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Potentiometric Investigations of Carbonate Ion Stability in Molten Cesium and Sodium Iodides

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The reaction of carbonate ion dissociation in molten CsI and NaI was studied in the temperature range from the melting point to 800 (CsI) and 830 °C (NaI) by a potentiometric method with the use of a membrane oxygen electrode as an indicator one. The dissociation constant of CO_3^{2-} in the molten iodides was found to increase with the temperature. p*K* values for CsI are 4.47 (650 °C), 4.23 (700 °C), 3.89 (750 °C), 3.44 (800 °C); those for NaI are 4.68 (700 °C), 4.39 (750 °C), 4.17 (800 °C), 3.92 (830 °C). The plots of p*K* vs reverse temperature are linear. Carbonate stability in molten CsI is lower than that in the NaI due to lower stability of Cs_2CO_3 compared with Na_2CO_3.

Cesium and sodium iodide melts are often used as starting materials (liquid media) for the growth of scintillation single crystals activated by various dopants (TlI, NaI for CsI and TlI for NaI crystals). The crystal quality is known to be dependent on their admixture composition. Most abundant oxide-containing admixtures, among which carbonates and hydroxides should be mentioned, result in absorption bands in UV and IR frequency ranges.[1,2] In addition, hydroxide admixtures in CsI scintillation single crystals lead to defect formation owing to their decay under exposure to γ irradiation[3] and this worsens the optical characteristics during the crystals' exploitation.

Nevertheless, the effect of oxygen-containing impurities on scintillation crystal properties cannot be stated to be only negative. Thus, carbonate ions have been found[4] to be usable for CsI crystal doping, and CsI (CO_3) scintillation crystals are now considered among the most promising ones.

From the what is said above it is clear that the stage of initial preparation of the molten media to the growth process should include either removal of the oxide-containing components if they are undesirable or, instead, the creation of conditions under which the desirable oxygen-containing dopants should be stable in ionic solvents.

Processes of the dissociation of oxygen-containing admixtures in molten salts are often described as acid−base reactions in frames of oxoacidity (Lux[5] definition):

$$B = A + O^{2-} \tag{1}$$

where B is an oxobase and A is the oxoacid. Lux introduced the pO parameter $pO \equiv -\log a_{O^{2-}} \sim -\log m_{O^{2-}}$ for the characterization of basic properties of melts; this parameter is considered to be similar to pOH in aqueous solutions.

Carbonate ions dissolved in ionic melts are able to exhibit the above-mentioned acid−base dissociation which occurs according to the equation

$$CO_3^{2-} = CO_2\uparrow + O^{2-} \tag{2}$$

and their stability may be characterized by the dissociation constant *K*

$$K = p_{CO_2} a_{O^{2-}} / a_{CO_3^{2-}} \tag{3}$$

(where p_{CO_2} is CO_2 pressure and $a_{O^{2-}}$ and $a_{CO_3^{2-}}$ are oxide ion and carbonate ion activities, respectively) or p*K* = −log *K*; the decrease of p*K* corresponds to reduction of the carbonate stability. Up to the present time there are no studies of carbonate behavior in molten cesium and sodium iodides although the data on equilibrium constants of reaction 2 in molten chloride melts based on alkaline and alkaline earth metal cations are well-known.[6−9] Recently we performed a study of carbonate dissociation equilibrium 2 in molten potassium halides (KCl, KBr, KI) at 800 °C.[10]

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The objective of the present work is to study equilibrium 2 in liquid NaI and CsI in the temperature range from temperatures near the melting point up to ~800 °C.

Experimental

"Caesium iodide extra pure 17-2" ("17-2" means that 17 impurities are controlled and content is less than 10^{-2} mas.%) and "sodium iodide extra pure 12-3" were used as the solvents. Before being melted, NaI and CsI were dried by careful heating of the commercial salts to 180 °C in air. After the melting, the ionic liquids were kept in an argon atmosphere for 1 h, and then a small amount of NH_4Cl was added into the melts to provide the removal of oxide ions according to the following equation:

$$NH_4Cl + O^{2-} \rightarrow NH_3\uparrow + H_2O\uparrow + 2Cl^- \qquad (4)$$

After this simple purification the melts were appropriate for the studies. Reaction 2 was studied at the following temperatures: 650, 700, 750, and 800 °C for CsI (mp 621 °C[11]) and 700, 750, 800, and 827 °C for NaI (mp 662 °C[11]). The investigation routine was as follows. First, it was necessary to calibrate the potentiometric cell

$$Pt|Ag|Ag^+, 0.1\ mol\ kg^{-1} + melt||melt + O^{2-}|YSZ|Pt(O_2) \qquad (5)$$

to obtain a calibration $E-$pO plot:

$$E = E° + RT/(zF)(pO) \qquad (6)$$

For this purpose known amounts of Lux base (KOH for CsI or NaOH for NaI) were added to the melt in argon atmosphere to provide pO values in the range from 1 to 4. As is known,[12] the membrane material (stabilized zirconia) is stable under these conditions and its solubility in the melts is too small.[13] Then the equilibrium emf of the potentiometric cell with a membrane oxygen electrode $Pt(O_2)|YSZ$ (yttrium stabilized zirconia) was fixed. The emf value was considered as stable if some consecutive measurement within 20 min showed its changes were less than 0.001 V and shift of the emf was absent. When a set of data necessary for the $E-$pO plot was obtained, we proceeded to the study of reaction 2.

To provide the equilibrium conditions, carbon dioxide was bubbled through the melts. Subsequent addition of the Lux bases was under these conditions (4 or 5 experimental points). Passing CO_2 led to the practically complete transformation of the hydroxides into the corresponding carbonates; in the case of NaOH it may be represented by the equation

$$2NaOH + CO_2\uparrow \xrightarrow{CO_2} Na_2CO_3 + H_2O\uparrow \qquad (7)$$

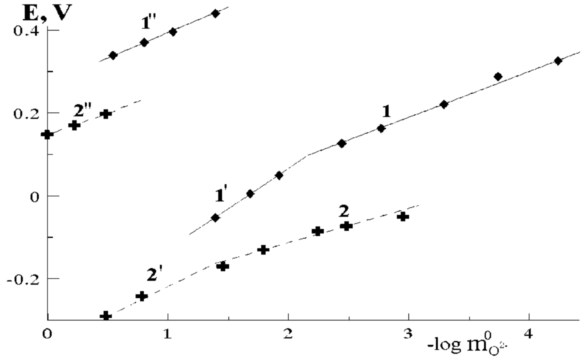

Figure 1. The dependence of emf (E) vs initial oxide ion molalities ($-\log m°_{O^{2-}}$) of the potentiometric cell with a membrane oxygen electrode Pt-(O_2)|YSZ: molten CsI at 700 °C in argon (1, 1′) and in CO_2 (1″); molten NaI at 830 °C in argon (2, 2″) and in CO_2 (2″).

The plots obtained in the CO_2 flow condition were $E = -\log m_{CO_3^{2-}}$ ones. Equilibrium O^{2-} molality was estimated from the calibration data:

$$m_{O^{2-}} = \exp\left(-2.3025\frac{zF(E - E°)}{RT}\right) \qquad (8)$$

The equilibrium constant of reaction 2 was calculated from eq 3.

The typical calibration results are presented in Figure 1. The calibration plots in argon atmosphere in CsI melt (plots 1, 1′) and NaI (plots 2, 2′) are simple enough to interpret: they consist of two plots of different slopes at all the temperatures, (i) 1.15RT/F at relatively low oxide ion concentration that corresponds to the reaction

$$0.5O_2\uparrow + 2e^- = O^{2-} \qquad (z = 2) \qquad (9)$$

and (ii) 2.3RT/F in more basic solutions,

$$0.5O_2^{2-}\uparrow + e^- = O^{2-} \qquad (z = 1) \qquad (10)$$

The latter slope is known[14,15] to be caused by peroxide ion, O_2^{2-}, formation at the Pt surface. Despite the sometimes considerable deviations of z (6) from the whole numbers 2 and, that is especially proper for iodide melts, from 1, it was possible to make conditional division of the slopes in the sections with ~1.15RT/F and ~2.3RT/F slopes. The calibration plots 1″ and 2″ obtained in CO_2 atmosphere were used for estimations of equilibrium constants of reaction 2.

These plots are without features complicating their interpretation, and their slopes (see Figure 1, plots 1″, 2″) agree with the stoichiometry of reaction 2. The pK values of reaction 2 were 4.47 (650 °C), 4.23 (700 °C), 3.89 (750 °C), and 3.44 (800 °C) for CsI and 4.68 (700 °C), 4.39 (750 °C), 4.17 (800 °C), and 3.92 (830 °C) for NaI; in all the cases the standard deviation does not exceed 0.04.

The results of carbonate dissociation studies in molten salts are sometimes compared with the corresponding values obtained from thermochemical data.[9] The latter values are

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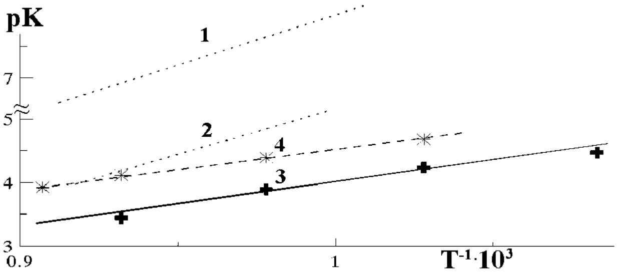

Figure 2. The temperature dependence of p*K*: (1) reaction of solid Na_2CO_3 decomposition to solid Na_2O and gaseous CO_2; (2) the same reaction where liquid Na_2CO_3 and Na_2O take part; (3) carbonate ion decomposition to oxide and CO_2 in molten CsI; (4) the same reaction in molten NaI.

often calculated for the equilibrium (molten sodium halides):

$$Na_2CO_{3,solid} = CO_{2,gas} + Na_2O_{solid} \quad (11)$$

the solid-phase reaction may be considered owing to an efficient lack of data on heat capacities of liquid components.

The calculated p*K* values of reaction 11 (Figure 2, plot 1) considerably differ from the experimental ones leading to the generally accepted conclusion about efficient deviations of carbonate solutions in molten halides from the ideal ones.[9] The plots of p*K* of reaction 2 vs reverse temperature are described by the following equations: $pK = -2.80 + (6.77 \times 10^3)T^{-1}$ for CsI and $pK = -1.49 + (6.01 \times 10^3)T^{-1}$ for NaI; as is seen from Figure 2, the slopes are approximately half those predicted by the thermochemical data (1.45×10^4). Ditto, these plots are practically linear, which shows changes of reaction 2 enthalpy to be small in the studied temperature ranges.

It should be noted that carbonate is less stable in molten CsI than in NaI melt. The reason consists of efficiently lower thermal stability of Cs_2CO_3 compared with Na_2CO_3 that may be confirmed by the dissociation pressures of CO_2 over the mentioned carbonates.[16] This is in good agreement with the results obtained by other investigators[17,18] where basicity of carbonate ions was studied in argon (without CO_2). From these results it may be found that basicities of carbonate ion solutions in CsI melt are higher than those of solutions based on molten NaI. From the cited works it follows that dissociation of carbonate ion in NaI is essentially incomplete even in inert atmosphere. In this relation our data are in good agreement with the conclusions which follow from.[14,15]

Conclusion

Carbonate ion is referred to weak Lux bases at 800 °C and under CO_2 pressure of 1 atm in molten cesium and sodium iodides. Its basic properties decrease from the former melt to the latter one owing to the lower stability of Cs_2CO_3 compared with Na_2CO_3.

The p*K* values decrease with the temperature and are approximated by the equations $pK = -2.80 + (6.77 \times 10^3)T^{-1}$ for CsI and $pK = -1.49 + (6.01 \times 10^3)T^{-1}$ for NaI. Plots of p*K* vs reverse temperature are linear, but the slope for NaI is less than that predicted from the thermochemical data.

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