Composition and synthesis development of building glass on the basis of non-standard raw materials

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Abstract. Colorless building glass on the basis of non-standard raw materials with the use of discolourers—cerium oxide and potassium nitrate—was synthesized. The regularities of the cerium oxide addition effect on the light transmittance of the glasses are shown when the proportion of Na2O is replaced by K2O. The results of ORP and iron oxide equilibrium investigation in glasses, improvement of light transmission by means of correction of ORP glass are presented. The physical and chemical properties of glasses are measured: thermal coefficient of linear expansion (TCLE), water resistance and crystallization ability of glasses. The recommended composition of a building glass on the basis of non-standard raw materials is presented.

1. Introduction
At present achievement of high and stable glass optical characteristics is becoming problematic, on the one hand taking into account the ever increasing requirements for glass quality, and on the other hand providing factories with high-quality raw materials, in particular quartz sand. The use of raw materials of the Ural region in glass production will significantly reduce the transportation costs and consequently reduce the cost of raw materials, if the quality of the final product is preserved at the same time.

In the mass manufacture of glass products, it is expedient to use inexpensive raw materials, but they have a high content of iron impurities. Many researchers consider it important to study the oxidation-reduction potential (ORP), the change in the equilibrium of iron oxide in glass [1-9]. Iron oxides are actively involved in oxidation-reduction processes in the building glass production. The conversion of iron compounds to the oxide form (III) which is less intense in coloring the glass can be achieved, mainly, by oxidation during the synthesis. Oxidation is carried out by introducing additional oxygen-containing components—discolourers.

Nonstandard raw materials contain coloring impurities which complicates the production of high-transparent glass. On the basis of such raw materials, the synthesis of glasses can be carried out by applying discolourers to improve the quality of the product. In addition, due to the increase in the thermal transparency of the glass mass, it is possible to reduce fuel consumption for maintaining near-bottom temperatures.

Currently, the widest agent in the colorless glass production is cobalt oxide and selenium which is not profitable for enterprises in our opinion. Both agents are physical discolourers which reduce the
transmission and operational properties of the glass [1]. It should also be noted that selenium is used with minimal iron content in the glass because of the risk of a brownish tinge. Modifying the glass compositions with decolorizing agents is an effective way of changing light transmittance and reducing the proportion of divalent iron. Thus, the problem of glass and charge composition development based on nonstandard raw materials is timely and relevant.

The purpose of the work is to develop a composition of charge based on nonstandard raw materials and synthesis of building glass with increased spectral characteristics.

2. Methodology
In the work traditional physical and chemical methods of research outlined in normative documents were used. The properties of synthesized materials were measured on the research and laboratory equipment of the UrFU and the institutes of the Ural Branch of the Russian Academy of Sciences, they are the following: light transmittance by a Shimadzu UV-2600 spectrophotometer (the Center for Collective Use "Spectroscopy and Analysis of Organic Compounds"), water resistance by Standard 10134.1-82, crystallization ability by the method of stable temperature drop, TCLE measurement by the quartz dilatometer DIL 402 C.

3. Results and discussion
In the work we used nonstandard raw materials. Their chemical composition is presented in Table 1. The synthesis of glasses was carried out in laboratory furnaces with silicate heaters in corundum crucibles. During the synthesis, the charge was held at 1450 °C for 3 hours. After obtaining a homogeneous melt, the billets were cast in the form of a flat plate of circular shape, after which they were annealed in a muffle furnace at 560-570 °C. 19 glass samples that were cut, ground and polished had plane-parallel surfaces with a thickness of 4 mm.

**Table 1. Chemical composition of raw materials, wt. %.

| Type of raw material                      | SiO₂ | Al₂O₃ | CaO | MgO | Na₂O | K₂O | SO₃ | Fe₂O₃ | Other |
|------------------------------------------|------|-------|-----|-----|------|-----|-----|-------|-------|
| Quartz sand Kamensk-Uralskoe field       | 98.52| 0.61  | 0.17| 0.04| 0.05 | 0.14| –   | 0.19  | 0.28  |
| Quartz sand Butkinskoe field             | 96.78| 1.43  | 0.13| 0.33| 0.38 | 0.60| –   | 0.15  | 0.20  |
| Dolomite "Krilosovo" Pervouralsk         | 1.00 | 1.00  | 33.60| 18.20| –    | –   | –   | 0.20  | 54.00 |
| Limestone Sosnovskoye field              | 0.70 | 1.03  | 54.20| –   | –    | –   | –   | 0.12  | 43.95 |
| Soda, Berezniki                          | –    | –     | –   | –   | 58.14| –   | –   | –     | 41.86 |
| Sodium sulfate                           | –    | –     | –   | –   | 43.49| –   | 56.11| –     | 0.40  |

All synthesized glasses have a variable colour: from blue to a colourless and slightly yellow. The physical and chemical properties of glasses are measured: TCLE, water resistance and crystallization ability of glasses. The TCLE of all investigated glasses is 90·10⁻⁷ C⁻¹. All glasses are to 4 class water resistance. The glass samples were not crystallized.

It has been established that the change in the light transmission of colorless glass and the disruption of the stability of the technological process is due to the total iron content [10–15], the equilibrium state of \( \text{Fe(II)} \leftrightarrow \text{Fe(III)} \). The course of the reaction in the glass mass is affected by the oxidation-reduction conditions (ORC) of the glass melting process. In the work it was found out that the ORC depends on the following parameters: ORP, bivalent iron fraction, thermal transparency index and basicity index [12].

ORP is estimated by reduction number (RN):
\[ RN = \sum Y_i \cdot P_i \]

\( Y_i \) — carbon number of the i-component of the charge;

\( P_i \) — mass of the i-component per 2000 kg of sand.

The Fe (II) fraction (dFe(II)) is determined by the spectral method (from the transmission curve) and is calculated by formula:

\[ dFe(II) = \frac{\lg \tau_\lambda}{LW \rho \chi_{Fe^{2+}}}, \]

where \( \tau_\lambda \) — the spectral transmittance of the sample at a wavelength \( \lambda = 1000 \) nm; \( L \) — sample thickness, cm; \( W \) — mass content of iron in glass in terms of metal, %; \( \rho \) — density of glass, g/cm\(^3\); \( \chi_{Fe^{2+}} \) — volume absorbance of bivalent iron, calculated at a concentration of 102 g/cm\(^3\) glass (at a wavelength of 1000 nm, it is equal to 3.60 cm\(^2\)/g).

An important indicator for glasses is the thermal transparency index (TTI) of the glass mass, determined in the infrared region of the spectrum at a wavelength of 1100 nm and calculated by the formula:

\[ TTI = 4.0 \cdot \tau_{1100}^{-1} \]

where \( \tau_{1100} \) — light transmittance of a sample with a thickness of 0.004 m at a wavelength of 1100 nm.

Table 2 presents some characteristics of the glasses and the composition of the discolourers.

| Mass content of discolourers, % | CeO\(_2\) | K\(_2\)O | Fe\(_2\)O\(_3\) | ORP | dFe(II) | TTI |
|-------------------------------|-----------|-----------|-----------------|-----|---------|-----|
| 1\(^t\)                      | -         | -         | 0.63            | 13.47 | 21.20  | 5.90 |
| 2\(^t\)                      | -         | -         | 11.00           | 38.68 | 4.92   | 8.85 |
| 5\(^t\)                      | 0.10      | 1.00      | 0.43            | 49.23 | 4.77   | 8.88 |
| 6\(^t\)                      | 0.10      | 2.00      | 40.34           | 50.90 | 5.14   | 8.80 |
| 7\(^t\)                      | 0.15      | 1.00      | 43.67           | 4.69  | 8.90   |
| 8\(^t\)                      | 0.15      | 2.00      | 43.67           | 4.69  | 8.90   |
| 9\(^t\)                      | 0.25      | 1.00      | 52.06           | 5.14  | 8.80   |
| 10\(^t\)                     | 0.25      | 2.00      | 52.06           | 5.14  | 8.80   |
| 11\(^t\)                     | 0.50      | 1.00      | 62.68           | 7.98  | 8.21   |
| 12\(^t\)                     | 0.50      | 2.00      | 70.12           | 4.27  | 8.99   |
| 13\(^t\)                     | 1.00      | 1.00      | 80.74           | 3.13  | 8.85   |
| 14\(^t\)                     | 1.00      | 2.00      | 80.74           | 3.13  | 8.85   |
| 15\(^t\)                     | -         | -         | 10.25           | -     | -      |
| 16\(^t\)                     | 0.10      | 0.50      | 0.24            | 14.20 | 22.43  | 8.00 |
| 17\(^t\)                     | 0.15      | 0.50      | 15.79           | 19.02 | 17.53  | 8.40 |
| 18\(^t\)                     | 0.25      | 0.50      | 27.20           | 17.53 | 8.40   |
| 19\(^t\)                     | 0.50      | 0.50      | 27.20           | 17.53 | 8.40   |

1 — Sand of Kamensk-Uralskoe field
2 — Sand of Butkinskoe field
It is shown that the values of dFe (II) in investigated glasses decrease with the addition of decolorizing agents from 26.28 to 3.13 %. On the base of the ORP result assessment the color and tinge of glass are predicted at the stage of batch preparation. In the glass charge the ORP changes to + 80.74, the overlapping of blue and yellow is observed that gives different tinge of green since iron in the glass is present simultaneously in the form of Fe²⁺ and Fe³⁺, the oxide form predominates.

Spectral characteristics for various additives are given and the effect of these additives on the process of discoloration of glass mass is given (Figure 1, 2). Analysis of the obtained curves shows that for sheet and container glasses synthesized without discoulerers, low light transmission in the visible region, starting at 550 nm, is observed. This indicates the presence largely Fe²⁺ in the glasses.

![Figure 1](image1.png)

**Figure 1.** Spectral curves of the glass transmission of the samples No 1, 2, 7, 8, 13, 14.

![Figure 2](image2.png)

**Figure 2.** Spectral curves of the glass transmission of the samples No 16–19.
One of the main criteria for estimating the oxidation-reduction state of the glass mass is the basicity of the glass which is expressed by the ratio of $\frac{Fe^{2+}\times 100}{Fe_{\text{total}}\%}$ [16-20]. This indicator gives an opportunity to objectively determine the actual change in the ORP of the glass mass. The dependence of the basicity indicator on the content of the discolourers of the K$_2$O-CeO$_2$ system is presented on the curves (Figure 3).

![Figure 3](image)

**Figure 3.** The change in the ratio of iron oxides to the content of cerium dioxide for sheet glass.

It is shown that the number of discolourers depends on the chemical composition of the charge and the content of iron oxide in the glass. A glass with a basicity index of more than 18% is classified as not discoloured, but with a basicity of less than 18% as difficult to bediscoloured. Proceeding from oxidation-reduction processes, the light transmittance, the proportion of Fe$^{2+}$ and Fe$^{3+}$, we recommend the optimal composition for the synthesis of colorless building glass (Table 3).

| Glass       | SiO$_2$ | Al$_2$O$_3$ | CaO | MgO | Na$_2$O | K$_2$O | SO$_3$ | CeO$_2$ | Fe$_2$O$_3$ |
|-------------|---------|-------------|-----|-----|---------|--------|--------|---------|-------------|
| Construction| 72,45   | 1,00        | 8,50| 3,50| 12,50   | 1,00   | 0,5    | 0,15    | 0,40        |

4. Conclusion

Modern ideas about the possibility of obtaining colorless transparent glass mass on the basis of nonstandard raw materials with the use of chemical discoloration are expanded. To increase the redox potential and the optical characteristics of the glass, it is recommended to use CeO$_2$ and K$_2$O as discolourers. With a minimum content of CeO$_2$=0.1% and K$_2$O=1.0% and an unchanged temperature of the melting of sheet glass, light transmission in the visible region of the spectrum increases from 84 to 89%, and at a maximum CeO$_2$=1% and K$_2$O=2% increases to 91.7%.

The mechanism of discoloration of high-iron glasses by introduction of the CeO$_2$-K$_2$O system is proposed, the former consists of the iron oxide equilibrium shift to the oxidized form due to the increase in the oxygen amount.

The effect of CeO$_2$ and K$_2$O oxides on the discoloration of iron-containing glasses was studied for the first time. With an increase in the amount of CeO$_2$ to 0.5%, the light transmission increases from 84 to 91%. The use of discolourers of the system CeO$_2$-K$_2$O does not impair the physical and chemical properties of the glasses investigated.

*ICCATS 2018*
The composition of glass based on nonstandard raw materials with discolourers is proposed to obtain a colorless sheet glass with high light transmittance (up to 90–91 %), the maximum permissible content of iron oxide in the charge on the basis of nonstandard raw materials is up to 0.4%.

References
[1] Guloyan Yu A 2003 Technology of glass and glassware (Vladimir: Transit-X ) p 480
[2] Levitin L Ya, Litvin V I, Tokarev V D, Yachevskii A V 2012 Increase of glass manufacturing efficiency using cullet in float-glass production J. Steklo and Ceramics 69 pp 143–145
[3] Fedorova V A 2010 Modern problems of obtaining high-transparency glasses J. Steklo and Ceramics 67 pp 82–85
[4] Min’ko N I, Binaliev I M 2013 Role of sodium sulfate in glass technology J. Steklo and Ceramics 69 pp 361–365
[5] Atkarskaya A B 2010 Effect of the oxidation – reduction potential on the proneness of glass to form bubbles J. Steklo and Ceramics 67 pp 99–104
[6] Flank A M, Lagarde P, Jupille J, Montigaud H 2011 Redox profile of glass surface J. Non-Crystalline Solids 357 pp 3200–3206
[7] Min’ko N I, Morozova I I 2014 Effect of the Redox Potential on the Cooking and Properties of Glass J. Steklo and Ceramics 71 pp 229–232
[8] Mulevanov S V, Nartsev V M 2014 Spectrophotometric Determination of the Redox State of Glass J. Steklo and Ceramics 71 pp 148–151
[9] Klement R, Kraxner J, Liska M 2009 Spectroscopic analysis of iron doped glasses with composition close to the E-glass: a preliminary study – Ceramics J. Silikaty 53 pp 180–183
[10] Atkarskaya A B, Zaitseva M I 2005 Redox Equilibrium of Iron in Silicate Glasses J. Steklo and Ceramics 62 pp 304–307
[11] Kiyan V I, Atkarskaya A B 2006 Dynamics of the redox state of the melt in the continuous production of clear glass J. Steklo and Ceramics 63 pp 249–253
[12] Fedorova V A 2000 Combined Evaluation of the Role of Impurities and Small Additives in Glass Production J. Steklo and Ceramics 57 pp 272–274
[13] Kiyan V I, Mashir Yu I, Atkarskaya A B 2000 Change in the redox potential of a glass melt upon introducing a melting catalyst into the glass batch J. Steklo and Ceramics 57 pp 78–80
[14] Atkarskaya A B, Kiyan V I 2001 Reasons for Variations in Glass Melt Diathermancy in an Operating Tank Furnace J. Steklo and Ceramics 58 pp 335–337
[15] Fedorova V A 2012 Cerium dioxide and its behavior in various types of glasses J. Steklo Mira 5-6 pp 16–18
[16] Zhernovaya N V, Min’ko N I, Onishchuk V I, Mel’nikova L I 2000 Effect of the redox potential of the glass batch and cullet on the tinting of industrially produced glass containing iron oxides J. Steklo and Ceramics 57 pp 84–86
[17] Guloyan Yu A 2004 Conditions for Transformation and Equilibrium of Iron Oxides in Glass Melting J. Steklo and Ceramics 61 pp 3–5
[18] Min’ko N I, Atkarskaya A B, Myagkaya A A, Tret’yakov I V 2011 Stabilizing the spectral properties and technologies of glass J. Steklo and Ceramics 68:87
[19] Min’ko N I, Morozova I I 2014 Scientific and engineering problems of construction and technological utilization of man-made waste (Belgorod: GTU named V.G. Shukhov) pp 42–49
[20] Agureev S A, Levitin L Ya, Tokarev V D 2014 Efficient Control Regimes for the Thermal and Technological Process of Glassmaking in Tank Furnaces for Float-Glass Production J. Steklo and Ceramics 70 pp 347–349