

Dehydration of alkali metal iodides in vacuum

D.S.Sofronov, B.V.Grinyov, A.Yu.Voloshko, V.G.Gerasimov^{},
E.M.Kisil, N.N.Smirnov, O.V.Shishkin*

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine
^{*}V.Karazin Kharkiv National University, 4 Svobody Sq.,
61077 Kharkiv, Ukraine

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The behavior of lithium, sodium, and cesium iodides under heating in vacuum has been studied using baric method and spectrometry. Water release into the gas phase has been found to occur from the materials within various temperature ranges. The water release at the alkali metal iodides seems to be connected with decomposition of the impurity phase containing hydroxyl groups.

Исследовано поведение йодидов лития, натрия и цезия при нагревании в вакууме методами барического и спектрометрического анализа. Показано, что для рассматриваемых соединений выделение воды в газовую фазу наблюдается в различных температурных интервалах. Выделение воды при нагревании йодидов щелочных металлов, по-видимому, связано с разложением примесной фазы, содержащей гидроксильные группы.

The functional materials on the basis of the alkali metal iodides are applied widely in the science and technique [1, 2]. The main problem at manufacturing of these materials is the formation of impurities during raw material preparation connecting with the salt hydrolysis process under heating and formation of oxygen-containing impurities [3]. The problem to be when developing the drying technology for such materials, it is necessary not only to provide high rates of dehydration reaction, but also to prevent hydrolysis. Vacuum dehydration is among the ways to solving this problem.

Lithium iodide is known to form several crystallohydrates: $\text{LiI}\cdot\text{H}_2\text{O}$, $\text{LiI}\cdot 2\text{H}_2\text{O}$, and $\text{LiI}\cdot 3\text{H}_2\text{O}$ [4]. The decomposition of $\text{LiI}\cdot 2\text{H}_2\text{O}$ and $\text{LiI}\cdot 3\text{H}_2\text{O}$ to monohydrate proceeds without hydrolysis. The attempts to break off the last water molecule from crystallohydrate without hydrolysis have appeared unsuccessful. The dehydration of lithium iodide crystallohydrate in vacuum gives a product with the LiOH content 0.025 to 0.08 % [5]. Melting with excess iodine does

not prevent the hydrolysis. Sublimation of the salt in vacuum (0.01 Torr) at 800–850°C results in the product with the water content of 0.01 to 0.02 % [6].

In the system $\text{NaI}-\text{H}_2\text{O}$, several crystallohydrates have been found: $\text{NaI}\cdot 5\text{H}_2\text{O}$ (existing at temperatures lower than -31.5°C), dihydrate $\text{NaI}\cdot 2\text{H}_2\text{O}$ (from -13.5 to 68°C) showing an invariant transition point to NaI at 68°C and 74.8 % NaI [7] or 68.2°C and $P_{\text{H}_2\text{O}} = 6.32$ кПа [8], and metastable $\text{NaI}\cdot x\text{H}_2\text{O}$ showing an invariant transition at 60°C and 74.5 % NaI . According to [9], the metastable form exists within 30–40°C range at supposed $x = 0.5$.

Cesium iodide is known to not form crystallohydrates, and there are no literature data on the removal of residual water therefrom.

The first publication considering specific features of vacuum dehydration sodium iodide crystals was appeared only in 1991 [11]. The heat treatment of sodium iodide crystals has shown that water molecules

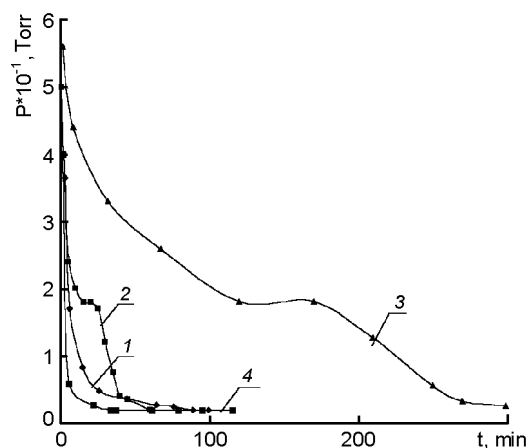


Fig. 1. Variation of pressure in vacuum system during pumping-out at ambient temperature for alkali metal iodides: Lil (1), NaI (2), NaI·2H₂O (3) and Csl (4).

leave the surface of single crystals at 150 and 300–350°C [11], as has been confirmed by mass-spectrometry. These were in contradiction with the literature ones. Dehydration of sodium iodide containing a small amount of water (0.2 %) as an impurity in the crystalhydrate carried out in vacuum has shown a peak at 127–347°C with a maximum at 240°C in the pressure-temperature dependence [3]. This was interpreted as decomposition of high-temperature binding of sodium iodide with water. However, no data were submitted to identification of the relevant compounds.

The purpose of this work was to study the behavior of lithium, sodium, and cesium iodides at heating in vacuum and identification of the baric analysis responses. The study was out using a method based on recording of pressure in the system under continuous pumping-out of the decomposition volatile products [3, 12] and spectrometry [13]. The sample mass was varied from 30 to 100 g. The philosophy of measurement is described in [14]. The salt samples were charged into quartz ampoules which were connected to the vacuum system. The heating was carried out in a small-sized furnace at temperature steps of 6–8°C with holding at least 3 min at each step. The pressure variations in vacuum system were fixed by a manometric valve according to the vacuum gauge indications. The water removal was monitored using a spectrometer connected to the vacuum system and tuned to characteristic frequency of water molecules (325152.82 MHz [15]).

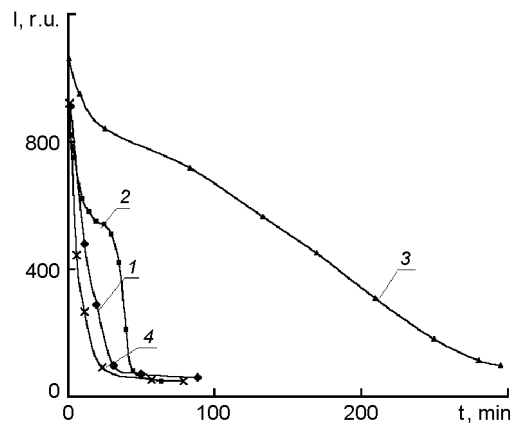


Fig. 2. Intensity of the molecular water spectral absorption line during the heat treatment of: Lil (1), NaI (2), NaI·2H₂O (3) and Csl (4).

It follows from the data obtained that the dehydration of the metal alkali iodides in vacuum at ambient temperature proceeds practically at the same manner (Fig. 1): after pumping-out of atmospheric air, a certain arises pressure in the system due to water transition to the gas phase. The fact that the system pressure is associated directly with the release of water molecules from the salts into the gas phase is confirmed by spectrometric measurements (Fig. 2), from which it follows that the intensity change of the molecular water absorption and the pressure changes in the system are similar in character. In accordance with reduction of water content, the vacuum in the system raises up to a limiting value. The attainment of the ultimate vacuum characterizes the discontinuance of water release from the salts under the experiment conditions. At the subsequent heating of salts, the gas release from the salts is observed in various temperature ranges.

So for the lithium iodide sample dehydration at the temperature of 25°C (Fig. 3), the baric response is observed at heat treatment in two temperature ranges: 30–95°C with a maximum at 65°C and 100–160°C with a maximum at 140°C. Both those signals of spectrometer correspond to water release. The signal at temperature exceeding 280°C is not associated with water release into the gas phase, since no changes on the molecular water absorption wavelength are recorded. This peak seems to be associated with the release of elementary iodine (I₂) that is observed visually as an intense coloration of the ampoule walls that is characteristic for iodine.

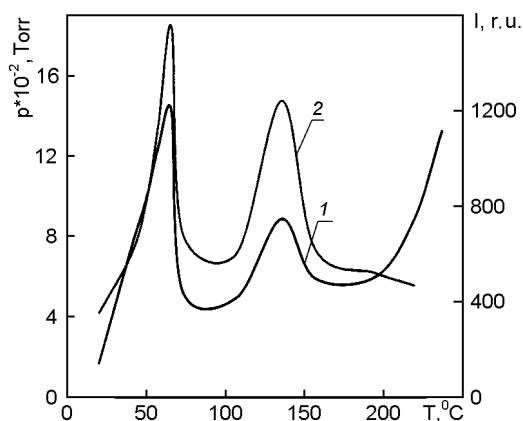


Fig. 3. Variation of pressure in vacuum system (1) and intensity of the molecular water spectral absorption line (2) during the heat treatment of lithium iodide.

Heating of sodium iodide (Fig. 4, curve 1) results in gas release from the salt in temperature ranges 180–280°C (maximum at 230°C) and 280–450°C (maximum at 350°C). According to spectrometric data, these peaks are associated with the molecular water release (Fig. 4, curve 2). In case of heat treatment of a sample obtained after dehydration of sodium iodide crystallohydrate at ambient temperature (Fig. 4, curve 3,4), no gas release is observed.

As to cesium iodide, the following peaks are observed at heat treatment in the pressure-temperature dependence (Fig. 5): at 120–160°C (a maximum at 150°C), 160–240°C, and 240–290°C (a maximum at 275°C). According to spectrometric data, the pressure changes as well as and in case of lithium and sodium iodides, are caused by molecular water release into the gas phase.

It follows from the data obtained that the observed release of water at high-temperature heat treatment is peculiar to all alkali metal iodides. Moreover, the gas release is observed both from substances forming (lithium and sodium iodides) and not forming crystallohydrates (iodide of cesium). The following regularity is traced: in a series $\text{LiI} > \text{NaI} > \text{CsI}$, the water amount being released at heating decreases the water amount being released at heating decrease. Which determined by weight method. Content of high-temperature water in the LiI , NaI and CsI samples has made about 0.1%, 0.03–0.05% and less 0.01% accordingly. The same sequence is found as to ability of the substances to crystallohydrate formation and the tendency to hydrolysis [13]. In the case of lithium iodide (that is strongly

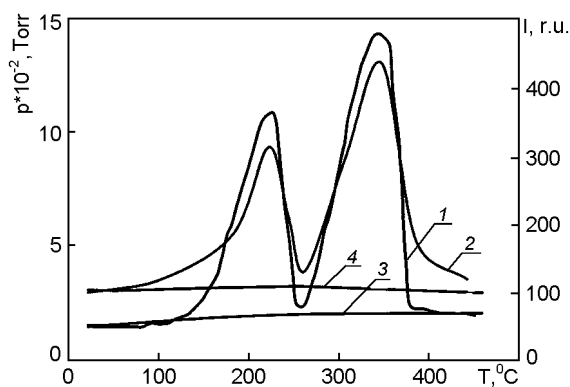


Fig. 4. Variation of pressure in vacuum system and intensity of the molecular water spectral absorption line during the treatment of sodium iodide samples (1, 2) and of sodium iodide crystallohydrate at ambient temperature (3, 4) .

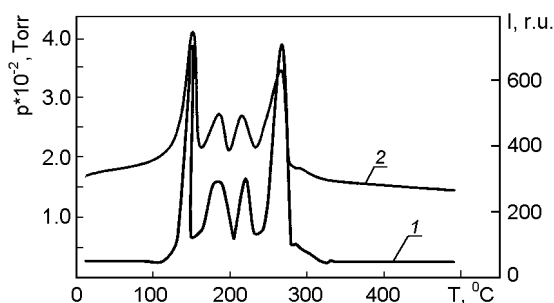


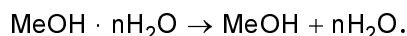
Fig. 5. Change of pressure in empty space - system (1) and absorption line molecule of water (2) during heat treatment is model of cesium iodide.

hygroscopic), the water release into gas phase occurs already at a weak heating while for cesium iodide (not hygroscopic and forming no crystallohydrates), the water release is observed only under considerable heating and in narrow temperature ranges. Thus, it is possible to suppose that the reason of occurrence of high-temperature water is similar for all alkali iodides.

On the other hand, for all compounds under consideration, the water release is observed within a rather wide temperature range (for LiI , 25–160°C; NaI , 180–450°C; CsI , 120–290°C). Several peaks are seen, thus evidencing that the water release process parameters vary as the temperature increases. It is well known that OH^- -groups present in the initial compounds may be a water source. So, the purified lithium iodide contains about $(3 \text{ to } 8) \cdot 10^{-2} \%$ of alkali [5], the sodium iodide, about $10^{-3} \%$. The hydroxides, in turn, form crystallohydrates of the following compositions:

$\text{LiOH}\cdot 2\text{H}_2\text{O}$, $\text{NaOH}\cdot \text{H}_2\text{O}$, $\text{CsOH}\cdot \text{H}_2\text{O}$ [16]. Under heat treatment thereof, the following regularity is observed [17]: in a sequence from lithium to cesium, ability to retain crystallohydrate water increases and the stability of the hydroxide itself is reduced. $\text{LiOH}\cdot 2\text{H}_2\text{O}$ can be completely dehydrated by heating up to 200°C with formation of anhydrous hydroxide stable up to its melting point. The crystallohydrate of cesium hydroxide is dehydrated at higher temperatures up to the melting point, and the last portions of water are very difficult to remove.

In our case, the water release temperature ranges ($180\text{--}280^\circ\text{C}$ for sodium iodide and $120\text{--}240^\circ\text{C}$ for cesium iodide) are likely connected with decomposition of hydroxide crystallohydrate according to reaction:



Water release from sodium and cesium iodides at $280\text{--}450^\circ\text{C}$ and $240\text{--}290^\circ\text{C}$, respectively, may be related to decomposition of OH^- -groups:



This hypothesis is testified by [15].

Thus, the observed water release at heating of lithium, sodium, and cesium iodides seems to be a consequence of decomposition of the relevant hydroxides initially present in the raw salts.

The results obtained can form a basis for the further studies in thermochemistry of crystallohydrates and for synthesis of high-purity anhydrous compounds, and also can be used in development of technological processes for dehydration of alkali metal halides.

References

1. M.E.Globus, B.V.Grinyov, Inorganic Scintillators: Novel and Traditional Materials, Akta, Kharkov (2001) [in Russian].
2. Functional Materials for Science and Engineering: A Collection of Works, ed. by V.P.Seminozhenko, Inst. for Single Crystals Publ., Kharkov (2001) [in Russian].
3. V.I.Goriletsky, B.V.Grinyov, B.G.Zaslavsky et al., Crystal Growth, Akta, Kharkiv (2001) [in Russian].
4. R.Ripan, Chimia Metalelor, Vol. 1. Edutira didact. si pedagog., Bucuresti, **1**, (1969).
5. N.I.Pirogov, Zh. Prikl. Khim., **29**, 1128 (1956).
6. I.V.Tananaev, S.M.Petushkova, G.V.Shpineva, Zh. Neorg. Khim., **3**, 1071 (1958).
7. A.N.Kirgintsev, L.N.Trushnikova, V.G.Lavrent'ev, Water Solubility of Inorganic Substances, Khimia, Leningrad (1972) [in Russian].
8. P.Digemans, Rec.Trav.Chim., **57**, 144 (1938).
9. I.van der Elskan, E.Zander, Z. Anorg. Allgem. Chem. **322**, 181 (1963).
10. A.M.Podorozhny, N.A.Korobkin, V.V.Safonov et al., Zh. Neorg. Khim., **33**, 13 (1988).
11. B.V.Grinyov, Yu.B.Poltoratsky, O.V.Tuchin, V.L.Yankelevich, Atomnaya Energia, **70** (1991).
12. V.V.Boldyrev, Methods for Study the Thermal Decomposition Kinetics of Solids, Tomsk Univ. Publ., Tomsk (1958) [in Russian].
13. S.F.Dubko, B.A.Efremov, A.A.Katrich, Radiofiz. and Radioastron., **3**, 368 (1998).
14. B.V.Grinyov, V.G.Gerasimov, A.I.Voloshko et al., Functional Materials, **11**, 575 (2004).
15. The I.P.L. Submillimeter, Millimeter, and Microwave Spectral Line Catalog, is accessible via anonymous ftp at spec.jpl.nasa.gov or via our home page at <http://spec.jpl.nasa.gov>.
16. L.S.Itkina, Lithium, Rubidium, and Cesium Hydroxides, Nauka, Moscow (1973) [in Russian].
17. N.M.Glinka, General Chemistry, Khimia, Leningrad (1985) [in Russian].

Зневоднювання йодидів лужних металів у вакуумі

**Д.С.Софронов, Б.В.Гриньов, А.Ю.Волошко, В.Г.Герасимов,
О.М.Кисіль, М.М.Смірнов, О.В.Шишкін**

Досліджено поведінку йодидів літію, натрію та цезію при нагріванні у вакуумі методами баричного та спектрометричного аналізу. Показано, що для цих сполук спостерігається вивільнення води у газову фазу у різних температурних інтервалах. Вивільнення води при нагріванні йодидів лужних металів, можливо, пов'язано з розкладом домішкової фази, яка містить гідроксидні групи.