Processes of Europium Oxide Dissolution in Molten Alkali Metal Iodides

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The interactions of Eu^{2+} with oxide ions and the processes accompanying dissolution of Eu_2O_3 in molten CsI and NaI at 700 °C were studied by a potentiometric method and sequential addition method with electrochemical control of the saturation. An electrochemical cell with a membrane oxygen electrode $Pt(O_2)|ZrO_2(Y_2O_3)$ was used for determination of the equilibrium molality of O^{2-}. The solubility products of EuO are equal to $P_{EuO} = 7.94 \cdot 10^{-14}$ $mol^2 \cdot kg^{-2}$ in molten CsI and $2.24 \cdot 10^{-9}$ $mol^2 \cdot kg^{-2}$ in molten NaI. In the latter melt EuO is referred to as a weak base since its dissociation constant is $2.0 \cdot 10^{-6}$. The interaction of Eu_2O_3 with both molten iodides leads to the formation of EuO and O^{2-} in the solutions, which contain approximately $4 \cdot 10^{-4}$ $mol \cdot kg^{-1}$ EuO in CsI and $4 \cdot 10^{-3}$ $mol \cdot kg^{-1}$ EuO in NaI melts, and the dissociation of EuO in the melts is suppressed. The behavior of Eu oxo-species in the iodide melts is subjected to predictions of the Pearson “hard” and “soft” acids and bases concept. The admixtures formed by Eu_2O_3 dissolution in the molten iodides essentially affect the luminescence properties of single crystals grown from the saturated solutions as compared with the pure iodides. The obtained thermodynamic data permit consideration of Eu^{2+} as a good scavenger for the CsI melt, but it is not available for molten NaI.

Introduction

The current progress in material science of scintillators is connected with single crystals based on Eu-containing alkali and alkaline earth metal halides. Although such materials as SrI_2:Eu or CsI:Eu have long been known to be scintillation materials,[1,2] their thorough investigation started only several years ago. This renaissance of interest in materials forgotten a long time ago is due to new possibilities of deep purification of chemicals. For instance, SrI_2 of 5 N purity doped with 6 % Eu^{2+} possesses a light yield exceeding 100 000 photons·MeV^{-1},[3] whereas SrI_2:Eu obtained from chemicals of reagent quality does not differ from the material obtained by Hofstadter[1] and its light yield is only 30 000 photons·MeV^{-1}.[4] Unfortunately, there is no information about the admixtures decreasing the working parameters of this and similar scintillators.

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

The purpose of the present work is to study processes of the interactions of Eu^{2+} with O^{2-} and dissolution of Eu_2O_3 in molten alkali metal iodides and to clear up some features connected with the behavior of Eu oxo-species in CsI and NaI melts.

Experimental Section

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

NaI (“Tekhnoprom”, Saki, Ukraine 99.99 %) was used after drying in a vacuum (1 Pa) by slow heating from room temperature to 250 °C.

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

Anhydrous EuI_2 was prepared by dissolution of Eu_2O_3 in aqueous HI (reagent quality), and then NH_4I (reagent quality), taken in a molar ratio 2:1 to Eu, was added to the solution. The obtained solution was evaporated and dried up to the formation of a brown powder ($EuI_3 + NH_4I$ with traces of I_2 and water). This powder was carefully heated in vacuum up to the beginning of I_2 evaporation, which started at 200 °C owing to the following reaction:

$$EuI_3 \xrightarrow{t\ >\ 200\ °C,\ vacuum} EuI_2 + \frac{1}{2}I_2\uparrow \tag{1}$$

At the end of the decomposition reaction, the process of NH_4I sublimation commenced, accompanied with HI formation in the hot zone and additional purification of EuI_2 from oxygen-containing admixtures according to

$$2HI\uparrow + O^{2-} \rightarrow H_2O\uparrow + 2I^- \tag{2}$$

and the admixture oxide ions were removed from the final powder.

The processes of the interaction of Eu^{2+} with O^{2-} and dissolution of Eu_2O_3 in molten CsI were studied by controlling the equilibrium molality of O^{2-} concentration in the melt. The

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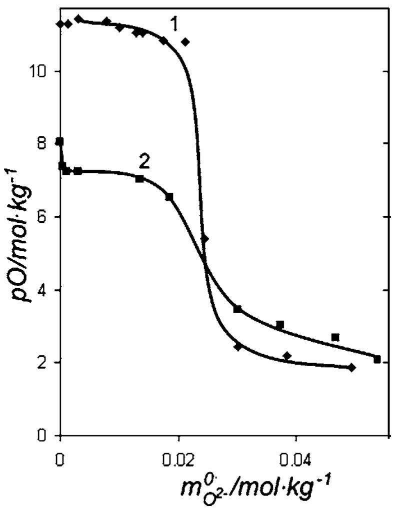

Figure 1. Potentiometric titration curves of Eu^{2+} (EuI_2) with O^{2-} in molten CsI (curve 1, $m^0_{Eu^{2+}} = 0.022$ mol·kg^{-1}) and NaI (curve 2, $m^0_{Eu^{2+}} = 0.029$ mol·kg^{-1}) at 700 °C.

scheme of the potentiometric cell for this determination is as follows:

$$(-)\mathrm{Pt}|\mathrm{Ag}|\mathrm{Ag}^+ + \mathrm{MeI}||\mathrm{MeI} + \mathrm{O}^{2-}|\mathrm{YSZ}|\mathrm{Pt}(\mathrm{O}_2)(+) \tag{3}$$

(where Me = Na or Cs and YSZ is the solid electrolyte of 0.9 ZrO_2 + 0.1 Y_2O_3 composition) and its construction is described in detail elsewhere.[8] The cell (eq 3) was initially calibrated with known amounts of strong base (KOH)

$$2\mathrm{KOH} \rightarrow 2\mathrm{K}^+ + \mathrm{O}^{2-} + \mathrm{H_2O}\uparrow \tag{4}$$

to obtain the dependences of electromotive force (emf) versus equilibrium oxide ion molality ($m_{O^{2-}}$ or pO $\equiv -\log a_{O^{2-}} \approx -\log m_{O^{2-}}$, where $a_{O^{2-}}$ is the activity of O^{2-} in the melt studied). The potentiometric titration and the sequential addition method (SAM) routines are described elsewhere.[8,9] To provide an inert atmosphere in the cell, high-purity (99.99 %) Ar was used.

Results and Discussion

EuO Solubility in Molten Iodides. EuO solubility in the molten iodides was determined by the potentiometric titration method. The following reaction

$$\mathrm{Eu}^{2+} + \mathrm{O}^{2-} = \mathrm{EuO}\downarrow \tag{5}$$

was studied. For this purpose, the amount of EuI_2, approximately corresponding to 0.03 mol·kg^{-1} Eu^{2+}, was added to both melts. The titration was performed by the addition of KOH ($^1/_2O^{2-}$) and measurement of the equilibrium emf (and, hence, pO). The initial amount of KOH was very low (on the order of 10^{-4} mol·kg^{-1}), which was necessary to obtain the results in a nonsaturated solution region, if the latter exists.

The potentiometric titration curves are presented in Figure 1. According to their form (the absence of a sharp pO drop at the first addition of the titrant in curve 1), EuO can be referred to as a practically insoluble oxide in molten CsI, and the magnitude of the pO drop at the equivalence point (approximately 8 pO units) allows supposition of an extremely low solubility product value for EuO. In contrast, the potentiometric curve in molten NaI (Figure 1, curve 2) has a sharp drop of pO at small titrant additions (so-called '"nonsaturated solution section") that allows EuO to be considered as a merely soluble oxide in the said melt. After the third addition the melt becomes saturated, and one can observe an inclined section before the equivalence point. The form of the titration curve in this case permits the conclusion that the solubility of EuO in NaI is appreciably higher in comparison with the CsI melt (the potentiometric curve drop at the equivalence point is near 5.5 pO units).

Table 1. Experimental and Calculated Parameters Obtained for the Potentiometric Titration of Eu^{2+} (EuI_2, 0.022 mol·kg^{-1}) with O^{2-} in Molten CsI at 700 °C

$m^0_{O^{2-}}$ / mol·kg^{-1}	pO / mol·kg^{-1}	pK'_{EuO} / mol·kg^{-1}	pP'_{EuO} / mol^2·kg^{-2}
0.0001	11.31	8.97	12.97[a]
0.0014	11.29	10.12	12.98[a]
0.0030	11.47	10.67	13.19[a]
0.0079	11.38	11.13	13.23[a]
0.0101	11.18	11.11	13.10[a]
0.0128	10.97	11.11	13.00[a]
0.0140	10.97	11.21	13.06[a]
0.0174	10.69	11.26	13.02[a]
0.0213	10.66	12.15	13.82
0.0244	3.73		
0.0301	2.42		
0.0384	2.20		
0.0495	1.87		

[a] These points were chosen for averaging pP'_{EuO}.

The thermodynamic parameters of eq 5 in the molten iodides were calculated on the basis of the consumption of O^{2-}. This value was calculated from the initial molality of O^{2-} ($m^0_{O^{2-}}$) and the equilibrium pO value as

$$\Delta m_{O^{2-}} = m^0_{O^{2-}} - m_{O^{2-}} = m^0_{O^{2-}} - 10^{-\mathrm{pO}} \tag{6}$$

From this value, the solubility product (P'_{EuO})

$$P'_{EuO} = m_{Eu^{2+}} m_{O^{2-}} = (m^0_{Eu^{2+}} - \Delta m_{O^{2-}}) \cdot 10^{-\mathrm{pO}} \tag{7}$$

and the dissociation constant (K'_{EuO})

$$K'_{EuO} = \frac{m_{Eu^{2+}} m_{O^{2-}}}{m_{EuO}} = \frac{(m^0_{Eu^{2+}} - \Delta m_{O^{2-}}) \cdot 10^{-\mathrm{pO}}}{\Delta m_{O^{2-}}} \tag{8}$$

were calculated. The experimental and calculated values are presented in Tables 1 (CsI) and 2 (NaI).

The data presented in Table 1 testify that all the solutions obtained by addition of O^{2-} to Eu^{2+} solutions in molten CsI are saturated, that is, even the first small amount of the titrant (KOH) causes the precipitation of EuO from the melt. Indeed, consideration of the changes of pK'_{EuO} together with the increase of $m^0_{O^{2-}}$ shows that there is directional shift of the calculated value (increase), whereas pP'_{EuO} oscillates randomly near a certain average value. Such a behavior of the calculated values confirms the formation of the saturated solution.[10] So, the solubility product index of EuO, pP_{EuO}, is estimated as 13.1 ± 0.2 (13.1 ± 0.5 at the confidence level $p = 0.95$), that corresponds to $7.94 \cdot 10^{-14}$ mol^2·kg^{-2}. Such a value shows that EuO is practically insoluble in molten CsI.

Table 2. Experimental and Calculated Parameters Obtained for the Potentiometric Titration of Eu^{2+} (EuI_2, 0.029 mol·kg^{-1}) with O^{2-} in Molten NaI at 700 °C

$m^0_{O^{2-}}$ / mol·kg^{-1}	pO / mol·kg^{-1}	pK'_{EuO} / mol·kg^{-1}	pP'_{EuO} / mol^2·kg^{-2}
0.0001	8.04	5.58[a]	9.56
0.0005	7.38	5.69[a]	7.91
0.0011	7.25	5.83[a]	8.79[b]
0.003	7.22	6.27	8.79[b]
0.0135	7.03	6.94	8.81[b]
0.0185	6.54	6.74	8.47[b]
0.0302	3.47		
0.0373	3.02		
0.0468	2.69		
0.0539	2.08		

[a] These points were chosen for averaging pK'_{EuO}. [b] These points were chosen for averaging pP'_{EuO}.

As for EuO behavior in molten NaI, the thermodynamic data obtained for the first three points in Table 2 allow an estimate the dissociation constant index as $pK_{EuO} = 5.70 \pm 0.12$ (5.70 ± 0.5 at $p = 0.95$); that is, EuO is a weak base in molten NaI.

All the remaining points belong to the saturated solution region and the solubility product index can be obtained from these data as $pP_{EuO} = 8.65 \pm 0.13$ (8.65 ± 0.4 at $p = 0.95$). Going from the above thermodynamic data, it is possible to find the concentrations of nondissociated EuO (s_{EuO}) in the saturated solution from the following equation:

$$s_{EuO} = \frac{P_{EuO}}{K_{EuO}} = \frac{2.24 \cdot 10^{-9}}{2.00 \cdot 10^{-6}} = 1.12 \cdot 10^{-3}\ \mathrm{mol \cdot kg^{-1}}$$

$$\log s_{EuO} = -2.95 \pm 0.7 \qquad (9)$$

To finish the consideration of the potentiometric titration data, it should be noted that the accuracies of the determined thermodynamic parameters are appreciably worse than in molten chlorides because of additional difficulties of measurements in melts possessing strong reducing properties, owing to the simultaneous presence of the I^- and Eu^{2+} ions.

Eu_2O_3 Solubility in Molten Iodides. The results reported in the previous section permit determination of the solubility product value of EuO, that is, the parameter connected with the behavior of the ionized part of the dissolved oxide. However, a part dissolved in the melt without dissociation in the case of CsI cannot be determined by the direct potentiometric titration. In order to estimate the fraction of nondissociated oxide in the saturated solution, the sequential addition method (SAM) described in ref 11 seems more appropriate.

This method consists of the addition of some amounts of the oxide studied to the melt and the measuring the equilibrium emf. The oxide is added up to saturation, which results in the minimum or plateau in the pO−*pm* plot (see Figure 2). Such a plot gives the possibility to make some conclusions.

First, the point denoted in Figure 2 by arrow s_1 corresponds to the amount of Eu_2O_3 dissolved in the melt only partially, so some quantity of the oxide remains nondissolved. Such a partial dissolution results in an essential decrease of the Eu_2O_3 particle size, and its solubility increases according to the Ostwald−Freundlich rule. Subsequent additions of Eu_2O_3 lead to increasing average size of Eu_2O_3 particles, and its solubility decreases (whereas pO increases). The abscissa of the s_1 point (pm = 3.7) yields a value of Eu_2O_3 solubility of $2.0 \cdot 10^{-4}$ mol·kg^{-1}. It should be noted that this value is in good agreement with the results of quantitative analysis fulfilled by the polarographic method. Second, the pO value at saturation is equal to 3.72, which corresponds to the equilibrium oxide ion molality near $1.95 \cdot 10^{-4}$ mol·kg^{-1}. To ascribe this O^{2-} concentration to a certain chemical process, additional studies are required.

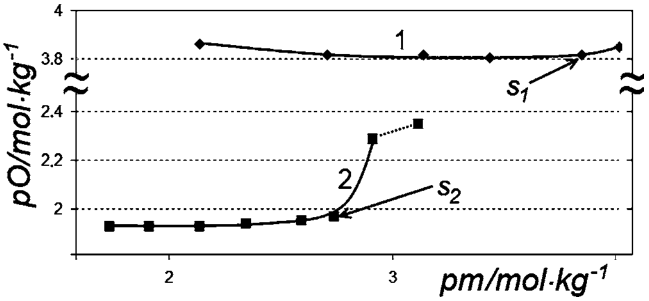

Figure 2. Dependence of pO vs −log $m^0_{Eu_2O_3}$ (≡ pm) at the addition of Eu_2O_3 to molten CsI (curve 1) and NaI (curve 2) at 700 °C. s_1 and s_2 arrows designate points of saturation in CsI and NaI, respectively.

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

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

$$Eu_2O_3\downarrow + 2I^- \rightarrow 2EuO + O^{2-} + I_2\uparrow \qquad (10)$$

and this equilibrium is completely shifted to the right. The molality of EuO in this saturated solution is equal to $4.0 \cdot 10^{-4}$ mol·kg^{-1}.

Since the concentration of Eu_2O_3 dissolved in CsI ($2.0 \cdot 10^{-4}$ mol·kg^{-1}) coincides with the equilibrium molality of O^{2-} ($1.9 \cdot 10^{-4}$ mol·kg^{-1}), it means that reaction 10 is the only process generating oxide ions, and EuO dissociation according to

$$EuO_{dissolved} \rightarrow Eu^{2+} + O^{2-} \qquad (11)$$

is suppressed.

Figure 3 answers the other question: do such low concentrations of the participants of reaction 10 affect the properties of CsI? The first maximum in the crystal polluted with Eu_2O_3 is located at 312 nm, whereas the pure material possesses a similar maximum at 305 nm. From ref 12 it follows that the formed amount of oxide ions in the melt ($2.0 \cdot 10^{-4}$ mol·kg^{-1}) makes this scintillator slower. The second sequence of the said pollution is a rather intensive band caused by Eu^{2+} or vacancies.[13] Hence, if the CsI melt is kept in contact with Eu_2O_3, then the single crystal grown from this melt possesses appreciably distinguished luminescent characteristics as compared with the undoped material.

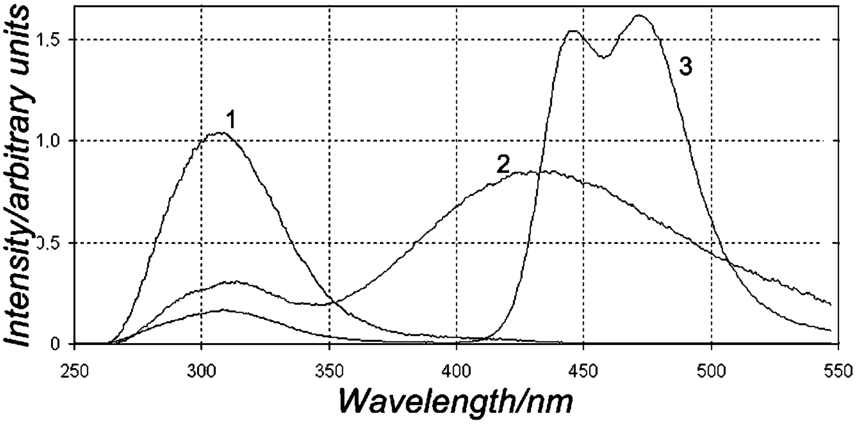

Figure 3. Radioluminescence spectra: curve 1, CsI crystals grown without dopants; curve 2, crystal grown from the saturated solution of Eu_2O_3 in CsI; curve 3, crystal grown from the saturated solution of Eu_2O_3 in NaI. The excitation source is ^{241}Am.

Now let us return to Figure 2 and consider the results for the NaI melt. Speculations similar to those in the case of molten CsI permit us to conclude that the saturation of the melt is achieved at $pm = 2.85$ (s_2 point), that is, EuO molality is near $2.8 \cdot 10^{-3}$ and $\log s_{EuO} = -2.55$ (assuming that the dissolution of Eu_2O_3 in iodide melts causes reduction of Eu^{3+} to Eu^{2+}; see eq 10). When it is taken into account that the error of the dissociation constant determination is rather high (eq 9), the obtained results are close.

Hence EuO has a slight solubility in molten NaI; however, if Eu^{2+} is used as an activator the precipitation of EuO from the melt prepared from the commercial NaI (concentration of $\hat{I}^{2-}$ less than 10^{-3} mol·kg^{-1}) is hardly possible since the potential EuO concentration is less than that in the saturated solution ($2.8 \cdot 10^{-3}$ mol·kg^{-1}). This reason makes Eu^{2+} (EuI_2) unavailable for removal of oxygen-containing admixtures from NaI.

Considering the effect of the ionic solvents on the solubility of EuO shows that the observed increase of solubility in the CsI−NaI sequence can be explained in terms of Pearson's HSAB (hard and soft acids and bases) concept.[14] Indeed, the equilibrium

$$EuO\downarrow + \; n\mathrm{Me}^{+} \leftrightarrows Eu^{2+} + \mathrm{Me}_n\mathrm{O}^{n-2} \qquad (12)$$

is affected by the "hardness" of the alkali metal cation and Na^+ is a harder acid than Cs^+. Therefore, the stability of $\mathrm{Me}_n\mathrm{O}^{n-2}$ complexes in NaI should be higher than in CsI, and the equilibrium of reaction 12 is shifted to the right, which in turn causes increased oxide solubility. Since hard acids react with nondissociated oxide in the melt, the stronger interaction of Na^+ with the oxide results in the increase of nondissociated EuO solubility from $4 \cdot 10^{-4}$ mol·kg^{-1} in CsI to $2.8 \cdot 10^{-3}$ mol·kg^{-1} in NaI.

The increased solubility of EuO in NaI as compared with CsI affects the luminescence spectrum of the single crystal grown from the saturated solution (Figure 3, curve 3). There are two neighbor bands in the spectrum with maxima located at (447 and 473) nm, and both bands are connected with Eu species: the shorter-wave band could be ascribed to luminescence of Eu^{2+} surrounded only by iodide ions, whereas the second one arises from O^{2-} ions entering Eu^{2+} surroundings in concentrated solutions of EuO. Seemingly, both bands are present in the saturated solution of Eu_2O_3 in the CsI crystal since the band at 435 nm is asymmetric, however, the intensity of the latter band is very small, caused by a relatively low concentration of EuO in the said solution.

Conclusions

As found by the potentiometric titration method, the solubility product index of EuO, pP_{EuO}, is 13.1 ± 0.3 ($P_{EuO} = 7.94 \cdot 10^{-14}$ mol^2·kg^{-2}) and EuO is practically insoluble in molten CsI at 700 °C. The solubility product of EuO in molten NaI is considerably higher: $pP_{EuO} = 8.65 \pm 0.13$ ($P_{EuO} = 2.24 \cdot 10^{-9}$). The value of the dissociation constant of EuO in NaI is $K_{EuO} = 2 \cdot 10^{-6}$.

Dissolution of Eu_2O_3 in the CsI melt is accompanied by oxidation of the melt and formation of EuO and O^{2-} in the solution. The saturated solution contains $4 \cdot 10^{-4}$ mol·kg^{-1} EuO and $1.9 \cdot 10^{-4}$ mol·kg^{-1} O^{2-}; under these conditions the dissociation of EuO is completely suppressed. The solubility of EuO in NaI determined by this method is $2.8 \cdot 10^{-3}$ mol·kg^{-1}.

The radioluminescence spectrum of a CsI single crystal grown from the saturated solution of Eu_2O_3 in CsI corresponds to superimposition of those for undoped CsI polluted with O^{2-} and CsI:Eu solid solution. Essentially higher solubility of EuO in molten NaI leads to formation of a double band in the corresponding spectrum. Both bands are ascribed to Eu^{2+} ions:, one band is caused by Eu^{2+} in the CsI matrix whereas the other is connected with Eu oxo-species in the saturated solution of Eu_2O_3 in NaI.

The obtained data mean that Eu^{2+} ions (EuI_2) are a good scavenger in the CsI melt but are inappropriate in the case of molten NaI.

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