

On the behavior of europium oxocompounds in molten CsI

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Interactions of Eu^{2+} with oxide ions and processes accompanying dissolution of Eu_2O_3 in molten CsI at 700°C were studied by potentiometric method and sequential addition method. Electrochemical cell with a membrane oxygen electrode $\text{Pt}(\text{O}_2)|\text{ZrO}_2(\text{Y}_2\text{O}_3)$ was used for the determination of equilibrium molality of O^{2-} . Solubility product of EuO is equal to $P_{\text{EuO}} = 7.94 \cdot 10^{-14} \text{ mol}^2 \cdot \text{kg}^{-2}$; i.e., EuO is practically insoluble in molten CsI. Interaction of Eu_2O_3 with CsI leads to formation of EuO and O^{2-} in the solution. Saturated solution contains approximately $4 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ EuO and $2 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ of O^{2-} , the dissolved EuO is non-dissociated. These admixtures essentially affect luminescence properties of single crystals grown from the saturated solution of Eu_2O_3 in CsI as compared with pure CsI.

Взаимодействие ионов Eu^{2+} с оксид-ионами и процесс растворения Eu_2O_3 в расплаве CsI при 700°C изучены титриметрическим методом и методом последовательных добавок. Электрохимическая ячейка с мембранным кислородным электродом $\text{Pt}(\text{O}_2)|\text{ZrO}_2(\text{Y}_2\text{O}_3)$ использовалась для измерения равновесной концентрации O^{2-} . Величина произведения растворимости EuO $P_{\text{EuO}} = 7,94 \cdot 10^{-14} \text{ моль}^2 \cdot \text{кг}^{-2}$ позволяет отнести EuO к оксидам, практически нерастворимым в расплаве CsI. Взаимодействие Eu_2O_3 с CsI ведет к образованию EuO и O^{2-} в растворе. Насыщенный раствор содержит приблизительно $4 \cdot 10^{-4} \text{ моль} \cdot \text{кг}^{-1}$ EuO и $2 \cdot 10^{-4} \text{ моль} \cdot \text{кг}^{-1}$ O^{2-} , EuO в этом растворе не диссоциирует. Образующиеся примеси существенно изменяют люминесцентные свойства монокристаллов CsI, выращенных из насыщенного раствора Eu_2O_3 в CsI по сравнению с чистым йодидом цезия.

1. Introduction

The present-day situation in material science of halide scintillators is characterized by considerable increase of attention of investigators to compositions based on Eu-containing alkali and alkaline earth metal halides. Although such materials as $\text{SrI}_2:\text{Eu}$ or $\text{CsI}:\text{Eu}$ were known as scintillation materials long since [1, 2], their thorough investigations started some years ago. The main reason of this consists in new possibilities

of deep purifications of chemicals. For instance, SrI_2 of 99.999 % purity doped with 6 % Eu^{2+} demonstrates light yield more than 100,000 photons/MeV [3], whereas the similar scintillator obtained from SrI_2 of reagent quality does not differ from the material obtained in [1] and possesses the light yield only 30,000 photons/MeV [4]. There is no information about admixtures decreasing the working parameters of the said scintillator.

The second direction of europium halide (mainly, EuI_2) use is the treatment of the traditional Tl-doped alkali metal halides to suppress afterglow, which may be ascribed to presence of some oxygen-containing admixtures. Although this approach is successful in some cases [5, 6], the mechanism of Eu^{2+} ion action on the melt properties remains unclear.

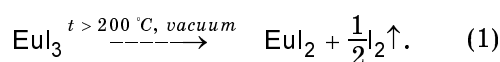
The purpose of the present work is to study processes of interaction of Eu^{2+} with O^{2-} and dissolution of Eu_2O_3 in molten CsI .

2. Experimental

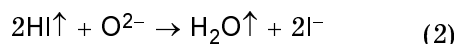
CsI (Aldrich, 99.999 % of CsI) with the total molality of oxygen-containing admixtures equal to $5\text{--}7 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ of O^{2-} (after melting) was used for the experiments. The total concentration of O^{2-} was determined by reverse titration procedure described elsewhere [7].

Eu_2O_3 (Stanford Material Corporation, OX63-5N, 99.999 % of Eu_2O_3) was used without purification.

Anhydrous EuI_2 was prepared by dissolution of Eu_2O_3 in aqueous HI (reagent quality) and NH_4I (reagent quality) taken in molar ratio 2:1 to Eu was added to the solution. The obtained solution was evaporated and dried up to formation of brown powder ($\text{EuI}_3 + \text{NH}_4\text{I}$ with traces of I_2 and water). This powder was carefully heated in vacuum to beginning of I_2 evaporation, which started at 200°C owing to the following reaction



At the end of the decomposition reaction the process of NH_4I sublimation started, the sublimation process was accompanied with HI formation in hot zone and additional purification of EuI_2 from oxygen-containing admixtures that could be described by the scheme:



and admixture oxide ions were replaced from the final powder.

The processes of interaction of Eu^{2+} with O^{2-} and dissolution of Eu_2O_3 in molten CsI were studied by control of equilibrium molality of oxide ion concentration in the melt. The potentiometric cell for this determination may be presented by the following scheme

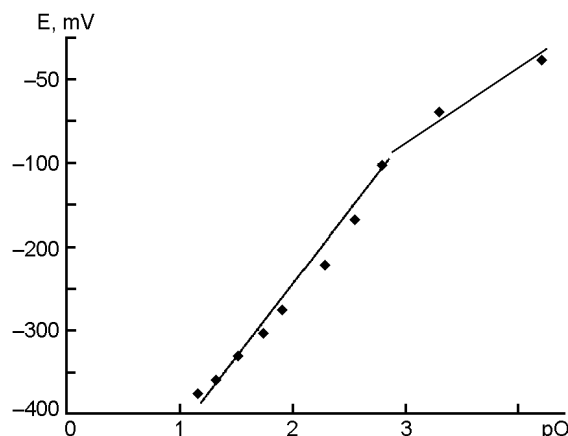
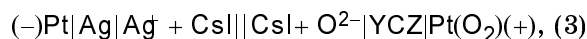


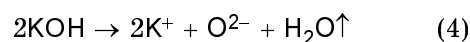
Fig. 1. The calibration dependence of $emf(E)$ vs. pO of cell (3) in molten CsI at 700°C .



(where YCZ is yttria stabilized zirconia, $0.9 \text{ ZrO}_2 + 0.1 \text{ Y}_2\text{O}_3$) and its construction is described in detail elsewhere [8]. The descriptions of the potentiometric titration routine and the sequential addition method (SAM) are presented there, too. To provide inert atmosphere in the cell high pure (99.99) Ar was used.

3. Results and Discussion

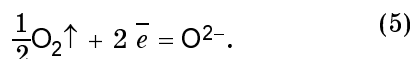
E-pO calibration plot. As a rule, quantitative investigations of behavior of oxygen species in molten salts require preliminary calibration of measuring devices against equilibrium O^{2-} concentration in the melt. We performed the calibration of cell (3) in molten CsI at 700°C adding to the pure melt known amount of KOH , which was considered as a strong Lux base, i.e., its dissociation according to the scheme:



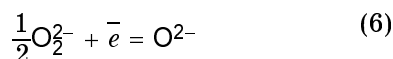
was complete in dry atmosphere.

The plot of $emf(E)$ of cell (3) vs. pO ($pO \equiv -\log a_{\text{O}^{2-}} \approx -\log m_{\text{O}^{2-}}$, $a_{\text{O}^{2-}}$ and $m_{\text{O}^{2-}}$ activity and molality of O^{2-} , respectively) is presented in Fig. 1 as is seen it consists of two linear sections which slopes are close to $1.15 \text{ RT}/F$ (theoretical value is 96.3 mV at 700°C) at high pO values and $2.3 \text{ RT}/F$ (theoretical value is 193 mV at 700°C) at low pO . The inflection point is described by the following coordinates: $pO = 2.75$ and $E = -85 \text{ mV}$. Such a form of the calibration plot is usual for $\text{Pt}(\text{O}_2)|\text{YSZ}$ oxygen electrode in molten salts [9]. The upper section of the plot cor-

responds to occurrence of two-electron process on the electrode, which is expressed by the following equation:



The increase of O^{2-} concentration in the melts results in the formation of stable peroxide ions at the electrode surface and the character of the electrode process is changed and the so-called one-electron reversibility



takes place.

The sections are approximated by the following equations obtained by least squares method:

$$E = -345(\pm 51) + 88(\pm 15) \cdot pO, \text{ mV}, \quad (7)$$

at $pO > 2.75$,

$$E = -556(\pm 11) + 149(\pm 5) \cdot pO, \text{ mV}, \quad (8)$$

at $pO < 2.75$.

The slopes of the plots are somewhat lower comparing with the corresponding theoretical values, this takes place for molten halides possessing strong reduction properties. The same reason causes the shift of the inflection point from $pO = 3$ (molten chlorides) to lower values in molten iodides owing to the decrease of oxidant (O_2^{2-}) stability in solutions with reduction properties.

On EuO solubility in molten CsI. The determination of EuO solubility in molten CsI was performed by the potentiometric titration method. The reaction:



was studied. For this purpose amount of EuI_2 , corresponding to $0.025 \text{ mol}\cdot\text{kg}^{-1}$ of Eu^{2+} was added the melt. The titration was performed by additions of KOH ($1/2 \text{ O}^{2-}$) and measuring of the equilibrium *emf*. The initial amount of KOH was very small ($10^{-4} \text{ mol}\cdot\text{kg}^{-1}$) that was necessary to obtain results in non-saturated solution region, were it exists.

The usual and differential titration curves are presented in Fig. 2. According to their form (the absence of sharp pO drops at the first additions of the titrant) EuO can be referred to practically insoluble oxide in molten CsI and the magnitude of pO drop at the equivalence point (approximately 8 pO units) allows to suppose ex-

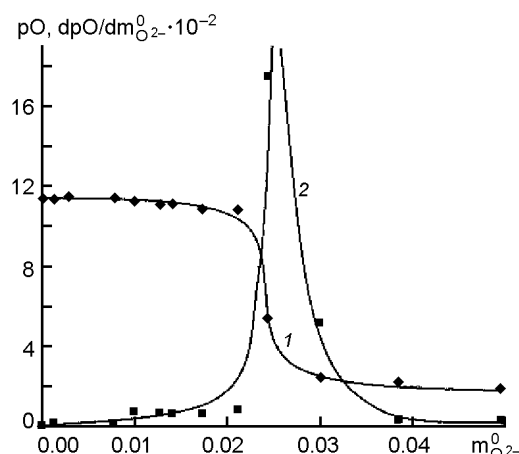


Fig. 2. Usual (1) and differential (2) curves of potentiometric titration of Eu^{2+} (EuI_2 , $0.03 \text{ mol}\cdot\text{kg}^{-1}$) with O^{2-} in molten CsI at 700°C .

tremely low solubility product value for EuO.

The calculations of thermodynamic parameters of equilibrium (9) were made on the basis of consumption of oxide ion. From the obtained equilibrium *emf* the pO value was obtained from equation (7) at $E > -85 \text{ mV}$ and from equation (8) at $E < -85 \text{ mV}$. Than the consumption of O^{2-} was calculated from the initial molality of O^{2-} ($m_{\text{O}^{2-}}^0$) as

$$\Delta m_{\text{O}^{2-}} = m_{\text{O}^{2-}}^0 - m_{\text{O}^{2-}} = m_{\text{O}^{2-}}^0 - 10^{-pO}. \quad (10)$$

From this values solubility product (P'_{EuO}):

$$P'_{\text{EuO}} = m_{\text{Eu}^{2+}} \cdot m_{\text{O}^{2-}} = (m_{\text{Eu}^{2+}}^0 - \Delta m_{\text{O}^{2-}}) \cdot 10^{-pO}, \quad (11)$$

and dissociation constant (K'_{EuO})

$$K'_{\text{EuO}} = \frac{m_{\text{Eu}^{2+}} \cdot m_{\text{O}^{2-}}}{m_{\text{EuO}}} = \frac{(m_{\text{Eu}^{2+}}^0 - \Delta m_{\text{O}^{2-}}) \cdot 10^{-pO}}{\Delta m_{\text{O}^{2-}}} \quad (12)$$

were calculated. The experimental and calculated values are presented in Table.

These data give evidence that all the solutions obtained by addition of O^{2-} to Eu^{2+} solutions in molten CsI are saturated, i.e., even the first small addition of KOH causes the precipitation of EuO. Indeed, the considering changes of pK'_{EuO} together with the increase of $m_{\text{O}^{2-}}^0$ shows that there is directed shift of the calculated value (in-

Table. Experimental and calculated parameters obtained at the potentiometric titration of Eu^{2+} (Eu_2 , $0.02 \text{ mol}\cdot\text{kg}^{-1}$) with O^{2-} in molten CsI at 700°C

$m_{\text{O}^{2-}}^0$	pO	pK'_{EuO}	pP'_{EuO}
0.0001	11.31	8.97	12.97*
0.0014	11.29	10.12	12.98*
0.0030	11.43	10.63	13.15*
0.0079	11.36	11.11	13.21*
0.0101	11.20	11.13	13.13*
0.0128	11.04	11.18	13.07*
0.0140	11.04	11.28	13.13*
0.0174	10.82	11.39	13.15*
0.0213	10.80	12.28	13.95
0.0244	5.39	—	—
0.0301	2.42	—	—
0.0384	2.20	—	—
0.0495	1.87	—	—

Note. Points chosen for averaging pP'_{EuO} are designated with asterisks.

crease) where as pP''_{EuO} oscillates randomly near some average value. According to [10] such a behavior of the calculated values confirms the formation of the saturated solution. So, the solubility product index of EuO , pP_{EuO} is estimated as 13.1 ± 0.2 that corresponds to $7.94 \cdot 10^{-14} \text{ mol}^2 \cdot \text{kg}^{-2}$. Such a value allows to refer EuO to oxides practically insoluble in molten CsI .

On Eu_2O_3 solubility in molten CsI . Investigations performed in the previous section give us possibility to determine the solubility product value of EuO , i.e., parameter connected with the behavior of ionized part of dissolved oxide. However, a part of a solid substance is dissolved in the melt without dissociation. In order to estimate the fraction of the non-dissociated oxide in the saturated solution the sequential addition method described in [11] seems more appropriate.

This method consists in adding some amounts of the oxide studied to the melt with the measuring equilibrium emf . The oxide is added up to saturation, which results in minimum in $E-pm$ plot as it is shown in Fig. 3. Such a plot gives possibility to make some conclusions.

The first, the point designated in Fig. 3 by arrow 1 corresponds to amount of Eu_2O_3 , which is dissolved in the melt only partially and some quantity of the oxide remains non-dissolved. The partial dissolution results in the essential decrease of Eu_2O_3 particle size and its solubility ac-

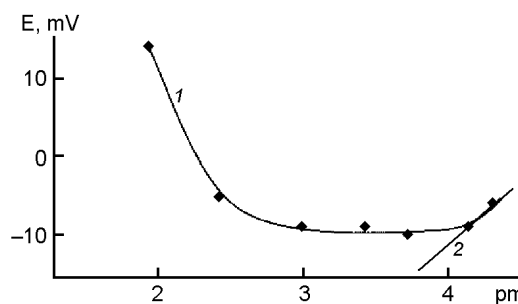


Fig. 3. The dependence of emf vs. $-\log m_{\text{Eu}_2\text{O}_3}^0 \equiv pm$ at the addition of Eu_2O_3 to molten CsI at 700°C (SAM). Arrow 1 designates point where the addition is partially dissolved and arrow 2 is the estimated point where the saturation is achieved.

cording Ostwald-Freundlich rule increases. The following additions of Eu_2O_3 lead to increase of the average size of Eu_2O_3 particles and its solubility decreases (and emf increases). Point 2 obtained by cross-section of horizontal line corresponding to the minimal emf in the plot with the inclined line corresponding to the $E-pm$ dependence in non-saturated solutions designates the point of the saturation, where $pm = 3.7$, i.e., $2.0 \cdot 10^{-4} \text{ mol}\cdot\text{kg}^{-1}$ of Eu_2O_3 . It should be noted that this value is in good agreements with the results of quantitative analysis fulfilled by polarographic method. The second, the emf value at saturation is equal to -10 mV and this value allows to found pO and equilibrium oxide ion molality

as 3.72 and $1.95 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$, respectively. To ascribe this O^{2-} concentration to a definite process the additional studies are required.

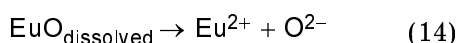
Although Eu^{3+} ions are known to be unstable in iodide melts, the valence state of Eu in molten CsI should be cleared. Therefore, we performed the growth of single crystal from CsI melt saturated with products of Eu_2O_3 interaction with this melt by Bridgman-Stochbarger method. The radioluminescence spectrum of the grown sample is presented in Fig. 4 (curve 2). It contains two bands: the first with the maximum located at 312 nm corresponds to self-luminescence of undoped CsI (see Fig. 4 curve 1) and the second one with maximum at 435 nm can be ascribed to Eu^{2+} luminescence ($5d-4f$ transition). The bands in long-wave region, especially at $\lambda > 550 \text{ nm}$, which could be referred to Eu^{3+} luminescence are not observed.

So, we can conclude that the process of Eu_2O_3 dissolution in molten CsI is accompanied with the reaction:



and this equilibrium is shifted to the right completely. The molality of EuO in this saturated solution is equal to $3.6 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$.

Since concentration of dissolved in CsI Eu_2O_3 ($1.8 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$) coincides completely with the equilibrium molality of O^{2-} ($1.9 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$), it follows that reaction (13) is only a process generating oxide ions and the dissociation of EuO according to reaction



is suppressed.

Fig. 4 gives the answer on another question: do such low concentrations of the participants of reaction (14) affect the properties of CsI. The first maximum in the crystal polluted by Eu_2O_3 is located at 312 nm whereas pure material possesses the similar maximum at 305 nm and from [12] it follows that the formed amount of oxide ions in the melt ($2.0 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$) makes this scintillator slower. The second sequence of the said pollution is intensive enough band originated by Eu^{2+} [13]. Hence, if CsI melt is kept in contact with Eu_2O_3 , then grown from this melt single crystal possesses appreciably distinguished luminescent characteristics.

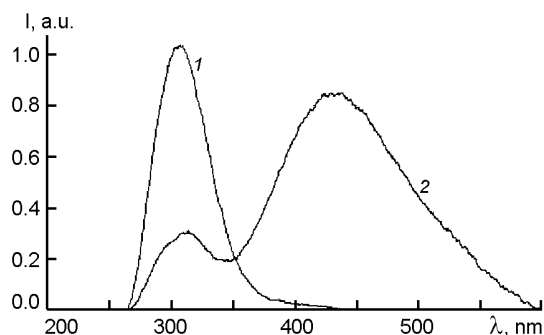


Fig. 4. Radioluminescence spectra of CsI crystals grown without dopants (1) and grown from the saturated solution of Eu_2O_3 in the melt, source ^{241}Am .

4. Conclusions

Solubility product index of EuO, pP_{EuO} , has been found by potentiometric titration method to be 13.1 ± 0.2 and $P_{\text{EuO}} = 7.94 \cdot 10^{-14} \text{ mol}^2 \cdot \text{kg}^{-2}$ that allows to consider EuO as practically insoluble in molten CsI at 700°C .

Dissolution of Eu_2O_3 in CsI melt is accompanied with oxidation of melt and formation of EuO and O^{2-} in the solution. Saturated solution contains of $3.6 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ EuO and $1.9 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ of O^{2-} , the dissociation of EuO under these conditions is completely suppressed.

Radioluminescence spectrum of CsI single crystal grown from the saturated solution of Eu_2O_3 in CsI shows that corresponds to superimposition of those for undoped CsI polluted with O^{2-} and CsI:Eu solid solution.

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Про поведінку оксосполук європію у розплаві CsI

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Взаємодія іонів Eu^{2+} з оксид-іонами і процес розчинення Eu_2O_3 у розплаві CsI при 700°C були вивчені титриметричним методом і методом послідовних добавок. Електрохімічна комірка з мембранним кисневим електродом $\text{Pt}(\text{O}_2)|\text{ZrO}_2(\text{Y}_2\text{O}_3)$ була використана для визначення рівноважної концентрації O^{2-} . Величина добутку розчинності EuO $P_{\text{EuO}} = 7,94 \cdot 10^{-14}$ моль²·кг⁻² дає змогу віднести EuO до оксидів, практично нерозчинних у розплаві CsI. Взаємодія Eu_2O_3 з CsI веде до утворення EuO і O^{2-} у розчині. Насичений розчин містить приблизно $4 \cdot 10^{-4}$ моль·кг⁻¹ EuO та $2 \cdot 10^{-4}$ моль·кг⁻¹ O^{2-} , EuO у цьому розчині не дисоціює. Домішки, що утворюються істотно змінюють люмінесцентні властивості монокристалів CsI, вирощених з насиченого розчину Eu_2O_3 у CsI порівняно з чистим йодидом цезію.