

Peculiarities of molten KBr-2 SrBr₂ mixture deoxidization under the action of reactive gas medium

*O.L.Rebrov¹, V.L.Cherginets¹, T.P.Rebrova¹, T.V.Ponomarenko¹,
A.G.Varich¹, O.I.Yurchenko², V.V.Soloviev³*

¹Institute for Scintillation Materials, National Academy of Sciences of Ukraine, 60 Nauky Ave., 61001 Kharkiv, Ukraine

²V.N. Karazin Kharkiv National University, 4 Svobody Sq., 61022 Kharkiv, Ukraine

³Yury Kondratyuk Poltava Polytechnic National University, 24 Pershotravnevy Pr., 36011 Poltava, Ukraine

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The process of the oxygen-containing admixtures removal from molten mixture KBr-2 SrBr₂ (deoxidization) was studied by emf method in the cell with transference at 973 K. The deoxidization was performed by passing bromine vapor through the melt containing carbon suspension (graphite or active coal powder). The membrane oxygen electrode Pt(O₂)YSZ (YSZ — 0.9ZrO₂ + 0.1Y₂O₃) was used for the determination of equilibrium and current concentrations of oxide ions, O²⁻, at the running of the studied processes. The chemical stage of the deoxidization process in the molten KBr-2 SrBr₂ was found to undergo the kinetics of the 2nd order with the respect to O²⁻ ions. The rate constant value for the case of graphite powder use was estimated as 1.34·10⁵ kg·mol⁻¹·min⁻¹. The use of the active coal resulted in the increase of the rate of KBr-2 SrBr₂ deoxidization process by approximately 25 per cent, although, it did not affect the melt purification limit. The latter fact is an essential argument confirming the achieving of the chemical equilibrium in the studied system. The minimal equilibrium concentration of O²⁻ after the finishing of the deoxidization process was 3.6·10⁻⁷ mol·kg⁻¹. The obtained results are in good agreement with those obtained for the chloride melt of the same cation composition (KCl-2 SrCl₂), that is a common trend for the deoxidization of chloride and bromide melts in the reactive gas medium.

Keywords: potassium bromide, strontium bromide, melts, purification, carbobromination.

Особливості розкислення розплаву KBr-2 SrBr₂ у реактивному газовому середовищі. *О.Л.Ребров, В.Л.Чергинець, Т.П.Реброва, Т.В.Пономаренко, А.Г.Варич, О.І.Юрченко, В.В.Соловійов*

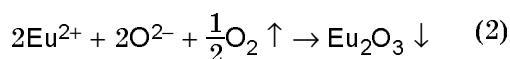
Методом ЕРС у колах з переносом досліджено процес видалення оксигенвмісних домішок з розплаву KBr-2 SrBr₂ при температурі 973 К. Розкислення розплаву проводили парою бром у присутності вуглецю (порошок графіту або активного вугілля). Для визначення поточної концентрації оксид-іонів при перебігу процесів використано мембранний кисневий електрод Pt(O₂)YSZ (YSZ — 0.9 ZrO₂ + 0.1Y₂O₃). Встановлено, що хімічна стадія процесу розкислення описується кінетичним рівнянням її порядку відносно іонів O²⁻. Значення константи швидкості реакції при використанні графіту оцінено як 1,34·10⁵ кг·моль⁻¹·хв⁻¹. Застосування активного вугілля пришвидшує швидкість процесу розкислення розтопу KBr-2 SrBr₂ приблизно на 25 %, але на ступінь його очищення від оксигенвмісних домішок не впливає. Це свідчить про встановлення

в системі хімічної рівноваги. Мінімальна рівноважна концентрація O^{2-} після очищення дорівнює $3,6 \cdot 10^{-7}$ моль·кг $^{-1}$. Отримані результати задовільно узгоджуються з даними для хлоридного розплаву з таким же катіонним складом ($\text{KCl}-2 \text{SrCl}_2$), що є загальною тенденцією для розкислення хлоридних і бромідних розплавів у реактивному газовому середовищі.

1. Introduction

The congruent compounds of alkali and alkaline earth halides attract considerable attention of material scientists working on the development of new effective scintillation materials activated with europium (Eu^{2+}) addition [1–3] since the latter is partially or perfectly isomorphic for alkaline earth cations (Ca^{2+} , Sr^{2+} and Ba^{2+}). In addition, the alkali metal halide part of the solid solutions provides a considerable decrease of the corresponding single crystals hygroscopicity and, therefore, the increase of the operation time of the detecting devices made of them.

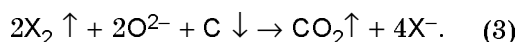
Such single crystals are usually obtained by growth from the melt of a corresponding stoichiometric composition. While the growth techniques vary, the main requirement for the growth melt is the removal of oxygen-containing admixtures, since their interaction with the added dopant (EuX_2 , where X is Cl, Br or I) leads to the formation of insoluble EuO or, at the presence of O_2 , Eu_2O_3 :



(this remains true at the addition of other rare-earth halides of RX_2 or RX_3 compositions, where R is the rare earth metal).

The above interactions lead to the decrease of the actual dopant concentration in the growth melt, and, hence, in the final crystal. This, in its turn, causes the worsening of the optical properties of the crystals and the decrease of their scintillation efficiency.

Carbohalogenation is considered as the most convenient way for the removal of oxygen-containing admixtures from different halide melts. This method consists in the passing of free halogen through the melt containing suspended carbon powder. The reaction which takes place at such a treatment can be described by the following equation:



For the chloride melts the practical realization of the carbohalogenation process is essentially simplified since in this case tetrachloromethane, CCl_4 , can be used. The latter presents itself the perhalogenated derivative of methane with high enough vapor pressure at the room temperature which breaking down temperature is near 500°C [4], serving simultaneously as the origin of both carbon and chlorine. The heterogeneous process (3) is used for the deoxidization of bromide melts and for iodide melts the carbohalogenation treatment seems to be too complicated to apply due to the absence of volatile periodinated derivatives and very low vapor pressure of iodine at temperatures close to the room one.

The purpose of the present work is the investigation of the course of the carbohalogenation (carbobromination) process of the molten $\text{KBr}-2 \text{SrBr}_2$ mixture corresponding to the KSr_2Br_5 congruent compound possessing the melting point of 572°C [5]. According to [5] the scintillation material $\text{KSr}_2\text{Br}_5:\text{Eu}^{2+}$ containing 3.5 mole per cent of the activator possesses the absolute light yield of 75000 photons per MeV that is twice as much as the corresponding parameters of the widely used NaI:Tl scintillator (38000 photons per MeV).

An additional point of interest of the presented research is that although the similar investigations in molten alkali bromide mixtures and $\text{KBr}-\text{BaBr}_2$ melts are known [6], the carbobromination investigations in SrBr_2 -containing melts were not performed yet.

2. Experimental part

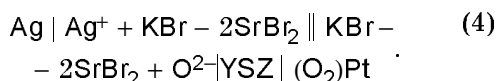
Before the experiments potassium, strontium and ammonium bromide (99.5 mas.% of the main substance) were dried in drying oven at 160°C .

Pure bromine (99 mas. % of Br_2) was kept over anhydrous sulfuric acid (99 mas. % of H_2SO_4) for a week and then was separated from H_2SO_4 in separating funnel.

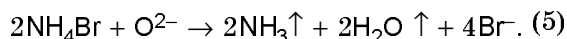
Argon of high purity (O_2 content less than $2 \cdot 10^{-3}$ vol. %) was dried by passing it through the sorption column with phosphorus oxide (V).

The investigations were performed in the electrochemical cell, being the quartz cruci-

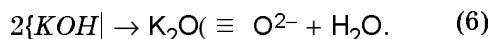
ble closed by cover made of chamotte. In the cover there were holes for the membrane oxygen electrode $\text{Pt}(\text{O}_2)|\text{YSZ}$ (where YSZ the solid electrolyte of $0.9\text{ZrO}_2 + 0.1\text{Y}_2\text{O}_3$ composition), the silver reference electrode $\text{Ag}|\text{Ag}^+$ immersed in the bromide melt containing $0.1 \text{ mol}\cdot\text{kg}^{-1}$ of Ag^+ , alundum tube for gas supply (either pure argon or argon saturated with Br_2 vapor) and the hole for entering weights of solid substances (KOH , NH_4Br). The principal scheme of the cell is as follows:



For each experiment 50 g of the $\text{KBr}-2\text{SrBr}_2$ melt charge (9.7 g of KBr and 40.3 g of SrBr_2) were weighted in the alundum crucible and the crucible was placed in the electrochemical cell which further was inserted into tube furnace. Then the supply of argon was switched on and the furnace with the electrochemical cell was heated to 700°C (973 K). After the temperature stabilization ammonium bromide was added to the melt for the removal of oxygen-containing admixtures which were present in the initial reagents or were formed at the charge heating as a result of oxidation or pyrohydrolysis. This deoxidization process can be presented by the following common scheme:



Before the carbobromination investigations the electrochemical cell (4) was calibrated with weights of KOH (99 mas. % of the main substance) serving as a source of oxide ions. As is known [7], under the experimental conditions (temperature is 973 K , dry argon atmosphere) potassium hydroxide completely dissociates in melts according to the equation:



The weights of KOH were recalculated into oxide ion molalities ($m_{\text{O}^{2-}}$, $2\text{KOH} \equiv \text{O}^{2-}$) and into $p\text{O}$ values ($p\text{O} \equiv -\log m_{\text{O}^{2-}}$). After the addition of each weight the equilibrium emf value (E , V) was measured. The measurements were performed by the Poggendorff method with the use of P-309 potentiometer. The emf value was considered as equilibrium one if its oscillations within 10 min did not exceed 0.001 V and the directed emf shift (drift) was absent.

The kinetics of $\text{KBr}-2\text{SrBr}_2$ melt carbobromination were studied after the calibra-

tion. For this purpose either graphite powder (with the specific surface of approximately $700 \text{ m}^2\cdot\text{g}^{-1}$, BET) or active coal (both in quantity of 0.5 g) were added to the bromide melt. Then the bubbling of argon saturated with bromine vapor started. "Argon + Br_2 " gas mixture was obtained by the passing of argon through the saturator with the dried bromine thermostated at the temperature of 0°C (vapor pressure of Br_2 was 8.6 kPa). The rate of the gas mixture passing through the melt was $150 \text{ cm}^3\cdot\text{min}^{-1}$ which provided the constant concentration of bromine in the atmosphere over the studied melt. The emf measurements were taken each 30 sec for first 10 min, each minute from 10 to 20 min and each 2 min after 20 minutes of the carbobromination process.

3. Results and discussion

The calibration $emf (E) - p\text{O}$ plot:

$$E = E_0 + \theta \cdot p\text{O}, \quad (7)$$

(where E and E_0 the measured and the standard emf values of cell (4), V ; θ the slope, V) in $\text{KBr}-2\text{SrBr}_2$ melt at 973 K presents single section which treatment by the least squares method yields to the following regression:

$$E = 0.345(\pm 0.018) + 0.085(\pm 0.008) \cdot p\text{O}, V, \quad (8)$$

(here and after the standard deviations are used for the statistical estimations of the results). This dependence was further used for recalculation of emf values into $p\text{O}$ ones.

The " $p\text{O} - \text{time}$ " dependences obtained at the running of the carbobromination of the $\text{KBr}-2\text{SrBr}_2$ melt at 973 K are shown in Fig. 1 and an example of the experimental and derived data is presented in Table.

The presented data show that within 45 minutes of carbobromination process the oxide-ion concentration in the 50 g of $\text{KBr}-2\text{SrBr}_2$ melt decreases down to $3.6 \cdot 10^{-7} \text{ mol}\cdot\text{kg}^{-1}$. Similarly to other halide melts [8, 9] the course of the carbobromination can be conditionally divided into three sections:

— the first section (1a in Fig. 1) corresponds to the situation when the oxide ion concentration in the treated melt is considerably higher than the concentration of the dissolved bromine which is instantly consumed in the reaction with O^{2-} according to Eq. 3;

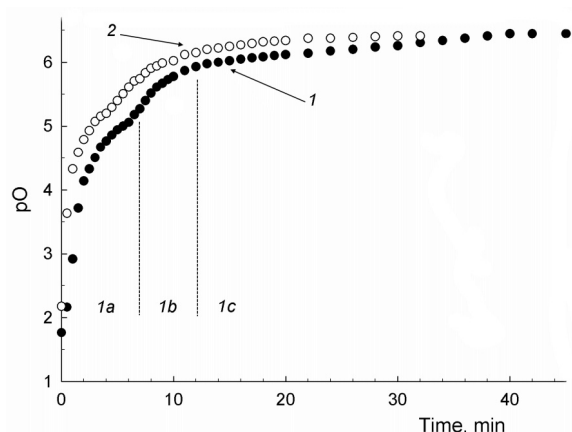


Fig.1. The dependences of pO vs. time during at the $KBr-2 SrBr_2$ melt carbobromination at 973K with the use of different carbon sources: 1 — graphite powder, 2 — active coal powders. Stages 1a, 1b and 1c are explained in the text.

— at the second section (1b in Fig. 1) the oxide ion concentration in the melt becomes comparable or less than that of dissolved bromine (at $pO \geq 5$) and the running of the deoxidization process is limited by the chemical reaction in the melt;

— at the third section (1c in Fig. 1) the rates of competing processes of deoxidization and contamination of the melt with oxygen-containing admixtures equalize and the dependences in Fig. 1 reach a plateau. Another possible explanation is that the system reaches the state of chemical equilibrium.

The existence of these stages is confirmed by the calculations of kinetics of the carbobromination process. The differential Van't Hoff method was used to determine

the kinetic orders of the limiting stages of the process. It consisted in the construction of dependencies of the process rate logarithm ($\log w$) vs. the logarithm of O^{2-} molality ($\log m$) corresponding to this rate. The kinetic orders can be determined as the slopes of such dependencies. The differential Van't Hoff method is universal and, in contrast to the integral methods, it permits to determine the kinetic orders of the processes even in the cases if they are of non-integer values.

To simplify the results' treatment we made some assumptions on the basis of the Lagrange mean value theorem which gave us the possibility to transform instantaneous values of the rates and the molalities into corresponding average values obtained in the short time intervals. Applied to the obtained experimental results this theorem can be formulated in such a form: if the dependence of oxide ion molality against the time, $m(t) = f(t)$ is a continuous function on the closed interval $[t_1, t_3]$ and differentiable on this interval (smooth function) than there exists a point t_2 in this interval such that:

$$-w(m) = m'(t_2) = \frac{m(t_3) - m(t_1)}{t_3 - t_1}. \quad (9)$$

Since the experimental dependences are smooth and the time intervals are short enough we made a non-thermodynamic assumption that the molality in the point t_2 to which the derivative (9) is referred to is the averaged value of the oxide ion molalities measured in points t_1 and t_3 , i.e.:

Table. The experimental data obtained as a result of $KBr-2 SrBr_2$ melt carbobromination at 973 K with the use of graphite powder as a source of carbon

Time, min	pO	Time, min	pO	Time, min	pO	Time, min	pO
0.0	1.76	5.5	5.00	12.0	5.93	26.0	6.20
0.5	2.16	6.0	5.06	13.0	5.98	28.0	6.24
1.0	2.92	6.5	5.18	14.0	6.00	30.0	6.26
1.5	3.72	7.0	5.27	15.0	6.02	32.0	6.31
2.0	4.14	7.5	5.40	16.0	6.05	34.0	6.34
2.5	4.33	8.0	5.52	17.0	6.07	36.0	6.38
3.0	4.51	8.5	5.61	18.0	6.08	38.0	6.41
3.5	4.67	9.0	5.67	19.0	6.11	40.0	6.45
4.0	4.76	9.5	5.73	20.0	6.12	45.0	6.45
4.5	4.86	10.0	5.78	22.0	6.14		
5.0	4.94	11.0	5.87	24.0	6.18		

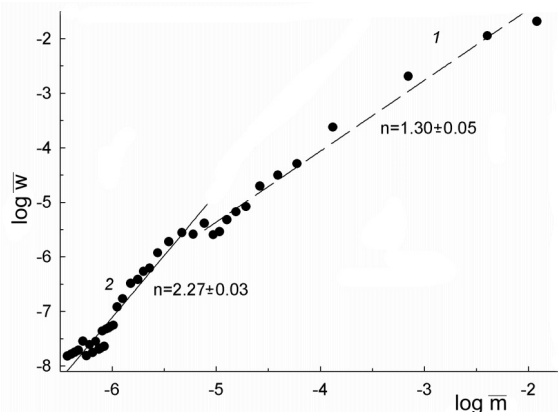


Fig.2. The dependence of the carbobromination process of KBr-2 SrBr₂ vs. oxide ion concentration at 973K, $\log \bar{w} = f(\log \bar{m})$, for the case of graphite powder use as carbon source.

$$m(t_2) = \frac{m(t_3) - m(t_1)}{2}. \quad (10)$$

The dependence of the averaged rates of the carbobromination process against the averaged molalities $-\log \bar{w} = f(-\log \bar{m})$ constructed on the basis of the experimental data (Fig. 2) can serve as the most ponderous argument for the division of $pO = f(t)$ dependences into sections with different limiting stages. It should be emphasized that, according to the Van't Hoff equation, $n = \partial(\log w) / \partial(\log m)$ written in designations of this work, the slopes of dependences 1 and 2 in Fig. 2 are the corresponding kinetic orders (n) of the limiting processes.

It can be seen that at the initial stage of carbobromination process (section 1 in Fig. 2) the kinetic order value is close to 1, however, the deviation from 1 is statistically significant ($n = 1.30 \pm 0.05$). This agrees with the results obtained in other chloride and bromide melts, e.g. [6]. This section corresponds to the section 1a in Fig. 1 where the oxide ion molality considerably exceeds the bromine concentration in the treated melt.

The section 2 in Fig. 2 corresponds to the stage 1b where the chemical reaction in the melt is the rate-limiting process and its kinetic order is close to 2 ($n = 2.27 \pm 0.03$).

Finally, the points situated in the bottom left corner of the diagram correspond to the "plateau" in Fig. 1.

The data corresponding to the section 2 gives the possibility to calculate the rate constants of the carbobromination processes

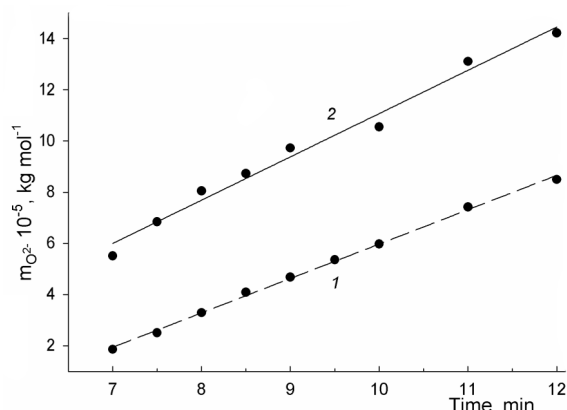


Fig. 3. The dependences of inversed oxide-ion molality vs. time, $m_{\text{O}^{2-}}^{-1} = f(t)$, at the performing of KBr-2 SrBr₂ carbobromination at 973 K with the use of different carbon sources: 1 — graphite powder, 2 — active coal powders.

which experimental data $pO = f(t)$ are presented in Fig. 1.

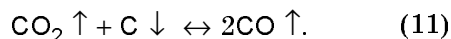
As is known, in the case of the process of the second order the dependence of the inverse molality against the time, $m_{\text{O}^{2-}}^{-1} = f(t)$, is linear and the slope is nothing but the rate constant.

These dependences are presented in Fig. 3 and to eliminate errors for data close to the "plateaus" (essential superimposition of processes running in inverse direction) the treatment times are chosen from 7 to 12 min that agrees with the division made in Fig. 1.

Both dependences in Fig. 3 are linear with the correlation coefficients r_{xy} of 0.999 (7 degrees of freedom) and 0.992 (6 degrees of freedom) for dependences 1 and 2, respectively. The rate constants are estimated as $(1.34 \pm 0.02) \cdot 10^5 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ (the graphite powder) and $(1.69 \pm 0.08) \cdot 10^5 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ (the active coal powder). The obtained results permit to make some conclusions about the running of the carbobromination process which is referred to heterogeneous ones. It should be mentioned again that the specific surface of the graphite powder is $700 \text{ m}^2 \cdot \text{g}^{-1}$ whereas the similar value for active coal powder is estimated within $1800\text{--}2200 \text{ m}^2 \cdot \text{g}^{-1}$ according to handbook data.

Since, according to the data of Fig. 1, the degree of purification of KBr-2 SrBr₂ is not dependent on the specific surface of the used carbon source the plateau in Fig. 1 arises as a result of the achieving of chemical equilibrium first of all in the gaseous

phase (bromine, oxygen admixture and carbon oxides), i.e., the reaction (3) is accompanied with the following process:



In the other case the increase of the deoxidization rate should result in higher degrees of the purification and, hence, lower residual oxide ion concentrations.

It is seen, that at the use of the active coal powder for deoxidization of the bromide melt only a certain part of the coal "works". In the opposite case the process rate should be approximately 3 times as much as the rate of the carbobromination process performed with the use of the graphite powder (1800–2200 $\text{m}^2 \cdot \text{g}^{-1}$ vs. 700 $\text{m}^2 \cdot \text{g}^{-1}$). Therefore, for these processes there exists an "effective specific surface" which is lower than the value declared in the technical documentation on the ingredient (from the comparison of the rate constants the value of "effective specific surface" can be estimated as $\sim 900 \text{ m}^2 \cdot \text{g}^{-1}$). Ditto, the admixtures originated by the "natural raw" (active coal) can negatively affect the purity and, hence, functional properties of the final product, especially if this concerns the treatment of growth melts for the obtaining of optical crystals of various usage.

As to the agreement of the obtained results with the similar data obtained for KCl-2 SrCl₂ melt at the same temperature, it should be noted that in the case of the KBr-2 SrBr₂ the final pO value after the finishing of the deoxidization process is equal to 6.45 (6.8 in the chloride analog) and the decimal logarithms of the rate constants ($\log k$) are 5.13 and 5.26, respectively. The obtained data are close enough and are in good agreement with the cases of other chloride and bromide melts of the same cation compositions. For example, for KBr–BaBr₂ (0.76:0.24) and KCl–BaCl₂ (0.76:0.24) melts pO values after the finishing of the carbohalogenation process are the same ($pO = 6.3$) and $\log k$ values are 5.08 and 5.03, respectively [9]).

Conclusions

The chemical stage of the purification of the KBr-2 SrBr₂ melt from oxygen-containing admixtures using carbobromination (action of bromine vapor in the presence of carbon suspension in the melt) is characterized by 2nd kinetic order with the respect to O²⁻ ions.

The rate constant value of the carbobromination of the KBr-2 SrBr₂ melt at 973 K was estimated as $1.34 \cdot 10^5 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ for the case of graphite powder used as the source of carbon. The use of active coal instead of the graphite leads to some increase of the deoxidization rate, however, in this case the limit of purification (residual oxide-ion concentration after the purification) remains unchanged and is equal to $3.6 \cdot 10^{-7} \text{ mol} \cdot \text{kg}^{-1}$.

The results obtained in the KBr-2 SrBr₂ melt are close to the corresponding data for the chloride analog of KCl-2 SrCl₂ composition. The close values of the kinetic parameters and the limits of oxide ion concentration after the purification for chloride and bromide melts with the same cation composition is observed for other molten systems based on alkali and alkaline halide mixtures.

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