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On features of deoxidization of CsI melt with zirconium getter

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Interaction of Zr getter with oxygen-containing admixtures being most abundant in molten alkali metal iodides (deoxidization) is studied. Reaction of Zr with oxide ions (in form of the corresponding alkali metal oxide) is characterized by very negative enthalpy and Gibbs energy values that make the deoxidization process very favorable. Practically the interaction leads to decrease of O^{2-} concentration by a factor of ca. 6. Interaction of Zr with carbonate ions is shown both by the calculations and by experiment ещ lead to the formation of carbon particles (suspension) in the melts that causes certain limitations of the getter treatment for the purification of practically used growth iodide melts.
Keywords: cesium iodide, melt, deoxidization, zirconium.

Исследовано взаимодействие металлического циркония (геттер) с наиболее распространенными кислородсодержащими примесями (раскисление) в расплавленных йодидах щелочных металлов. Реакция циркония с оксид-ионами (в форме соответствующего оксида щелочного металла) характеризуется отрицательными значениями энтальпии и свободной энергии Гиббса, что свидетельствует о термодинамической выгодности процесса раскисления. Практически это взаимодействие приводит к снижению равновесной моляльности оксид-ионов в расплаве йодида цезия приблизительно в 6 раз. Экспериментально показано и подтверждено расчетом, что реакция циркония с карбонат-ионами приводит к образованию частиц углерода (суспензия), что налагает некоторые ограничения на применение геттеров для раскисления практически используемых йодидных расплавов.

Особливості розкислення розтопу CsI цирконієвим геттером. *Ю.М.Дацько, Т.П.Реброва, В.Л.Чергинець, В.О.Науменко, О.Л.Ребров, П.В.Матейченко, І.М.В'юник*.

Досліджено взаємодію металічного цирконію (геттер) з найбільш поширеними оксигенвмісними домішками (розкислення) у розтоплених йодидах лужних металів. Реакція цирконію з оксид-іонами (у формі відповідного оксиду лужного металу) характеризується негативними значеннями ентальпії і вільної енергії Гібса, що свідчить про термодинамічну вигідність процесу розкислення. Практично ця взаємодія веде до зниження рівноважної моляльності оксид-іонів у розплаві йодиду цезію приблизно у 6 разів. Експериментально показано і підтверджено розрахунками, що реакція цирконію з карбонат-іонами веде до утворення частинок вуглецю (суспензія), що накладає деякі обмеження на застосування геттерів для розкислення йодидних розтопів, що використовуються на практиці.

1. Introduction

Single crystals of undoped cesium iodide are widely used for precision measurements in high-energy physics [1, 2]. However, for this purpose the crystal should possess good performance and high radiation hardness. These properties are known to be essentially dependent on the technology of crystal obtaining (the growth procedure, purity of the raw). In particular, the presence of admixtures increases the fraction of the slow components in the scintillation pulse that makes the scintillator slower.

Oxygen-containing admixtures are the most abundant ones and their appearance in the growth melt and, hence, in the obtained crystals is caused by interactions of the initial CsI with traces of water, oxygen and carbon dioxide which are contained either in the atmosphere or in the salt (hygroscopic moisture, organic admixtures). It makes the treatment (deoxidization) of the melt to be the most important procedure immediately preceding the crystallization process (crystal growth).

The deoxidization of halide melts can be performed by two common ways: the treatment in the reactive gas atmosphere and the precipitating deoxidization.

The common drawback of treatment of iodide melts in reactive gas atmosphere consists in supply or formation *in situ* of very aggressive substances such as HI or I_2, which cause intensive corrosion of metal parts of equipment. Because of this reason the use of gases for purification of iodide melts in manufacturing conditions seems undesirable.

In this relation the precipitating deoxidization recently proposed in our work [3] presents more available way of iodide melt purification since addition of deoxidizing dopants does not result in the formation of aggressive gases. The destruction of the most abundant oxygen-containing admixtures OH^- and CO_3^{2-} by action of cation acids:

$$Mg^{2+} + 2OH^- \rightarrow MgO\downarrow + H_2O\uparrow, \qquad (1)$$

$$Mg^{2+} + CO_3^{2-} \rightarrow MgO\downarrow + CO_2\uparrow \qquad (2)$$

results only in formation of gases which are atmosphere components. It should be noted that the above mentioned admixtures (hydroxide and carbonate) are formed because of interaction of water and carbon dioxide with CsI raw or melt at the stages preceding the crystal growth:

$$2H_2O\uparrow + 2I^- \rightarrow 2OH^- + 2HI, \qquad (3)$$

$$CO_2\uparrow + \frac{1}{2}O_2\uparrow + 2I^- \rightarrow CO_3^{2-} + I_2\uparrow. \qquad (4)$$

Therefore, the gases yielded as products of reactions (1) and (2) do not create additional contamination of the growth atmosphere.

The use of cation acids, nevertheless, has disadvantages connected with the existence in the melt of the cation-scavenger and the product of its interaction with oxygen containing admixtures. The first, since the addition of the dopant should be equal to the total concentration of the admixtures and the excess of the scavenger should worsen the quality of the grown CsI crystal. The second, the formed metal oxide stays in contact with the iodide melt and can be partially dissolved. Therefore, only cations forming oxides with extremely low solubilities in melts (Mg^{2+}, Y^{3+}) can be recommended for the purification [3].

The Red-Ox variation of the precipitating deoxidization consisting in the treatment of purified melt by a metal-getter [4] is free from the former drawback proper to cations-scavengers: the refractory metal itself is insoluble in the melt and cannot contaminate the melt and crystals. The Red-Ox variation was checked on Zr–CsI (Aldrich, 5N) system and the high efficiency of Zr getter was confirmed.

Nevertheless, some questions connected with this way of the purification remain. Taking into account very high reducing properties of Zr it can be assumed that gases yielding due to decomposition of the main oxygen-containing admixtures may react with the remaining metal with formation of gaseous hydrogen (from H_2O) and solid carbon (from CO_2) and the presence of the latter product is especially undesirable.

The purpose of the present work consists in investigation of interaction of Zr with CsI melt prepared from the raw with higher level of contamination by oxygen-containing admixtures than CsI Aldrich, 5N.

2. Experimental

Cesium iodide of two kinds of quality was used in the studies of deoxidization process and the crystal growth: CsI supplied by Aldrich with the mass fraction of the main substance of 0.99999 (kept for a year)

Table. Thermodynamic parameters of interactions between some oxoderivatives of alkali metals with zirconium at 1000 K

No.	Reaction	Type of calculation	ΔH, kJ·mol^{-1}	ΔG, kJ·mol^{-1}
6	$2Na_2O + Zr \rightleftarrows 4Na + ZrO_2$	2nd Ulich	−268.1	−341.6
7	$2K_2O + Zr \rightleftarrows 4K + ZrO_2$	2nd Ulich	−373.9	−458.4
8	$2Cs_2O + Zr \rightleftarrows 4Cs + ZrO_2$	2nd Ulich	−403.7	−471.3
9	$2Na_2CO_3 + Zr \rightleftarrows Na_2O + ZrO_2 + C$	accurate	−395.8	−335.8
10	$Na_2CO_3 + 1.5Zr \rightleftarrows 2Na + 1.5ZrO_2 + C$	accurate	−514.3	−504.6
11	$CO_2\uparrow + Zr \rightleftarrows ZrO_2 + C$	accurate	−696.8	−511.8

and the reagent of "extra pure" quality produced by Technoprom, Saki (kept for 2 years). The different term of the storage should provide different degree of contamination by oxygen-containing admixtures because of process (4). Concentrations of carbonate ion in the said chemicals (raw) were *ca.* $5\cdot10^{-4}$ mol·kg^{-1} (Aldrich) and *ca.* $1.5\cdot10^{-3}$ mol·kg^{-1} (Technoprom).

Zr shavings were obtained from the metal of 4N purity. Before the experiment they were treated by diluted HCl (4N) to remove the traces of other metals which may remain on the surface after mechanical treatment. In the potentiometric experiments we used amounts of Zr providing surface area *ca.* 0.5 cm^2.

The study consisted of the following experiments:

— a weight of the metal shaving was added to molten CsI heated to 973 K, and the decrease of oxide ion concentration in the melt was detected by a potentiometric method with the use of an electrode reversible to oxide ion;

— commercial CsI salt and the metal shaving was placed in a growth ampoule which then was heated to 973 K. The melt with the metal pieces was kept under vacuum for a day; after that a single crystal was grown from the melt by the Bridgman method.

— the surface of the getter after crystal growth or deoxidization process was studied by SEM.

For studying the processes of "getter-melt" interaction *in situ* we used the potentiometric cell with a membrane oxygen electrode $Pt(O_2)|YSZ$ (where YSZ the 0.9 ZrO_2–0.1 Y_2O_3 ceramics):

$$Ag|Ag^+(0.1M),CsI \vdots\vdots CsI,O^{2-}|YSZ|(PtO_2). \quad (5)$$

The presented potentiometric cell was first calibrated with known weights of KOH serving as a donor of oxide ions since its dissociation in molten salts:

$$2OH^- \rightarrow H_2O\uparrow + O^{2-} \quad (6)$$

occurred completely in dry inert atmosphere. This gave us possibility to obtain the dependence of *emf* of cell (4) on pO ($p \equiv -\log m_{O^{2-}}$, where $m_{O^{2-}}$ the equilibrium molality of oxide ions in CsI melt). The plot was further used for recalculation of the *emf* values obtained at the deoxidization process into $m_{O^{2-}}$ and pO.

Microphotographs were made using JSM 6390 LV scanning electron microscope with a MAX^N X-ray microanalysis system.

3. Results and discussion

Thermodynamic predictions

As is known, zirconium possesses considerable affinity to oxygen and the heat of formation of ZrO_2 is *ca.* 550 kJ·mol^{-1} per 1 oxygen [5]. Therefore, at high temperatures it is able to displace even the most active alkali metals from their oxocompounds. Thermodynamic analysis performed using existing data on sodium and potassium compounds (2nd Ulich approximation, Δc_p = const) [5] permit to construct the scheme of interactions in molten salts which can give an imagination about processes taking place during halide melt deoxidization (see Table). Temperature 1000 K was chosen since melting of alkali metal iodides occurs in the vicinity of the said temperature.

As seen from this Table, all the processes with participation of oxocompounds and metallic zirconium are characterized by very negative free Gibbs energies. This means

that the equilibrium state of all listed processes should be shifted to the right side.

Comparison of thermodynamic parameters for reactions of Na_2O, K_2O and Cs_2O with metallic zirconium gives possibility to state that the difference between standard enthalpies of their formation is the main part of difference in ΔG or ΔH of the said reactions. The thermodynamic favorability of these process increases going from Na_2O to Cs_2O and it means that purification with getters is the most effective in the case of cesium halides.

These speculations are referred to partial pressure of 1 atm and naturally, that under vacuum volatile alkali metal will be evaporated from the melt providing completeness of the corresponding chemical reactions. For example, reaction:

$$2Na_2O + Zr \rightleftarrows 2Na_{2,gas} + ZrO_2 \qquad (7)$$

is characterized by $\Delta G = -293.4$ kJ·mol^{-1} at 1000 K.

As to reaction of CO_2 or carbonate ions with Zr, it should to note that these compounds will be decomposed completely. Nevertheless, a question arises, what amount of the oxygen-containing admixtures (existing, mainly, as carbonates) will affect the quality of the grown single crystals due to the decomposition with formation of carbon.

Interaction of Zr with oxygen-containing admixtures in molten CsI

The addition of Zr to CsI (Aldrich) placed in the potentiometric cell causes the sequential rise of pO (Fig. 1, curve *1*) that means decrease of oxide ion concentration in the melt up to a certain point where a plateau begins (Fig. 1, line *2*). The plateau section corresponds to moment when the surface of zirconium is completely covered by interaction products that stops the following running of the deoxidization process.

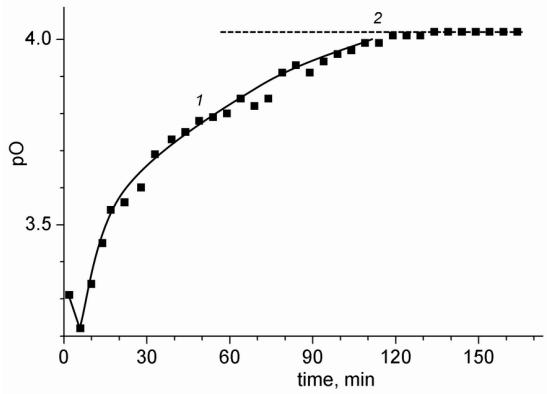

Fig. 1. The dependence of pO vs. time for process of deoxidization of CsI melt by zirconium getter at 973 K: *1* — the section where the purification occurs, *2* — the plateau section.

Knowing the initial and final concentration of oxide-ion before (the starting pO value) and after purification (pO value at the plateau) and the square of surface of the shaving permits to estimate the surface capacity of the used Zr getter with respect to oxygen as 0.42 mol·m^{-2} [6]. The concentration of oxide ion during the purification process is decreased by a factor of 6, i.e., the deoxidizing action of the getter on CsI melt is effective enough and the time of the treatment should be not less than 2 h.

The initial stage can be considered as an irreversible process, therefore, its running

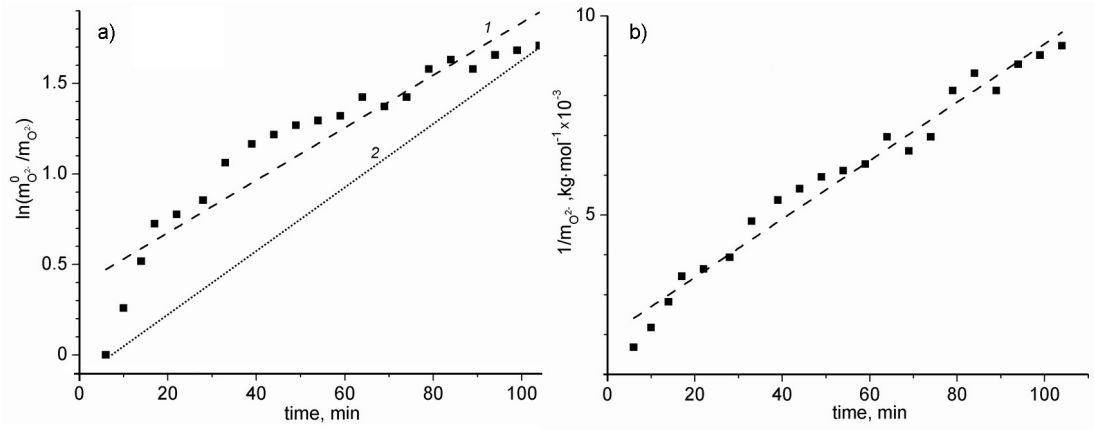

Fig. 2. The dependences of oxide ion concentration vs. time for process of deoxidization of CsI melt by zirconium getter at 973 K made for determination of kinetic parameters: a — 1st order dependence, $\ln m_{O^{2-}} = f(t)$, *1* — approximation by least squares method; b — 2nd order dependence, $1/m_{O^{2-}} = f(t)$.

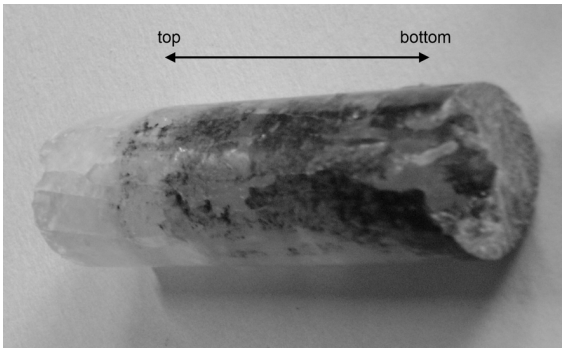

Fig. 3. Photo of CsI single crystals grown from the melt contaminated with carbonate ion.

should be subjected to the known kinetic regularities. Since we can determine current concentration of only oxide ion the running of the process can be described by pseudo-order, i.e., power in which oxide ion concentration enters in the kinetic equation of the following general form:

$$w = k \cdot m_{O^{2-}}^{n} \qquad (8)$$

where k the rate constants of the purification process.

The necessary data for the estimation of the process kinetics are presented in Fig. 2. It should be noted that, although the dependence of $\ln m_{O^{2-}}$ against time (proper to reactions of the 1st order) can be considered as practically linear (approximation line *1*, $r_{xy} = 0.931$ at 19 degrees of freedom) one can see that actually this dependence is somewhat convex to ordinate axis that is obvious if we consider position of the experimental points comparing with line *2* (Fig. 2a). The similar behavior is observed to "pO — time" dependence (Fig. 1) which is similar to the discussed logarithmic one (Fig. 2a).

Contrary, the dependence of $1/m_{O^{2-}}$ vs. time is linear with small oscillations of the experimental parameters near the approximation line ($r_{xy} = 0.985$ at 19 degrees of freedom) (Fig. 2b). These speculations help us to determine the pseudo-order of interaction "Zr — oxygen admixtures" as second, and the slope, 73.3±7 $kg \cdot mol^{-1} \cdot mol^{-1}$ is the rate constant of this process. The obtained result corresponds completely to stoichiometry of reaction (8) that leads to formation of ZrO_2. On the other hand such value of pseudo-order can confirm that reaction (8) is the limiting stage of the process whereas the reduction of CO_2 to carbon can not be detected by potentiometric method since this reaction is not accompanied with

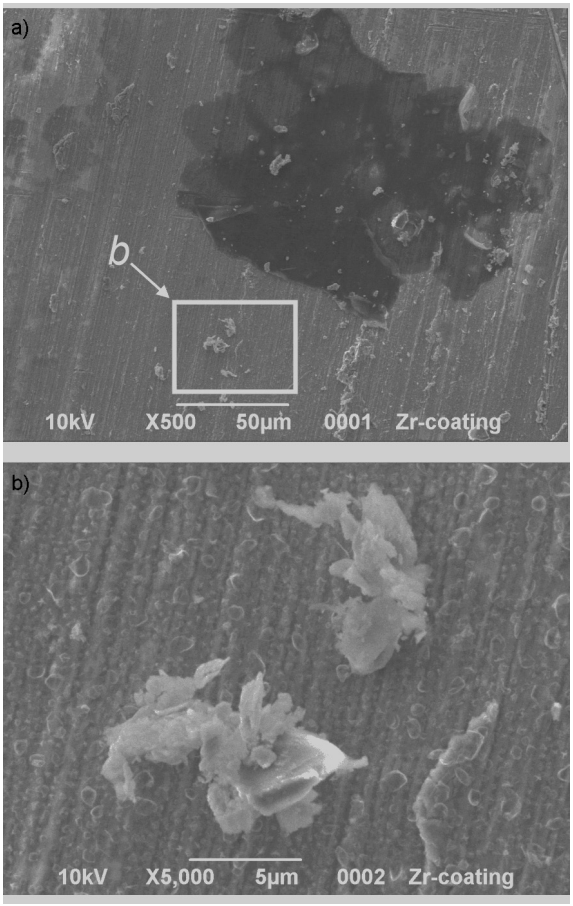

Fig. 4. SEM photographs of surface of Zr shaving used for deoxidization of CsI melt: a — carbon particle, b — ZrO_2 particles.

formation or fixation of oxide ions in molten CsI.

For treatment of CsI (Technoprom) with Zr pO changes were insignificant because of very high concentration of carbonate and they did not permit to make quantitative estimations.

Detection of products of "Zr — oxygen admixtures" interaction

To state what products are formed as a result of destruction of oxygen-containing admixtures by the metal getter, we performed the growth of CsI single crystals in quartz ampoules with addition of Zr shaving to the initial melt. In the case of Aldrich raw the crystal remained completely transparent and possessed scintillation parameters which were described elsewhere [4].

The result of treatment of more contaminated with carbonate Saki raw (which was kept for more long time) deserves special figure (Fig. 3).

As is seen, the bottom part of the grown single crystals contains appreciable amount of black inclusions (suspension) which is displaced to the ampoule walls during the growth process. Analysis showed that this is carbon soot containing ZrO_2. It means, that zirconium getter can be used for additional deep purification of "fresh" iodide raw of high purity, however, it is not usable for the purification of melts prepared from the raw appreciably contaminated by carbon-containing admixtures (carbonates, organic salts) because of destruction of the latter with the formation of suspended carbon.

To get more information about the deoxidization process we obtained SEM photo of the zirconium surface after the interaction (Fig. 4).

The surface on the shaving is covered by particles of ZrO_2 (Fig. 4a) and carbon (Fig. 4b), and the quantitative analysis of the sample of shaving gives the following ratio: Zr — 24.0 at.%, O — 45.2 at.% and C — 30.1 at.%, i.e. there is ZrO_2 and C as the main interaction products. Ditto, there is a definite amount of sodium on the Zr surface, ca. 0.51 at.%. Simply it means that the formed ZrO_2 serves as additional sorbent for sodium and the chemisorption process takes place according to the following equation:

$$2Na^+ + O^{2-} + ZrO_2\downarrow \rightleftarrows Na_2ZrO_3\downarrow \qquad (9)$$

leading to the formation of sodium zirconate which is insoluble in molten alkali metal halides (excluding lithium salts because of their strong affinity to oxide ion [7]). This reaction also gives the evidence of effective usage of dispersed ZrO_2 (powder) for removal of sodium admixtures from molten cesium halides.

4. Conclusions

Processes of interaction of Zr with the most abundant oxygen-containing admixtures (alkali metal oxides and carbonates) were demonstrated by thermodynamic analysis to possess very negative Gibbs energy values that makes the said deoxidization process very favorable. Practically the interaction leads to decrease of O^{2-} concentration by a factor of ca. 6.

The reaction running is described by kinetic equation of the second pseudo-order. The rate constant of the deoxidization process and the surface capacity of zirconium with respect to oxygen in molten CsI are determined.

Interaction of zirconium with carbonate ions is shown both by the calculations and by experiment to lead to the formation of carbon particles (suspension) in the melts that causes certain limitations on use of getters for the purification of practical growth iodide melts. ZrO_2 formed as one of the deoxidization process products shows acidic properties and fixes sodium probably, in the form of Na_2O to insoluble sodium zirconate.

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