

Mass-spectrometric study of thermal desorption processes at vacuum heating of lithium iodide used to LiI(Eu) crystal growing

D.S.Sofronov, A.Yu.Voloshko, O.V.Shishkin

State Scientific Institution "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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The thermal desorption at vacuum heating of fused LiI used to grow crystals has been studied using mass spectrometry. Water has been found to be released at 30–100 and 100–170°C due to decomposition of the residual hydrate as well as oxygen above 200°C. The oxygen release may be caused by decomposition of an impurity formed due to the hydrate dehydration.

Проведено масс-спектрометрическое исследование процесса термодесорбции при нагревании в вакууме плавленного иодида лития, используемого для выращивания монокристаллов. Установлено, что имеет место выделение воды при 30–100 и 100–170°C, связанное с разложением остатков гидрата, а также выделение кислорода при нагревании свыше 200°C. Возможно, что выделение кислорода связано с разложением примеси, образовавшейся при обезвоживании гидрата.

LiI(Eu) crystals find use as neutron detectors [1]. The purity grade of the initial salt is among the main factors affecting the performance of the crystals. This is true, in particular, for the content of oxygen-containing impurities (CO_3^{2-} , OH^- , and O^{2-}) that is defined by the salt production pre-history. Lithium iodide is produced conventionally by treatment of pure lithium carbonate solution with hydroiodic acid at a temperature below 77°C or by treatment of lithium sulfate solution with barium iodide. Lithium iodide is released from aqueous solutions as $\text{LiI}\cdot 3\text{H}_2\text{O}$ crystal hydrate. The dehydration thereof into anhydrous high-purity product is an extremely difficult operation. Water removal occurs at elevated temperatures and is complicated by the hydrolysis resulting in lithium hydroxide or lithium oxide formation [2, 3]. The final product obtained by dehydration in air or in vacuum contains the LiOH impurity. The melting in the presence of excess iodine does not prevent the hydrolysis. The dehy-

dration in a hydrogen iodide flow during 1.5 to 2 h results in formation of a product containing water in an amount of 2 to 3 mass. %. The vacuum sublimation (0.01 Torr, 800–850°C) provides the water content lowering down to 0.01 or 0.02 mass. % [2]. Moreover, a contact with water vapor causes formation of the hydrate due to a high hygroscopicity of lithium iodide.

Thus, it is just water molecules and hydroxyl groups that are to be expected as the main oxygen-containing impurities in lithium iodide. Accordingly, in the course of the salt preparation to crystal growing (its heating up to melting), the hydrate decomposition is possible resulting in formation of water molecule accompanying with the salt hydrolysis and hydroiodic acid release. The former baric and spectrometric studies of the initial raw material for the crystal growing have shown [4] that the heating in vacuum causes water release within two temperature ranges, namely, 30–95°C (with

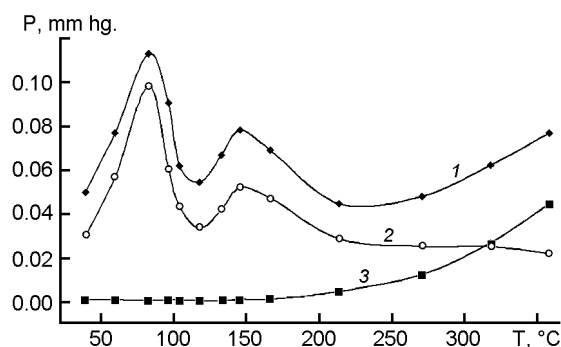


Fig. 1. Variation of the total pressure (1), partial pressure of H_2O (2) and oxygen (3) during heating of lithium iodide.

a maximum at 65°C) and $100\text{--}160^\circ\text{C}$ (with a maximum at 140°C). At the same time, the pressure in the vacuum system increases as the salt is heated up to above 280°C , that increase being not connected with the water release. That is, another gaseous species may be released. That substance is presumably hydrogen iodide that is formed due to lithium iodide hydrolysis in water vapor. This work is aimed at the study of processes occurring during lithium iodide heating in vacuum.

In the work, fused lithium iodide available in sealed ampoules and being used to grow single crystals was studied using the mass spectrometry [5]. A sample of 10 to 50 g weight was placed in a quartz ampoule that was the evacuated down to the utmost vacuum ($5 \cdot 10^{-2}$ Torr). Then the sample was heated to 420°C at the heating rate of $150^\circ\text{C}/\text{h}$. During the heating, the pressure changes as well the gas atmosphere composition were recorded using an IPDO-2 mass spectrometer. It follows from the mass-spectrometric data that there are two water release peaks within $30\text{--}95^\circ\text{C}$ and $100\text{--}170^\circ\text{C}$ ranges (Fig. 1). The results agree well with the former spectrometric data [4] and are most likely due to the decomposition of the hydrate impurity that was formed in the contact with water vapor. At temperatures exceeding 200°C , the oxygen release into the gas phase is found that is intensified considerably above 280°C . No hydroiodic acid was seen to be released.

The oxygen release may be due to decomposition of iodate impurity formed according to the reaction scheme [6]



Lithium iodate is known to melt at 435°C [7]. A pure transparent melted lithium io-

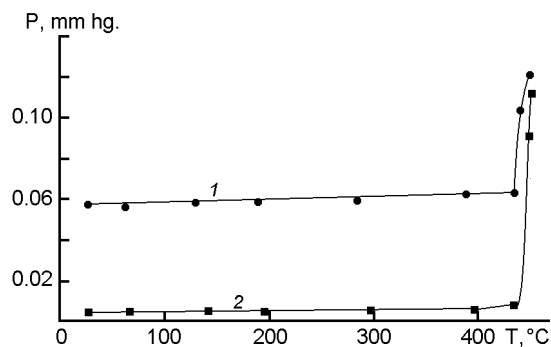


Fig. 2. Variation of the total pressure (1) and oxygen partial pressure (2) during heating of lithium iodate.

date starts to decompose above 450°C under release of oxygen bubbles; above 460°C , iodine vapor is released, too. Moreover, a weight loss has been reported to be observed within $240\text{--}420^\circ\text{C}$ range that is due to a partial decomposition of the salt. Thus, it is just the lithium iodate impurity decomposition that could explain the oxygen release during lithium iodide heating. To check that hypothesis, the lithium iodate decomposition in vacuum was studied using mass spectrometry (Fig. 2). Its decomposition accompanied by oxygen formation has been found to proceed at 450°C . No gaseous species were released within the $240\text{--}420^\circ\text{C}$ range. No water vapor was observed to be released, too. The results obtained indicate that the oxygen release from the studied lithium iodide samples above 200°C cannot be associated with lithium iodate decomposition.

Thus, when the fused lithium iodide is heated in vacuum, water vapor is released within $30\text{--}95^\circ\text{C}$ (with a maximum at 65°C) and $100\text{--}160^\circ\text{C}$ (with a maximum at 140°C) ranges due to decomposition of the hydrate impurity; moreover, oxygen is released above 200°C . The oxygen release is associated most likely with decomposition of an impurity that was formed in the course of lithium iodide hydrate decomposition. Identification of that impurity requires a further investigation and is necessary to provide the high quality of lithium iodide crystals.

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**Мас-спектрометричні дослідження процесів
термодесорбції при нагріванні у вакуумі йодиду
літію, використовуемого для вирощування
монокристалів LiJ(Eu)**

Д.С. Софронів, О.Ю. Волошко, О.В. Шишкін

Проведено мас-спектрометричні дослідження процесу термодесорбції при нагріванні плавленого йодиду літію, придатного для вирощування монокристалів. Встановлено, що при нагріванні його у вакуумі відбувається виділення води при 30-100 та 100-170°C, яке пов'язане з розкладанням залишків гідрату, а також виділення кисню при нагріванні більш 200°C. Виділення кисню можливо пов'язано з розкладанням домішки, яка утворилася в результаті зневоднення гідрату.