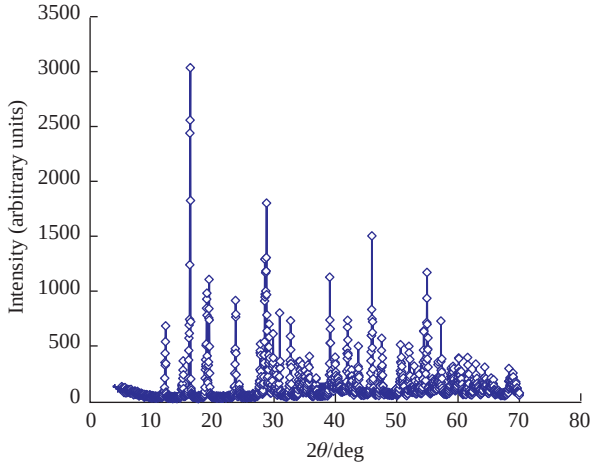


Figure 2 XRD pattern of the $Na_2W_2O_7$ single crystal.

was compared with the enthalpy of dissolution of sodium carbonate. A 0.2 M NaOH solution was chosen as the solvent. We measured the enthalpies of dissolution of sodium carbonate and sodium ditungstate and obtained the following values: $\Delta_{sol}H^0(Na_2CO_3) = -27.39 \pm 0.57$ kJ mol^{-1} ($n = 6$) and $\Delta_{sol}H^0(Na_2W_2O_7) = -47.29 \pm 0.71$ kJ mol^{-1} ($n = 6$). Each value was calculated from six parallel experiments. Uncertainties were calculated for 95% confidence intervals using critical values of Student's *t*-distribution. Next, based on the measured experimental data, we calculated the enthalpy of the reaction:

$$Na_2CO_3 + 2WO_4^{2-} + H_2O = CO_3^{2-} + Na_2W_2O_7 + 2OH^-, \quad (1)$$
$$\Delta_{sol}H^0 = 19.90 \pm 0.91 \text{ kJ mol}^{-1}.$$

Based on the obtained experimental data and published data for H_2O, WO_4^{2-} (solution), CO_3^{2-} (solution), Na_2CO_3 and OH^- (solution), taken from the reference book,[21] we calculated the standard enthalpy of formation of sodium ditungstate, which was $\Delta_f H^0(Na_2W_2O_7) = -2405.04 \pm 1.27$ kJ mol^{-1}.

Further, to confirm the reliability of our data, we used a test thermochemical cycle in which the standard enthalpy of formation of sodium ditungstate is calculated from the following reaction:

$$Na_2W_2O_7 + 2OH^- = 2Na^+ + 2WO_4^{2-} + H_2O. \quad (2)$$

The enthalpy of dissolution of sodium ditungstate was measured by us, and the data on the enthalpies of formation of H_2O, as well as Na^+, WO_4^{2-} and OH^- ions, were taken from the reference book.[21] As a result of the calculation, it was found that the standard enthalpy of formation of sodium ditungstate in accordance with reaction (2) is $\Delta_f H^0(Na_2W_2O_7) = -2405.68$ kJ mol^{-1}. As can be seen, within the limits of uncertainty, the value obtained using the test cycle coincides with the value measured by us in the first thermodynamic cycle. This indicates the reliability of our data.

Previously, the standard enthalpy of formation of sodium ditungstate was measured for a polycrystalline sample[22] and the resulting value was $\Delta_f H^0(Na_2W_2O_7) = -2405.38$ kJ mol^{-1}. Thus, the standard enthalpy of formation of a single crystal of sodium ditungstate measured by us agrees well with the known standard enthalpy of formation of a polycrystalline sample of sodium ditungstate. This confirms the reliability of the value obtained in this work.

It is very important to note that single crystals should be used to measure the basic characteristics, since polycrystalline samples may contain amorphous phases that cannot be identified using X-ray phase analysis. Therefore, data for polycrystalline samples can be determined with errors.

Next, to calculate the lattice enthalpy of $Na_2W_2O_7$, we used the Born–Haber cycle presented below:

$$2Na(s) + 2W(s) + 3.5O_2(g) = Na_2W_2O_7(s) + \Delta_f H_3^0, \quad (3)$$

$$2Na^+(g) = 2Na(s) + 2\Delta_r H_4^0, \quad (4)$$

$$2W^{6+}(g) = 2W(s) + 2\Delta_r H_5^0, \quad (5)$$

$$7O^{2-}(g) = 3.5O_2(g) + 7\Delta_f H_6^0. \quad (6)$$

Using the Hess law on the basis of reactions (3)–(6) one can obtain:

$$2Na^+(g) + 2W^{6+}(g) + 7O^{2-}(g) = Na_2W_2O_7(s) + \Delta_{lat}H^0, \quad (7)$$

where $\Delta_{lat}H^0$ is the lattice enthalpy, which was calculated as follows: $\Delta_{lat}H^0 = \Delta_f H_3^0 + 2\Delta_r H_4^0 + 2\Delta_r H_5^0 + 7\Delta_r H_6^0$. Enthalpies of reactions (4)–(6), *i.e.*, enthalpies of formation of ions, were taken from the reference book.[21] Then the calculated lattice enthalpy of $Na_2W_2O_7$ was $\Delta_{lat}H^0(Na_2W_2O_7) = -49030$ kJ mol^{-1}.

Finally, the stabilization energy of the $Na_2W_2O_7$ single crystal was calculated. The stabilization energy is the enthalpy of formation of $Na_2W_2O_7$ from simple oxides, in this case Na_2O and WO_3. The standard enthalpy of formation of a single crystal of sodium ditungstate was measured by us. The standard enthalpies of formation of Na_2O and WO_3 required for the calculation were taken from the handbook.[21] Then the stabilization energy is equal to $\Delta_{st}H^0 = -304.93 \pm 1.54$ kJ mol^{-1}. Hence it follows that the single crystal of sodium ditungstate is thermodynamically stable with respect to decomposition into simple oxides, which makes it promising for application.

One of the important areas in materials science is the search for correlations between thermodynamic and functional properties in order to understand in which direction functional properties change when thermodynamic properties vary. In our study, the synthesized single crystal proved to be a scintillation crystal. One of the important functional properties of a scintillation single crystal is the luminescence wavelength. Previously, the luminescence properties were measured for single crystals of sodium dimolybdate and sodium ditungstate.[23] The luminescence emission wavelength for sodium dimolybdate is 650 nm, and for sodium ditungstate it is 540 nm. The enthalpy of the crystal lattice of sodium dimolybdate, calculated by us from reference data,[21] is $\Delta_{lat}H^0(Na_2Mo_2O_7) = -54730$ kJ mol^{-1}. The lattice enthalpy of sodium ditungstate was calculated by us in this work and takes the following value: $\Delta_{lat}H^0(Na_2W_2O_7) = -49030$ kJ mol^{-1}. As can be seen, an increase in the lattice enthalpy correlates with an increase in the luminescence wavelength. This makes it possible to predict in which direction the luminescence wavelength will change with a change in the lattice energy. This is very important for creating materials with predetermined functional properties.

Thus, a $Na_2W_2O_7$ single crystal was grown by the low-temperature-gradient Czochralski technique from precursors (Na_2CO_3, WO_3) that were highly purified. It was shown that the single crystal has high radiation purity. Solution calorimetry was used to determine the standard enthalpy of formation of a $Na_2W_2O_7$ single crystal, the lattice enthalpy and the stabilization energy. It was shown that sodium ditungstate is thermodynamically stable with respect to decomposition into simple oxides, which makes it promising for application. It was shown that the luminescence wavelength increases from 540 nm for $Na_2W_2O_7$ to 650 nm for $Na_2Mo_2O_7$ with an increase in the lattice enthalpy from −49030 kJ mol^{-1} ($Na_2W_2O_7$) to −54730 kJ mol^{-1} ($Na_2Mo_2O_7$). This makes it possible to predict the direction of change in the luminescence wavelength with a change in the lattice enthalpy.

The content of impurities in $Na_2W_2O_7$ was determined by atomic emission spectral analysis on an iCAP-6500 spectrometer. According to the analysis performed, the crystal showed high radiation purity. Thus, the content of K, Ra, Th and U was 91 ppb, 54 ppb, 45 ppt and 8 ppt, respectively.

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