International Journal of Thermophysics, Vol. 26, No. 4, July 2005 (© 2005)
DOI: 10.1007/s10765-005-6726-4

Temperature Measurement: Christiansen Wavelength and Blackbody Reference[1]

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The aim of this paper is to propose simple and reliable methods to measure temperatures exceeding 1500°C by pyrometry on dielectric heteropolar compounds. By adopting a spectroscopic approach based on a knowledge of the material (chemical composition, texture, size), it is suggested first to work at the Christiansen wavelength that is nearly independent of temperature, the texture, and the shape. Second, recent developments concerning plate blackbodies that are operable up to 1600 K are presented. Such compact systems are suitable to be installed in industrial heating devices in order to easily calibrate the pyrometer.

KEY WORDS: blackbody; black metal; Christiansen wavelength; heteropolar dielectric material.

1. INTRODUCTION

Pyrometric temperature determination is—according to ITS 90 [1]—the only technique used for temperature measurements above the freezing point of silver. But this method requires an accurate knowledge of the emittance of the material under consideration, at least at the working wavelength(s) of the pyrometer. In semitransparent materials and more particularly in most of dielectrics, often used in the conception of high temperature devices (furnace, thermal shield), emittance depends not only on temperature and wavelength but also on the thickness and the texture

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[1] Paper presented at the Seventh International Workshop on Subsecond Thermophysics, October 6–8, 2004, Orléans, France.

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of the material, its chemical composition, and the presence of impurities. Therefore, the accurate determination of the spectral emittance is difficult, and particularly in the semitransparent region that generally covers a spectral domain going from the mid-infrared to the visible. Since commercial pyrometers are often working in this spectral region, the measurement of the temperature appears particularly intricate. Moreover, the usage of a pyrometer involves its calibration with blackbody radiation as a reference. However, such systems are often expensive, bulky, difficult to manipulate, and sometimes sophisticated [2]. This brief overview shows the need to adopt alternative strategies to simplify pyrometric high-temperature measurements.

To overcome this difficulty, we have first developed a special setup dedicated to measurements of the spectral emittance of oxide compounds, homogenous or heterogeneous, up to 2600 K, and within a large spectral range (10 to 12,500 cm^{-1} or 1000 to 0.8 μm). In this paper, we will outline the key role of the "Christiansen wavelength" for the temperature determination [3]. It is a peculiar wavelength at which the material behaves like a blackbody, in the case of heteropolar dielectric compounds. At the same time, still in order to simplify pyrometric measurement, we have developed a nearly "blackbody" coating working up to 1600 K over a large spectral range. This coating is made with a black oxide, already used for the same application but at the lowest temperature [4]. It allows the design of a compact, efficient, and low cost device that is easy to set-up in an industrial process. In this paper the experimental apparatus will be briefly presented. Also, in this paper we will discuss how these innovations help to make the high-temperature measurements easier.

2. EXPERIMENTAL SETUP

Normal spectral emittance measurements are performed on a device based on a Bruker IFS 113 V interferometer. A detailed description is given in Ref. 3. The spectrometer is equipped with several detectors, allowing measurements from 10 to 12,500 cm^{-1}, i.e., from 0.8 to 1000 μm. Heating of the sample is carried out with a CO_2 laser ($\lambda = 10.6\,\mu\mathrm{m}$, $\O_{\mathrm{beam}} = 10\,\mathrm{mm}$) that allows heating of a dielectric sample up to 2600 K. For lowest temperatures, namely between 500 and 1200 K, we developed a thin homogeneous resistive heater based on an aluminosilicate ceramic tile [5]. We can use two methods to deduce the spectral emittance. The first, called the indirect method, is based on the second Kirchhoff law;

$$\varepsilon\,(\sigma, T) = 1 - R\,(\sigma, T) - T\,(\sigma, T) \tag{1}$$

where $\varepsilon(\sigma, T)$ is the normal spectral emittance, $R(\sigma, T)$ is the normal spectral reflectance, and $T(\sigma, T)$ is the normal spectral transmittance. In Eq. (1) σ corresponds to the wave number and T to the temperature. The second method, the so-called direct method, is based on the definition of the normal spectral emittance, previously evoked. According to the conception of our device [3], the latter method consists of measuring both the flux emitted by the sample,$\Phi_{\text{sample}}(\sigma, T)$, and by a blackbody reference, $\Phi^{\circ}(\sigma, T)$ (given by a commercial blackbody furnace Pyrox PY 5 in our case),

$$\varepsilon(\sigma, T) = \frac{\Phi_{\text{sample}}(\sigma, T)}{\Phi^{\circ}(\sigma, T)} \tag{2}$$

Redundancy of both methods had been established up to 1300 K, since the indirect method, involving a tubular furnace as the heating instrument, only performs up to this temperature [3]. However, this comparison on homogeneous compounds such as single crystals or glasses, allows us to validate the measurements realized with the direct method.

3. CHRISTIANSEN WAVELENGTH OF SEVERAL KINDS OF MATERIALS

In the following we introduce briefly some considerations about the Christiansen wavelength that is typical for heteropolar dielectric materials [6, 7]. Let us first consider the case of a homogeneous and non-diffusive plate of thickness d which is optically polished. One can demonstrate as already described in Ref. 8 that

$$\varepsilon(\sigma, T) = \frac{(1 - \rho(\sigma, T))\left(1 - e^{-4\pi\, k(\sigma, T) d}\right)}{1 - \rho(\sigma, T)\; e^{-4\pi\, k(\sigma, T) d}} \tag{3}$$

where $k(\sigma, T)$ is the extinction coefficient of the material and $\rho(\sigma, T)$ is the reflectivity defined at the interface air/material. Then $\rho(\sigma, T)$ is defined by the Fresnel relation, given for normal incident light to the material surface, by the following expression:

$$\rho(\sigma, T) = \left| \frac{\tilde{n}(\sigma, T) - 1}{\tilde{n}(\sigma, T) + 1} \right|^2 \tag{4}$$

where $\tilde{n}(\sigma, T)$ is the complex optical index, defined by ($\tilde{n}(\sigma, T) = n(\sigma, T) + ik(\sigma, T)$ $n(\sigma, T)$ is the real refractive index). Now the Christiansen wavelength is defined as the wavelength $\lambda_{\text{Christiansen}}$ where the refractive index is unity and for which the extinction coefficient is very low. Thus, at this peculiar wave number $\sigma_{\text{Christiansen}}$, Eq. (4) yields $\rho(\sigma_{\text{Christiansen}}, T) \cong 0$. If

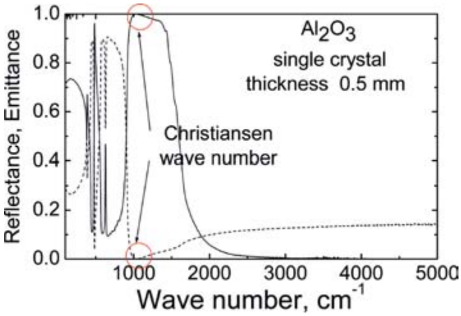

Fig. 1. Normal spectral reflectance (dotted line) and normal spectral emittance (solid line) of alumina (0.5 mm thick) at $T = 300\,\mathrm{K}$. The Christiansen frequency is indicated by circle.

the thickness of the material is sufficient, the value of the exponential term in Eq. (3) tends to zero. Therefore, at $\sigma_{\mathrm{Christiansen}}$, $\varepsilon\,(\sigma_{\mathrm{Christiansen}}, T) \cong 1$, i.e., at this characteristic wave number, a semitransparent compound can emit electromagnetic waves like a blackbody (see Fig. 1). Note that for common heteropolar materials (alumina, silica, spinel, carbide, nitride), this property is true for thicknesses larger than 100 μm. It is due to their absorption mechanisms occurring in the far-infrared range (lattice vibration). Therefore, the Christiansen wave number is just localized after the high wave-number limit of the phonon range as one can see in Fig. 1 for the case of an alumina single crystal (thickness = 500 μm, $T = 300\,\mathrm{K}$).

Such a standard wave number is very helpful for the determination of the spectral emittance by the direct method as we had explained in Ref. 3. It allows us to determine the temperature of the heating sample by using the interferometer as a pyrometer. We present in Fig. 2 the temperature dependence of the spectral emittance of an alumina single crystal, under normal atmosphere, up to the melting point. Note that the Christiansen wave number shifts slightly to lower wave numbers upon heating caused by an anharmonicity effect and thermal dilatation. It is independent or weakly dependent on temperature which is a preponderant advantage for making measurements in a large domain of temperature. Indeed, the variations of the emittance level in the mid-infrared range fully justify the use of the Christiansen wave number. When the compound becomes granular, becoming therefore porous which is the case for a ceramic, and if one asumes the same thickness criterion evoked previously in this section, this remarkable wave number remains present in the spectrum as shown in Fig. 3. Thus, these examples show the importance to work at this char-

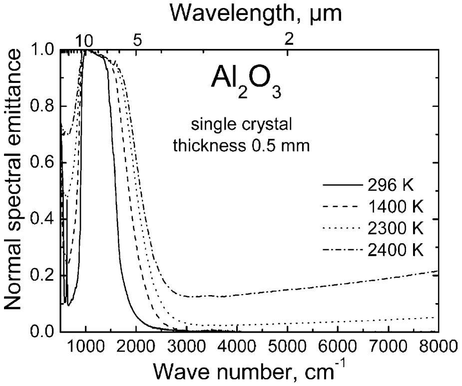

Fig. 2. Temperature dependence of the normal spectral emittance of alumina (0.5 mm thick) obtained by the direct method up to 2400 K (solid line: 296 K, dashed line: 1400 K, dotted line: 2300 K, dashed-dotted line: 2400 K).

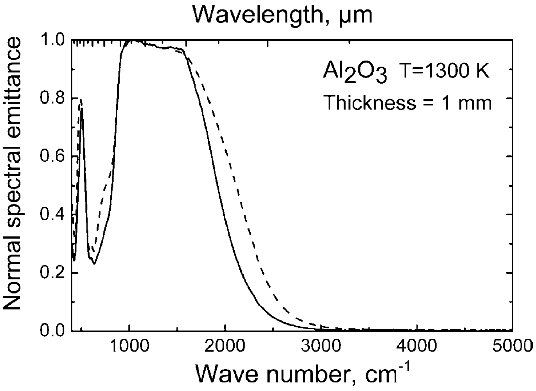

Fig. 3. Comparison between normal spectral emittance of alumina (1 mm thick) obtained for a single crystal (solid line) and a ceramic (dashed line) at 1300 K by the direct method.

acteristic wave number, where a dielectric behaves like a blackbody over a large domain of temperature and for different textures. It is then interesting to know this wavelength not only to make thermophysical studies at the laboratory scale but also to measure temperature for high-temperature industrial processes.

4. HIGH EMISSIVE COATING UP TO 1600 K

4.1. Thermo-optical Properties of Black Metal

Another challenging experience is to enlarge the spectral range where a material can emit electromagnetic waves like a blackbody. In this sense black metal materials exhibit a rather interesting behavior. Therefore, black metals of general formula $Ln_2MO_{4+\delta}$, where Ln is a rare earth, M is a transition metal, and δ is the amount of oxygen excess, present strong absorption mechanisms not only in the visible (from 12,500 to 25,000 cm^{-1}) but also in the whole infrared range, i.e., 10 to 12,500 cm^{-1}[9]. In the case of $Pr_2NiO_{4+\delta}$, it has been shown that, for $\delta >$ 0, the absorption mechanism remains sufficiently significant up to 1300 K to confer a high spectral emittance [10, 11]. The amount of oxygen excess is crucial to preserve these properties, since the stoichiometric compound ($\delta = 0$) does not present interesting optical properties in the mid-infrared range. Such a behavior is highlighted in Fig. 4 which presents several values of the absorption coefficient $K(\sigma, T)$; $K(\sigma, T)$ is given by

$$K(\sigma, T) = 4\pi\, k(\sigma, T)\ \sigma \tag{5}$$

where σ is the wave number. The values reported here have been obtained by fitting experimental reflectivity spectra measured on a $Pr_2NiO_{4+\delta}$ single crystal, with the aid of a dielectric function model well adapted to reproduce the optical response of conductive media [9, 10, 12]. It clearly shows, by using Eq. (3) and the corresponding reflectivity spectra [10], that a fictive single crystalline layer must be opaque for thicknesses larger than 2.5 μm and for temperatures up to 1300 K, which demonstrates that it is a surface property. By using this predictive information, $Pr_2NiO_{4+\delta}$ has been applied to enhance the radiative performances of an industrial infrared heater that was initially made of an aluminosilicate ceramic tile routinely working at T = 1000 K [4]. After the tile was covered by using the ultra-spray pyrolysis process [4, 5], it can be shown that its radiative behavior tends to that of a blackbody (98%). This spectacular result is not only due to the polaronic absorption but also to the rough morphology of the layer which consists of by an assembly of spheres of 20 to 30 μm diameter [4]. It allows us to build a compact and light "blackbody" system, coming in the form of a disc (Ø = 10 mm) and designed in its first version to work at, at least, $T = 1000$ K.

4.2. Chemical Stability of Pr_2 $NiO_{4+\delta}$

To make pyrometric calibrations at higher temperature with larger thin plates, we have first investigated the chemical stability of this oxide

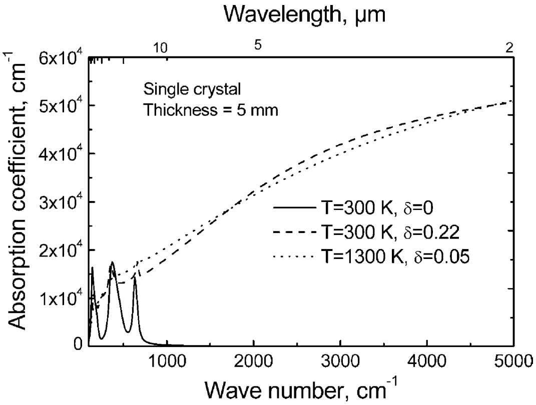

Fig. 4. Temperature dependence of the absorption coefficient of a single crystal of $Pr_2NiO_{4+\delta}$, within the ab plane (solid line: 300 K, $\delta = 0.0$; dashed line: 300 K. $\delta = 0.22$, dotted line: 1300 K, $\delta = 0.05$). All the curves have been obtained by using the fit of the experimental reflectivity spectra with the help of a dielectric function model [9].

up to 1600 K. Thermogravimetric analysis (TGA) measurements of powder have been made with a symmetrical balance of high sensitivity (TGA 24-24, Setaram, Lyon, sensitivity ±1 μg) to follow the oxygen over-stoichiometry evolution (δ) [13]. We have analyzed a fine black powder obtained before by following a modified sol-gel route [14]. Therefore, by varying the atmosphere of these studies (Ar, air), we have observed that δ ranges between 0.22 at $T = 300$ K to a value always superior to 0.05 up to 1600 K (Fig. 5). This means that the polaronic density remains sufficiently high to preserve the desired optical properties up to these temperatures. Although thermogravimetric measurements up to the melting of this compound should be done, one can expect, by extrapolating our actual mass loss data, that this compound is very suitable for building a thin plate blackbody that is able to work at more severe thermal conditions.

From these results, we have recently developed a system by using a chemical route for making the rough deposit [11]. This route is actually applied in the field of the solid oxide fuel cells [15, 16]. We produce a paste by mixing the appropriate amount of $Pr_2NiO_{4+\delta}$ powder with an organic media whose use is well known in the field of the solid oxide fuel cell [11]. The paste is then applied with a brush on the substrate ($40 \times 40\,mm^2$) and *ex situ* annealed up to 1473 K during one hour in a muffle furnace. An X-ray diffractogram (XRD) confirms that the deposit is

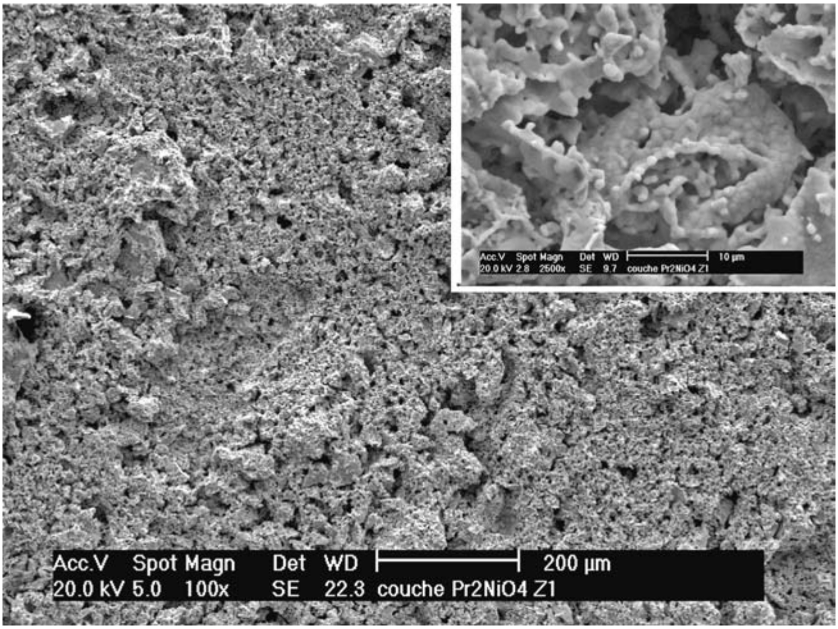

Fig. 5. SEM photograph of a rough deposit of $Pr_2NiO_{4.22}$ on a ceramic tile (×100). On the top right corner, the deposit is observed with a higher magnification (×2500).

composed of $Pr_2NiO_{4+\delta}$. Scanning electronic microscopy (SEM) photography shows that the layer is nicely spaced out as one can see in Fig. 5. This complex texture is appropriate to generate micro-blackbody cavities. Finally we obtain an optical response nearly equal to the one of the blackbody (0.97) up to 1340 K. Limitation of this system lies on the choice of the ceramic substrate that is damaged at the highest temperatures used. To overcome this latter difficulty, different kinds of substrates are actually tested. In addition, enhancement of the texture is planned to reach higher values of the spectral emittance (Fig. 6).

5. CONCLUSION

To facilitate pyrometric high temperature measurements, we have adopted a spectroscopic approach based on the knowledge of the material (chemical composition, texture). In particular concerning the actual temperature measurement at the surface of a dielectric sample, we suggest here to work at the "Christiansen wavelength,"

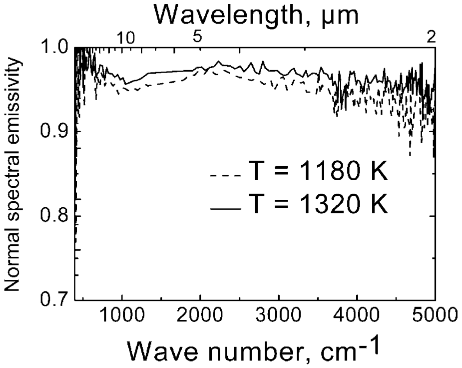

Fig. 6. Normal spectral emissivity of the $Pr_2NiO_{4.22}$ deposit at T = 1180 K (dashed line) and T= 1320 K (solid line).

(i) a wavelength at which spectral emittance exceeds 0.999, making the temperature measurement highly accurate and reliable, under usual thicknesses, and

(ii) a wavelength which is independent or weakly dependent on temperature.

At this specific wavelength, the material's surface emits like a blackbody *independent of its shape and texture.*

What is more of a remarkable property is emphasized over a larger spectral range, when we look carefully at the thermo-optical properties of the black metal family. Such compounds have great potential for use in the design of thin plate blackbodies, being able to work at 1600 K. Current experimental work is continuing to consolidate this promising first result.

ACKNOWLEDGMENTS

The author thanks Dr. A. Douy (CRMHT-Orléans) for supplying the $Pr_2NiO_{4+\delta}$ powder and E. Veron (CRMHT Orléans) for the XRD and SEM characterization. G. Duneau (ITECH System, Onzain, France) is acknowledged for providing the ceramic substrate.

REFERENCES

1. H. Preston-Thomas, *Metrologica* **27**:3 (1990).
2. S. A. Ogarev, B. B. Khlevnoy, M. L. Samaylov, V. I. Shapoval, and V. I. Sapritsky, *Proc. TEMPEKO* (2004).

3. O. Rozenbaum, D. De Sousa Meneses, S. Chermanne, Y. Auger, and P. Echegut, *Rev. Sci. Instrum.* **70:**4020 (1999).
4. B. Rousseau, A. Sin, F. Weiss, P. Odier, M. Chabin, and P. Echegut, *Appl. Phys. Lett.* **79:**3633 (2001).
5. B. Rousseau, D. De Barros, J. La Manna, F. Weiss, G. Duneau, P. Odier, D. De Sousa Meneses, Y. Auger, P. Melin, and P. Echegut, *Rev. Sci. Instrum.* **75:**2884 (2004)
6. R. Bowling Barnes and L. Lyman Bonner, *Phys. Rev.* **49:**732 (1936).
7. C. F. Bohren and D. R. Huffmann, *Absorption and Scattering of Light by Small Particles* (Wiley Interscience, New York, 1983).
8. R. Siegel and J. R. Howell, *Thermal Radiation of Heat Transfer* (Taylor and Francis, Bristol, Pennsylvania, 1992), pp. 970–985.
9. F. Gervais, *Mat. Sci. Eng.* **39:**22 (2002).
10. B. Rousseau, *Ph. D. Thesis* (University of Orléans, 2001).
11. B. Rousseau, A. Douy, E. Veron, and P. Echegut, private communication.
12. B. Rousseau, J. M. Bassat, A. Blin, M. S. De Oliveira, P. Odier, C. Marin, and P. Simon, *Solid State Sci.* **6:**1131 (2004)
13. C. Allançon, J. Rodriguez-Carvajal, M. T. Fernandez-Diaz, P. Odier, J. M. Bassat, J. P. Loup, and J. L. Martinez, *Z. Phys. B* **100:**85 (1996).
14. P. Holtappels and C. Bagger, *J. Eur. Ceram. Soc.* **22:**41 (2002).
15. J. Yeon Yi and G. Man Choi, *J. Eur. Ceram. Soc.* **24:**1359 (2004).
16. A. Douy and P. Odier, *Mat. Res. Bull.* **24:**1119 (1992).