

Thermal radiation of chromium-doped glass melts

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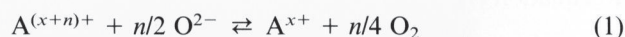
Glass melts are semitransparent radiators whose emission depends on the type and concentration of colouring ions in the melt. Furthermore the temperature profile in the melt especially in regions near the surface is of major importance. In this study, numerical calculations based on experimentally determined absorption coefficients of chromium-doped melts are presented. The model used is that of an isothermal glass melt layer covered by a further layer with a constant temperature gradient. The effect of temperatures, layer thickness and concentrations on the emission spectra is described. Emission spectroscopy should enable the quantitative determination of colouring ions in the melt as well as of the temperature profile near the melt surface.

Wärmestrahlung von chrom-dotierten Glasschmelzen

Glasschmelzen sind semitransparente Strahler, deren Emission von der Art und Konzentration färbender Ionen in der Schmelze abhängt. Weiterhin ist das Temperaturprofil in der Schmelze, speziell in oberflächennahen Bereichen von großer Bedeutung. In dieser Untersuchung werden numerische Berechnungen vorgestellt, die auf experimentell bestimmten Absorptionskoeffizienten von chrom-dotierten Schmelzen basieren. Das verwendete Modell ist das einer isothermen Schicht, die von einer weiteren Schicht mit konstantem Temperaturgradient bedeckt wird. Die Abhängigkeit der Emissionsspektren von Temperaturen, Schichtdicken und Konzentrationen wird beschrieben. Emissionsspektroskopie sollte die quantitative Bestimmung färbender Ionen in der Schmelze als auch von oberflächennahen Temperaturprofilen ermöglichen.

1. Introduction

Light emission of glass melts at high temperatures is of high importance for the industrial melting process. It widely determines the temperature distribution in an industrial glass tank. Glass melts are semitransparent radiators whose emissivities strongly depend on the type and concentration of colouring ions. The most important colouring ions are ions of transition elements, such as iron or chromium, and occur in more than one oxidation state, i.e. they are polyvalent. Since the transmission spectra of glasses, containing polyvalent ions, exhibit distinct absorption bands, the emissivity strongly depends on the wavelength. Absorption coefficients themselves also depend on temperature [e.g. 1 and 2]. Furthermore, redox ratios of polyvalent elements may depend on the temperature because the respective equilibrium constants, K , may be shifted as an effect of temperature [3 and 4]:



$$K = \frac{[A^{x+}]}{[A^{(x+n)+}]} [O_2]^{n/4} \quad (2)$$

where A^{x+} and $A^{(x+n)+}$ are the polyvalent element in its reduced and oxidized state, and $[A^{x+}]$ and $[A^{(x+n)+}]$ are the concentrations of the redox states of the polyvalent elements present in the melt.

This paper provides a study on the numeric calculation of emission spectra from glass melts doped with polyvalent elements. The calculations are based on experimentally determined temperature-dependent extinction coefficients $\varepsilon(\lambda, T)$ and are carried out for isothermal glass melts as well as for melts possessing a temperature gradient near the surface.

2. Blackbody radiation and emission of semitransparent materials

The radiance of a blackbody is described by Planck's radiation law.

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Der ausführliche Schlußbericht „Emissionsspektroskopie an Glasschmelzen zur quantitativen Bestimmung färbender Ionen“ (AiF-Nr. 12064 B) kann bei Bedarf über die Bibliothek der Deutschen Glastechnischen Gesellschaft (DGG) bestellt werden.

$$L_B = \frac{c_1}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{c_2}{\lambda} \cdot T\right) - 1} \quad (3)$$

where L_B is the blackbody radiation, λ is the wavelength, T is the temperature, $c_1 = 2h \cdot c_0^2 = 1.91 \cdot 10^{-16} \text{ W m}^2 \text{ sr}^{-2}$ and $c_2 = (h \cdot c_0)/K = 1.43 \cdot 10^{-2} \text{ m K}$.

For a blackbody, the absorption as well as the emission coefficients are infinite. In the case of semitransparent radiators, absorption and emission coefficients are finite. The absorption of a layer possessing the thickness x is described by Lambert-Beer's law:

$$\alpha = 1 - e^{-a(\lambda)x} \quad (4)$$

where α is the absorption and $a(\lambda)$ is the absorption coefficient. It should be noted that the absorption coefficient also depends upon the temperature. Furthermore, reflection of light at the boundary melt/gas atmosphere has to be taken into account. Here, the Fresnel equation is valid,

$$R = \left(\frac{n-1}{n+1}\right)^2 \quad (5)$$

where n is the refractive index.

The radiance of an isothermal melt with the thickness d is then given by [5]:

$$L_x = (1-R)L_B \int_0^d a(\lambda) \exp(-a(\lambda) \cdot x) dx. \quad (6)$$

Integration of equation (6) in the isothermal case leads to equation (7):

$$L_x = (1-R)L_B(1 - \exp(-a(\lambda) \cdot d)). \quad (7)$$

For $n = 1.5$, $(1-R)$ is around 0.96 (see equation (5)). In the case of absorption coefficients larger than zero and infinite thickness of the melt, the emission is $0.96 \cdot L_B$, i.e. disregarding the reflection of light at the boundary melt/atmosphere, the radiance of the melt is equal to the blackbody radiation. For an absorption coefficient equal to zero, the melt does not emit light at all. For a practical purpose, i.e. when absorption coefficients and/or the thickness of the melt are too large, emission spectra do not provide any information on absorptivities and hence on the species occurring in the melt. If, however, $0 < a(\lambda) \cdot x \ll \infty$, emission of light increases with increasing absorption coefficients. In that $a(\lambda) \cdot x$ range, emission spectra may provide information on the species present in the melt.

3. Emission of a semitransparent radiator for a nonisothermal case

In the following, a nonisothermal case is considered. The model used is an isothermal melt of the thickness

d_i covered by a layer with the thickness d_n in which a constant temperature gradient occurs. The temperature at the surface is smaller than in the bulk. For this case, equation (6) has to be rewritten:

$$L_x = (1-R) \int_0^{d_i+d_n} L_B(x) \cdot a(\lambda, x, T) \cdot \exp(-a(\lambda, x, T) \cdot x) dx. \quad (8)$$

Since L_B as well as $a(\lambda)$ depend on the temperature, they depend on x in the nonisothermal case. For the most temperature profiles, equation (8) can no longer be solved analytically and a numerical solution is necessary. If the isothermal part of the melt is large enough, so that $a \cdot x$ can be considered as infinite, this part of the melt will act as a blackbody-like radiator. The gradient layer with the thickness d_n then will absorb more light than it will emit. Hence, the relative intensity of light, L_x/L_B will be smallest at those wavelengths where the absorption coefficient is largest. It should be noted that, depending on the temperature profile in the melt, its thickness and $a(\lambda)$, the emission of light can be smallest at wavelength where the absorption coefficients are smallest (e.g. for a thin isothermal layer), but light emission can also be largest at smallest absorption coefficients as described for a nonisothermal case.

4. Numerical calculation of emission spectra

Emission spectra of chromium-containing glass melt were calculated using experimentally determined absorptivity coefficients and their temperature dependencies. Each absorption band of Cr^{6+} as well as of Cr^{3+} were described by a Gaussian band

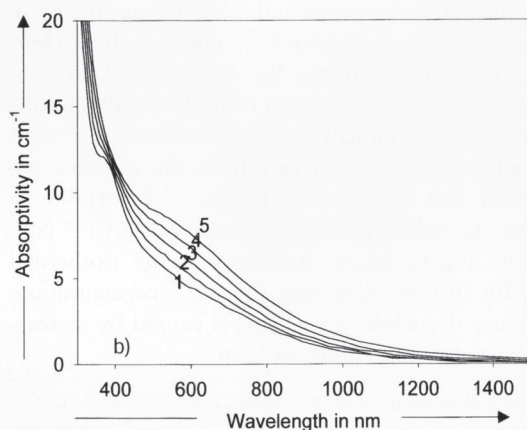
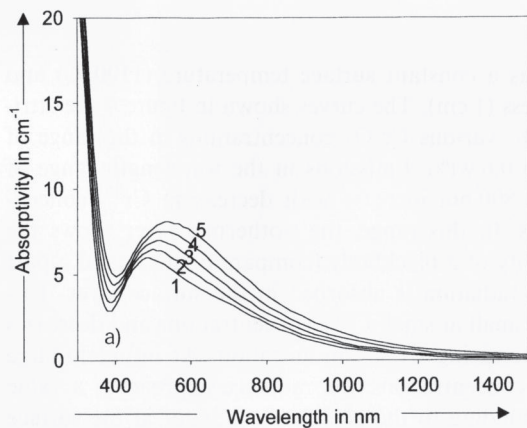
$$a(\lambda) = a_0 \cdot \exp\left[-\frac{1}{2} \left(\frac{\nu - a_1}{a_2}\right)^2\right] \quad (9)$$

where ν is the wave number, a_0 , a_1 and a_2 are constants, representing height, position and half-width of the absorption band, respectively. All together, one line of Cr^{6+} and two lines of Cr^{3+} [6] and the UV cut were taken into consideration. The attributed parameters and their temperature dependences are summarized in table 1. It should be noted that the redox ratio $\text{Cr}^{6+}/\text{Cr}^{3+}$ strongly affects the spectra.

Figures 1a and b show absorption spectra of glass melts in the temperature range from 900 to 1300 °C for a melt with 0.3 wt% Cr^{3+} and a melt containing both 0.005 wt% Cr^{6+} and 0.295 wt% Cr^{3+} , respectively. For the melt solely containing Cr^{3+} , distinct maxima are observed in the range of 480 to 500 nm. The maximum is shifted to larger wavelengths while increasing the temperature [7]. The absorptivity in the entire wavelength range shown increases with the temperature. Also the

Table 1. Temperature dependence of the height a_0 , position a_1 and half-width a_2 of the absorption bands calculated from experimental data, $[\text{CrO}_3]$ and $[\text{Cr}_2\text{O}_3]$ represent the concentration of the chromium species

	Cr^{6+}	Cr^{3+}	Cr^{3+}
λ_{max} in nm at 25 °C	365	450	656
a_0 in cm^{-1}	$0.28 - (8.3 \cdot 10^{-5} \cdot T) [\text{CrO}_3]$	$0.0012 \frac{\left(1 + \exp\left(-\frac{0.15}{kT}\right)\right)}{\left(1 - \exp\left(-\frac{0.15}{kT}\right)\right)} [\text{Cr}_2\text{O}_3]$	$0.0011 - 1.87 \cdot T \cdot [\text{Cr}_2\text{O}_3]$
a_1 in m^{-1}	$2.76 \cdot 10^6 - (92.5 \cdot T)$	$2.2 \cdot 10^6 + 111.8 \cdot T - 0.17 \cdot T^2$	$1.54 \cdot 10^6 - 53.19 \cdot T$
a_2 in m^{-1}	$10^5 \frac{\left(1 + \exp\left(-\frac{0.824}{kT}\right)\right)}{\left(1 - \exp\left(-\frac{0.824}{kT}\right)\right)}$	$0.168 \cdot 10^5 \frac{\left(1 + \exp\left(-\frac{0.11}{kT}\right)\right)}{\left(1 - \exp\left(-\frac{0.11}{kT}\right)\right)}$	$1.46 \cdot 10^5 + 127 \cdot T$



Figures 1a and b. Experimentally determined absorptivities of glass melts as a function of the wavelength and the temperature; curve 1: 900 °C, curve 2: 1000 °C, curve 3: 1100 °C, curve 4: 1200 °C, curve 5: 1300 °C. Figure a: melt with 0.3 wt% Cr as Cr_2O_3 ; figure b: melt with 0.005 wt% Cr as CrO_3 and 0.295 wt% Cr as Cr_2O_3 .

UV cut is shifted to larger wavelengths. In the melt containing Cr^{6+} , well pronounced maxima are no longer

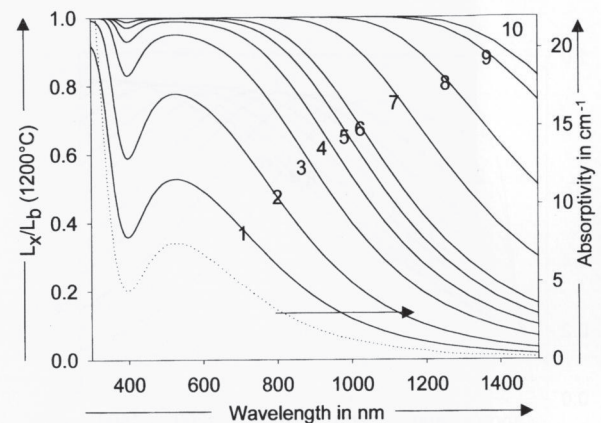


Figure 2. Calculated emission spectra (referenced to a black-body radiation at 1200 °C) for isothermal glass layers (1200 °C) of different layer thicknesses; curve 1: 0.1 cm, curve 2: 0.2 cm, curve 3: 0.4 cm, curve 4: 0.6 cm, curve 5: 0.8 cm, curve 6: 1 cm, curve 7: 2 cm, curve 8: 4 cm, curve 9: 8 cm and curve 10: 10 cm. Dotted line shows absorptivity values. The melt contains 0.3 wt% Cr_2O_3 .

observed, because of the additional absorption band caused by Cr^{6+} whose maximum occurs in the wavelength range of 400 to 450 nm, i.e. at wavelengths where in figure 1a the minimum occurs.

Figure 2 shows calculated emission spectra of glass melts which only contain Cr^{3+} for the isothermal case (1200 °C) (reflectance neglected). Here, the thickness of the glass layer was varied and the bottom of the glass container was assumed to be fully transparent (and does not show emission of light). The relative emissivity L_x/L_B increases with increasing layer thickness until it is unity at all wavelengths attributed to larger absorption coefficients, the limiting value being reached already at a smaller layer thickness. At layer thickness < 1 cm, a distinct minimum is observed which is attributed to the

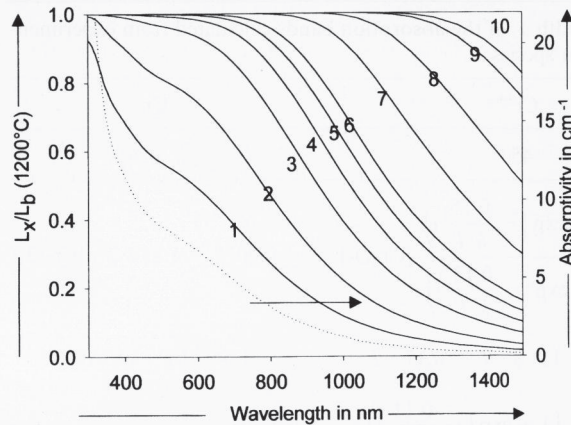


Figure 3. Calculated emission spectra (referenced to a blackbody radiation at 1200°C) for isothermal glass layers (1200°C) of different layer thicknesses. Notes to curves are given in caption to figure 2. The glass melt contains 0.005 wt% Cr as CrO_3 , and 0.295 wt% Cr as Cr_2O_3 .

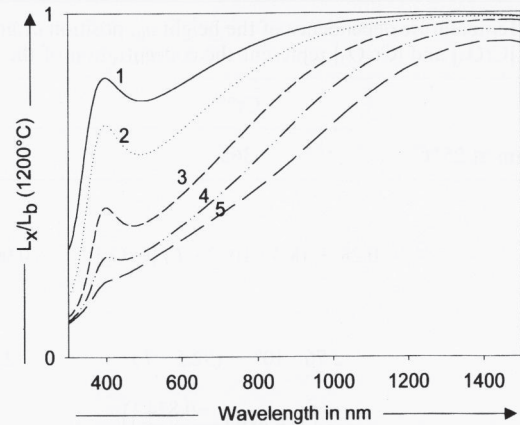


Figure 5. Calculated emission spectra for the nonisothermal case: isothermal glass layer (1200°C, thickness: 10 cm), covered by layers with a constant temperature gradient (surface temperature: 1100°C), gradient layer thicknesses: curve 1: 0.1 cm, curve 2: 0.2 cm, curve 3: 0.5 cm, curve 4: 1 cm, curve 5: 2 cm. The melt contains 0.3 wt% Cr as Cr_2O_3 .

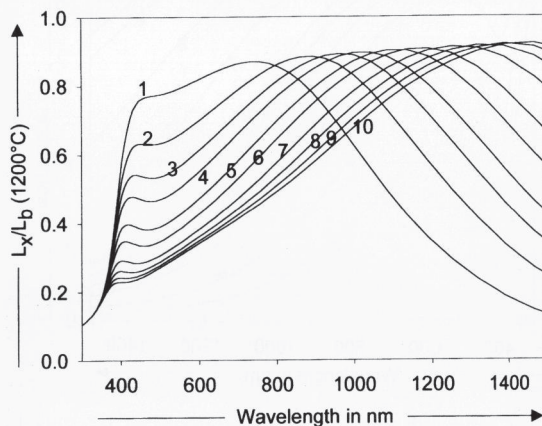


Figure 4. Calculated emission spectra for the nonisothermal case: isothermal glass layer (1200°C, thickness: 10 cm), covered by layers with a constant temperature gradient (surface temperature: 1100°C, thickness: 1 cm). Cr concentrations (as Cr_2O_3): curve 1: 0.02 wt%, curve 2: 0.05 wt%, curve 3: 0.075 wt%, curve 4: 0.1 wt%, curve 5: 0.15 wt%, curve 6: 0.2 wt%, curve 7: 0.3 wt%, curve 8: 0.4 wt%, curve 9: 0.5 wt%, curve 10: 0.6 wt%.

minimum in the absorption coefficient at around 400 nm.

Figure 3 shows calculated emission spectra of glass melts containing the same quantity of chromium, however 0.005 % is present as Cr^{6+} . At small layer thickness, the larger emission at wavelengths attributed to Cr^{6+} (≈ 400 nm) is clearly seen. By analogy to figure 2, at larger wavelengths, the radiance approaches that of a blackbody.

Figure 4 shows calculated emission spectra of a melt with an isothermal layer of constant thickness (10 cm) and temperature (1200°C) and a gradient layer which

also has a constant surface temperature (1100°C) and thickness (1 cm). The curves shown in figure 4 are attributed to various Cr_2O_3 concentrations in the range of 0.02 to 0.6 wt%. Emissions in the wavelength range of 350 to 800 nm increase with decreasing Cr^{3+} concentrations. In this range, the isothermal layer shows the emissivity of a blackbody (compare figure 2) and a part of this radiation is absorbed in the surface layer. This part is small at small Cr^{3+} concentrations and decreases with increasing Cr^{3+} concentration. At infinitely large Cr_2O_3 concentrations, the radiance approaches a value corresponding to the blackbody radiator at the surface temperature. At large wavelengths > 1400 nm, the emission increases with increasing Cr^{3+} concentration. Here, at low Cr^{3+} concentrations, the emissivity of the isothermal layer is lower than that of a blackbody and the absorption of the gradient layer is of minor importance. With increasing Cr^{3+} concentration, the radiance increases. In the middle wavelength range (1000 to 1400 nm), the radiance first increases with the Cr^{3+} concentration due to larger emissions in the isothermal layer. With further increasing the Cr^{3+} concentration, the radiance decreases again. This is caused by increasing absorptions in the gradient layer.

In the calculated emission spectra shown in figure 5, the thickness of the gradient layer is varied, while the surface temperature (1100°C), the thickness of the isothermal layer (10 cm) and its temperature (1200°C) are kept constant. The melt considered solely contains Cr_2O_3 (0.3 %). Also here, a distinct minimum, due to the absorptivity of Cr^{3+} is observed at wavelengths of around 450 nm, and a maximum at around 400 nm. The thinner the surface layer, the larger the emissivity.

Figures 6 and 7 show calculated emission spectra for the nonisothermal case for a glass melt solely containing Cr^{3+} and a glass melt containing both Cr^{6+} and Cr^{3+} .

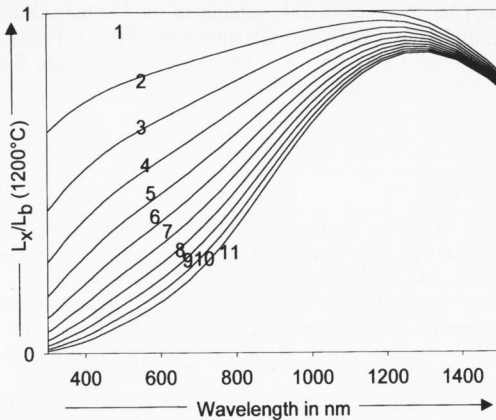


Figure 6. Calculated emission spectra for the nonisothermal case: isothermal glass layer (1200°C, thickness: 10 cm), covered by layers of different surface temperatures (thickness: 1 cm). Surface temperatures: curve 1: 1200°C, curve 2: 1180°C, curve 3: 1160°C, curve 4: 1140°C, curve 5: 1120°C, curve 6: 1100°C, curve 7: 1080°C, curve 8: 1060°C, curve 9: 1040°C, curve 10: 1020°C, curve 11: 1000°C. The melt contains 0.295 wt% Cr as Cr_2O_3 and 0.005 wt% Cr as CrO_3 .

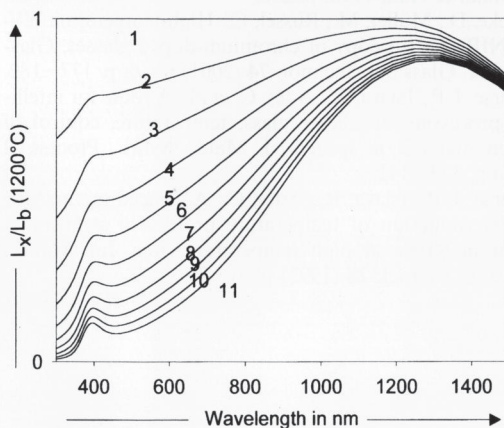


Figure 7. Calculated emission spectra for the nonisothermal case: isothermal glass layer (1200°C, thickness: 10 cm), covered by layers of different surface temperatures (thickness: 1 cm). Notes to curves are given in caption to figure 6. The melt contains 0.3 wt% Cr as Cr_2O_3 .

By analogy to figures 2 and 3, an isothermal glass melt layer possessing the thickness d_i was considered. In this case, we assumed $d_i = 10$ cm and the bottom of the crucible containing the melt to be fully transparent. The isothermal melt is covered by a melt layer in which a constant temperature gradient occurs. This model is fully described by the temperature of the isothermal layer, T_i , the surface temperature, T_n , and the thicknesses of both layers, d_i and d_n . In our case, the surface temperature, T_n is smaller than the temperature of the isothermal layer. Figures 6 and 7 show these emission spectra for $T_i = 1200^\circ\text{C}$, $d_i = 10$ cm and $d_n = 1$ cm for different surface temperatures in the range of 1000 to 1200°C. The emission spectra of the isothermal layer itself would be equal to the blackbody radiation (compare figures 2 and 3). The emissivity in the UV range de-

creases strongly with decreasing surface temperature. This is due to the large absorptivities in this wavelength range and to the drastically decreasing UV emissions with decreasing temperature. At wavelengths > 1400 nm, the surface temperature has a minor effect on the emissivity, because in this wavelength range the absorptivity is small and the intensity of the emitted radiation does not depend as strongly on temperature as at smaller wavelengths. Here, the emissivity is mainly due to the isothermal layer. The maximum observed at around 1200 to 1250 nm is due to a moderate absorptivity of the melt. Here the radiance of the thick isothermal layer is not strongly absorbed by the surface layer.

In figure 7 the maximum in the emissivity observed at around 400 nm is caused by the minimum in the absorptivity which occurs at approximately the same wavelength (see figure 1a). The minimum observed at around 450 nm is attributed to the maximum in the absorptivity, i.e. the absorption of Cr^{3+} . By contrast, in figure 6, attributed to a melt with 0.005% Cr^{6+} , neither a maximum, nor a minimum is seen. At the high temperatures supplied, also the absorption spectra does not exhibit a minimum (see figure 1b). It should be noted that the presence of Cr^{6+} is clearly seen from the spectra.

5. Discussion

The radiance from a semitransparent isothermal layer of molten glass increases with the absorptivity and finally approaches the radiance of a blackbody of the same temperature. Thus, the emitted radiance (normalized to the blackbody radiation) is large at wavelengths where the absorptivity is high. This situation changes notably with the occurrence of a thermal gradient layer at the surface. If the absorptivity within this layer is large, the emission spectra approaches that attributed to the blackbody radiation at the surface temperature. This is especially observed at wavelengths < 350 nm as well as at large concentrations of absorbing ions or thicker gradient layers. If otherwise the absorptivity at a certain wavelength is small, the effect of the gradient layer is of minor importance and the spectrum is dominated by the emitted radiance of the isothermal layer beneath.

The shape of an emission spectra strongly depends on the type and concentration of absorbing ions and the temperature profile in the melt. As shown in the calculated emission spectra of melts containing only Cr_2O_3 or both Cr_2O_3 and CrO_3 , species occurring in the melt can quantitatively be determined from the spectra in the case of melt layers (if the bottom of the glass container is transparent). This case, however, is of minor importance for industrial glass melts. Here, the temperature at the surface usually is not the same as in the bulk and the bottom of the glass container is not transparent. In an industrial glass furnace, the temperature at the surface is higher than in the bulk due to the irradiative heating by

the burners. In the feeder, however, the surface temperature should be lower than in the bulk. In the numerical calculations presented in this paper, an isothermal glass layer with a temperature of 1200°C (typical for the feeder) was considered. This layer was covered by a thinner layer with a lower temperature. Within this layer, a constant gradient was assumed. The emission spectra were drastically affected by this layer. If the absorption spectra of the melt show well pronounced absorption bands, the emission spectra also in the nonisothermal case are notably affected by absorbing ions present in the melt. In contrast to the isothermal case, the emission of the system isothermal layer/gradient layer does not necessarily increase with the absorptivity. If within this system the absorptivity increases, the emission also increases up to a certain value. This value is smaller than that attributed to the blackbody radiation of the isothermal layer. If the absorptivity further increases, the absorption in the surface layer assumes increasing importance and finally the emission approaches that of a black body at the surface temperature.

Careful analysis of emission spectra should enable one to determine concentrations of absorbing ions as well as temperature profiles in regions near surface in a slightly other way than it is described in [8 and 9]. For this purpose, absorptivities and their dependencies upon temperature must be known.

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