

UV/VIS-Spectroscopy of molten slags and glasses (up to 1600 °C)

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Abstract

The aim of this research project is to obtain information about the molecular structure of liquid oxide melts (systems silicates and aluminates) by application of spectroscopical methods. The chemical structure is correlated with the properties of the oxide melts (e.g. basicity, redox-state, equilibria). Spectroscopical methods are also suitable for the control of melts during the running process. For these investigations, spectroscopical methods have been developed: absorption- (wavelength range 220 up to 780 nm) and reflection- (wavelength range 250 up to 550 nm) spectroscopy for research studies up to 1600 °C at different oxygen partial pressures. We are just working on the reflection spectroscopical measurements.

Measurements at slags with 3d-cation with and without (eigen-absorption) dopings have been investigated. The eigen-absorption is extraordinarily high in liquid silicates and is connected with the dissociation of these silicates.

Slags systems of CaO-SiO₂; CaO-MgO-SiO₂ ; CaO-Al₂O₃-SiO₂ and CaF₂-CaO-Al₂O₃ which have been doped with oxides of different 3d-cations: Fe₂O₃ [Fe²⁺/Fe³⁺]; Cr₂O₃ [Cr⁶⁺- species]; and CoO [Co²⁺] with mass contents 0.80 % up to 50 % and slags without doping.

Fe³⁺ and Cr⁶⁺ (as chromate species) have very intensive charge transfer bands (CT-bands). The position of the Fe³⁺-CT-bands and the eigen-absorption depend on the basicity of the liquid slags. With an increase of basicity, a strong red shift of the bands has been measured, which has been quantitatively evaluated. The height and the long-wave decrease (Urbach range) of the Fe³⁺-bands depend on the redox state of the slag. In liquid slags, the Cr⁶⁺-species is spectroscopically detectable as Cr₂O₇²⁻- anion, whilst in the glassy slags at room temperature the CrO₄²⁻-anion does exist. The Cr₂O₇²⁻- anion is not stable in liquid slags and in a diffusion-controlled thermal dissociation, gaseous CrO₃ is evaporated.

Within the VIS range, the intensive d-d-absorption bands of the tetrahedral Co²⁺(O²⁻)₄-complex are strongly lowered with an increase of temperature.

By quantitative evaluation of the spectra, the dissociation degree and the dissociation enthalpy have been determined as a function of the temperature up to a temperature above the liquidus temperature.

Experimental methods

The experimental setup consists of a Xe-lamp (1000 W), with a dispersive monochromator system (UV/VIS-spectrometer). The main part is a self-constructed high-temperature cell (see **figure 1**) for the preparation of thin films (film thickness of about $d=(0.12\pm0.02)$ mm, depending on the viscosity of liquid slags) for UV/VIS-absorption spectroscopy [1;2]. The synthetic slags are premelted, powered and strewn on an electrically heated Pt70Rh30-net consisting of 0.12 mm strong wires. The net has 250 meshes/cm² each with an area of 0.5x0.5 mm² and a total transparency of 65 %. The vertically oriented net is stretched between two clamps made of copper which also serve contemporarily as electric contacts. The construction offers the advantage to correct automatically the thermal expansion of the net by the weight of the lower movable contact, thus avoiding the bending of the net. The temperature of the slag sample is detected by using a PtRh18-thermocouple with a wire diameter of 60 μ m. The thermocouple is inserted into the melt inside a mesh.

The high-temperature cell can also be used for reflection-spectroscopical studies of “optically thick” melts, preferably of CaO-SiO₂ slag melts with high contents of FeO_n (up to 30 % Fe₂O₃ ; all mass contents in %).

The high-temperature cell is integrated in the UV/VIS-spectrometer (**figure 2**) which consists of a 1000 W xenon short arc lamp, a double-monochromator and a semiconductor-detector. The lamp is mounted in an appropriate housing with a spherical reflector and a quartz condensor system to maximize the light output of the source. A lock-in-amplifier and a chopper prevent the perturbation of the measurement by the not negligible UV/VIS-radiation of the melt. The observable wavelength range (wavelength: λ ; wavenumber: $\nu=1/\lambda$; A : absorbance) is between 200 nm ($\nu=50,000$ cm⁻¹) and 750 nm ($\nu=13,333$ cm⁻¹).

The comparison to high-temperature spectra is possible by recording spectra of quenched samples at room temperature with the same optical systems as the high-temperature ones. For recording the reflection spectra, the UV/VIS reflection spectrometer MCS 525 (manufacturer Zeiss Jena) has been used. The reflection spectrometer works with a flash lamp system. The flash energy amounts to 0.6 J (250 nm to 550 nm), the flash duration amounts to 10⁻⁶ s (each scan). The flash is led by quartz glass wave guides and focused by a quartz lens system on the surface of the liquid slag. The illuminated surface amounts to approximately 20 mm². The reflected beam is coupled into a second receiver wave guider in an angle of 0°. The light signal is led into a dispersive system and analyzed by a diode array. For determining the reflection spectrum, two reference materials have been used: barium sulfate standard (comparison with an ideal diffused reflector) and a planar platinum surface (comparison with an ideal mirror reflector).

Eigen-absorption of the slags

To approach the spectroscopical behaviour of silicate melts, the optical absorption mechanism of silicates has been investigated (“eigen-absorption”). In a silicate matrix, the electronic transition, which is responsible for the high-energy absorption, occurs between the bond and the anti-bond level ($\sigma\rightarrow\sigma^*$ -transition) with an energy of 11.7 eV ($\nu=94,340$ cm⁻¹). The $n\rightarrow\sigma^*$ -transition (n : non-binding electrons) of the non-bridging oxygen in the terminal $\equiv\text{Si-O}^-$ -groups is shifted down to 10.5 eV ($\nu=84,746$ cm⁻¹) [3]. This influence of terminal, non-bridging $\equiv\text{Si-O}^-$ -groups gains a high importance, once the samples are constituted of several components such as CaO, MgO and Al₂O₃ (investigated systems

CaO-Al₂O₃-SiO₂ and CaO-MgO-SiO₂). The main part of the UV-absorption (lower energy absorption part) is caused by charge-transfer-transitions from a non-binding n-state to an unoccupied Me^{x+}-orbital (Me^{x+}: Ca²⁺, Mg²⁺, Al³⁺ ...). The decreasing content of SiO₂ in the samples will automatically increase the content of terminal ≡Si-O⁻-groups. This electron transition changes strongly under the influence of temperature, as discussed below in the molten slag section. The bases of the UV-absorption (*A*=absorbance) of liquid silicates and the interpretation of the strong increase of the UV-absorption within the wavenumber range at about 50,000 cm⁻¹ have been represented in detail in [6].

With an increase of temperature, silicates with a high content of terminal ≡Si-O⁻ show a strong increase of the UV-absorption: **figure 3**. With the increase of basicity one can notice a strong red-shift of the low-energy edge of the absorption band (Urbach tail). The reasons for this phenomenon are the fluctuation of the Madelung-potential and the dissociation of the bonding ≡Si-O⁻...Meⁿ⁺. An important criterion for the UV absorption behaviour of solid silicate glasses is the cutoff wavenumber ν_{cut} [3]. For the wavenumber ν_{cut} , the (decadic) absorption coefficient α_{ν} gets the value $\alpha_{\nu}=50 \text{ cm}^{-1}$ in the long-wave range of an absorption band (Urbach-range). In this case (see figure 3) ν_{cut} is fixed as $A_{\nu}=\alpha_{\nu}d=0.6$ for $d=0.012 \text{ cm}$ (*A*=absorbance). At room temperature, there is a direct linear relation between ν_{cut} and the optical basicity $A(\text{Pb}^{2+}/20 \text{ }^{\circ}\text{C})$ [7;8] of solid silicates (systems CaO-Al₂O₃-SiO₂ and CaO-MgO-SiO₂). This behaviour can be explained theoretically [3]. In the liquid CaO-Al₂O₃-SiO₂-slag (1500 °C), ν_{cut} shifts dramatically from the far UV range to the near UV/VIS range: from about 75,000 cm⁻¹ to 30,000 cm⁻¹ (strong red shift). Furthermore, the mentioned simple connection between $\nu_{\text{cut}}(1500 \text{ }^{\circ}\text{C})$ and $A(\text{Pb}^{2+}/20 \text{ }^{\circ}\text{C})$ does not exist anymore. These deviations can be explained as follows: In glassy aluminates and silicates, Al³⁺ has a coordination number $CN(\text{Al}^{3+})=4$ (tetrahedral coordination), which has been determined by IR-spectroscopical investigations. With an increase of temperature, the Al-O-complexes dissociate by decreasing their coordination number from $CN(\text{Al}^{3+})=4$ to $CN(\text{Al}^{3+})=3$ [17]. In molten silicates and aluminates, the dissociation equilibrium is:



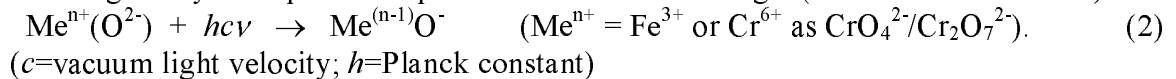
In molten silicates Al-O-complexes are integrated in the Si-O-network as follows:

AlO_4^{5-} as $(\equiv\text{Si-O})_4\text{Al}^{3+}$ and AlO_3^{3-} as $(\equiv\text{Si-O})_3\text{Al}^{3+}$, O^{2-} has the function of a network transformer, forming ≡Si-O⁻-groups. In liquid CaO-Al₂O₃-SiO₂-slags, this leads to an additional strong red shift of the cutoff wavenumber caused by the component Al₂O₃.

Charge transfer spectra of Fe³⁺

Introduction

Topic of interest are the charge-transfer transitions (CT-bands in the wavelength range 230 - 400 nm) in melts, which are doped with Fe₂O₃ or Cr₂O₃ at constant oxygen partial pressures. For a short time, there is a charge transfer between the metal cation and the oxide ligand by absorption of a photon $h\nu$ in the UV-range (metal reduction bands):

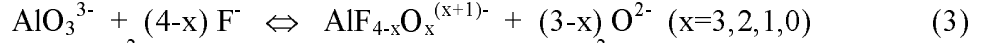


These CT-bands are very intensive (extinction coefficients of $\varepsilon_{10}=10^6$ up to $10^7 \text{ cm}^2/\text{mol-Me}^{n+}$) [4].

CT-spectra of Fe³⁺

The position and the shape of the Fe³⁺-CT-absorption bands (electron-transitions $\pi \rightarrow t_{2g}$ and $\sigma \rightarrow e_g$ in $\text{Fe}^{3+}(\text{O}^{2-})_6$, broad overlapping bands) offer the possibility to determine the basicity of the oxide melts (with an increase of basicity, there is a measurable red shift):

figure 4. In CaF₂-containing CaO-Al₂O₃, a strong red shift has been measured, **figure 5.** The following equilibrium causes a high basicity:



The displacement of the O²⁻-ions increases the activity of the O²⁻- ions. In the spectra, no hint about F⁻-complexes like Fe³⁺(F⁻)₄ or Fe³⁺(F⁻)₆ does exist[5;6].

d-d-transitions in the Co²⁺ (3d⁷-cation)

Introduction

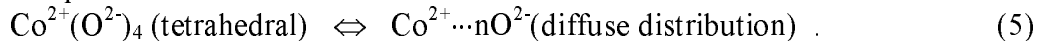
CoO-doped silicates have an intensive blue colour which is caused by the d-d-transition ⁴A₂(F)→⁴T₁(P) (splitted into three absorption maxima by the spin-orbit coupling in Co²⁺) of the tetrahedral complex Co²⁺(O²⁻)₄ (O²⁻ is bound in the Si-O-network). The weak coordinative bondings, which are responsible for the formation of this complex, can be dissolved by thermal energy. Because the O²⁻-ligand can not be arranged in a rigidly geometric way and there are two different types of O²⁻-ligands [terminal O²⁻ bond as ≡Si-O⁻ and O²⁻ bound as ≡Si-O-Si≡], the fine structure bands overlap. Thus, as a rule, in glassy silicates only three maxima can be observed [9...11]. The O²⁻-ligand sphere, given as ≡Si-O⁻ and ≡Si-O-Si≡, produces an electric field so that the tetrahedral symmetry of the electric ligand field is reached approximately.

Usually in spectroscopy, the field strength parameter *Dq* is used with wavenumber unit cm⁻¹ because this quantity is proportional to the energy. For Co²⁺ in glassy silicates and borates in tetrahedral coordination, *Dq* is approximately 380 cm⁻¹ [3;10..12]. The value of *Dq* is inversely proportional to *R*⁵_{Co-O} (*R*_{Co-O} = Co-O-ligand distance) [9;10] and directly proportional to the integral of the radial wave function that describes the interaction of the d-electrons on Co²⁺ with the ligand field.

With an increase of temperature, the bond distance *R* becomes fuzzy [13;14] as a consequence of the ligand fluctuation and the oscillation ligand - central cation. Furthermore, the symmetry is increasingly disturbed. Because *Dq* depends very much on *R*_{Co-O} and on the symmetry of the complex, *Dq* moves towards the value zero. This is equivalent to the dissociation of the complex and is connected to the loss of the *LFSE*. From the measured value of *Dq*, the *LFSE* can be calculated in the following way: In the tetrahedral d⁷-Co²⁺-high-spin complex, four electrons are situated in the lower energy level and three electrons are situated in the upper energy level (see figure 1), so that one gets the following correlation for the *LFSE*: *LFSE* = - 4·(6 *Dq*) + 3·(4 *Dq*) = - 12 *Dq*. Converted to thermochemical quantities, one gets the following equation for the dissociation energy *E_d* (*N_A*=Avogadro's number) :

$$E_d = 12 Dq \cdot h \cdot c \cdot N_A \quad (4)$$

For the tetrahedral Co²⁺-complex in silicates, this leads to *E_d*=54 kJ/mol-Co²⁺. The dissociation equilibrium in silicates can be described as follows:



Structure of the d-d-bands

In **figure 6**, the absorption spectra for the silicates 54.5CaO+45.5SiO₂ (all mass contents in %) doped with 1.5 % CoO {liquidus temperature 1680 K, *d*=(0.12±0.01) mm} are shown at different temperatures. Below the liquidus temperature the sample is in the glassy state. The band system, observed at 16,800 cm⁻¹ (293 K), is assigned to the ⁴A₂(F)→⁴T₁(P) transition of the Co²⁺(O²⁻)₄-complex. The strong spin-orbit coupling in Co²⁺ is a result of the orbital ligand field in the splitting into three spin-orbital levels. The central band at 16,800 cm⁻¹ is approximately the mean value of the two partial bands at 18,600 cm⁻¹ and 15,500 cm⁻¹ (293 K). The aim of this work is to prove the thermic dissociation of the tetrahedral Co²⁺(O²⁻)₄ up to 1750 K via spectroscopical measurements.

Because the silicate tends to crystallization in the temperature range above 1150 K, the absorption spectra above 1150 K up to the formation of the molten phase overlap with scattering effects sometimes.

Determination of the dissociation degree from the spectroscopical data

From the spectra, the dissociation degree and the dissociation enthalpy can be calculated under the following assumptions:

a) The measured value for the absorbance $A(T)$ of a band at a given temperature is proportional to the concentration of the $\text{Co}^{2+}(\text{O}^{2-})_4$ -complex c_c :

$$A(T) \propto c_c . \quad (6)$$

b) At room temperature, the complex dissociation is approximately equal to zero. Therefore, at room temperature, the absorbance is proportional to the total Co^{2+} -concentration c_t :

$$A(293 \text{ K}) \propto c_t . \quad (7)$$

c) c_t is constant and the sum of Co^{2+} in the dissociated state c_d and c_c :

$$c_t = c_d + c_c . \quad (8)$$

The dissociation degree β , which is defined as the quotient $\beta = c_d / c_t$, can be determined from the equations (6) to (8) as follows:

$$\beta = 1 - \frac{A(T)}{A(293 \text{ K})} . \quad (9)$$

Figure 7 shows the analysis concerning the dissociation degree β depending on the temperature using the bands in the wavenumber ranges at about $16,800 \text{ cm}^{-1}$ and $18,900 \text{ cm}^{-1}$. In the liquid state, the value of β tends to 1 for higher temperatures. The dissociation degree amounts to $\beta \approx 0.8$, when the liquidus temperature is exceeded. The band maxima in the wavenumber ranges $16,800 \text{ cm}^{-1}$ and $18,900 \text{ cm}^{-1}$ have been analyzed, because both bands can be measured clearly separated from each other and they interfere less with the thermic background radiation.

Determination of the dissociation enthalpy from the spectroscopical data

The coefficient of dissociation $K_d(T)$ has to be defined according to the equilibrium (5):

$$K_d = c_d / c_c . \quad (10)$$

The dependence of $K_d(T)$ on the temperature T and the dissociation enthalpy ΔH_d are related in the following way:

$$\frac{\partial \ln K_d}{\partial 1/T} = \frac{-\Delta H_d}{R} . \quad (11)$$

By use of equations (6) to (9) and equation (10), the coefficient of dissociation can be determined from the spectroscopical data as follows:

$$K_d = \frac{A(293 \text{ K})}{A(T)} - 1 . \quad (12)$$

In **figure 8**, the corresponding representations according to equation (12) and using the conception of (11) are shown for the silicate $54.5\text{CaO}+45.5\text{SiO}_2$ (mass content in %) doped with 1.5 % CoO. Respectively, two linear ranges are clearly perceptible: The range of lower temperatures, room temperature up to approximately 1250 K, and 1250 K up to approximately 1750 K. From this, the values for ΔH_d are calculated respectively:

$\Delta H_d(293 \div 1250 \text{ K}) = (27 \pm 1) \text{ kJ/mol-Co}^{2+}$ and $\Delta H_d(1250 \div 1750 \text{ K}) = (78 \pm 10) \text{ kJ/mol-Co}^{2+}$.

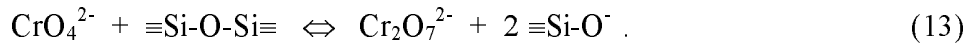
In the temperature range below 1250 K, there are significant differences between the determined values for the dissociation enthalpy and the dissociation energy which can be calculated from the ligand field theory by use of the absorption spectra: $E_d > \Delta H_d$. The

probable reason for this is the following: During the complex dissociation, the repulsive energy between the four oxygen ligands is released {exothermic contribution to the dissociation reaction, see equation (5), [9]}. In the calculation of E_d , this energy part is disregarded. Because of the stimulation of the thermic vibrations central cation-ligand, this repulsive energy of the ligands becomes more positive with an increase of temperature.

In CaO-SiO₂-slags, $\equiv\text{Si-O}^-$ and $\equiv\text{Si-O-Si}\equiv$ - groups are also involved in the complex reaction. A stepwise dissociation of the complexes can be observed. First, the thermodynamically more instable complexes with predominantly $\equiv\text{Si-O-Si}\equiv$ -ligands and the then more stabile complexes with a higher content of $\equiv\text{Si-O}^-$ -ligands dissociate. In addition to the *LFSE*, the $\equiv\text{Si-O}^-$ -ligand field has a higher electrostatic field effect (Madelung-potential), which stabilizes the complexes.

CT- spectra of Cr⁶⁺ (as chromate species)

Figure 9 shows the absorption spectra at 1500 °C and 20 °C for the 54.5CaO+45.5SiO₂-slag. Spectra of Cr₂O₃-containing CaO-SiO₂-slags indicate two strong CT-transitions of CrO₄²⁻: $2t_2(\sigma) \rightarrow 3t_2(\pi^*)$ at $\nu=36,800 \text{ cm}^{-1}$ and $t_1(\pi) \rightarrow 3t_2(\pi^*)$ at $\nu=27,300 \text{ cm}^{-1}$ at room temperature. For the molten CaO-SiO₂-slags {1500 °C, $p(\text{O}_2)=0,21 \text{ bar}$ }, the spectrum changes its appearance totally: The spectrum becomes similar to the spectrum of the dichromate-anion Cr₂O₇²⁻. The following equilibrium in the liquid slag state determines the spectrum:

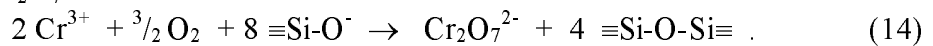


Literature data [15] show similar spectra of CrO₃ dissolved in silicates. In the vitreous, highly polymere Na₂O·9B₂O₃ matrix, the dichromate anion has also been proven at room temperature [16].

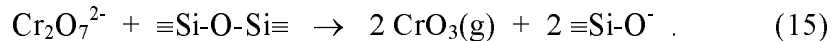
At lower oxygen partial pressures, the chromates will be reduced to Cr³⁺ and Cr²⁺.

Time resolved spectra, **figure 10**, (time interval of 90 min) studies of Cr₂O₃ containing silicate slags under higher oxygen partial pressure have yielded a decrease of the absorption band of Cr₂O₇²⁻ depending on the time. The reason for this behaviour is the evaporation of the volatile CrO₃(g) out of the molten slag.

Formation of the Cr₂O₇²⁻ anion:



Evaporation of CrO₃(g):



The decrease in the CrO₃ content in this experiment can also be monitored by the absorbance change $A(t)$ at a fixed wavenumber ($\nu=27,027 \text{ cm}^{-1}$) at 1500 °C.

$A(t)$ is proportional to the average CrO₃-concentration in the slag layer. By curve fitting of $A(t)$ at a constant wavelength to an equation for the diffusion process in the layer with $d=0.012 \text{ cm}$, the chemical diffusion coefficient is obtained: $D(\text{Cr}^{3+}/\text{Cr}^{6+})=3.5 \cdot 10^{-7} \text{ cm}^2/\text{s}$.

UV/VIS-Reflectance measurements

Introduction und preliminary remarks

In the wavenumber range at about $\nu \approx 30,000 \text{ cm}^{-1}$, molten silicates with a high content of Fe₂O₃ have extraordinarily high (decadic) optical absorption coefficients α_ν [1;2;5;6]. CT-transitions of Fe³⁺ in an oxide matrix are the reason for this phenomenon. α_ν is a function of the wavenumber. The reflectance R_ν is relevant for the reflection behaviour of a regularly reflecting surface. According to equation (16), R_ν can be calculated from the real refractive index n and the dimensionless absorption coefficient $k_\nu=\alpha_\nu/(\nu \cdot 4\pi)$ as follows:

$$R_v = \frac{(n-1)^2 + k_v^2}{(n+1)^2 + k_v^2}. \quad (16)$$

R_v is the measurable spectral reflectance degree for an reflection angle of 0° . For high values of k_v , R_v tends to the value 1. The absorption coefficient α_v consists of two parts: The first part is the absorption by the liquid slag matrix $\alpha_v(\text{slag})$. The second predominant part is the absorption in the near UV-range caused by the CT-transitions of the Fe^{3+} -ion $\varepsilon_v(\text{Fe}^{3+}) \cdot c(\text{Fe}^{3+})$ { ε_v =molar decadic extinction coefficient; $c(\text{Fe}^{3+})$ =molar concentration }.

From this, α_v can be calculated: $\alpha_v = \alpha_v(\text{slag-matrix}) + \varepsilon_v(\text{Fe}^{3+}) \cdot c(\text{Fe}^{3+})$.

From the spectroscopical CT-data for liquid $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2$ -slags, k_v can be estimated to a value between 0.5 and 1.0 ($\nu \approx 30,000 \text{ cm}^{-1}$) for a slag with contents of Fe_2O_3 between 40 and 60 % (mass ratio $\text{CaO/SiO}_2=1.2$). In the wavenumber range at about $\nu \approx 30,000 \text{ cm}^{-1}$ this leads to increased reflection values of $R_v=0.09$ up to 0.18 (superposition of anomalous with normal dispersion) and whilst for Fe_2O_3 -free slags the value is only $R_v \approx 0.05$ (preponderant normal dispersion).

The real refractive index n depends only insignificantly on the wavenumber ($n \approx 1.5 \div 1.7$; [18]). From measurements of the electrical conductivity, it is known that $\text{CaO-SiO}_2\text{-FeO}_n$ -melts have p-semiconductive properties depending on the oxygen partial pressure (formation of a redox system $\text{Fe}^{2+}/\text{Fe}^{3+}$ [19]). This leads to an additional increased optical reflection in the liquid state. These are the initial considerations of our research studies with which we are occupied currently.

Spectral reflectance of liquid $\text{CaO-SiO}_2\text{-FeO}_n$ -slags

Figure 11 shows the reflection-spectrum of a $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3$ -slag (air atmosphere) with the composition $32.7\text{CaO}+27.3\text{SiO}_2+40.0\text{Fe}_2\text{O}_3$ (mass content in %) in the wavenumber-range $40,000 \text{ cm}^{-1}$ (UV) up to $20,000 \text{ cm}^{-1}$ (VIS). In this wavenumber-range the visible thermal radiation, which is emitted by liquid slags (up to 1600°C), is insignificant. This holds especially for the UV-range at about $\nu \approx 30,000 \text{ cm}^{-1}$. In the wavenumber-range between $40,000 \text{ cm}^{-1}$ and $20,000 \text{ cm}^{-1}$ the reflection signals are undisturbed. The abnormally high reflectance of liquid slags in the UV-range is recognizable. It is caused by the CT-transitions of the pair $\text{Fe}^{3+} \dots \text{O}^{2-}$ [see photochemical reaction, equation (2)]. The strong increase of the reflectance at $\nu \approx 30,000 \text{ cm}^{-1}$ is caused by the exponential decrease of α_v (Urbach range) with an decrease of the wavenumber. The relation between UV/ VIS-reflectance of liquid slags with high contents of FeO_n and MnO_n (influence of the redox-state/oxygen partial pressure) are the subject of our research work.

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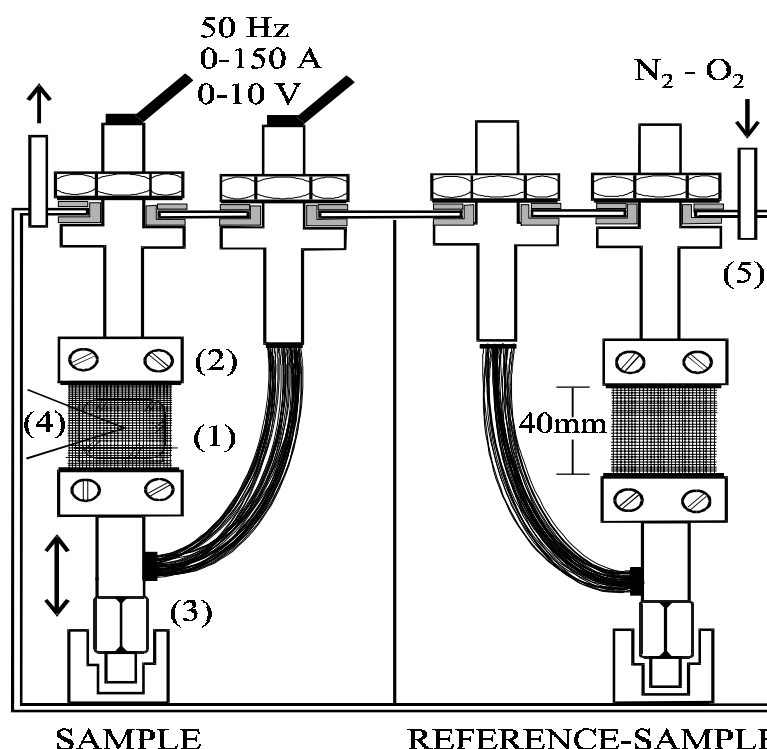


Figure 1: High-temperature cell: (1) Pt70Rh30-net, stable up to 1700 °C, (2) upper electrical contact, (3) moveable lower electrical contact, (4) PtRh18-thermocouple, (5) gas inlet

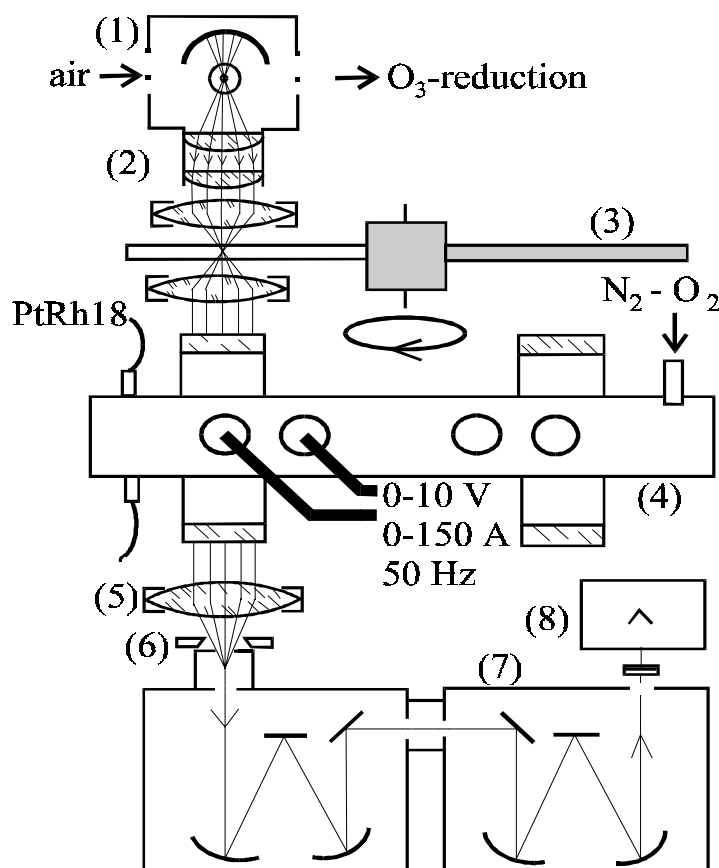


Figure 2: UV/VIS-Spectrometer: (1) 1000 W-Xe-lamp, (2,5) UV-grade fused silica condensor lenses, (3) chopper, (4) high-temperature cell, (6,7) double monochromator, (8) Si-detector with lock-in-amplifier and data acquisition system

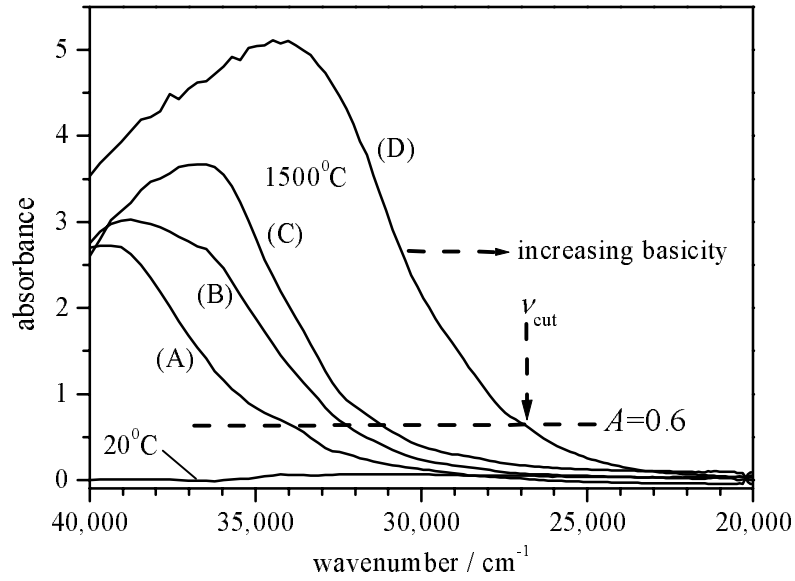


Figure 3: UV/VIS-absorption spectra (eigen-absorption) of different slags at 1500 °C, N₂-atmosphere [$p(\text{O}_2) \approx 10^{-5}$ bar], liquidus-temperature 1350 up to 1430 °C, $d = (0.12 \pm 0.02)$ mm, **(A):** 20CaO+60SiO₂+20Al₂O₃ / 1500 °C, **(B):** 32.5CaO+35SiO₂+32.5Al₂O₃ / 1500 °C, **(C):** 42CaO+38SiO₂+20Al₂O₃ / 1500 °C, **(D):** 45CaO+10SiO₂+45Al₂O₃ / 1500 °C, **20 °C:** comparison of the liquid state with the glassy quenched slag **(D)** .

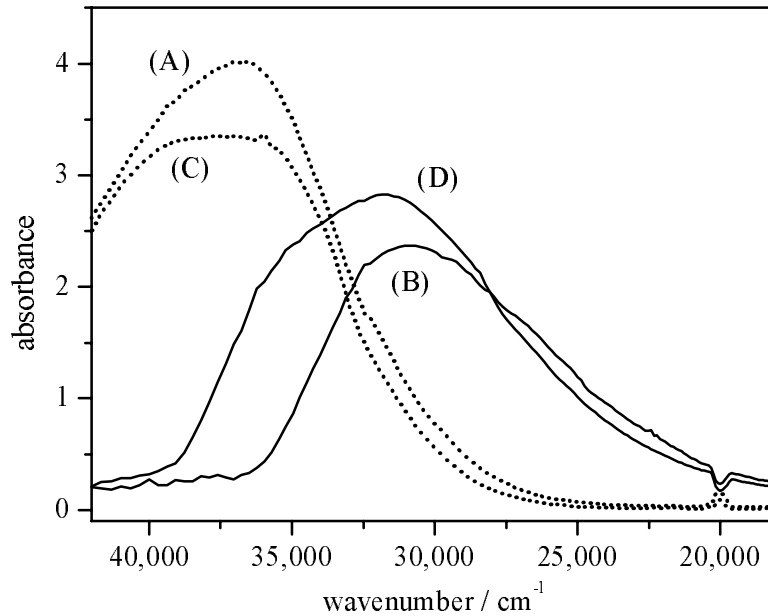


Figure 4: UV/VIS-spectra of slags, doped with an Fe₂O₃ mass content of 0.80 % , in air, oxidation degree $N(\text{Fe}^{3+})/N_0(\frac{1}{2}\text{Fe}_2\text{O}_3) = 0.70 \dots 0.80$, $d = (0.12 \pm 0.02)$ mm, **(A):** 45CaO+10SiO₂+45Al₂O₃ / 20 °C / vitreous state, **(B):** 45CaO+10SiO₂+45Al₂O₃ / 1500 °C / liquid state, **(C):** 20CaO+60SiO₂+20Al₂O₃ / 20 °C / vitreous state, **(D):** 20CaO+60SiO₂+20Al₂O₃ / 1500 °C / liquid state. The absorbance value contributed by the undoped matrix (no Fe₂O₃) has been subtracted.

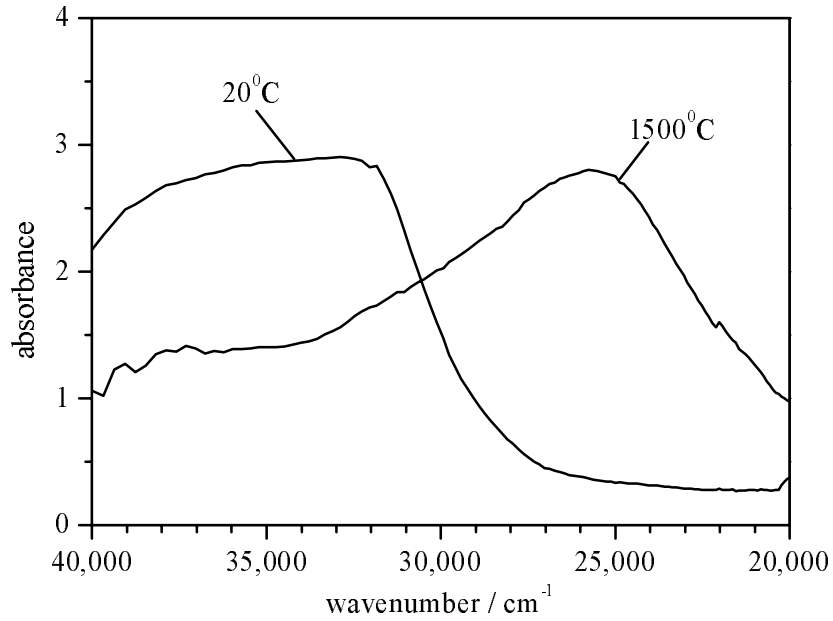


Figure 5: UV/VIS-spectra of slag $47\text{CaO}+33\text{Al}_2\text{O}_3+20\text{CaF}_2$ doped with 0.8 % Fe_2O_3 (mass content in %), solid state at 20 °C (quenched) and in the liquid state at 1500 °C, in air, oxidation degree $N(\text{Fe}^{3+})/N_0(1/2\text{Fe}_2\text{O}_3)>0.95$, $d=(0.12\pm0.02)$ mm. The absorbance value contributed by the undoped matrix (no Fe_2O_3) has been subtracted.

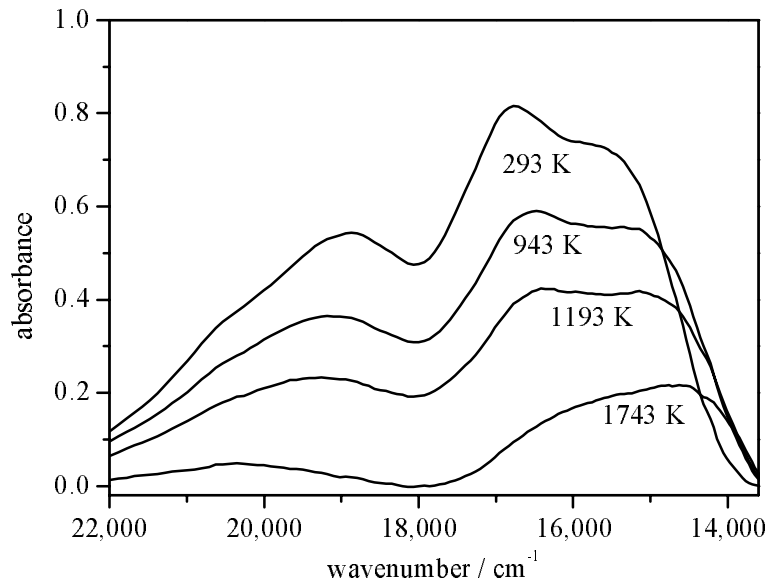


Figure 6: VIS-absorption spectrum of the silicate $54.5\text{CaO}+45.5\text{SiO}_2$ (mass content in %), doped with 1.5 % CoO , in air. d-d-electron transition $^4\text{A}_2(\text{F})\rightarrow^4\text{T}_1(\text{P})$ in the complex $\text{Co}^{2+}(\text{O}^{2-})_4$; parameter: 293 K up to a temperature above the liquidus temperature. Below the liquidus temperature (=1680 K) the samples are in the glassy state. $d=(0.12\pm0.02)$ mm

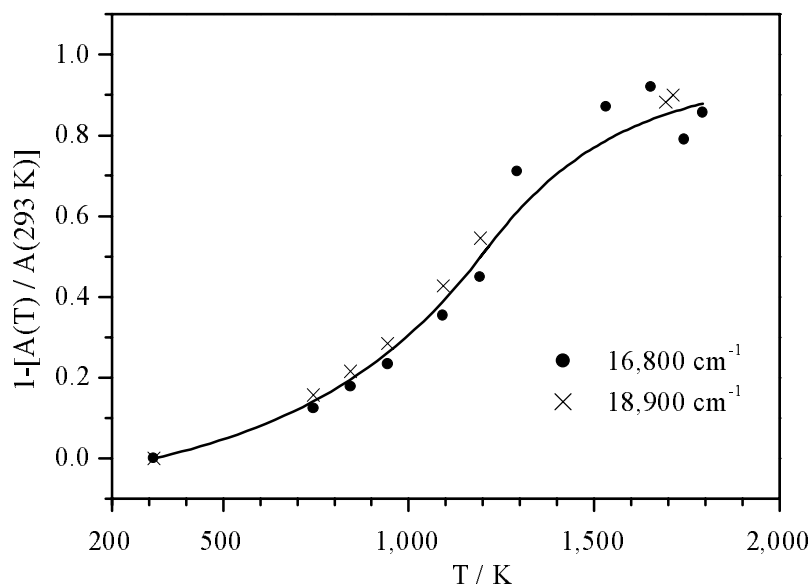


Figure 7: Dissociation degree of the complex $\text{Co}^{2+}(\text{O}^{2-})_4$ depending on the temperature 54.5CaO+45.5SiO₂ (mass content in %), doped with 1.5 % CoO, in air; calculated according to equation (9) from the height of the absorbance maxima for partial bands at ~16,800 and at ~18,900 cm⁻¹.

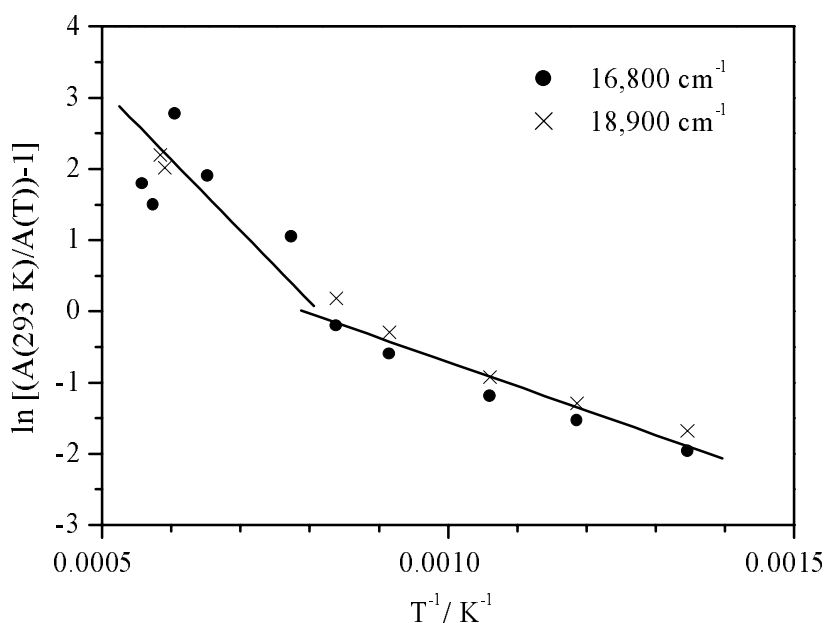


Figure 8: Determination of the dissociation enthalpy for the $\text{Co}^{2+}(\text{O}^{2-})_4$ -complex according to equations (11) and (12) in the silicate matrix 54.5CaO+45.5SiO₂ (mass content in %) doped with 1.5 % CoO, in air. The dependency of the absorbance maxima on the temperature has been analyzed at ~16,800 and at ~18,900 cm⁻¹.

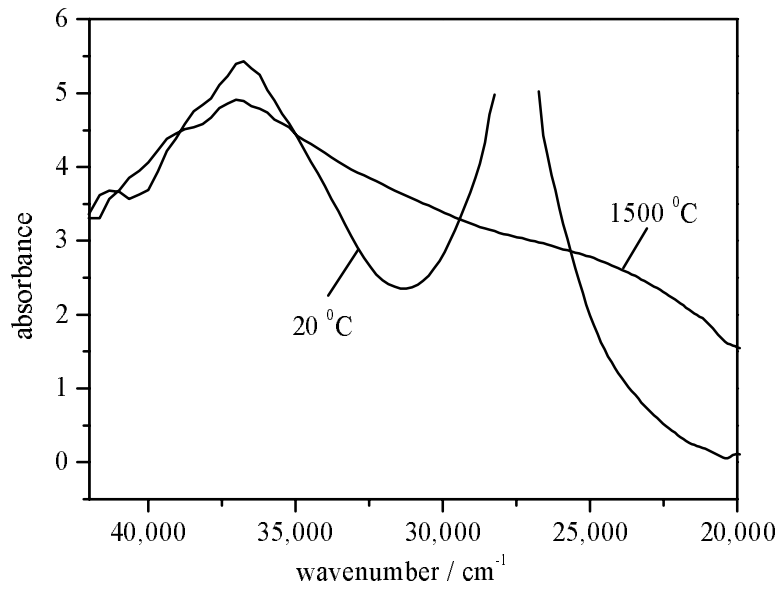


Figure 9: UV/VIS-absorption spectra of a slag with a mass content (%) of 54.5CaO +45.5SiO₂, doped with 2.0 % Cr₂O₃ in air, $d=(0.12\pm0.02)$ mm, oxidation degree $N(\text{CrO}_3)/N_0(\frac{1}{2}\text{Cr}_2\text{O}_3)=0.27$, **(A):**1500 °C / liquid state, **(B):**20 °C / glassy state

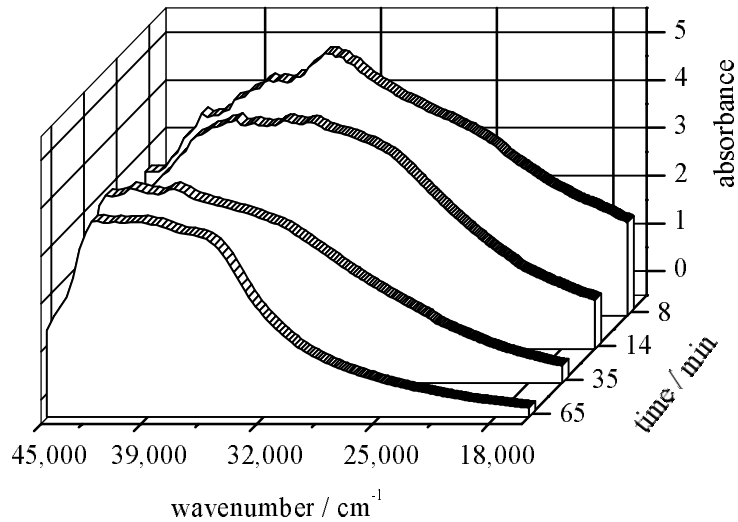


Figure 10: Time resolved UV/VIS absorption spectra of a slag with a mass content (%) of 54.5CaO+45.5SiO₂, initially doped with 2.0 % Cr₂O₃ in air, $d=(0.12\pm0.02)$ mm, oxidation degree $N(\text{CrO}_3)/N_0(\frac{1}{2}\text{Cr}_2\text{O}_3)=0.27$, 1500 °C / liquid state. Diffusion controlled evaporation of the volatile CrO₃: calculated chemical diffusion coefficient $D(\text{Cr}^{3+}/\text{Cr}^{6+})=(3.5\pm0.5)\cdot10^{-7}$ cm²/s, obtained from the absorbance as a function of time at the constant wavelength 370 nm ($\nu=27,027$ cm⁻¹).

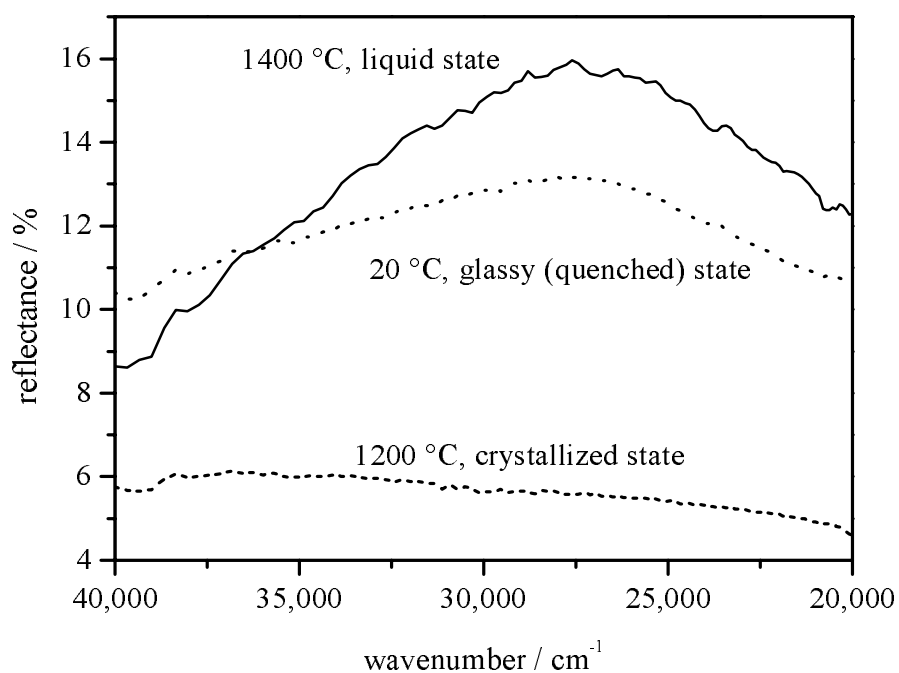


Figure 11: UV/VIS-reflection-spectrum of a CaO-SiO₂-Fe₂O₃-slag (air atmosphere) with the composition 32.7CaO+27.3SiO₂+40.0Fe₂O₃ (mass content in %); reference: polished Pt-surface