

High-temperature UV-VIS-NIR absorption and emission spectroscopy of soda-lime-silica glasses doped with Nd₂O₃

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Absorption spectra were recorded from a glass with the basic composition 16Na₂O · 10CaO · 74SiO₂ doped with 4 wt% Nd₂O₃ at temperatures in the range from 25 to 1400 °C. The effective width of the observed absorption peaks increased with increasing temperature, while the peak positions remained nearly constant. Some absorption coefficients decreased with temperature while that at a wavelength of 657 nm increased notably. Emission spectra were recorded from glass melts exhibiting a temperature gradient at the surface (cold surface). The spectra showed distinguished minima at those wavelengths where the absorption maxima occurred. Numerical simulation of the emission spectra assuming a constant temperature gradient at the surface is in agreement with the experimental spectra.

1. Introduction

At high temperatures, glass melts are semi-transparent radiators, whose emissivities strongly depend on the type and concentration of colouring ions present. In comparison to melts and glasses doped with transition metal ions, those containing rare earth elements show much narrower absorption lines [1 and 2]. Thus, also light emissions of melts doped with rare earth elements should occur in a narrower wavelength range. Wavelength, absorption coefficients and full width at half maxima attributed to a certain absorption line, in the case of transition metals, strongly depend on the temperature. In the case of rare earth elements, 5 s and 5 p orbitals are fully occupied and shield the 4 f orbitals whose excitations are responsible for the absorption lines observed [1 and 2]. Hence, in the case of rare earth elements the effect of both the host glass composition and the temperatures should be less pronounced than in the case of transition metal ions [3 to 5]. Light emission from glass melts at high temperatures is of special importance for the melting process and widely determines the temperature distribution in an industrial glass tank [6 and 7]. Furthermore, light emitted from the melt might provide information on the composition of the melt, i. e. the concentration of colouring ions present [8 and 9]. Hence emission spectroscopy can be a valuable tool for quality control. In the case of polyvalent elements, not only information on the total concentration of these elements can be obtained but also on their redox ratios [9].

This paper provides a study on the absorptivity of Nd₂O₃-doped soda-lime-silica glass as well as on its emiss-

ivity at high temperatures. The spectra obtained were numerically simulated assuming an isothermal melt as well as using a layer model exhibiting a temperature gradient at the surface.

2. Theory

Light emission from a blackbody is described by Planck's radiation law

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

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

While in the case of a blackbody, absorption and emission coefficients are infinite, for a semitransparent radiator, they become finite. The absorption of a layer with the thickness x is described by Lambert-Beer's law

$$\alpha = 1 - e^{-a(\lambda)x} \quad (2)$$

where α is the absorption and $a(\lambda)$ the absorption coefficient, which depends upon temperature. Taking into account the reflection at the boundary melt/gas atmosphere ($R = ((n - 1)/(n + 1))^2$), the radiation of a semitransparent radiator, L_x , with the thickness, d , can be described as follows [10]:

$$L_x = (1 - R) \int_0^d L_B \cdot a(\lambda) \exp(-a(\lambda) \cdot x) dx \quad (3)$$

In the isothermal case, the integration of equation (3) leads to equation (4):

$$L_x = (1 - R) L_B (1 - \exp(-a(\lambda) \cdot d)). \quad (4)$$

If the product $a(\lambda) \cdot d$ is large, $\exp(-a(\lambda) \cdot d)$ approaches zero and $L_x = (1 - R) \cdot L_B$, i. e. for $n = 1.5$: $L_x \approx 0.96 \cdot L_B$. In this case, the emitted light does not provide any information on $a(\lambda)$, i. e. on the melt composition.

In the case of nonisothermal melts, equation (3) cannot be solved analytically, since L_B and $a(\lambda)$ are affected by the temperature and hence depend on x [8].

$$L_x = (1 - R) \int_0^d L_B(x) \cdot a(\lambda/x) \exp(-a(\lambda, x) \cdot x) dx. \quad (5)$$

In the following, a constant temperature gradient at the surface was assumed: an isothermal part of the melt (thickness: d) is covered by a layer with the thickness d_n in which a constant temperature gradient occurs. The temperature is lowest at the surface. In sections 3 and 4, results of a numerical simulation of equation (5) are presented using the model described above. As already pointed out in [8], an isothermal layer large enough will act as black body. Then the gradient layer will absorb more light than it emits, and the intensity of the emitted light be smallest at those wavelengths where the absorption is largest [8].

3. Experimental

A glass with the basic composition $16\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot 74\text{SiO}_2$ doped with 4 wt% Nd_2O_3 was melted from reagent-grade raw materials Na_2CO_3 , CaCO_3 , Nd_2O_3 and SiO_2 in a high-frequency furnace in a platinum crucible using a maximum temperature of 1500 °C. The glasses were cast on a graphite mould, preheated to 600 °C and subsequently cooled using a cooling rate of 30 K/h.

Temperature-dependent absorption spectra were recorded in the temperature range of 25 to 1400 °C using a halogen lamp as light source. The light was reflected by a planar mirror, passed a chopper (frequency: 113 s^{-1}) and subsequently the sample. The transmitted light was reflected by 90° by an offaxis parabolic mirror (focal distance: 45 cm) and focused to the entrance slit of a monochromator TRIAX 320 (Jobin-Yvon, Edison, NY (USA)). The sample was placed in a heating chamber of a microscope heating stage (TS 1500 Linkam, Waterfield (UK)). An Si-detector was used; the signals were given to a lock-in amplifier SR 830 (Stanford Research Systems, Sunnyvale, CA (USA)) adjusted to the chopper frequency. The samples had a diameter of 6 mm and were 1 to 2 mm thick. The experimental equipment is shown in figure 1.

High-temperature emission spectra were recorded using the equipment schematically shown in figure 2. The crucible containing the Nd_2O_3 -doped melt was located in a high-frequency furnace. The emitted light was reflected by an offaxis parabolic mirror, passed a chopper and focused on

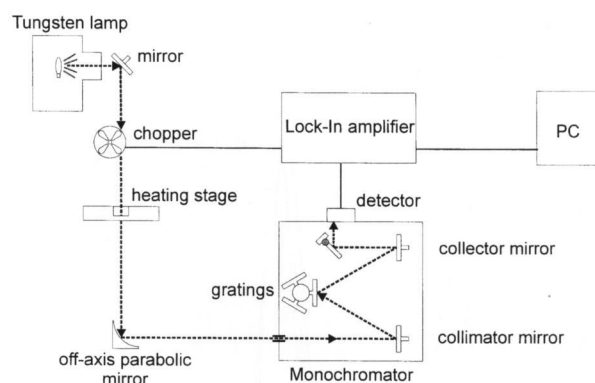


Figure 1. Schematic drawing of the apparatus used for high temperature UV-VIS-NIR absorption spectroscopy.

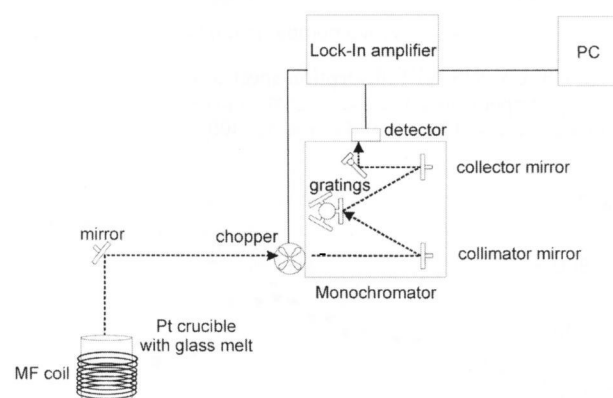


Figure 2. Schematic drawing of the apparatus used for high temperature VIS-NIR emission spectroscopy.

the entrance slit of the monochromator. Detector, lock-in amplifier and monochromator were the same as described above. Emission spectra were recorded from samples with different melt layer thicknesses (1, 2 and 3 cm) from (nearly) isothermal melts and melts with a temperature gradient at the surface. The temperature gradient was measured using thermocouples pinned at the wall of platinum crucible containing the melt.

4. Results

Figure 3 shows UV-VIS-NIR absorption spectra of the neodymium-doped sample at different temperatures. At room temperature, absorption bands at 512, 526, 584, 628, 687, 746, 806 and 875 nm are observed. The peaks at 584, 746, 804 and 875 nm possess more or less pronounced shoulders. With increasing temperature, the peaks at 584, 746 and 806 nm get more symmetric. The peaks at 512 and 526 nm observed in the spectrum recorded at room temperature can no longer be distinguished, that at 512 nm appears as shoulder. The intensity of the peak observed at 657 nm at 1400 °C is much larger than at lower temperatures. The increase of the effective line width (defined as $\int a(\lambda) d\nu/a_{\text{maximum}}$) with increasing temperature is illustrated in figure 4. The effect of temperature on some absorption coefficient is shown in figure 5. The absorption coefficient of the peak at a wavelength of 585 nm remains nearly constant in the entire temperature range studied.

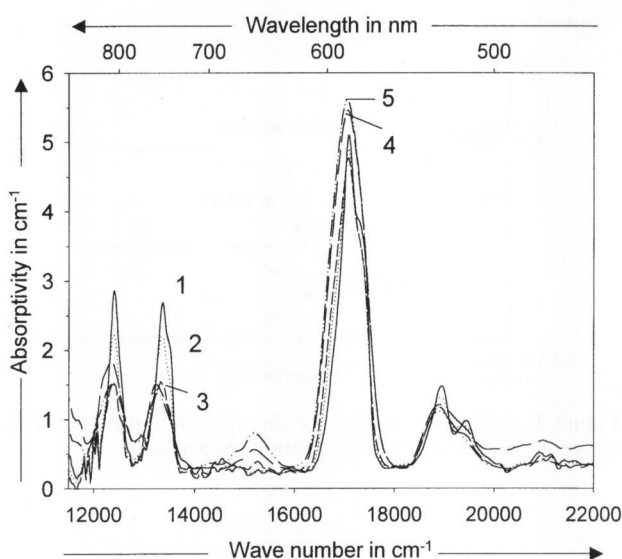


Figure 3. UV-VIS-NIR absorption spectra of the Nd_2O_3 -doped melt at temperatures of curve 1: 25°C, curve 2: 400°C, curve 3: 800°C, curve 4: 1200°C and curve 5: 1400°C.

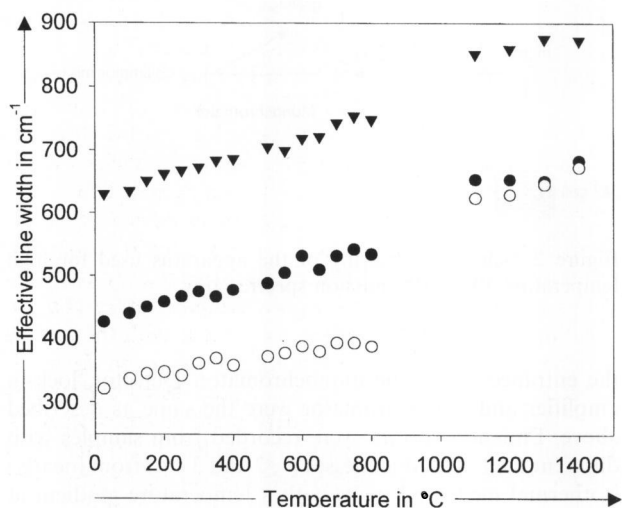


Figure 4. Effective line width of the absorption bands as a function of the temperature; \blacktriangle : 585 nm, \bullet : 746 nm and \circ : 804 nm.

Those attributed to the bands at 750 and 806 nm decrease with increasing temperature. The intensity of the peak observed at 657 nm at 1400°C is much larger than at lower temperatures.

Wavelengths attributed to the absorption maxima are not strongly affected by the temperature. The position of the peak at 585 nm remains constant within the limits of error even at 1400°C, while in the case of the peaks at 748 and 806 nm, a slight shift to larger wavelengths is observed (6 and 5 nm, respectively). The effective linewidth increases with temperature; in the case of the peak at 750 nm, the width increases from 420 to 680 cm^{-1} , i. e. by around 60%.

In figure 6, emission spectra of (nearly) isothermal glass melt layers with a thickness of 1, 2 and 3 cm are shown. The spectra are not normalized to the spectral sensitivity of the Si-detector used. The intensities of the emitted light are approximately the same for melts with thicknesses of 2 and 3 cm, however, there are wavelength-dependent differences.

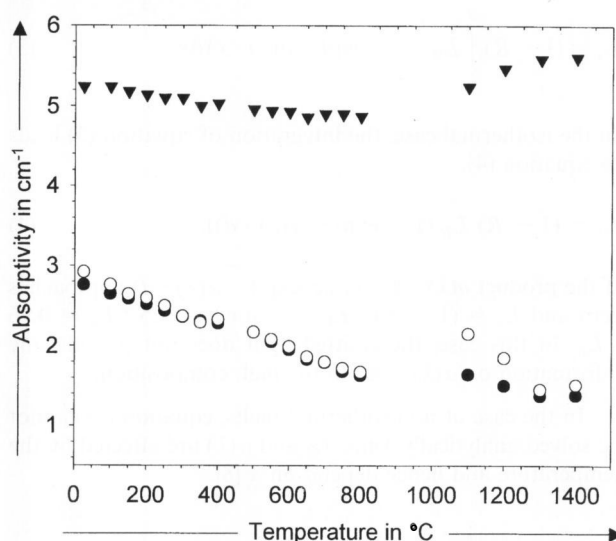


Figure 5. Absorption coefficients of the bands as a function of the temperature; \blacktriangle : 585 nm, \bullet : 746 nm and \circ : 804 nm.

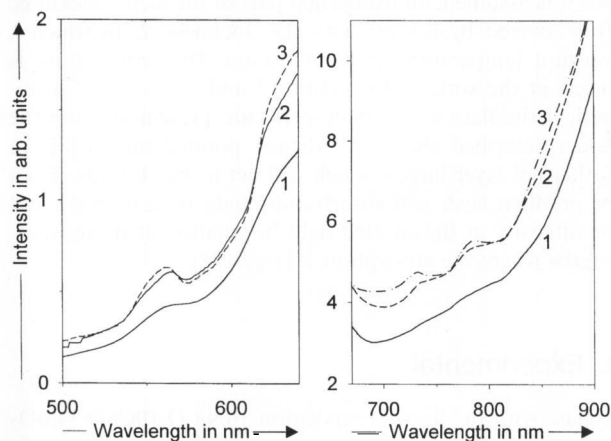


Figure 6. Emission spectra of the (nearly) isothermal Nd_2O_3 -doped glass melt layers with different thicknesses for two scales; curve 1: 1 cm, curve 2: 2 cm and curve 3: 3 cm.

The intensities at a melt layer thickness of 1 cm are smallest. In the spectra attributed to layer thicknesses of 2 and 3 cm, there are distinct minima (570 to 630 nm, 730 to 780 nm and 790 to 850 nm). The minimum at 570 to 630 nm is also observed in the spectrum of the melt with 1 cm thickness. The maxima in the spectrum increase with increasing layer thickness.

Figure 7 shows emission spectra of nonisothermal melts of different thicknesses (1, 2 and 3 cm). Notable differences to figure 6 are observed. First, the light intensities are smaller than in figure 6 at the same thicknesses. Second, the distinct minima already observed in figure 6 are more pronounced. The minima in the emission spectra occur at those wavelengths where large absorptivities are observed in the absorption spectra.

In the melt without cooling and in that which was cooled at the surface, temperatures were measured. In the melt without cooling, the temperature at the surface is around 15 K lower than in the bulk. In the cooled melt, a temperature of 80 K lower than in the bulk was measured

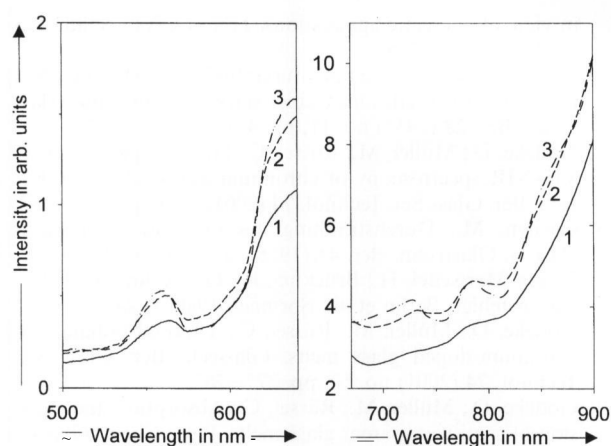


Figure 7. Emission spectra of the surface-cooled Nd₂O₃-doped glass melt layers with different thicknesses for two scales; curve 1: 1 cm, curve 2: 2 cm and curve 3: 3 cm.

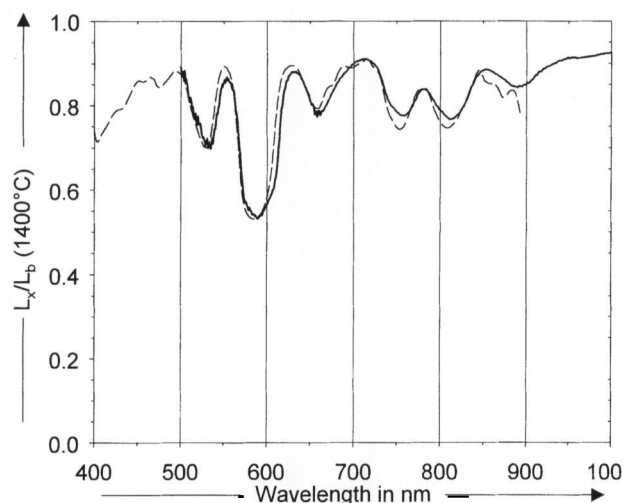


Figure 8. Emission spectrum of the surface-cooled melt (figure 7, curve 3) divided by that of the melt without cooling (figure 6, curve 3) (full line). The layer thickness in both cases was 3 cm. Simulated emission spectrum is shown by the dashed line.

near the surface; it increases in the bulk and at a depth of around 14 mm, the bulk temperature is reached.

Figure 8, curve 1 shows the emission spectrum of the surface-cooled melt (layer thickness: 3 cm, see figure 7, curve 3) which was divided by that of the uncooled melt with the same layer thickness (figure 6, curve 3). It is seen that the minima occur at the same positions where the absorption maxima occur. Minima attributed to the absorption lines of 530, 585, 660, 760 and 800 nm are observed. In figure 8, dashed line, a numerically calculated emission spectrum is shown. For the calculation, a surface temperature of 1320 °C and a bulk temperature of 1400 °C were considered, the temperature was assumed to change linearly within a layer thickness of 14 mm. As it is seen, a good agreement of the measured emission spectra is obtained.

5. Discussion

The absorption peaks observed at room temperatures occur at the same wavelengths already reported in the literature.

According to [2], the peaks at 526 and 584 nm are attributed to the $^4I_{9/2} \rightarrow ^4G_{7/2}$ and $^4I_{9/2} \rightarrow (^4G_{5/2}, ^2G_{7/2})$ transitions, respectively. Those at 628 and 687 nm are caused by the $^4I_{9/2} \rightarrow ^2H_{11/2}$ and $^4I_{9/2} \rightarrow ^4F_{9/2}$ transitions, while those at 746, 806 and 875 nm are attributed to the $^4I_{9/2} \rightarrow ^4(F_{7/2}, ^2H_{9/2})$, $^4I_{9/2} \rightarrow (^4F_{5/2}, ^2H_{9/2})$ and $^4I_{9/2} \rightarrow ^4F_{3/2}$ transitions, respectively. The only absorption line getting more intense while increasing the temperature is that at 657 nm.

In comparison with absorption lines of transition metal ions, the shifts observed are small. Also the effect of temperature on the effective line widths is small ($\leq 60\%$). This is caused by the fully occupied 5 s and 5 p orbitals of Nd³⁺ which shield the 4 f orbitals [2]. The knowledge of the effect of temperature on the absorptivities is a prerequisite for the numerical calculation of emission spectra.

Emission spectra were recorded from melts with different thicknesses. If the surface was not cooled, already a slight decrease in temperature was observed at the surface (≈ 15 K). Hence, strictly speaking, the melts were not ideally isothermal. This can be shown in the spectra (see figure 6). At wavelengths, where the absorptivity of the melt is large, minima occur. This is better pronounced at larger melt thicknesses. Nevertheless, an increase in intensity with increasing melt layer thickness is observed, which shows that a layer thickness of 1 cm with the absorptivities occurring is too small to act as a black body radiator. However, there are only slight differences in the light emission of melts which are 2 and 3 cm thick. In the surface-cooled glass, the minima observed at wavelengths where the melts exhibit large absorptivities are much better pronounced. That is due to the much larger temperature gradient occurring at the surface. Now, the emission at which wavelengths absorption occurs is smaller in the 3 cm thick sample than in the 2 cm thick sample. Nevertheless, at wavelengths where the absorptions are small, the emissions increase with the sample thickness. The emission spectrum shown as in figure 8, dashed line, was numerically calculated using experimentally determined temperature-dependent absorptivities. A bulk with a constant temperature of 1400 °C covered by a gradient layer was used as model. The surface temperature (1320 °C) was identical with that experimentally determined. To obtain figure 8, full line, the spectrum shown as curve 3 in figure 7 was divided by that shown as curve 3 in figure 6. Here, it was assumed that this curve is attributed to the black body radiation of an infinitely thick isothermal glass melt. Since also the melt which was not cooled at the surface exhibited a small temperature gradient, which is also seen from the minima in the spectrum, this model is not exactly right. Nevertheless, the experimental spectrum obtained as described is in good agreement with the numerically calculated one. The positions of the absorption minima are equal within the limits of error. The intensities for the peaks at 540, 585 and 657 nm are also in agreement, slight deviations are observed at 750 and 810 nm. Here, the intensities of the calculated spectrum were smaller than those of the simulated spectrum. It should be noted that also the position of the peak at 657 nm was the same in both cases.

6. Conclusions

The effect of temperature on the absorption spectra of Nd³⁺-doped glasses is much smaller than that reported

from transition metal ions. The wavelengths attributed to the respective absorption peaks are nearly independent of temperature. Emission spectra, recorded from melts exhibiting a surface colder than the bulk, exhibited distinguished minima at wavelengths at which the melt shows absorption maxima. Numerically simulated emission spectra of melts exhibiting a temperature gradient at the surface are in agreement with the experimental spectra.

7. References

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