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Activation of Quartz Grain Surface with Chloride Ions

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ABSTRACT

Alteration of technological and optical states of glass activated with chloride ions, entered to the surface of quartz sand and quartz grain by way of sodium chloride was investigated in the article. Concentration optimum of activating agent was determined.

Keywords: Activating Agent of Surface; Flor Ion; Quartz Sand; Grain; Optical Transmission

The present paper is concerned with certain methods of improving optical properties of special-purpose glasses: soda-lime glasses used for making solar batteries and very-high-purity quartz glasses. The raw materials used for making photovoltaic glass are known for strict requirements to be made on their iron content (0.012%). Quartz glass, by virtue of its structure and when containing impurities and admixtures, is furthermore capable of undergoing some considerable changes in its properties and possibly structure.[1,2]

As the assessment criterion the variation of iron content, as well as of the optical transmission of the glass, which had been molten using sand and quartz grains activated with chloride ions, has been taken. The research works carried out featured the introduction of chloride ions directly onto the quartz raw material at the batch preparation stage. A 0.1 mass % NaCl solution has been used for this purpose.

The objectives pursued by introducing chloride ions by way of a solution are as follows:

-to obtain an uniform per-quartz-grain distribution of the active admixture.

- to remove the iron impurities during the process of melting a multicomponent glass or quartz.

1. Soda-lime Glass

Sand chlorination has been carried out at the stage of the batch preparation in using the raw material with a 0,015% iron content.

A 0.1% NaCl water solution has been prepared preliminarily. Sand has been further poured with the NaCl water solution at 4% batch moisture content and stirred thoroughly. The sand has been dried at 40°C and 120°C. Quartz grains having a porous and crumbling surface get coated with a uniform chloride-ion containing layer.

The theoretical chemical interreactions to take place at the quartz grain surface are as follows:

$$Fe_2O_3 + 3NaCl + 3H_2O \rightarrow FeCl_3\uparrow + 3Na(OH) + Fe(OH)_3, \quad (1)$$

$$NaOH + SiO_2 \rightarrow Na_2SiO_3, \quad (2)$$

Electron microscopic studies of the activated quartz grain surface and the resulting coating layer content by scanning electron microscopy method and using an electron probe X-ray spectroscopic microanalyzer have been carried out.

Microphotographs of the sample surface have been 0made at various magnifications. In **Figure 1**a microphotograph of the sand grains is shown without chloride ions applied.

In that microphotograph the crystal-form grains are visible having clearly defined borders and cracks.

A qualitative elemental analysis has shown the quartz grains without NaCl treatment to be represented by the following principal elemental composition: Si, O, C, Al, Fe (s. **Figure 3(a)**). The qualitative elemental composition has changed after the chloride-ion treatment due to appearance of Cl and Na on the grain surface (s. **Figure 3(b)**).

Glasses have been molten at 1450°C using the batch without chlorine and with 0.1; 0.2; 0.5% NaCl admixtures.

In all obtained glasses the ferric oxide residual has been determined and the integral optical transmission has been measured in the range between 300 nm and 2500 nm for the purpose of determining the sunlight transmission.

The total ferric oxide percentage in the initial glass has been determined at 0.0148% and it has decreased by 18% down to 0.0122% for the glass that has been activated with 0.1% NaCl. On further increasing the introduction of the activator, the process of the ferric oxide content decrease has decelerated and its percentage has been determined at 0.0120% and 0.0117% when having introduced 0.2% and 0,5% of chloride ions, correspondingly.

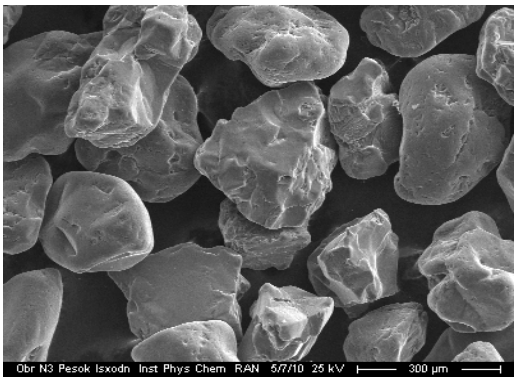
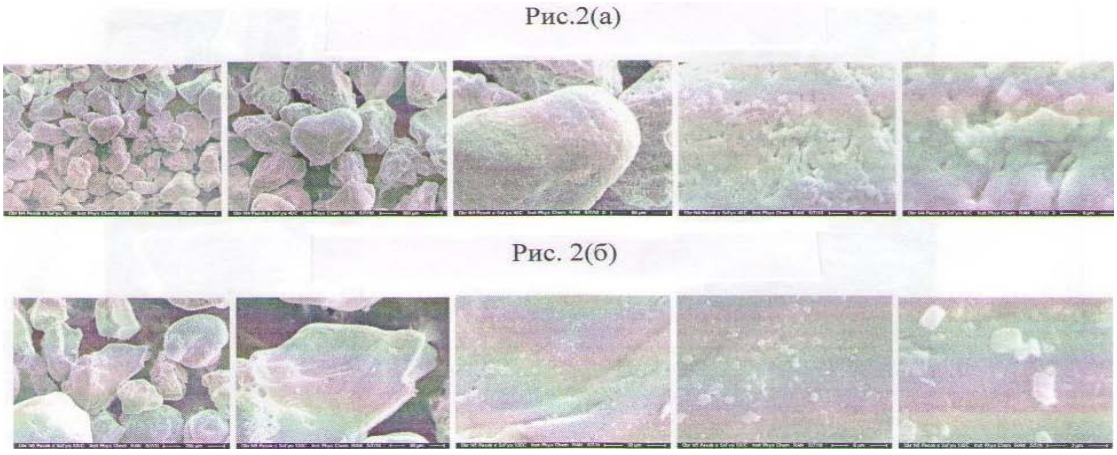
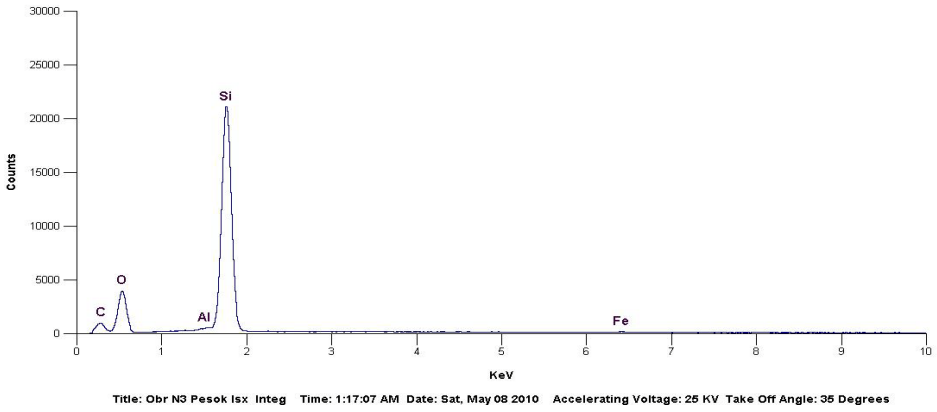


Figure 1. Microphotograph of quartz grains.

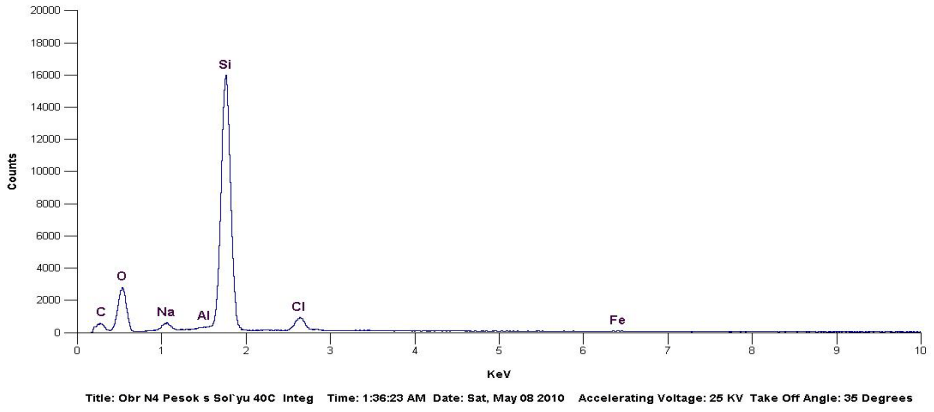


а – material dried at 40˚C; b – material dried at 120˚C

Figure 2. Microphotographs of quartz grains activated with 0.1% NaCl.



(a)



(b)

а – surface without chloride ion activation ; б - surface activated with chloride ions

Figure 3. Qualitative elemental composition of quartz sand grain surface.

A reduction in the content of iron impurities due to formation and volatilization of $FeCl_3$ according to the above-stated reaction has thus been observed in all the glasses under study. The iron impurities partly remain in glass what is apparently attributed to time and temperature factors.

Optical transmission of glasses, which has been measured in the range between 300 nm and 2500 nm, has shown that a 0.1% chloride ion admixture results in an effective increase of the optical transmission of glass from 89% up to 91.8% and in case the admixture percentage is increased up to 0.5% the optical

transmission of the glass remains practically constant (s. **Figure 5**).

An optimal activator concentration has thus been determined to be equal to 0.1% of chloride ions for the low initial iron content glasses.

2. Quartz Glass

Quartz grains have been doped using 0.1% and 0.5% NaCl solution concentrations by introducing the salt solution onto the quartz grain surface followed by solution drying at 350°C. Quartz grains have been further molten in an oxyhydrogen furnace. The doped quartz grains have been observed to be low-melting raw material with a resulting increase of the melting speed from 1.3 kg/h up to 1.5 kg/h at 2000°C. It should be noted that while melting 0.5% NaCl doped quartz grains the formation of semitransparent flocks has been observed, whereas the cooled glass melt has turned white dramatically and become opaque which is likely to be due to glass crystallization. Crystallization is known to take place when glass, being a non-stoichiometric product, is doped with some chemical components capable of changing the system by shifting it to stoichiometry (crystallization). Such components can be either chloride ions or sodium cations. Therefore glasses have been under study doped with other chloride ion concentrations and various cationic components.

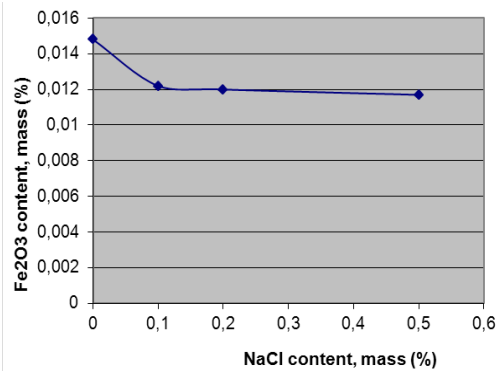


Figure 4. Ferric oxide – vs- activator admixture percentage curve.

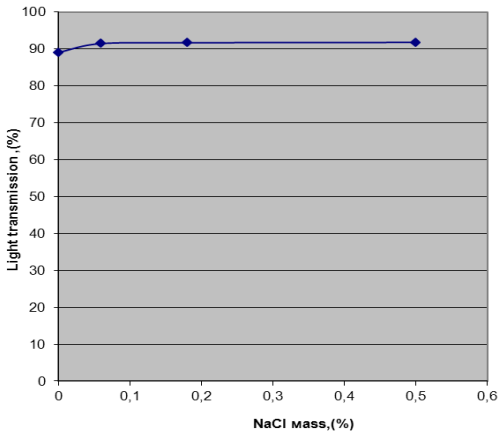


Figure 5. Optical transmission of glass –vs - activator percentage curve.

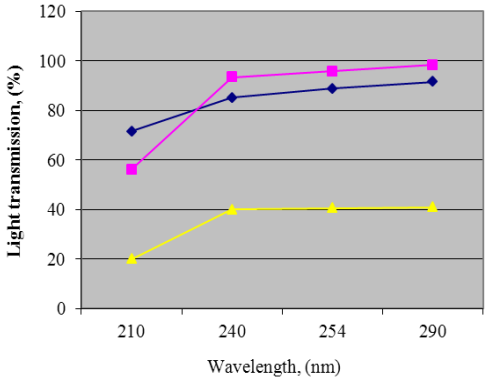


Figure 6. Optical transmission behavior of glass: 1 – initial glass sample; 2 – sample of glass; activated with 0.1% Nacl; 3 - sample of glass; activated with 0.5% NaCl (crystallized glass).

In activating the quartz grain surface with 0.1% NaCl the glass melt has remained transparent both during its melting and after cooling. The mass percentage of iron impurities and sodium has been determined in the initial and doped glass that have changed in the ratios as shown in the table below.

Glass description	Content of admixtures/impurities 10^{-4}, mass %	
	Na	Fe
Initial glass	9.87	2.7
Glass activated with 0.1% NaCl	12.07	0.6
Glass activated with 0.5% NaCl	17.2	1.7

As evident from the table, chloride ion doping of quartz grains enhances the initial material purity in decreasing the iron content by a factor of 1.5-4. Increased percentage of sodium admixtures has contributed to a favorable glass melt viscosity change and a resulting melting speed increase from 1.3kg/h up to 1.5kg/h.

Optical transmission values of the glasses under study in UV and visible part of spectrum have been determined. Increased optical transmission of the quartz glass activated with chloride ions is observed, especially in UV part of spectrum (s. **Figure 6**).

Industrial melting of quartz glass has been carried out using a melting discharge coefficient of 1.18 while its rated value being equal to 1.3. The glass block obtained is of first-rank quality. The drawn tube is of good quality, the glass is easily formed and may be recommended for making blown glassware, e. g. high-intensity light source envelopes.

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