

## Mass-spectrometric studies of the charge for CdWO<sub>4</sub> crystal growth

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The cadmium tungstate charge has been tested by mass-spectrometry. The charge criterion quality is the absence of ammonia-containing impurities that form ammonia and hydroxide under decomposition. The preliminary heat treatment in air at 700°C favors the removal of organic impurities, ammonium salts, and hydroxides.

Проведено тестирование шихты вольфрамата кадмия масс-спектрометрическим методом. Критерием качества шихты является отсутствие аммониевых примесей, разлагающихся с образованием аммиака и гидроксидов. Предварительная термическая обработка шихты в атмосфере воздуха при температуре 700°C способствует удалению органических примесей, аммониевых солей и гидроксидов.

The high-efficiency scintillators based on cadmium tungstate (CdWO<sub>4</sub>) single crystals are used widely in X-ray tomography, radiation monitoring devices, and spectrometric devices for ionizing radiation recording. They also are a material of good prospects for recording of rare processes in experiments intended to search for double beta decay and dark matter. In this connection, the manufacturing of said crystals with high scintillation characteristics is an actual task. The present impurities (about 10<sup>-4</sup> wt, %) may influence considerably the transmission, light yield, energy resolution, and afterglow of CdWO<sub>4</sub> crystals [1].

The cadmium tungstate crystals grown by Czochralski technique show sometimes a greenish tint [2, 3]. The crystal coloration may be associated with several factors, including the following: presence of uncontrolled impurities [4, 5]; light scattering on colloidal particles [6]; the melt stoichiometry violation due to high volatility of cadmium oxide resulting in enrichment of the melt in tungsten oxide and WO<sub>3</sub> segregation as a phase [2, 7, 8]; the tungsten valence lowering due to redox reactions running during the charge preparation

and/or the crystal growing. At present, there is no common opinion about the actual causes of the crystal green color. The coloration results most likely from a combination of the above factors. The initial salts are controlled as a rule for the metal content (the cationic composition) while the impurity anions are set aside due to difficulties in the analytical determination. It has been noted in practice that the use of raw materials differing in ionic composition results in crystals differing in characteristics, although the concentrations of cations are within the allowed limits in all the cases.

The mass-spectrometric measurements of thermal desorption are among informative methods to study processes running during a substance heating. Before, the thermal desorption of CdWO<sub>4</sub> was studied within 100–800°C temperature range, and it was shown that during the heating, vacancies are probably formed in the cationic sublattice but not in the oxygen one. The initial salts were not studied.

To understand the processes running during the cadmium tungstate heating, its testing for thermal desorption is of both scientific and practical interest. The testing

was carried out by mass-spectrometric technique described in [10, 11] in detail. Three samples of raw  $\text{CdWO}_4$  were studied: Sample #1 — the initial material resulting in green-colored crystals (the salt synthesized from aqueous solutions of cadmium nitrate and ammonium para-tungstate); Sample #2 — the Sample #1 pre-treated for 5 h in air at  $700^\circ\text{C}$ ; and Sample #3 — the raw material that has given a colorless crystal (the salt synthesized from oxides by solid-phase technique). All three salt samples were stoichiometric and approximately of the same composition with respect to cationic impurities. The total content of controllable impurities did not exceed  $10^{-3}$  wt, %. The samples to be studied of 30 g mass were loaded into a quartz ampoule that was evacuated down to  $10^{-2}$  Torr residual pressure and then heated up to  $800^\circ\text{C}$  at the temperature raise rate of  $200^\circ\text{C}$  per hour. The gas phase composition was monitored using an IPDO-2 mass-spectrometer. The mass-spectrometric measurement results are presented in Figs. 1–6.

According to the experimental data, the following compounds are released during heating of the Sample #1 (Figs. 1 and 2): water within two temperature ranges ( $30\text{--}300^\circ\text{C}$  with a maximum at  $110^\circ\text{C}$  and  $400\text{--}700^\circ\text{C}$  with a maximum at  $590^\circ\text{C}$ );  $\text{NH}_3$  and  $\text{H}_2$  at  $200\text{--}600^\circ\text{C}$ ;  $\text{N}_2$  at  $200\text{--}500^\circ\text{C}$  as well as at heating above  $600^\circ\text{C}$ ;  $\text{CO}$  within temperature ranges of  $300\text{--}500^\circ\text{C}$  and  $500\text{--}800^\circ\text{C}$ , an insignificant increase in  $\text{CO}_2$  content being also observed at  $300\text{--}700^\circ\text{C}$ ; hydrocarbons of varying composition at  $300\text{--}600^\circ\text{C}$ . In contrast to the Sample #1, when testing the salt Sample #2 pre-treated in air, the following phenomena were observed (Figs. 3 and 4): water desorption within a single temperature range ( $300\text{--}300^\circ\text{C}$ ); intense  $\text{N}_2$  release above  $700^\circ\text{C}$ ;  $\text{CO}$  release at  $600\text{--}800^\circ\text{C}$  only and  $\text{CO}_2$  release at  $30\text{--}300^\circ\text{C}$  and  $500\text{--}800^\circ\text{C}$ ;  $\text{O}_2$  release within the whole temperature range studied. The testing of the Sample #3 has shown that water vapor, carbon dioxide and carbon monoxide were released in the temperature ranges of  $30\text{--}400^\circ\text{C}$ ,  $450\text{--}800^\circ\text{C}$ , and  $370\text{--}700^\circ\text{C}$ , respectively. In addition, small amounts of hydrogen and hydrocarbons were observed to be released at  $450\text{--}700^\circ\text{C}$ .

It is to note that when all the Samples #1, 2, and 3 are heated in vacuum above  $400^\circ\text{C}$ , a black film with metallic glance is deposited onto cold wall of the quartz ampoule. According to the chemical analysis data, the film consists of metallic cadmium.

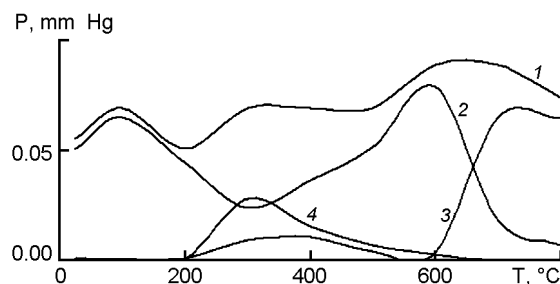


Fig. 1. Variation of the total pressure (1) and partial pressures of  $\text{H}_2\text{O}$  (2),  $\text{N}_2$  (3) and  $\text{NH}_3$  (4) during heating of the Sample #1 salt in vacuum.

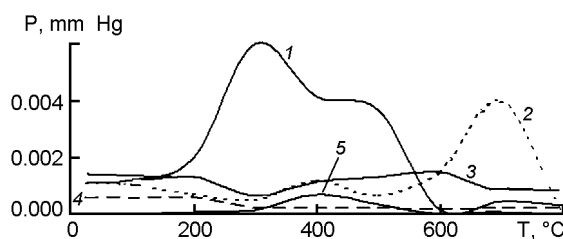


Fig. 2. Variation of the partial pressures of  $\text{H}_2$  (1),  $\text{CO}$  (2),  $\text{CO}_2$  (3),  $\text{O}_2$  (4) and hydrocarbons (5) during heating of the Sample #1 salt in vacuum.

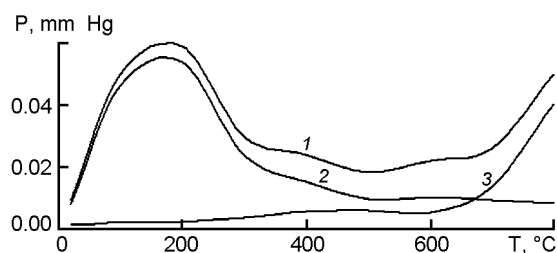


Fig. 3. Variation of the total pressure (1) and partial pressures of  $\text{H}_2\text{O}$  (2) and  $\text{N}_2$  (3) during heating of the Sample #2 salt in vacuum.

However, the treatment of the Sample #3 resulted in formation of several dark islands on the ampoule wall, the Sample #1 gave a continuous mirror-like coating along the whole perimeter of the 7–10 cm height ampoule.

Let us consider the possible processes running during the cadmium tungstate heating.

**Water vapor release.** Water is released within two temperature ranges: 30 to  $400^\circ\text{C}$  (typical of all the samples studied) and  $400$  to  $700^\circ\text{C}$  (for the Sample #1). The  $30\text{--}400^\circ\text{C}$  range is wide enough to interpret the water release. First of all, adsorbed water molecules are removed from the cadmium tungstate particle surface. This hypothesis is confirmed by the fact that said

temperature range is typical of all the samples tested. In the case of impurities forming crystal hydrates (which cadmium tungstate does not form), the hydrates should be decomposed during the heat pre-treatment, so a change in the mentioned temperature range should be expected. However, the pre-treatment for 5 h at 700°C does not cause any variation in the water release character within the first temperature range.

Water release within the second temperature range (400 to 700°C) is observed only for the Sample #1. That range corresponds to decomposition of the II Group metal hydroxides [12]. The pre-heating favors the decomposition of hydroxide impurities while no water release is observed during the subsequent heating. Thus, the heat pre-treatment favors the removal of hydroxide impurities.

$\text{NH}_3$ ,  $\text{N}_2$  and  $\text{H}_2$  release at 200–600°C. These compounds are released, first of all, at testing of the Sample #1. This fact is connected in first turn to the salt preparation pre-history (cadmium tungstate being obtained in aqueous solution). The synthesis in solution is accompanied by capturing of the mother liquor and unreacted raw materials, in particular, ammonium salts which, being decomposed above 200°C, cause the  $\text{NH}_3$  release. The  $\text{N}_2$  and  $\text{H}_2$  release at those temperatures is due to  $\text{NH}_3$  decomposition [13]. The heat pre-treatment provides the removal of ammonium-containing impurities from the initial charge.

*Hydrocarbon release.* The presence of said compounds in the course of cadmium tungstate heating evidences the initial contamination of the raw materials with organic impurities. The organic impurities are present both in Sample #1 and Sample #3. Their decomposition starts at temperatures exceeding 200°C due to pyrolysis reactions with formation of various hydrocarbons [14] (the total hydrocarbon amounts are presented in Figs. 2 and 6, curves 5 and 4, respectively). The decomposition of organic compounds under heating of cadmium tungstate is similar to that for sodium iodide and is considered in detail in [15]. Furthermore, the pyrolysis processes may cause formation of  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ . An insignificant  $\text{CO}_2$  and  $\text{CO}$  release is observed at 300–700 and 300–500°C, respectively (Fig. 2). The  $\text{CO}$  release within the 550 to 800°C range is due more likely to chemisorption [16]. Perhaps the hydrogen release also takes place at the decomposition of organic impurities but its amount is small as compared to that

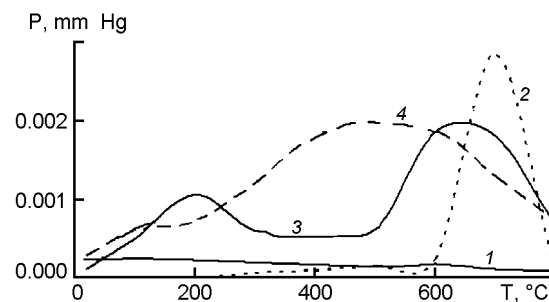


Fig. 4. Variation of the partial pressures of  $\text{H}_2$  (1),  $\text{CO}$  (2),  $\text{CO}_2$  (3), and  $\text{O}_2$  (4) during heating of the Sample #2 salt in vacuum.

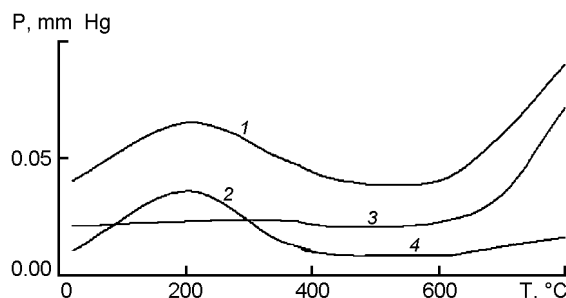


Fig. 5. Variation of the total pressure (1) and partial pressures of  $\text{H}_2\text{O}$  (2) and  $\text{N}_2$  (3) during heating of the Sample #3 salt in vacuum.

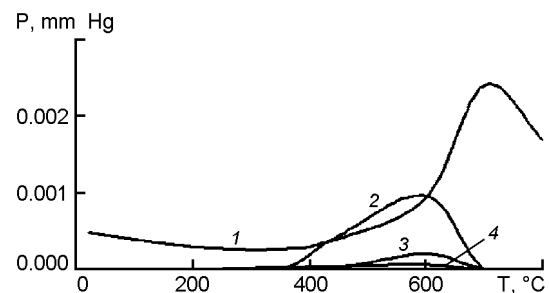


Fig. 6. Variation of the partial pressures of  $\text{CO}$  (1),  $\text{CO}_2$  (2),  $\text{H}_2$  (3) and hydrocarbons (4) during heating of the Sample #3 salt in vacuum.

formed due to ammonium decomposition. The heat pre-treatment (Sample #2) favors the complete oxidation of organic impurities.

$\text{N}_2$  release above 600°C. The  $\text{N}_2$  release under heating of cadmium tungstate charge above 700°C is a rather unexpected phenomenon. The nitrogen release character above 600°C is essentially independent of the sample pre-history (Samples #1 and #3) and pre-treatment (Sample #2). Perhaps it is due to desorption of the chemisorbed nitrogen from the cadmium tungstate particle surface [16].

Thus, basing on the testing results, a qualitative distinction of the charge consists in the presence of ammonium-contain-

ing impurities decomposing under ammonia formation that may cause a violation of cadmium tungstate stoichiometry and reduction of W(VI) as well as in the presence of hydroxides decomposing under water formation. The preliminary heat treatment of the initial cadmium tungstate charge in air at 700°C favors the charge purification from organic impurities, ammonium salts, and hydroxides.

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## Мас-спектрометричні дослідження шихти для отримання кристалів CdWO<sub>4</sub>

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Проведено тестування шихти вольфрамату кадмію мас-спектрометричним методом. Критерієм якості шихти є відсутність домішок амонієвих сполук, які розкладаються з утворенням аміаку та гідроксидів. Попередня термічна обробка шихти в атмосфері повітря при температурі 700°C сприяє видаленню органічних домішок, амонієвих сполук та гідроксидів.