

On the formation of oxide species in melts of CsCl–LiCl–YCl₃ system

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Interactions of oxide ions with Li⁺ (CsCl+LiCl system) and Y³⁺ (CsCl–LiCl+YCl₃ system) at 700°C have been studied by potentiometric method using a Pt(O₂)|ZrO₂(Y₂O₃) oxygen electrode to determine the equilibrium O²⁻ molality. The addition of Li⁺ to CsCl melt results in O²⁻ fixation in Li₂O complex, $K_{Li,2} = (2.11 \pm 0.04) \cdot 10^3$ (molality scale). The solubility product of Li₂O in 2CsCl–LiCl melt is $K_s = 0.22 \text{ mol}^3 \cdot \text{kg}^{-3}$. Addition of Y³⁺ to 2CsCl–LiCl causes the formation of YO⁺ complex, $K_{Y,1} = (3.11 \pm 0.05) \cdot 10^2$. The formation of YO⁺ retards the purification of CsCl–LiCl+YCl₃ melt from oxide impurities which worsen the quality of rare-earth based scintillation single crystals.

Взаимодействия оксид-ионов с катионами Li⁺ (система CsCl+LiCl) и Y³⁺ (система CsCl–LiCl+YCl₃) при 700°C изучены потенциометрическим методом с использованием кислородного электрода Pt(O₂)|ZrO₂(Y₂O₃) для определения равновесной моляльности O²⁻. Прибавление Li⁺ к расплаву CsCl ведет к связыванию O²⁻ в комплексы состава Li₂O, $K_{Li,2} = (2.11 \pm 0.04) \cdot 10^3$ (моляльная шкала). Произведение растворимости Li₂O в расплаве 2CsCl–LiCl равно $K_s = 0.22 \text{ моль}^3 \cdot \text{кг}^{-3}$. Введение Y³⁺ в расплав 2CsCl–LiCl приводит к образованию комплексов YO⁺, $K_{Y,1} = (3.11 \pm 0.05) \cdot 10^2$. Образование YO⁺ замедляет процесс очистки расплава CsCl–LiCl+YCl₃ от кислородсодержащих примесей, ухудшающих качество сцинтилляционных монокристаллов на основе галогенидов редкоземельных металлов.

1. Introduction

Scintillators based on alkali and rare-earth (RE) metal halides are among the modern materials being under extensive development. There are a lot of publications devoted to such materials of different compositions, the papers [1, 2] should be mentioned as the most recent ones. These materials can be obtained by two ways. The dry way includes only mixing ultrapure anhydrous halides and the crystal growth. The wet method consists in dissolution of RE oxides (the most available commercial form of RE compounds) and alkali metal halides in the corresponding acid, evaporation, drying, and calcination of the raw. The raw

material so obtained is used to grow crystals. From the viewpoint of expenses, the latter way is considerably cheaper but its use results often in that the obtained scintillators are worse in quality than in the case of the dry method. The main reason for this is connected with the difficulties of purification of the raw from traces of oxygen-containing admixtures and moisture. To solve this problem, it is necessary to know certain properties of corresponding raw and growth melt, e.g., their ability to fix oxide ions and quantitative characteristics of that process [3]. Such information is absent, excluding [4] where some properties of KCl–NaCl–CeCl₃ system are reported, how-

ever, the said system is not of any practical importance.

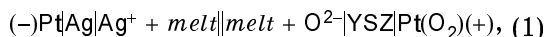
CLYC, or $\text{Cs}_2\text{LiYCl}_6:\text{Ce}$, is now one of the most attractive mixed scintillators. Thorough investigations of that material shows that its light yield varies between 9,600 [5] and 21,600 photons per MeV [6] and it depends on the way of the crystal obtaining. Most probable reason of such variation is the formation of lithium and yttrium oxo compounds in melt and, hence, the presence thereof in the solid crystal. However, there is no information about interactions of Li^+ and Y^{3+} cations with oxo anions in CsCl-LiCl-YCl_3 system.

The study of interaction of $\text{CsCl}+x\text{LiCl}$ ($x = 0-0.5$) and $2\text{CsCl-LiCl}+y\text{YCl}_3$ ($y = 0-1$) molten systems with O^{2-} to determine the main forms of oxocomplexes and the corresponding equilibrium constants is the purpose of this work.

2. Experimental

CsCl of reagent quality with the total molality of oxygen-containing admixtures $10^{-4} \text{ mol}\cdot\text{kg}^{-1}$ of O^{2-} (after melting) was used for the experiments without purification. LiCl was obtained by dissolution of excess Li_2CO_3 (extra pure, 99.99 % Li_2CO_3) in aqueous HCl of reagent quality. Then, after addition of NH_4Cl (0.5 mole per 1 mole of LiCl), the solution was evaporated, dried and calcined in vacuum at stepwise temperature increase up to 500°C . YCl_3 was prepared by dissolution of Y_2O_3 (pure) in excess (5 %) of hydrochloric acid and NH_4Cl (4 mole per 1 mole of YCl_3) was added to the formed solution. This solution was dried and heated in vacuum up to 600°C with holding at 200 and 400°C for 1 h. KOH was of reagent quality, prior to the experiment it was melted and kept in Ar atmosphere for 2 h at 600°C .

The interaction of Li^+ and Y^{3+} with O^{2-} in the above-mentioned melts were studied by determination of equilibrium molal concentration of oxide ion in the melt. The potentiometric cell for those studies is presented by the following scheme:



(where YSZ is $0.9 \text{ ZrO}_2 + 0.1 \text{ Y}_2\text{O}_3$ ceramics) and its construction is described in detail elsewhere [7]. The descriptions of the potentiometric titration routine and the sequential addition method (SAM) are presented there, too. To provide inert atmos-

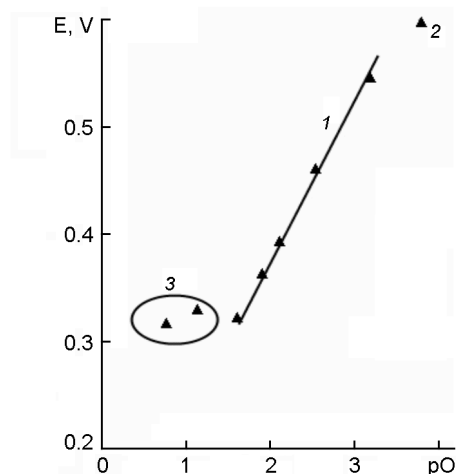


Fig. 1. Dependence of emf (E) of cell (1) vs. $p\text{O}$ in 2CsCl-LiCl melt at 700°C : 1, the calibration plot; 2, a point obtained at low O^{2-} molality; 3, the saturated solution region.

phere in the cell, high pure (99.99) Ar was used.

3. Results and discussion

Since 2CsCl-LiCl melt is an intermediate in the $\text{CsCl} \rightarrow 2\text{CsCl-LiCl} \rightarrow 2\text{CsCl-LiCl-YCl}_3$ sequence, we chose this melt as a reference one. The plot of emf (E) of the cell (1) vs. $p\text{O}$ ($p\text{O} \equiv -\log a_{\text{O}^{2-}} \approx -\log m_{\text{O}^{2-}}$, $a_{\text{O}^{2-}}$ and $m_{\text{O}^{2-}}$ are activity and molality of O^{2-} , respectively) is presented in Fig. 1. The slope of the $E-p\text{O}$ calibration plot is necessary to calculate the thermodynamic parameters of equilibria which is discussed in what follows.

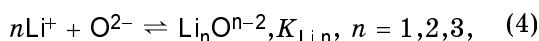
As is seen, the $E-p\text{O}$ plot contains some features. The points chosen for the calculations lie in line 1. Beside of these points, there are some features in the calibration data. The initial point (designated by 2) falls out from the plot since the "pure" melt contains oxide ion admixtures (of the order of $10^{-4} \text{ mol}\cdot\text{kg}^{-1}$) and this reason causes deviations of the actual O^{2-} molality from added amount of oxide ion donor, especially at low concentrations (here, $1.61 \cdot 10^{-4} \text{ mol}\cdot\text{kg}^{-1}$). Two points in oval (designated by 3) belong to the saturated solution region (the average emf value is equal to 0.323 V and $p\text{O} = 1.6$). This means that the 2CsCl-LiCl melt is characterized by upper basicity limit of $2.51 \cdot 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$, it is impossible to achieve higher O^{2-} concentrations in melt of such a composition. Taking into account that Li^+ molality in said melt is $2.97 \text{ mol}\cdot\text{kg}^{-1}$, it is possible to estimate the solubility product of Li_2O :

$$K_{s, Li_2O} = m_{Li^+}^2 \cdot m_{O^{2-}} = 2.97^2 \cdot 0.0251 = 0.22 mol^3 \cdot kg^{-3}. \quad (2)$$

The treatment of the plot 1 by the least squares method gives the following equation:

$$E = 0.099(\pm 0.02) + 0.139(\pm 0.01) \cdot pO \quad (P = 0.95). \quad (3)$$

Interactions in CsCl–LiCl system were studied by sequential additions of LiCl amounts to molten CsCl. To determine the equilibrium constants, we suppose that the addition of Li^+ to CsCl melt results in interactions:



and the balance of O^{2-} may be presented as

$$m_{O^{2-}} = m_{O^{2-}} \left(1 + \sum_{i=1}^3 K_{Li,i} \cdot m_{Li^+}^i \right). \quad (5)$$

It is important that this equation allows to obtain polynomial dependence which can be easily treated taking into account that

$$\frac{m_{O^{2-}}}{m_{O^{2-}}} = 10^{\frac{E^* - E_{CsCl}^0}{0.139}}, \quad (6)$$

where E^* is emf value of melt after Li^+ addition to pure CsCl, E_{CsCl}^0 is the emf of "pure" CsCl and 0.139 is the slope of E – pO plot (3):

$$10^{\frac{E^* - E_{CsCl}^0}{0.139}} \equiv \frac{m_{O^{2-}}}{m_{O^{2-}}} = 1 + \sum_{i=1}^3 K_{Li,i} \cdot m_{Li^+}^i. \quad (7)$$

Principal dependence of emf vs. logarithm of Li^+ molality is presented in Fig. 2 (plot 1). The slope of this plot is equal to 0.282 ± 0.015 V, i.e. exceeds twice that of the calibration plot. This can be explained by the formation of Li_2O as the main product of Li^+ – O^{2-} interactions in the chloride melt. Indeed, at the considerable excess of Li^+ (its molality in the melt is, at least, 1000 times higher than that of O^{2-}).

The expression for $K_{Li,n}$ constant is expressed as

$$K_{Li,n}^{-1} = \frac{m_{Li^+}^n \cdot m_{O^{2-}}}{m_{Li_nO^{n-2}}}. \quad (8)$$

Taking into account that Li^+ demonstrates relatively strong acidic properties,

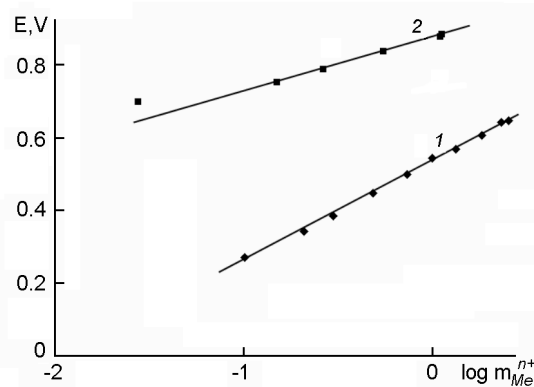


Fig. 2. Dependences of E, V vs. logarithm of Li^+ molality in CsCl+LiCl system (1) and Y^{3+} molality in CsCl–LiCl+ YCl_3 system (2) at $700^\circ C$.

we can assume that $m_{Li_nO^{n-2}} \approx m_{O^{2-}}^n = Li_nO^{n-2} = const$. This allows to rewrite the Eq.(8) in logarithmic form as

$$\log K_{Li,n}^{-1} = n \log m_{Li^+} + \log m_{O^{2-}} - \log m_{Li_nO^{(n-2)+}}. \quad (9)$$

Since $pO = -\log m_{O^{2-}}$, we get a relation between pO and $\log m_{Li^+}$

$$pO = const' + n \log m_{Li^+}. \quad (10)$$

So, the slope of line 1 $\left(\frac{\partial E}{\partial \log m_{Li^+}} \right)_T$ (Fig. 2) depends on the calibration plot slope $\left(\frac{\partial E}{\partial pO} \right)_T$ (0.139 V) in such a manner:

$$\left(\frac{\partial E}{\partial \log m_{Li^+}} \right)_T = n \left(\frac{\partial E}{\partial pO} \right)_T = n \cdot 0.139. \quad (11)$$

The same conclusion could be made after calculations according Eq.(7), $K_{Li,1}$ and $K_{Li,3}$ are statistically insignificant magnitudes. The dependence of $m_{O^{2-}}/m_{O^{2-}}$ vs. m_{Li^+} (points) and its polynomial approximation (curved line) are presented in Fig. 3a. As is seen, they are in a good agreement and $K_{Li,2}$ is calculated to be $(2.11 \pm 0.04) \cdot 10^3$ ($P = 0.95$).

The similar considerations were used for the calculation of equilibrium constants in $2CsCl$ – $LiCl$ + YCl_3 system. The slope of $E = \log m_{Y^{3+}}$ plot (Fig. 2, plot 2) is less than that of $E = \log m_{Li^+}$ and is equal to 0.148 ± 0.005 V. This means that the main product of the interaction is YO^+ .

The calculations of equilibrium constants were carried out for the following equilibria

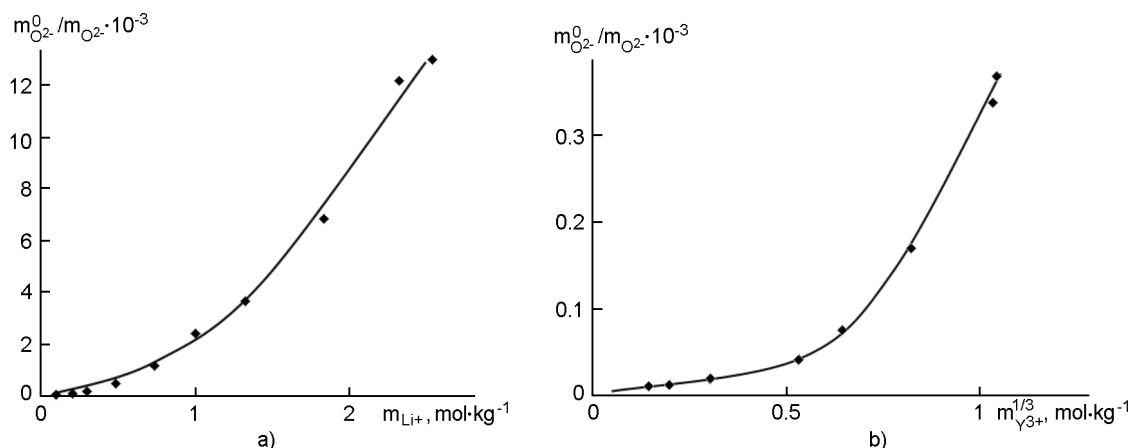
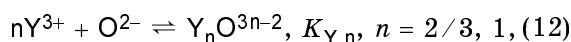


Fig. 3. Dependence of $m_{O_2-}^0/m_{O_2-}$ vs. molalities of Li^+ (m_{Li+}) in CsCl+LiCl system (a) and Y^{3+} ($m_{Y^{3+}}$) in CsCl-LiCl+YCl₃ system (b) at 700°C. The experimental values are designated by rhombs, the corresponding polynomial approximations are presented by curved lines.



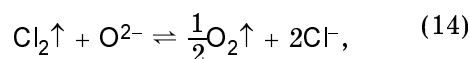
meaning $Y_{2/3}O = 1/3Y_2O_3$. The balance of O^{2-} molality (with the designation $m' = m_{Y^{3+}}^{1/3}$) may be presented as

$$10^{\frac{E^* - E_{CsCl-LiCl}^0}{0.139}} = \frac{m_{O_2-}^0}{m_{O_2-}} = 1 + K_{Y,2/3} \cdot m'^2 + K_{Y,1} \cdot m'^3. \quad (13)$$

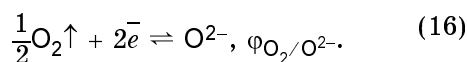
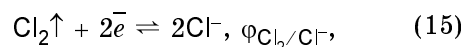
The dependence of $m_{O_2-}^0/m_{O_2-}$ vs. $m_{Y^{3+}}^{1/3}$ (points) and its polynomial approximation (curved line) are presented in Fig. 3b. The calculated and experimental data are in a good agreement and is $(3.11 \pm 0.05) \cdot 10^2$ ($P = 0.95$) whereas $K_{Y,2/3}$ is statistical zero. So, Y^{3+} demonstrates stronger acidic properties as compared to Li^+ . At considerable excess of Y^{3+} as compared to $m_{O_2-}^0$, YO^+ becomes the main form of the oxide ion existence in YCl₃ containing melts.

The formation of YO^+ as an intermediate substance in $Y_2O_3 \xrightarrow{-O^{2-}} 2YO^+ \xrightarrow{-2O^{2-}} 2Y^{3+}$ sequence explains the difficulties arising at CLYC melt purification. Indeed, the first stage of purification is the decomposition of Y_2O_3 accompanied by the formation of YO^+ ($YOCl$) in the solution. After this stage, the melt becomes transparent and colorless, however, the concentration of oxide ions therein remains high enough. The following removal of negatively charged O^{2-} ion from positively charged YO^+ is more difficult and just this stage retards considerably the purification process.

Another reason is essential for the Red-Ox purification processes. Indeed, the equilibrium of the main stage for such processes:



depends on electrochemical potentials of chlorine and oxygen electrodes, namely:



The potential of electrode reaction (15) against $Ag^+|Ag$ electrode is approximately equal to +0.84 V [8]. Potential of reaction (16) against $Ag^+|Ag$ electrode is seen from Fig. 2 as E . The condition of reaction (14) running to the right ($\varphi_{Cl_2/Cl^-} > \varphi_{O_2/O^{2-}}$) is valid for all the studied compositions excluding CsCl-LiCl-YCl₃ (2:1:1) melt ($\varphi_{O_2/O^{2-}} = +0.88$ V). This means that this melt cannot be purified from oxide ion traces, since the direct chlorination and carbohalogenation processes are retarded essentially as compared to melts based only on the alkali metal chlorides.

4. Conclusions

Interaction of molten CsCl-LiCl melt with oxide ion results in formation of Li_2O in the solution, $K_{Li,2} = (2.11 \pm 0.04) \cdot 10^3$ (molality scale). The solubility product of Li_2O in 2CsCl-LiCl melt is $0.22 \text{ mol}^3 \cdot \text{kg}^{-3}$. The main form of oxide ion fixation in melts of CsCl-

$\text{LiCl}-\text{YCl}_3$ is YO^+ complex, $K_{\text{Y},1} = (3.11 \pm 0.05) \cdot 10^2$. The formation of YO^+ retards the melt purification from oxide impurities. Owing to formation of YO^+ , visually transparent growth melts contain considerable amounts of oxide traces.

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Про утворення кисеньвмісних сполук у розплавах системи $\text{CsCl}-\text{LiCl}-\text{YCl}_3$

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Досліджено взаємодії оксид-іонів з катіонами Li^+ (система $\text{CsCl}+\text{LiCl}$) та Y^{3+} (система $\text{CsCl}-\text{LiCl}+\text{YCl}_3$) при 700°C потенціометричним методом з використанням кисневого електрода $\text{Pt}(\text{O}_2)|\text{ZrO}_2(\text{Y}_2\text{O}_3)$ для визначення рівноважної молярності O^{2-} . Додавання Li^+ до розплаву CsCl веде до зв'язування O^{2-} в комплекси складу Li_2O , $K_{\text{Li},2} = (2.11 \pm 0.04) \cdot 10^3$ (молярна шкала). Добуток розчинності Li_2O у розплаві $2\text{CsCl}-\text{LiCl}$ дорівнює $K_s = 0.22$ моль³·кг⁻³. Введення Y^{3+} у розплав $2\text{CsCl}-\text{LiCl}$ призводить до утворення комплексів YO^+ , $K_{\text{Y},1} = (3.11 \pm 0.05) \cdot 10^2$. Утворення YO^+ сповільнює процес очищення розплаву $\text{CsCl}-\text{LiCl}+\text{YCl}_3$ від кисеньвмісних домішок, що погіршують якість скінцифційних монокристалів на основі галогенідів рідкісноземельних металів.