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Heat capacity and phase transformation of cesium monomolybdate

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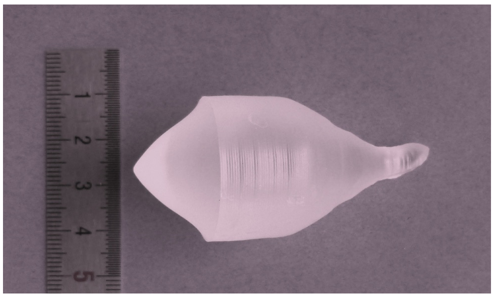
The Cs_2MoO_4 single crystal grown by the Czochralski method was characterized using X-ray diffraction analysis and its heat capacity was measured by differential scanning calorimetry in the temperature range of 319–900 K. It was found that the single crystal undergoes a phase transition at a temperature of 842 K, therefore it is promising for applications in the temperature range of 319–842 K.



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Compounds based on alkali metal (lithium, sodium and cesium) molybdates are promising materials for high-energy physics.[1–5] In addition, cesium molybdate is one of the components of radioactive waste in nuclear reactions.[6–8] Recently, much attention in the literature has been paid to the search for new materials for studying rare events, such as double neutrinoless beta decay and elastic coherent scattering of neutrinos on nuclei. The lithium molybdate crystal is one of the most used to search for double neutrinoless beta decay.[9–11] However, the problem is that lithium molybdate has low light output and is hygroscopic. It has been reported[12] that single crystals of sodium and cesium molybdates can become promising materials for searching for rare events.

To obtain high-quality single crystals of alkali metal molybdates, a detailed physicochemical analysis of the systems from which these single crystals are grown is necessary. In particular, thermodynamic studies play an important role, making it possible to calculate optimal synthesis temperatures, determine the stability and degradation of compounds, identify metastable single crystals, *etc.* Cesium molybdates single crystals are among the promising materials for various applications. The thermodynamics of cesium monomolybdate ceramics was studied in the cited works.[13–16] A single crystal of cesium monomolybdate was grown[17] by the traditional Czochralski technique and its scintillation properties were studied. There are no data in the literature on the heat capacity of the cesium molybdate single crystal, which was studied in this work. The purpose of this work was to measure the high-temperature heat capacity of a cesium monomolybdate single crystal using differential scanning calorimetry (DSC), as well as to determine the temperature and enthalpy of the phase transition.

A cesium molybdate single crystal for thermodynamic studies was grown using the low-temperature-gradient Czochralski technique.[†] Figure 1 shows a grown Cs_2MoO_4 single crystal.

Characterization of the Cs_2MoO_4 single crystal was carried out by X-ray diffraction analysis in accordance with the program described in previous articles.[18–20] The corresponding crystallographic characteristics and details of X-ray diffraction experiments are given in the footnote.[‡]

[†] A single crystal of cesium monomolybdate was grown from a melt using the low-temperature-gradient Czochralski technique. Precursors for growth were cesium carbonate Cs_2CO_3 (special purity 19-2, TU 6-09-4759-79, 99.99%) and highly purified molybdenum trioxide MoO_3. The cesium carbonate used for growth was heated at 500 K to constant weight to remove traces of moisture.

To grow a single crystal of cesium monomolybdate, the precursors were mixed in the ratio $Cs_2CO_3/MoO_3 = 1 : 1$. The growth of a Cs_2MoO_4 single crystal was carried out according to the chemical reaction: $Cs_2CO_3 + MoO_3 = Cs_2MoO_4 + CO_2\uparrow$. Single crystals were grown in platinum crucibles of 130 mm high and 70 mm in diameter. Before growing the single crystal, solid-state synthesis was performed. Solid-state synthesis was carried out in the same platinum crucibles from which the crystals were grown. The precursors were mixed and placed in a crucible. The crucible was closed with a platinum lid equipped with a tube. Then the crucible was placed in a three-zone resistance furnace, heated to 1000 K at a rate of 30 K h^{-1} and kept at this temperature for 5 h. The completeness of the solid-state reactions was monitored by observing the weight changes associated with CO_2 gas evolution and comparing them with the calculated weight changes. After completion of the solid-state reaction, the temperature was increased 5 K above the melting point at a rate of 70 K h^{-1}. The melt was kept at this temperature for more than 5 h to completely homogenize the melt. Cs_2MoO_4 crystals were grown in air using unoriented seeds. The process of growing crystals was carried out automatically.

The Cs_2MoO_4 single crystal was analyzed by atomic absorption spectrometry in an air–acetylene flame. The standard uncertainty was 0.1–0.7%. The results of chemical analysis showed that the Cs_2MoO_4 single crystal has a mass fraction purity of more than 99.2% and is described by the following composition: $Cs_{1.997 \pm 0.003}Mo_{0.998 \pm 0.002}O_4$.

According to the published data,[5] the luminescence wavelength of a Cs_2MoO_4 single crystal is 435 nm. It was found that the luminescence light yield of the Cs_2MoO_4 crystal at 10 K has the similar magnitude as that of the Li_2MoO_4 crystal.

[‡] *Crystallographic data for cesium monomolybdate*. Cs_2MoO_4, $M = 425.76$, crystal size 0.03 × 0.02 × 0.01 mm, orthorhombic, space group

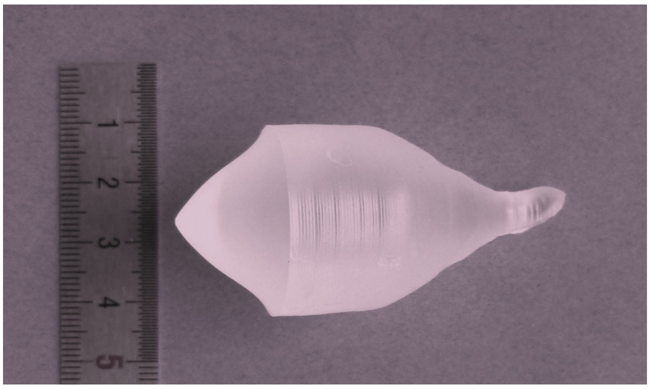

Figure 1 Grown single crystal of cesium molybdate.

Cs_2MoO_4 crystallizes in the orthorhombic system (Figure 2). The environment of the Mo(1) atom consists of four oxygen atoms forming a polyhedron in the form of a tetrahedron. The environment of the Cs(1) atom includes ten oxygen atoms located at the vertices of a polyhedron, which is a distorted bicapped square antiprism. The Cs(2) atom is surrounded by nine oxygen atoms arranged in a polyhedron classified as a monocapped square antiprism. Polyhedra are connected along triangular faces, edges or vertices to form a 3D frame. The Cs polyhedra are connected to each other along triangular faces, the Mo tetrahedra do not share O atoms with each other, and the Cs and Mo polyhedra are connected either along an edge or at a vertex. The lattice parameters of the Cs_2MoO_4 single crystal obtained in this work are in good agreement with the lattice parameters published previously:[5] $a = 8.606$, $b = 6.571$ and $c = 11.594$ Å.

The heat capacity of a single crystal of cesium monomolybdate in the temperature range of 319–900 K was measured by DSC at a heating rate of 6 K min^{-1} in a flowing argon atmosphere.[§] The experimental technique of DSC measurements was described in detail in previous articles.[21–23]

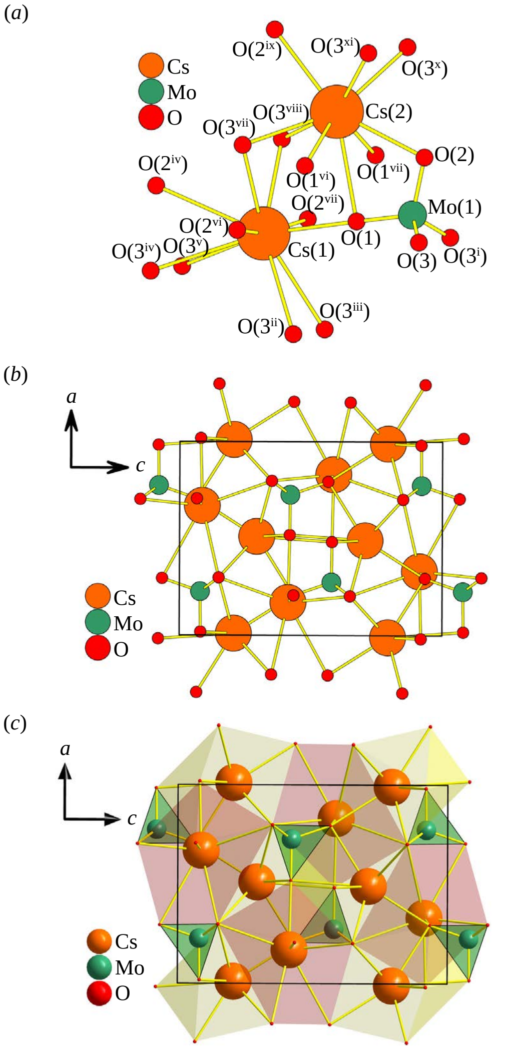

Figure 2 (*a*) Fragment of the crystal structure of Cs_2MoO_4, (*b*) projection onto the *ac* plane and (*c*) the same fragment where only polyhedra are shown.

When measuring the heat capacity of a Cs_2MoO_4 single crystal, three heating–cooling cycles were carried out. The data obtained in the second and third thermal cycles are in very good agreement with each other, but differ from the data obtained during the first heating. This was due to the fact that during the first heating the sample was annealed and absorbed impurities were removed.

The temperature dependences of the heat capacity of the Cs_2MoO_4 single crystal according to the data obtained in this work and the low-temperature heat capacity of the Cs_2MoO_4 powder measured earlier in another work[24] are presented in Figure 3.

In the Cs_2MoO_4 sample (see Figure 3), one phase transition was detected in the temperature range of 319–900 K. It should be noted that after the first, second and third heating cycles, the mass of the investigated samples practically did not changed. The phase transition temperature (T_{tr}), as well as the phase transition enthalpy (ΔH_{tr}) for the Cs_2MoO_4 single crystal, measured in this work, have the following values: $T_{tr} = 842.0 \pm \pm 0.4$ K and $\Delta H_{tr} = 5.35 \pm 0.16$ kJ mol^{-1}.

The previously measured[25] temperature and enthalpy of the phase transition in polycrystalline Cs_2MoO_4 are $T_{tr} = 841.3 \pm 0.4$ K and $\Delta H_{tr} = 4.6 \pm 0.1$ kJ mol^{-1}. Considering that the measurements in this work were performed on a single crystal, and in a previously published work[25] a polycrystalline sample was

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Pnma (no. 62), at 150(2) K: $a = 8.4927(13)$, $b = 6.5024(10)$ and $c = 11.533(2)$ Å, $V = 636.88(18)$ Å^3, $Z = 4$, $d_{calc} = 4.440$ g cm^{-3}.

X-ray diffraction analysis of single crystals was performed on a Bruker D8 Venture diffractometer (three-circle goniometer, Incoatec IμS 3.0 microfocus source, MoKα radiation, focusing and monochromatization with multilayer Montel mirrors, PHOTON III CPAD detector, resolution 768 × 1024). The sample temperature was maintained at 150(2) K using an Oxford Cryosystems Cryostream 800 plus cryostat. The intensity of reflections was measured by ω-scanning narrow (0.5°) frames. Absorption correction was introduced semi-empirically using the SADABS program package.[18] The structures were solved by the direct method and refined by full-matrix LSM in the anisotropic approximation for all non-hydrogen atoms using the SHELXL software package.[19] Images of the structures of the investigated compounds were obtained using Diamond 3.2 software.[20]

[§] The heat capacity of the samples was measured on a Netzsch DSC 404 F1 Pegasus® high-temperature differential scanning calorimeter in platinum crucibles with corundum liners and platinum lids at a heating rate of 6 K min^{-1} in a flowing argon atmosphere (20 ml min^{-1}). The samples were prepared by cutting a cylinder with a diameter of 5 mm and a thickness of 1 mm from the single crystal and placed in a platinum crucible. The tight fit of the cut cylinder to the crucible ensured good contact and good measurement accuracy.

The mass of the samples was weighed on an A&D GH-252 semi-micro analytical balances with an error of no more than 0.03 mg and amounted to 109.62 mg for Cs_2MoO_4. Before each thermal cycle, the working volume of the calorimeter was evacuated to a residual pressure of 1 Pa and purged several times with high-purity argon (99.999 vol%), containing 0.0001% O_2, 0.0005% N_2, 0.0004% H_2O, 0.00002% CO_2, 0.0001% CH_4 and 0.0001% H_2 as main impurities. Sapphire weighing 85.28 mg was used as a calibration sample. The measurement error for this calorimeter was estimated at 2–3%, which was confirmed by experiments with high-purity samples of platinum and sapphire.

As described in the DSC instructions, heat flow, temperature and sensitivity calibrations were performed by determining the temperature and enthalpy of fusion of the recommended samples at the same flow rate of the same gas as in the experiments and using the same samples.

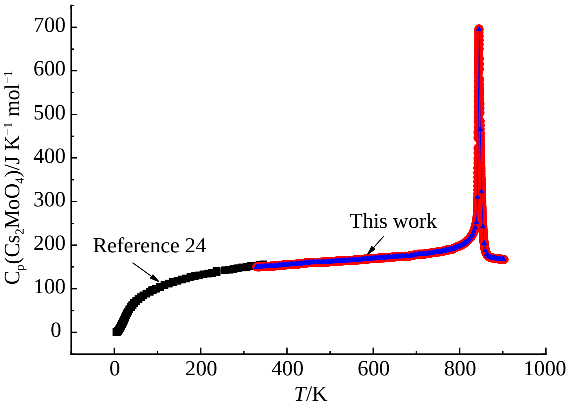

Figure 3 Temperature dependence of the heat capacity of a single crystal of Cs_2MoO_4 measured in this work during the first (blue line) and second (red line) heating, as well as low-temperature heat capacity data for Cs_2MoO_4 powder from ref. 24 (black line).

measured, it can be assumed that there is a good agreement between the data obtained here and the published data.[25] According to the data of that work,[25] the observed phase transition was associated with the transformation of the orthorhombic Cs_2MoO_4 polymorph into a tetragonal one. The heat capacity for single-crystalline Cs_2MoO_4 obtained in this work agrees with the heat capacity of polycrystalline Cs_2MoO_4 within 3%.

In this work, the heat capacity of a Cs_2MoO_4 single crystal, a material for high-energy physics, was measured for the first time. It was shown that the Cs_2MoO_4 single crystal is promising for application in the temperature range of 319–842 K.

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