Original Paper

Identification method for infrared absorption spectra of semitransparent media by their emission data
Application to lime–aluminosilicate glasses at high temperatures

Rino Fabris and Jean Christophe Huclin

Vétrotex International, Chambéry (France)

Mohamed Sakami and Michel Lallemand

Laboratoire d'Etudes Thermiques, ENSMA CNRS, Poitiers (France)

The infrared absorption spectra of four lime–aluminosilicate glasses have been studied at high temperatures in the spectral range 1 to 5 μm. The glass composition varies essentially by the FeO content. The effect of temperature is pointed out up to 1450 °C. The emission spectrometry technique used is applied to thin slabs of semitransparent materials heated in plane-parallel platinum crucibles exposed to strong temperature gradients. The absorption coefficient is identified, for each wavelength, by a non-linear constraint optimization technique. As an illustration of the major influence of the spectrum on the heat exchanges in semitransparent devices, a modeling of the combined conductive/radiative heat transfer is performed in a glass wall.

Identifizierung von Infrarotabsorptionsspektren halbdurchlässiger Materialien an Hand der Emissionsdaten. Anwendung auf Kalk–Alumosilicatgläser bei hohen Temperaturen

Die Infrarotabsorptionsspektren von vier Kalk–Alumosilicatgläsern wurden bei hohen Temperaturen im Spektralbereich 1 bis 5 μm untersucht. Die Glaszusammensetzung wies erhebliche Schwankungen des FeO-Gehaltes auf. Der Temperatureinfluß bis 1450 °C wird aufgezeigt. Die Emissionsspektrometrie wird auf dünne Platten aus halbdurchlässigem Material angewendet, die in planparallelen Platintiegeln aufgeheizt und dabei hohen Temperaturgradienten unterworfen waren. Der Absorptionskoeffizient wird für jede Wellenlänge mit Hilfe eines nichtlinearen Optimierungsverfahrens (mit Zwangsbedingung) ermittelt. Zur Illustration des überragenden Einflusses des Spektrums auf den Wärmeaustausch in halbdurchlässigen Medien wird ein Modell für den kombinierten Wärmeübergang durch Leitung und Strahlung in einer Glaswand entwickelt.

1. Introduction

During the melting of glass and most of the forming processes, i.e. in the temperature range between 1000 and 1500 °C, heat is transferred mainly by radiation (ratio of radiative flux/conductive flux >20) in the infrared spectral interval ranging from 1 to 5 μm. Thus, thermal modeling of coupled conduction/convection/radiation heat transfer of glass tanks or forming devices requires the knowledge of the optical data of the basic material, especially of the absorption spectrum and its evolution with temperature in the solid and liquid states.

There are three main spectrometry methods for the determination of absorption spectra, the reflection method [1 and 2], the transmission method [3 to 5] and the emission method [6 to 8]. The last one appears to be the most practical way at high temperatures, but it requires special care. Indeed, on the one hand, if the glass sample is directly introduced into a furnace, it is necessary to separate the proper emission from the spurious radiation of the heater and, on the other hand, if the

glass is studied by the thin plane-parallel crucible technique, high-temperature gradients are generated in the specimen and have to be account for in order to determine the true physical spectrum [9 to 11].

In the present work, the absorption spectra of four lime–aluminosilicate glasses are identified by their emission up to 1450 °C in the wavelength interval 1 to 5 μm. The experimental emission data is obtained in presence of controlled temperature gradients by an original thin crucible technique and a point-by-point non-linear identification process is used.

2. Principle of the experimental method

The glass samples are plane-parallel slabs of Semitransparent Materials (labelled STM) in non-isothermal situation. The specimens are deposited in a platinum crucible heated electrically up to 1450 °C. At each run, two different samples of glasses are simultaneously investigated. The first one is the studied sample and the other one is a reference glass (a high-cobalt containing glass) of very high opacity in the whole wavelength range (vis-

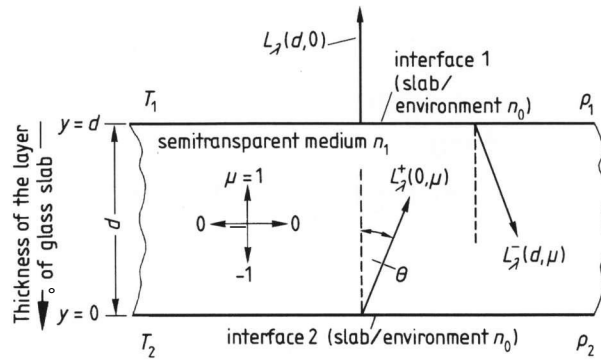Glastech. Ber. Glass Sci. Technol. 67 (1994) No. 4

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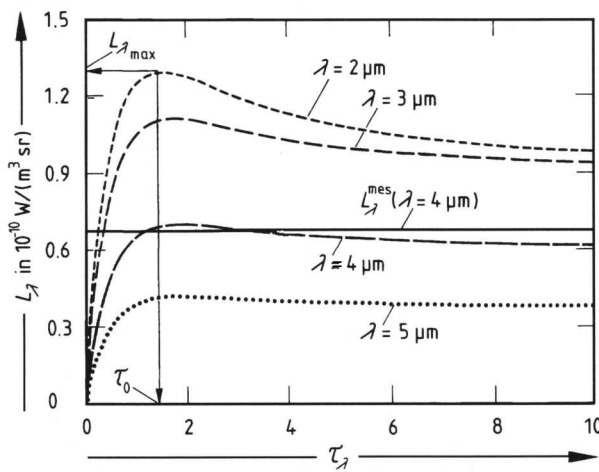Figure 1. Geometry of the plane-parallel semitransparent slab.

Figure 2. Theoretical spectral intensity L_λ as a function of the optical thickness τ_λ for different wavelengths.

ible and infrared). One assumes the temperature field in the slabs to be monodimensional.

When a temperature distribution is set up in a perfect plane-parallel semitransparent slab of thickness, d (figure 1) limited by two reflective boundaries, its internal spectral emission is governed by the Radiative Transfer Equation (RTE):

$$\frac{dL_\lambda(y)}{dy} + \kappa_\lambda L_\lambda(y) = n^2 \kappa_\lambda L_\lambda^0 [T(y)] \tag{1}$$

where $L_\lambda(y)$ is the monochromatic intensity, $L_\lambda^0 [T(y)]$ the local Planck function and κ_λ the absorption coefficient.

The problem consists, for a given wavelength, in the identification of the coefficient κ_λ, appearing in the differential equation (1), from the knowledge of the corresponding normal spectral outgoing intensity, $L_\lambda^{mes}(d)$.

The monochromatic normal emergent intensity of the slab is given by

$$L_\lambda(d) = \frac{(1-\varrho_1)}{[1-\varrho_1\varrho_2 \exp(-2\kappa_\lambda d)]} \cdot$$
$$\cdot \left\{ (1-\varrho_2) L_\lambda^0(T_f) \exp(-\kappa_\lambda d) + \right.$$
$$+ \kappa_\lambda \exp(-\kappa_\lambda d) \int_0^d L_\lambda^0 [T(y)]$$
$$\left. [\exp(\kappa_\lambda y) + \varrho_2 \exp(\kappa_\lambda y)] dy \right\} \tag{2}$$

where ϱ_1 and ϱ_2 are the reflectivities of the STM/air and the STM/crucible interfaces, respectively, and T_f is the crucible bottom temperature.

3. Identification method

The spectral absorption coefficient κ_λ of a glass may be obtained by an identification process through solving approximately the non-linear equation

$$L_\lambda(\kappa_\lambda, d) = L_\lambda^{mes}(d) \tag{3}$$

by the constrained optimization method [8]

$$\min \| L_\lambda(\kappa_\lambda, d) - L_\lambda^{mes}(d) \| \text{ subject to the conditions}$$
$$\| \kappa_\lambda d \| < b_\lambda \text{ and } \kappa_\lambda \in \text{Real} \tag{4}$$

where in the expression of $L_\lambda(\kappa_\lambda, d)$, given by equation (2), the measured temperature profile is inserted. In equation (4), b_λ is an a priori information chosen in such a way that for each wavelength equation (3) has a unique solution. In [11] equation (4) was approached by a Newton-Gauss iterative method; here a dichotomy method is used.

The a priori information is a result of the mathematical analysis of the model. In figure 2 the evolution of the theoretical intensity L_λ has been plotted as a function of the optical thickness, λ, or opacity, $\tau = \kappa_\lambda d$, for a set of wavelengths; the different curves were calculated with a mean specimen temperature of 1400 °C and a temperature difference of 200 K between its two interfaces. It is observed for some values of optical thickness that the two curves L_λ and L_λ^{mes} cross each other in two points, furthermore, L_λ passes through a maximum at τ_0. Accordingly, equation (3) has two mathematical solutions, one of them being physically irrelevant. But for $\tau < \tau_0$ the problem has a unique solution. Consequently, according to figure 2 one subjects the non-linear problem to the supplementary constraint $\tau < 1.7$. If no attention is paid to this special behavior, the solutions are dependent on the initially chosen values and wrong spectra may be recovered, as shown in figure 3.

As a matter of fact the proposed problem belongs to ill-posed problems (no unique solution, sensitivity to noise).

4. Experimental procedure

The glass sample holder is made up of pure platinum (($150 \times 30 \times 6$)mm^3); it is electrically heated by an ac current supply (figures 4a and b). Brass electrodes cooled

by water circulation are clamped on the side pieces and help to hold the device in place. The sample holder allows a three-dimensional displacement. The main platinum device provides four cylindrical crucibles (diameter 12 mm), each one of a different depth so that sample thicknesses can be achieved between 1.2 and 4 mm.

One assumes that in the longitudinal dimension no temperature gradients are present. On the other hand, since the glass slab exchanges heat simultaneously by natural convection and by radiation with the surroundings, a high temperature gradient results for the thickness of the slab. Small holes ($d/l = 0.5$ mm/5 mm) are drilled in the platinum in the vicinity of the glass/platinum interface in order to measure the bottom slab temperature by conventional pyrometry.

A complete sketch of the experimental facility is shown in figure 5. A water-cooled pipe is placed upon the glass sample, which serves to collect the useful infrared beam in the normal direction. Two diaphragms are connected to it in order to define the fixed solid angle of observation; it is helpful for elimination of spurious radiation coming from other samples and crucibles. The radiation beam is brought by a parabolic off-axis mirror which focuses on the entrance slit of a grating monochromator (a single-beam Perkin-Elmer 112 G connected to a microcomputer). Two kinds of detectors have been used, a PbS cell in the 1 to 2.6 µm region and a pneumatic detector of Golay for the 2.6 to 5 µm region. The chopping frequencies were 20 Hz and 1 kHz, respectively, for the Golay cell and the PbS detector. The electrical signal was analyzed by a lock-in amplifier EG&G 5206.

The emitted intensity of the sample is measured for each wavelength by determining the ratio between the emission of the sample and that of the reference medium, collected alternatively, by means of a sample holder translation from the sample to the reference glass, thus, providing the relative spectral emissivity

$$\varepsilon_\lambda^{\mathrm{rel}} = \frac{L_\lambda^{0\mathrm{mes}}}{L_\lambda^0(T_{\mathrm{ref}})} . \tag{5}$$

The surface temperature, T_{ref}, of the reference glass is measured by a pyrometer at 0.63 µm. Then, the surface temperature of the sample is deduced by comparison in the spectral opacity range of the reference glass emission and the sample emission, according to the relationship

$$\frac{(L_\lambda^{\mathrm{mes}})_{\mathrm{ref}}}{(L_\lambda^{\mathrm{mes}})_{\mathrm{gl}}} = \frac{L_\lambda^0(T_{\mathrm{ref}})}{L_\lambda^0(T_{\mathrm{gl}})} \tag{6}$$

where $L_{\lambda,\mathrm{gl}}^{\mathrm{mes}}$ and $L_{\lambda,\mathrm{ref}}^{\mathrm{mes}}$ denote the measured emission intensity of the sample in the opacity range of the spectrum (i.e. where the absorption is very strong) and the outgoing intensities. $L_\lambda^0(T_{\mathrm{ref}})$ and $L_\lambda^0(T_{\mathrm{gl}})$ are the Planck function at the temperature of the reference surface and of the studied glass, respectively.
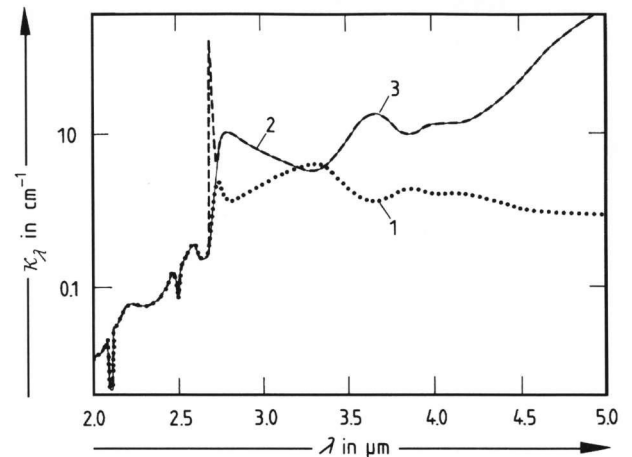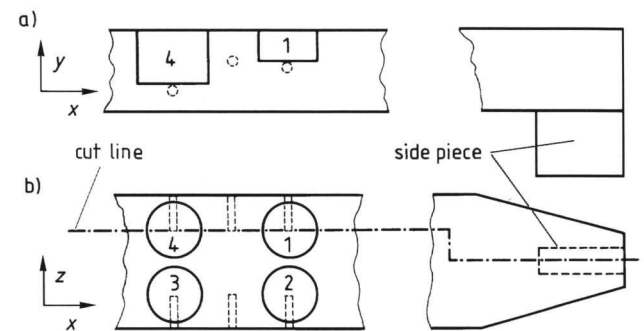

Figure 3. Comparison of the exact spectrum with the recovered spectra of a borosilicate glass as a function of the initial values for the non-linear identification process. Curve 1: recovered spectrum with the initial value $\tau_\lambda < \tau_0$, curve 2: recovered spectrum with the initial value $\tau_\lambda > \tau_0$, curve 3: exact spectrum.

Figures 4a and b. Schematic setup of a glass sample holder made up of pure platinum (($150 \times 30 \times 6$) mm³); a) cross-section in the $x-y$ plane, b) cross-section in the $x-z$ plane. Numbers 1 to 4 are glass crucibles. $-\cdot-\cdot$: cut line in the $x-z$ plane.
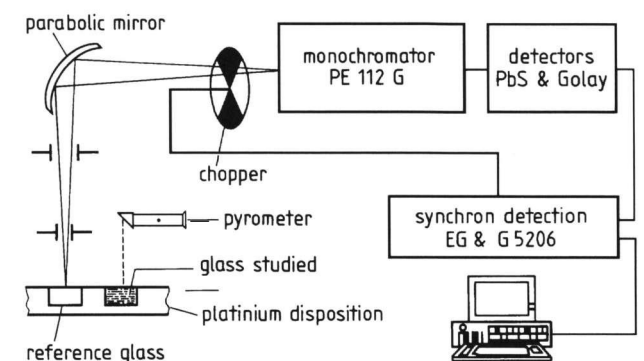

Figure 5. Experimental setup.

5. Studied glasses

The infrared absorption spectra of four lime–aluminosilicate glasses (whose compositions are reported in table 1) have been investigated by means of the emission of the non-isothermal glass slabs. These four glasses mainly differ in their ferrous iron content from which

Table 1. Glass compositions in wt%

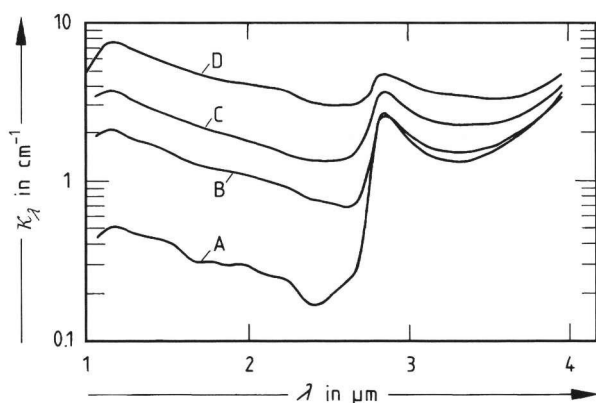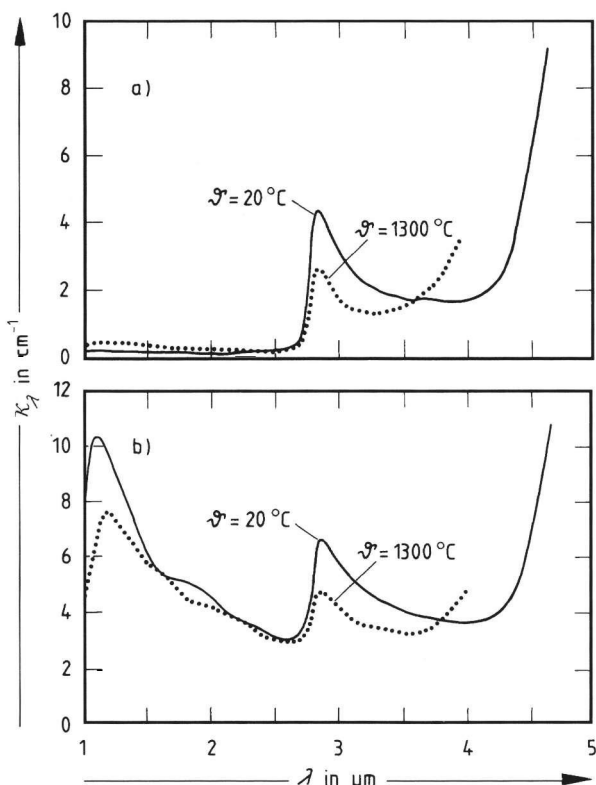| glass	SiO$_2$	Al$_2$O$_3$	CaO	C	Fe$_2$O$_3$	FeO
A	62	15	23	–	–	0.003
B	61.5	15	23	–	0.5	0.171
C	61.5	15	23	0.07	0.5	0.374
D	60	15	23	–	2	0.75

reference glass: E-glass with 2 wt% Co

Figure 6. Infrared absorption spectra of lime–aluminosilicate glasses A to D at 1300 °C.

Figures 7a and b. Comparison of the absorption spectra of lime–aluminosilicate glasses A and D at 1300 °C and at room temperature; a) glass sample A, b) glass sample D.

the absorption band centered around 1.2 μm originates which is of major interest for thermal application in glass manufacturing.
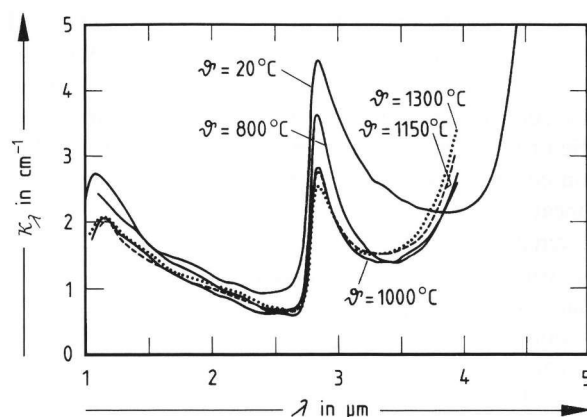

Figure 8. Absorption spectra of glass sample B at temperatures 20, 800, 1000, 1150 and 1300 °C.

The bottom face of the crucible was carefully polished and the normal reflectivity of the glass/platinum interface has been determined by the Fresnel formula taking into account the optical constants of both glass and platinum. The thickness of the glass layer was obtained by means of a video device which allows the optical control of the crucible fill up.

A temperature difference ranging from 100 K for the 1 mm thick crucible to 180 K for the 4 mm crucible was observed. All measurements have been performed in air at atmospheric pressure.

6. Identified spectra of lime–aluminosilicate glasses

For each wavelength of the investigated spectral range the emitted intensity is measured. Then, the temperature profile (assumed to be linear) is inserted in the expression of the theoretical intensity emission of the slab (equation (2)) and the optimization method (equation (4)) is developed according to the constraint $\tau < 1.7$ determined from figure 3.
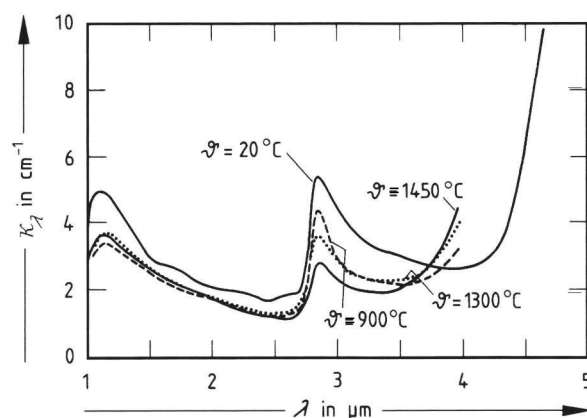

Figure 9. Absorption spectra of glass sample C at temperatures 20, 900, 1300 and 1450 °C.

In figure 6 the absorption spectra of the four specimens have been plotted in the wavelength range from 1 to 4 μm at 1300 °C. It can be seen that the four absorption spectra have the same trend, which are characteristic of the same vitreous network. The influence of the iron content, the only species which has been changed, appears clearly. A broad absorption band of Fe^{2+} ions centered around 1.1 μm can be noted, it is attributed to electronic transitions. Beyond 2.7 μm (the hydroxyl peak) the spectrum is due to atomic arrangement vibrations. From 2.7 to 4 μm the absorption coefficient is influenced by the concentration in hydroxyl groups [12 and 13]. Beyond 4.2 μm the observed strong increase of the spectra (the so-called thermal opacity range) is the high-frequency wing due to vibrations of the silica random lattice.

In figures 7 a and b the absorption spectra of glass specimens A and D at room temperature and at 1300 °C are reported and figures 8 and 9 display spectra for specimens B and C for different temperatures ranging from room temperature to 1450 °C. The main features are: the spectral shift of the opacity cut-off toward the short wavelength when the temperature increases [4 and 14] and, as a general trend, the lowering of the magnitude of all spectra, specially in the wavelength region from 2.7 to 4 μm. An exception is the clear glass (A) for which the converse effect is observed in the interval between 1 and 2.7 μm. However, the temperature effect on the absorption spectrum, even in the extreme temperature conditions, is weak when compared to the effect due to a small percent variation in the Fe_2O_3 content.

7. Application

The experimental results described in section 6. have been used to illustrate the influence of the ferrous band in the heat transfer of silicate glass. A plane-parallel glass wall is considered whose spectrum is of a variable magnitude in the spectral band from 1 to 2.7 μm. The wall has a thickness of 5 cm and exchanges heat by conduction and radiation only. The boundary conditions are as follows: One interface is at the fixed temperature, $\vartheta_1 = 1500$ °C, of emissivity $\varepsilon_1 = 0.4$, the other interface is exposed to a heat loss flux up to 100 kW/m², its emissivity is $\varepsilon_2 = 1$. The refractive index is taken as $n = 1.5$, the thermal conductivity of the medium is $k = 2$ W/(m K) and is assumed to be temperature-independent.

The absorption spectrum is divided into four gray bands

$\lambda = 0.5$ to 1.0 μm: $\kappa_\lambda = 0.01$ cm⁻¹;

$\lambda = 1$ to 2.7 μm: $\kappa_\lambda = 0.05, 0.5, 1.0$ and 3.0 cm⁻¹;

$\lambda = 2.7$ to 4.5 μm: $\kappa_\lambda = 2.5$ cm⁻¹;

$\lambda = 4.5$ to 15 μm: $\kappa_\lambda = 100$ cm⁻¹.

The one-dimensional coupled conductive/radiative heat transfer problem has been solved by a multiflux
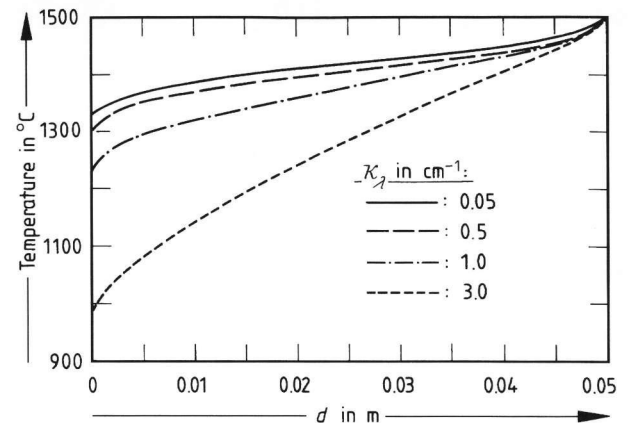

Figure 10. Influence of the 1 to 2.7 μm band on the temperature profile of a one-dimensional semitransparent wall. One temperature boundary is prescribed, the other is exposed to a constant heat loss.

method [9] and the results are shown in figure 10. It is demonstrated that the temperature gradient increases highly with the darkening of the second infrared spectrum band.

8. Conclusions

A special simple experimental emission spectrometry device has been used for the absorption spectra determination of semitransparent media. Its effectiveness increases highly with elevated temperature. It has the advantage to work in presence of important temperature gradients. Thanks to the non-linear proposed identification technique a clear identification of the spectrum is obtained.

9. Nomenclature
9.1. Symbols

b_λ	constraint factor
d	thickness in cm
k	thermal conductivity W/(m K)
L_λ	specific intensity in W/(m³ sr)
L_λ^0	Planck function in W/(m³ sr)
n	refractive index
STM	semitransparent medium (material)
T	temperature in K
y	abscissa
ε_λ	relative emissivity
$\varepsilon_1, \varepsilon_2$	wall emissivity
κ_λ	absorption coefficient in cm⁻¹
λ	wavelength in μm
ϱ_1, ϱ_2	reflectivity
τ	optical thickness or opacity
τ_{max}	maximum optical thickness

9.2. Superscripts

mes	measure
rel	relative

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9.3. Subscripts

f	bottom of crucible
gl	glass
λ	monochromatic quantity
ref	reference
1, 2	interfaces

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