Optical properties of silicate glass melts

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Typical examples of high temperature optical spectra of silicate glass melts are presented. The technological impact of these properties on the radiative heat transfer in industrial glass melting tanks is discussed.

Introduction

The high temperature properties of glass melts are of interest from both a scientific and a technological point of view. This contribution is focused on the high temperature characterisation of silicate glass melts by spectral optical methods. Some typical results of high temperature optical absorption measurements of silicate glass melts are presented. Compositional and redox effects on the glass melt optical properties are discussed. Furthermore, the technological importance of these properties for industrial glass manufacturing is illustrated, by assessing the impact of the high temperature spectral properties on the radiative heat transfer in semi-transparent glass melts.

Experimental method and exemplary results

The high temperature set-up for measurement of the spectral absorption of glass melts, developed at the TNO Institute of Applied Physics, is decribed in[1]. For minimising systematical errors in the high temperature aborption measurements, a sample holder with a variable optical path length in the glass melt sample is used. The spectral extinction coefficient $K(\lambda)$ at a certain temperature is calculated from the ratio between two transmittance spectra, recorded at different glass melt depths. The spectral melt properties of a large number of industrially produced silicate glasses have been measured, including:

- flint, green, amber and olive green soda lime glasses for containers
- soda lime float glass
- borosilicate glass for textile glass fibers (E-glass)
- Ba- and Sr- containing silicate glass, used for TV screens
- lead crystal glass

In general, the observed features in the high temperature glass melt spectra can be ascribed to a combination of absorptions due to

- electronic excitations in the glass matrix in the short wavelength region (< 1 µm), generally intensifying with temperature

- absorbing species in the glass, esp. colouring ions like Fe and Cr, and OH-groups in the intermediate wavelength region (1 – 4 µm),

- vibrational bands of the glass matrix for the long wavelength region (> 4 µm)

In fig. 1 the absorption spectra of a typical TV-screen glass composition, recorded at 1100, 1200, 1300 and 1400 °C, respectively, are compared to the absorption spectrum at room temperature (21 °C). The error in the high temperature absorption data is estimated to be maximum 5%.

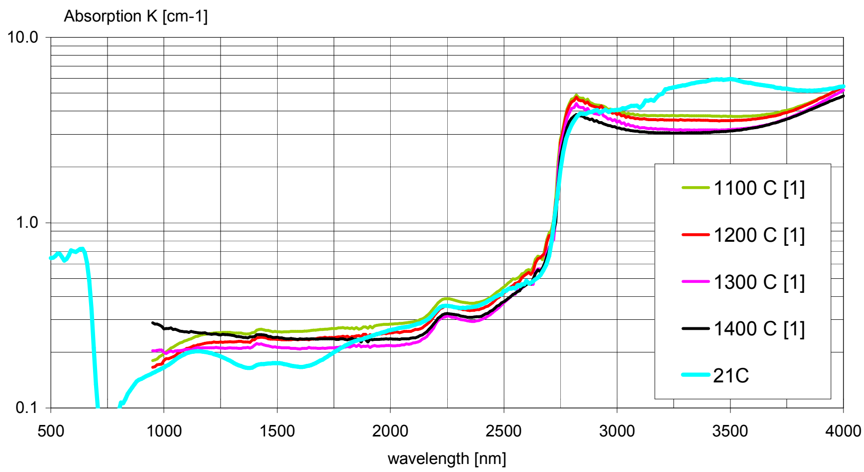

Fig. 1 Spectral absorption of TV screen glass at room temperature and at melt temperatures

Review of observed high temperature spectral features

The following observations, derived from a review of the high temperature spectra for all above mentioned silicate glass types, are of practical interest for industrial glass melting. A distinction is made between glasses/melts with relatively high and low iron contents. Spectra of glass melts with relatively high iron content (Fe_2O_3 > 0.05 wt%):

- For coloured container glasses (green, olive green and amber), float glass and borosilicate glass, the absorption band of Fe^{2+} around 1.0 - 1.1 µm and the free OH-absorption band around 2.8 µm dominate the spectra between 0.5 and 4 µm

- In general for these glasses, the absorption strength of the Fe^{2+} band decreases with temperature

- Green glass, containing both Fe- and Cr- ions, shows a deviating behaviour at high temperatures. For this glass the absorption around 1.0 – 1.1 μm increases with temperature.

Spectra of low-iron content glass melts (< 0.05 wt% Fe_2O_3):

- For low-iron content, oxidised glasses, esp. flint container, TV-screen and lead crystal glasses, the Fe^{2+} absorption band around 1.0 – 1.1 μm is virtually absent at high temperatures and only the free OH band remains clearly visible in the high temperatures spectra

- The absorption level of flint glass and TV-glass types between 0.5 and 2.5 μm is low (K typically varies between 0.04 and 0.4 cm^{-1}) and the spectral absorption of these 2 glass types in this wavelength region has a slight temperature dependence, only (cf. fig. 1)

- Lead crystal glass melts show a peculiar behaviour in the spectral region between 0.5 and 2.5 μm: the absorption increases about a factor 10 over this whole spectral region, when heating the glass from 1100 to 1400 °C. Apparently, the specific network structure of lead silicate glass melts results in an intensification of the electronic transitions of the matrix at elevated temperature.

Rosseland radiation conductivity

The main heat transfer mechanism in semi-transparent industrial glass melts is thermal radiation in the spectral region 1 - 4 μm. Therefore, detailed knowledge of the spectral optical properties of glass melts is required in order to understand, to model and to optimise the heat transfer and melting processes in industrial glass tanks. For comparing the radiative heat transfer characteristics of different glass types it is useful to define a so-called photon or radiation conductivity, by using the Rosseland or diffusion approximation. In this approach it is assumed that the glass melt system is optically thick for heat radiation. This implies that the mean free path of the photons, l_m (m), is small compared to the thickness d (m) of the glass melt system, where the mean free path of the photons is defined as the reciprocal value of the extinction coefficient K (m^{-1}): $l_m = 1/K << d$ (m) From an analysis of the high temperature spectra, it is concluded that the Rosseland diffusion approximation can be applied in practically all cases for modelling industrial glass melting tanks, where the glass bath depth is of the order of 100 cm. However, for modelling radiative heat transfer in the forehearth (typical depth 10 - 30 cm) of a glass furnace producing low iron content glass (e.g. flint container glass), the Rosseland approximation is no longer valid, since the condition: l_m << forehearth depth, is not satisfied. Other radiation models, like ray tracing and discrete transfer models, must be used for describing radiative heat transfer in such glass melt systems. The Rosseland radiation conductivity k_r is calculated from the spectra by numerically solving the following formula, with integration over the spectral region in which the glass melt is semitransparent (about 0.5 – 5 μm) [1, 2, 3]:

$$k_r = \int 4/3\, n^2 * (1/K(\lambda)) * (dM(\lambda)/dT) * d\lambda,$$

with:

n = refractive index of the glass melt

M = Planck's function of a black body radiator

T = absolute temperature (K)

The calculated photon conductivity of three low iron content glasses (TV-screen, lead crystaland flint container glass) is plotted as a function of temperature in figure 2.

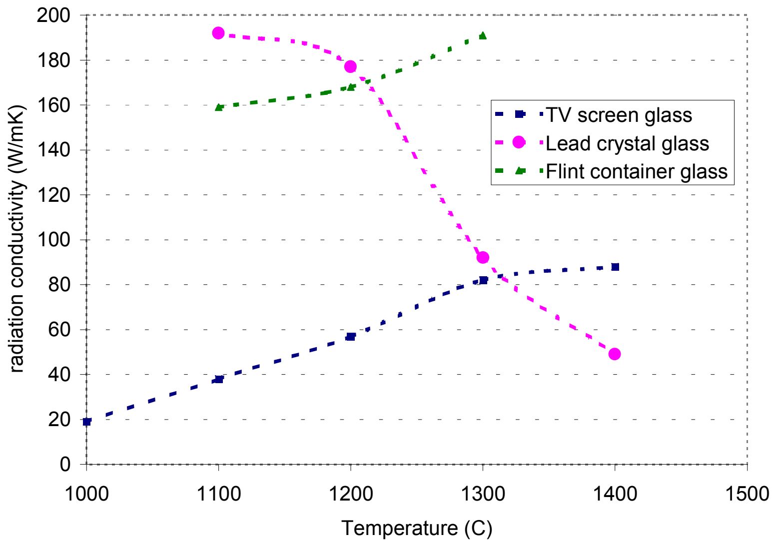

Fig. 2 Rosseland photon conductivity of different low–iron (< 0.05 wt% Fe2O3) oxidised glasses as a function of temperature

It can be seen in figure 2, that at temperatures below 1200 °C, the lead crystal glass has the highest radiation conductivity of the three low iron content glasses, wheras at temperatures higher than 1300 °C, the lead crystal has the lowest photon conductivity. The pronounced decrease of radiation conductivity with temperature for the lead crystal glass is caused by a strong increase in optical absorption with temperature, as mentioned above.

Effect of redox state on radiative heat transfer in glass melts

The optical absorption by Fe^{2+} ions has a large impact on the radiative heat transfer in industrial silicate glass melts. Since the Fe^{2+}-content is determined by the redox state of the glass, the redox state has a major effect on the photon conductivity at melt temperatures. This effect is illustrated in fig. 3, which shows the spectral absorption at 1200 °C of two float glasses with a similar chemical composition (total iron oxide content = 0.08 wt%), but with different redox states: The 'reduced' float glass has an iron redox ratio Fe^{2+}/ Fe_{tot} = 0.28 and the more 'oxidised' float glass has an iron redox ratio of 0.24 (room temperature ratio's). Due to this redox difference, the absorption of the reduced float glass in the spectral region 1 – 2.5 μm is higher than the corresponding absorption spectrum of the oxidised float glass, as can be seen in figure 3.

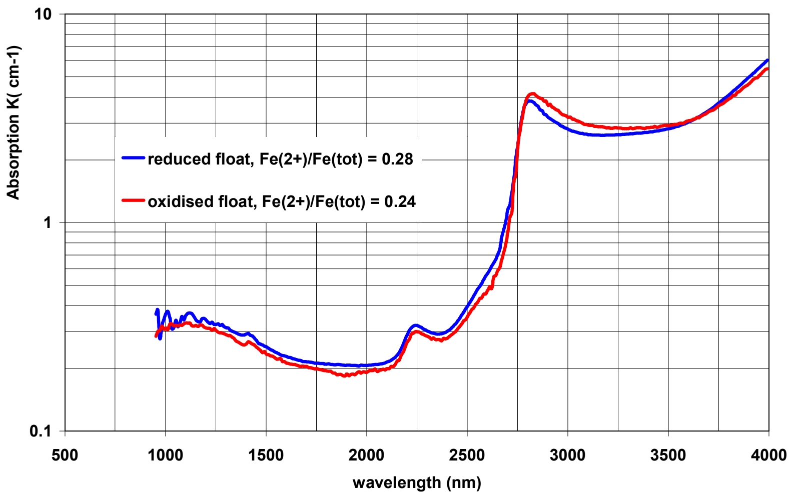

Fig 3 Absorption spectra at 1200 °C of two float glasses of different redox state

Using the spectra of fig. 3, the radiation conductivity at 1200 °C was calculated to be 56 W/mK for the reduced float glass and 73 W/mK for the oxidised float glass. So, a relatively small redox difference between two float glasses will have a large impact on the radiative heat penetration, when these glasses are melted in an industrial tank.

Concluding remarks

All the glass melts that have been studied show highest transmission in the wavelength region between 1 and 2.5 μm, i.e. the spectral region between the Fe^{2+} absorption band and the OH absorption band at 2.8 μm. This implies that heat radiation with a wavelength around 2 μm will have the largest penetration depth in the glass melt. Thus, for an effective radiative heat transfer from the combustion chamber of a fuel fired glass furnace into the glass melt, the burner flames should have a high radiative emission between 1 and 2.5 μm, especially for relatively 'dark' glass melts, like amber and green glasses. In general, gas flames have a considerably lower emissivity in this region than sooty oil flames. More luminous gas flames can be achieved by applying near stoichiometric or even reducing combustion conditions, which results in more soot formation.

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[1] Nijnatten, P.A. van, Broekhuijse, J.T. and Faber, A.J., *Spectral Photon Conductivity of glass at forming and melting temperatures*, Proceedings of the 5th ESG Conference, Prague, June 21 - 24, 1999.

[2] R.M. Potter and M.K. Choudhary, *Calculation of radiation thermal conductivity in silicate glass melts*, Proc. XVII ICG Congress, Beijing, 1995, Vol. 3, p 245 – 253

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