Mendeleev Communications

Mendeleev Commun., 2025, **35**, 705–707

Determination of enthalpies for potassium molybdate doped by gadolinium $K_5Gd(MoO_4)_4$

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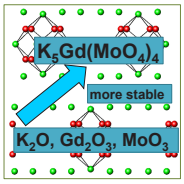
DOI: 10.71267/mencom.7829

For the first time, a standard formation enthalpy for the $K_5Gd(MoO_4)_4$ compound was measured by solution calorimetry. Stabilization energy and lattice enthalpy were calculated. It was shown that the compound is thermodynamically stable with respect to decomposition into simple oxides, which makes it promising for practical applications.



Keywords: potassium molybdate doped by gadolinium, formation enthalpy, stabilization energy, lattice enthalpy, solution calorimetry, solid state synthesis.

The class of polycrystalline and monocrystalline compounds based on alkali, rare earth and molybdenum oxides is very extensive.[1–10] These include, in particular, compounds of general formula $(A,Ln)_{2n}(MoO_4)_n$, where $n > 1$, A is alkali metal and Ln is lanthanide. Materials of this class are promising for remote diagnostics, remote exposure, optical communications, wide-field pulsed lasers, quantum electronics, *etc*. Materials with $n > 4$ are particularly promising because they have a high lattice energy and therefore increased stability. To create next-generation materials with improved functional characteristics, it is necessary to conduct extensive physicochemical, in particular, thermodynamic research. Since remote exposure and remote diagnostics are becoming increasingly important in global space, the necessity to explore the above compounds is increasing.

The standard formation enthalpy, entropy and heat capacity over a wide temperature range are the basic thermodynamic characteristics, which are necessary to predict or optimize the synthesis conditions of the above materials. The heat capacity for complex oxides can be well estimated by an additive sum of heat capacities for simple oxides.[11–13] The results of estimations of the values of standard formation enthalpies obtained using various models were contradictory in some cases. Therefore, it is preferable to measure experimentally the standard enthalpy of formation. The publication analysis has shown that there are no published thermodynamic data for the above-mentioned materials with $n > 4$. This is probably due to the fact that these compounds have been synthesized quite recently, and there are also sufficient difficulties associated with measuring the formation enthalpies for these compounds. Calorimetry is the main method for determining the formation enthalpies of complex oxides. The formation enthalpy of complex oxides is measured mainly by two calorimetric methods: dissolution calorimetry at room temperature and high-temperature reaction calorimetry.[14–17]

The purpose of this work was to create a thermochemical cycle, determine the standard formation enthalpy of potassium molybdate doped by gadolinium of the composition $K_5Gd(MoO_4)_4$, and calculate its lattice enthalpy. There is no published value for the standard formation enthalpy of $K_5Gd(MoO_4)_4$.

In the present paper, potassium gadolinium molybdate with the $K_5Gd(MoO_4)_4$ composition was synthesized.[†] The characterization of $K_5Gd(MoO_4)_4$[‡] was carried out by X-ray phase analysis in accordance with the technique described elsewhere.[18,19] The X-ray diffraction pattern is presented in Figure 1.

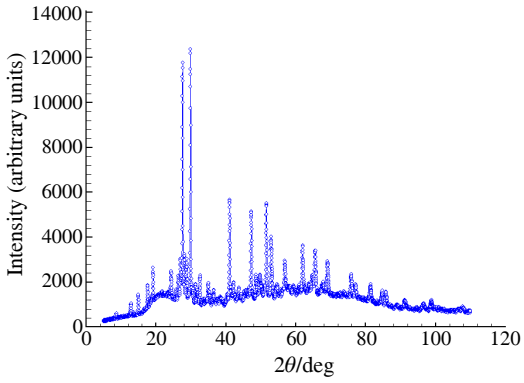


Figure 1 X-ray diffraction pattern for $K_5Gd(MoO_4)_4$.

[†] Potassium gadolinium molybdate $K_5Gd(MoO_4)_4$ was prepared by solid phase synthesis using modern equipment: a Fritsch Pulverisette 6 planetary mill, a PGR-400 press and an automatic SNOL 4/1300 furnace.

The starting materials for synthesis were potassium carbonate (K_2CO_3, high purity), gadolinium oxide (Gd_2O_3, high purity) and molybdenum(VI) oxide (MoO_3), which underwent deep purification according to the described procedure.[18] The starting materials necessary for synthesis were placed in a grinding corundum glass with a lid, where the grinding balls were also placed. The mixing speed varied from 110 to 250 rpm. After mixing, pressing into tablets was carried out. The resulting tablets were placed in a corundum boat and annealed in a SNOL 4/1300 muffle furnace. Annealing was carried out at of 823 K, with the heating rate of 2 K min^{-1}; to reach the synthesis temperature, the annealing time was 100 h.

[‡] X-ray diffraction analysis of $K_5Gd(MoO_4)_4$ was performed using Shimadzu XRD-7000 (CuK_α-radiation) at room temperature. It was shown that $K_5Gd(MoO_4)_4$ was an individual phase.

The enthalpy of dissolution of $K_5Gd(MoO_4)_4$ and precursors, which are necessary to construct a thermochemical cycle, were measured in an automated dissolution calorimeter with an isothermal jacket. The experimental methods and techniques were described in detail elsewhere.[20,21] The reliability of the calorimeter was checked using potassium chloride. The data on potassium chloride obtained using our calorimeter and the published data were in good agreement. The sample of potassium gadolinium molybdate for determining of dissolution enthalpy was about 0.1 g. The measurements were held in 1 M hydrochloric acid solution. The thermochemical cycle used to determine the standard formation enthalpy of $K_5Gd(MoO_4)_4$ was designed in such a way that dissolution enthalpies of K_2CO_3, $GdCl_3$ and H_2MoO_4 were compared with that of $K_5Gd(MoO_4)_4$. The scheme of the thermochemical cycle is given below:

$$2.5K_2CO_{3(s)} + 5HCl_{(sol)} = \\ = 5KCl_{(sol)} + 2.5H_2O + 2.5CO_{2(g)} + 2.5\Delta H_1^0, \quad (1)$$

$$GdCl_{3(s)} = GdCl_{3(sol)} + \Delta H_2^0, \quad (2)$$

$$4H_2MoO_{4(s)} = 8H^+_{(sol)} + 4MoO^{2-}_{4(sol)} + 4\Delta H_3^0, \quad (3)$$

$$K_5Gd(MoO_4)_{4(s)} + 8HCl_{(sol)} = \\ = 5KCl_{(sol)} + GdCl_{3(sol)} + 8H^+_{(sol)} + 4MoO^{2-}_{4(sol)} + \Delta H_4^0. \quad (4)$$

Using Hess's law, it is possible to write:

$$2.5K_2CO_{3(s)} + GdCl_{3(s)} + 4H_2MoO_{4(s)} = \\ = K_5Gd(MoO_4)_{4(s)} + 3HCl_{(sol)} + 2.5H_2O + 2.5CO_{2(g)} + \Delta H_5^0, \quad (5)$$

$$\Delta H_5^0 = 2.5\Delta H_1^0 + \Delta H_2^0 + 4\Delta H_3^0 - \Delta H_4^0. \quad (6)$$

The measured solution enthalpies for $K_5Gd(MoO_4)_4$, K_2CO_3, $GdCl_3$ and H_2MoO_4 were the following:

$$\Delta_{sol}H^0(K_2CO_3) = -56.54 \pm 1.43 \text{ kJ mol}^{-1},$$

$$\Delta_{sol}H^0(GdCl_3) = -170.51 \pm 0.71 \text{ kJ mol}^{-1},$$

$$\Delta_{sol}H^0(H_2MoO_4) = +7.49 \pm 0.75 \text{ kJ mol}^{-1},$$

$$\Delta_{sol}H^0[K_5Gd(MoO_4)_4] = -147.15 \pm 5.08 \text{ kJ mol}^{-1}.$$

The solution enthalpies were calculated as average values from six parallel calorimetric experiments. The uncertainty was calculated for the 95% confidence interval using the Student's coefficient.

Using Hess's law, we calculated the reaction enthalpy:

$$\Delta H_5^0 = -134.75 \pm 5.80 \text{ kJ mol}^{-1}.$$

To calculate the formation enthalpy for $K_5Gd(MoO_4)_4$ using the above reaction (5), the data on standard formation enthalpies for $GdCl_3$, HCl, H_2O, K_2CO_3, H_2MoO_4 and CO_2 are needed.

Data were taken from the reference online source[22] and were the following: $\Delta_fH^0(HCl) = -164.4 \pm 0.2$ kJ mol^{-1}, $\Delta_fH^0(GdCl_{3(s)}) = -1005.415 \pm 1.464$ kJ mol^{-1}, $\Delta_fH^0(CO_{2(g)}) = -393.513 \pm 0.046$ kJ mol^{-1}, $\Delta_fH^0(H_2O) = -285.829 \pm 0.040$ kJ mol^{-1}, $\Delta_fH^0(K_2CO_{3(s)}) = -1153.110 \pm 2.092$ kJ mol^{-1} and $\Delta_fH^0(H_2MoO_{4(s)}) = -1046.125 \pm 0.962$ kJ mol^{-1}.

Using the obtained ΔH_5^0 value and the published data on standard formation enthalpies of $GdCl_3$, HCl, H_2O, K_2CO_3, H_2MoO_4 and CO_2, the standard formation enthalpy for $K_5Gd(MoO_4)_4$ was calculated to have the following value:

$$\Delta_fH^0[K_5Gd(MoO_4)_{4(s)}] = -6015.89 \pm 6.63 \text{ kJ mol}^{-1}.$$

This standard formation enthalpy was determined for the first time.

Next, the stabilization energy ($\Delta_{st}H^0$) was calculated using the obtained standard formation enthalpy. To calculate the stabilization energy, the data on formation enthalpies of simple oxides K_2O, Gd_2O_3 and MoO_3 were needed.

The following data were taken from the reference online source:[22]

$$\Delta_fH^0(K_2O) = -362.334 \text{ kJ mol}^{-1},$$

$$\Delta_fH^0(Gd_2O_3) = -1820.458 \text{ kJ mol}^{-1},$$

$$\Delta_fH^0(MoO_3) = -745.170 \text{ kJ mol}^{-1}.$$

The stabilization energy was calculated as the enthalpy of the following reaction:

$$2.5K_2O + 0.5Gd_2O_3 + 4MoO_3 = K_5Gd(MoO_4)_4 + \Delta_{st}H^0. \quad (7)$$

In this case, the uncertainty for $\Delta_{st}H^0$ was calculated as a sum of uncertainties for enthalpies included in the above reaction.

The calculated stabilization energy for $K_5Gd(MoO_4)_4$ was the following:

$$\Delta_{st}H^0 = -1219.15 \pm 6.63 \text{ kJ mol}^{-1}.$$

Since the stabilization energy has a negative value, it can be concluded that the compound is thermodynamically stable with respect to decomposition into simple oxides. This makes this compound promising for practical applications.

One of the main thermodynamic functions of compounds is the lattice enthalpy, which allows one to conclude about stability of compounds. Below, we calculate the lattice enthalpy based on the measured standard formation enthalpy of the $K_5Gd(MoO_4)_4$ compound using the Born–Haber cycle:

$$5K_{(s)} + Gd_{(s)} + 4Mo_{(s)} + 8O_{2(g)} = K_5Gd(MoO_4)_4 + \Delta_fH^0_{1a}, \quad (1a)$$

$$5K^+_{(g)} = 5K_{(s)} + 5\Delta_rH^0_{2a}, \quad (2a)$$

$$Gd^{3+}_{(g)} = Gd_{(s)} + \Delta_rH^0_{3a}, \quad (3a)$$

$$4Mo^{6+}_{(g)} = 4Mo_{(s)} + 4\Delta_rH^0_{4a}, \quad (4a)$$

$$16O^{2-}_{(g)} = 8O_{2(g)} + 16\Delta_rH^0_{5a}. \quad (5a)$$

The Born–Haber cycle makes it possible to calculate the lattice enthalpy:

$$5K^+_{(g)} + Gd^{3+}_{(g)} + 4Mo^{6+}_{(g)} + 16O^{2-}_{(g)} = K_5Gd(MoO_4)_4 + \Delta_{lat}H^0_{6a}, \quad (6a)$$

where $\Delta_{lat}H^0_{6a} = \Delta_fH^0_{1a} + 5\Delta_rH^0_{2a} + \Delta_rH^0_{3a} + 4\Delta_rH^0_{4a} + 16\Delta_rH^0_{5a}$.

To calculate the lattice enthalpy, in addition to the standard formation enthalpy measured by us, the standard formation enthalpies of ions K^+, Gd^{3+}, Mo^{6+} and O^{2-} are required. The standard formation enthalpies of ions were taken from the reference online source[22] and were as follows: $\Delta_fH^0(K^+) = 507.7$ kJ mol^{-1}, Δ_fH^0 $(Gd^{+3}) = 4079.4$ kJ mol^{-1}, $\Delta_fH^0(Mo^{+6}) = 22463.9$ kJ mol^{-1} and $\Delta_fH^0(O^{2-}) = 905.8$ kJ mol^{-1}.

The obtained value of the lattice enthalpy was $\Delta_{lat}H^0_{6a} = -116985$ kJ mol^{-1}.

In this case, it was impossible to calculate the uncertainty for the lattice enthalpy, since uncertainties for values of formation enthalpies for ions K^+, Gd^{3+}, Mo^{6+} and O^{2-}, taken from reference[22] and used for calculation, were not reported.

Thus, the dissolution enthalpy of potassium gadolinium molybdate, potassium carbonate and molybdenum acid was measured in 1 M hydrochloric acid. The standard formation enthalpy, stabilization energy and lattice enthalpy were calculated. It was shown that the compound is stable with respect to decomposition into simple oxides, which makes it promising for applications in wide-field pulsed lasers.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

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Received: 19th May 2025; Com. 25/7829