https://doi.org/10.5281/zenodo.11216200

STUDYING EFFECTS OF CERIUM OXIDE ON OPTICAL PROPERTIES OF COLORLESS GLASS

A. Krauchuk, Yu. Paulıukevıch, A. Mozhjer, E. Trusova, L. Papko
Belarusian State Technological University, Sverdlova str. 13a, Minsk, Belarus
kravchuk@belstu.by

The actual problem of modern glassmaking is glass decolorization. Due to high competition on the market of glass containers, the requirements to transparency and tint of glass increase. Obtaining high transparency of glass is possible when it contains a minimum amount of coloring impurities, primarily iron ions that form a number of chromophoric centers. In order to eliminate the undesirable green tint associated with the presence of Fe^{2+} and Fe^{3+}, decolorizing agents are introduced into compositions of glasses [1–2]. Chemical decolorization is achieved by introduction of oxygen-containing compounds. Physical decolorization is achieved by introducing additional colorants that compensate for the coloring of green tones. A combination of coloring agents Se and CoO is traditionally used in the production of glass containers. The peculiarity of this decolorization is the reduction of total light transmittance of glass.

In glass production, cerium oxide (IV), which is a strong oxidizing agent that converts Fe^{2+} into Fe^{3+}, is successfully used as a decolorizer. The intensity of light absorption by Fe^{2+} ions is about 15 times higher than that of Fe^{3+}. At 1200–1400 ºC, cerium oxide decomposes $2CeO_2 \leftrightarrow Ce_2O_3 + 1/2O_2$, i.e. increases the oxidizing potential of the glass mass. The equilibrium is influenced by factors such as temperature, melting time and furnace atmosphere. Cerium oxide simultaneously with decolorization contributes to clarification of the glass mass.

The work aimed to study the effect of cerium oxide on optical properties of colorless container glass and to determine the optimal amount of a decolorizing agent.

On the basis of the basic composition of colorless container glass, raw compositions containing CeO_2 in the amount of 0.1–0.5 wt.% CeO_2 and KNO_3 in the ratio of 1 : 6, as well as CeO_2 in combination with Mn_2O_3 were obtained. Introduction of sodium and potassium nitrate into the composition of raw material mixtures was also tested. The content of impurity iron oxides in the composition of glasses was 0.07–0.1 wt.%.

The glass synthesis was performed at maximum temperature of 1500±10°C in a gas furnace for 2 h. The light transmission measurements in the wavelength range 330–1100 nm were performed by using spectrophotometer MS-122 PROSCAN.

On the spectral transmission curves (Fig.1) there are absorption bands with maxima at 380, 420 and 1100 nm that are specific to silicate glasses containing impurity iron oxides. The intense absorption band in the region of 630–1100 nm on the spectrum of glass of basic composition, not containing decolorizing agents, is associated with the presence of Fe^{2+} ions.

Introduction of cerium oxide causes the equilibrium to shift $Fe^{2+} \leftrightarrow Fe^{3+}$ to the right, which leads to an increase in light transmission in the visible and near-infrared spectral regions and smoothing of the spectrum. Such transformations of spectral curves in the visible, UV and IR regions are caused by changes in the oxidation state of iron and cerium ions in the glass mass. This reduces the intensity of color shades and finally glass decolorization is achieved. A pronounced decolorization effect is achieved at a ratio of $CeO_2 : Fe_2O_3 = 3 : 1$.

Thus, with Fe_2O_3 content of 0.07 wt.% in the glass composition it is necessary to introduce 0.2 wt.% CeO_2. The total light transmission reaches 87–88 %, which is higher than the values established by regulatory documents.

Increasing the amount of CeO_2 up to 0.5 wt.%, despite the increase of the total light transmission in the visible spectrum up to values of more than 88 %, is inexpedient, as it leads to appearance of a visually diagnosable yellow tint. There is a shift of the absorption band on the spectrum due to the presence of cerium ions, there is a strong increase in absorption in the ultraviolet and visible regions of the spectrum (330–400 nm), which is caused by the formation of Ce^{4+}–Ce^{3+}complex. In addition, the absorption at 380 nm, which is specific to the Fe^{3+} ion, is enhanced.

https://doi.org/10.5281/zenodo.11216200

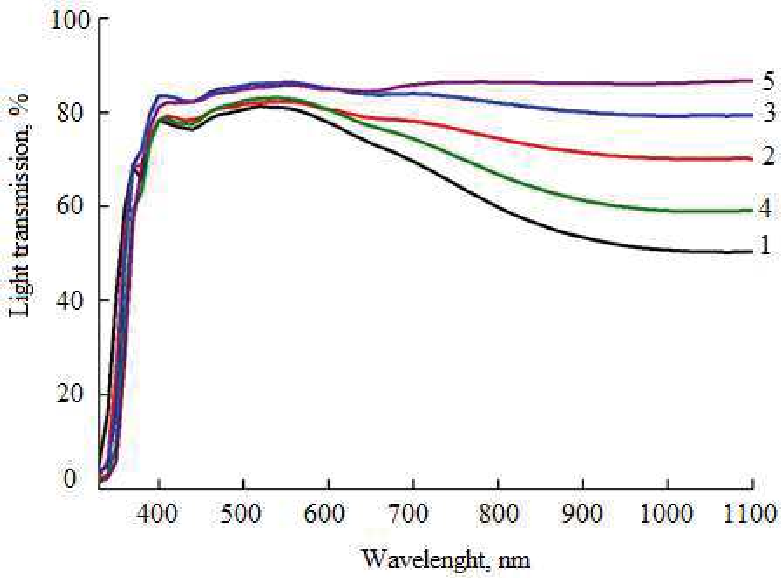

Figure 1 – Light transmission of glass, containing CeO_2, wt.%:
1 – 0.0; 2 – 0.1; 3 – 0.2; 4 – 0.3; 5 – 0.5

The effect of introduction of CeO_2 and composition of this oxide with KNO_3 is similar. Changes in spectra with increasing amount of cerium oxide in the composition of glasses are similar to those discussed above: the absorption band in the UV region expands the total light transmission in the visible region increases up to 82–86 % and in the IR region of the spectrum. Flattening of spectral curves in the visible region is achieved at CeO_2 concentration of 0.2–0.4 wt.% in glasses, while visually green and blue tints with increasing CeO_2 concentration up to 0.4 wt. % are not observed.

It is revealed that the addition of Mn_2O_3 in the amount of 0.1–0.5 wt.% does not visually provide a decolorizing effect in the conditions of laboratory melting. Mn_2O_3 decomposes in the range of lower temperatures – 950–1100 ° C, when the mobility of structural elements of the formed melt is low. As a result, the decolorization effect is weaker and is offset by other factors. The elimination of color shades was provided by application of the Mn_2O_3 – CeO_2 composition. The optimum content of these components was determined, including 0.1 wt.% Mn_2O_3 and 0.2 wt. % CeO_2. In general, the addition of Mn_2O_3 to CeO_2 is of interest from the point of view of reducing the cost of the decolorizing mixture.

When solving the problem of decolorizing container glass it is necessary to take into account that changes in the oxidation-reduction potential of the glass melt and its diathermancy due to the addition of decolorizing agents can disrupt the process of glassmaking and glass forming and lead to a decrease in performance and an increase in the defect rate of finished products, yet these phenomena are temporary. Negative consequences of the initial introduction of chemical decolorizing agents should be compensated by control actions: increasing the output, reducing the temperature in the furnace forehearth and other factors.

Thus, based on the study, the high efficiency of cerium oxide as a glass decolorizer was confirmed and the compositions of decolorizing compositions, including CeO_2 and KNO_3, CeO_2 and Mn_2O_3, were developed.

Reference

1. R. Conradt Fusion of Glass. Encyclopedia of Glass Science, Technology, History, and Culture. 2021. Vol. I. 53–64.
2. I. I. Al'baeva, S. G. Vlasova Decolorization of Glass Synthesized Using Local Raw Materials. Glass and Ceramics, 2017, 73, 361–364.