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PREPARATION OF NaCl : $CaCl_2$ + NaOH CRYSTALS

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In the last years several authors investigated the influence of the built in anions on the defect population in alkali halides. Fritz et al. [1] concluded from their results that a reaction must take place in KCl : KOH between divalent cation impurities, always present in the crystals and the anions; for instance $CaCl_2 + 2\,KOH = Ca(OH)_2 + 2\,KCl$. Gruzenski and Scott [2] suppose also that a reaction between divalent cation impurities and the deliberatly built in anions (SO_4^{2-}) explains their results.

To be able to investigate more profoundly the question of the occurence of such a reaction in crystals, it was necessary to grow crystals containing a high enough concentration of the respective anions and cations. The results achieved herein will be reported here.

EXPERIMENTAL PROCEDURE

The crystals NaCl : $CaCl_2$ + NaOH were grown by the Kyropoulos method in an inert atmosphere of dry commercial nitrogen. The nitrogen was not re-purified to remove eventual traces of oxygen or moisture. In Table 1 the amounts of $CaCl_2$ and NaOH are given which are added to the melt and the admixture content of the crystals. In addition some batches of NaCl melt, with $CaCl_2$ and NaOH added, as shown in Table 2, were allowed to solidify without pulling any crystals from the melt. After solidification, samples of material were taken from the upper part to establish their alkalinity. Also the alkalinity of samples of material from the bottom of the crucibles was established, immediatly after dissolving the samples and also after 24 hours. The calcium content was determined by spectroscopy (atom absorption). The alkalinity was established by titration in an inert atmosphere, according to Hatvani and Široká [3].

DISCUSSION OF RESULTS

The concetration of $CaCl_2$ and NaOH added to the melt and the actual admixture content of the crystals are found in Table 1. When the amount

Table 1.

Impurity content and analysis of the „effective segregation coefficients" of NaCl : $CaCl_2$ + NaOH crystals

Added to the melt [mol %]		Impurity content of the crystals [mol %]		Effective segregation coefficient of		Calculated impurity content of the melt [mol %]		Calculated quantity of reaction product in the melt [mol %]		Ratio of calculated quantities of
$CaCl_2$	NaOH	$CaCl_2$	NaOH	$CaCl_2$	NaOH	$CaCl_2$	NaOH	Ca^{2+}	OH^-	Ca^{2+} : OH^-
.5	1.0	.0487	.027	.09	.027	.063	.140	.437	.860	1 : 1.96
.5	.1	.1230	.0000	.24	.000	.250	.000	.250	.100	— *)
.5	.05	.1590	.0005	.32	.010	.360	.000	.140	.050	— *)
.1	3.0	.0000	.530	.00	.180	.000	2.800	.100	.200	1 : 2.0
.1	1.0	.0132	.053	.13	.053	.0132	.480	.087	.520	1 : 5.7
.1	.5	.0197	.034	.20	.068	.0197	.320	.080	.180	1 : 2.2
.1	.3	.0240	.016	.24	.053	.025	.170	.075	.130	1 : 1.8
.1	.1	.0350	.0003	.35	.003	.040	.000	.060	.100	1 : 1.7
<.1	.05	.0327	.0006	.33	.011	.038	.006	—	.044	—**)
.01	3.0	.0043	.205	.40	.068	.004	.150	.006	2.850	—
.01	.1	.0029	.0006	.30	.005	.003	.006	.007	.100	—
.01	.05	.0029	.0006	.30	.011	.003	.006	.007	.050	—

*) The solubility of $CaCl_2$ in NaCl is only .1 to .15 mol %.

**) No reliable value of the $CaCl_2$ quantity added to the melt is available.

Table 2. Alkalinity of NaCl : $CaCl_2$ + NaOH melt

Added to the melt [mol %]		Alkalinity of melt [mol %]
$CaCl_2$	NaOH	
.5	3.0	1.85
.5	1.0	.04
.5	.1	neutral
.1	.2	.072
.1	.10	neutral
.1	.05	neutral

of NaOH added to the melt simultaneously with a fixed quantity of $CaCl_2$ was increased, the calcium content of the crystals decreased. Likewise, at a hight enough $CaCl_2$ and fixed NaOH concentration in the melt a decrease of the alkalinity of the crystals was observed if the $CaCl_2$ concentration in the melt was increased. As a consequence, the „effective segregation coefficients" decrease (cf. Tab. 1). An anylsis of the NaCl : $CaCl_2$ + NaOH melt revealed that this decrease was due to the reaction of $CaCl_2$ and NaOH in the melt. Only if less $CaCl_2$ was added than corresponds to the stoichiometric ratio of the reaction $CaCl_2 + 2\,NaOH = Ca(OH)_2 + 2\,NaCl = CaO + H_2O + 2\,NaCl$ the upper part of the solidified melt was found to be alkaline (cf. Tab. 2). But if the $CaCl_2$ amoumt was half that of NaOH or more, the upper part of the melt was found neutral. The samples from the bottom of the crucible were also neutral in this case when titrated immediately after dissolution. But after 24 hours the solution became alkaline. These facts support the opinion expressed by Fritz et al. (loc. cit.) that the final product of the reaction is CaO (a white sediment they observed on the bottom of the crucible) which is insoluble in NaCl but might be hydrolized in due time in the NaCl solution.

Let us assume that the segregation coefficients are not altered by the presence of the other admixtures (see Andreev [4] and Rubínová [5]). Then after the removal of the quantity of $CaCl_2$ and NaOH which would correspond to the segregated quantity of $CaCl_2$ and NaOH in the crystal, the remaining $CaCl_2$ and NaOH in the melt should correspond to the stoichiometric ratio 1 : 2. This is approximately fulfilled as shown in Tab. 1, except when there is too much calcium in the melt as regards its solubility or when the calcium concentration is too low.

SUMMARY

If $CaCl_2$ and NaOH are added simultaneously into the NaCl-melt, a reaction takes place between the two components yielding an unsoluble sediment, most probably CaO. The $CaCl_2$ and NaOH are not completely transformed into CaO, though, especially if they are not in the stoichiometric ratio; a part of the still free $CaCl_2$ and NaOH is built in into the growing crystal, obviously in accord with the known segregation coefficients. From conductivity and dielectric loss measurements [6] it follows that the built in $CaCl_2$ and NaOH form Ca^{2+} and OH^- respectively at higher temperatures. At lower temperatures they combine and form $Ca(OH)_2$, i. e. a reaction is taking place in the crystal.

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