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Development of an Apparatus for the Determination of Spectral Reflectivity at High Temperatures in the Visible[1]

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The paper presents a reflectometer for high temperature measurements. In this apparatus, the directional-hemispherical spectral reflectivity is measured by comparing the optical response of the sample to white light with the response of a reference material. The reflected light, collected by an integrating sphere, is dispersed in a spectrograph and detected by an ICCD camera. This procedure allows the simultaneous measurement of the reflectivity in a large, continuous wavelength range (presently 510 to 860 nm). An electrical resistance heater is used to heat the samples up to about 1200 K; for higher temperatures a flash-lamp pumped dye laser is used. To avoid laser induced plasma generation, the integrating sphere is placed inside a vacuum chamber, which also allows measurements under a controlled atmosphere. The response of the apparatus is calibrated to an absolute scale which allows the determination of the sample temperature by fitting the thermal emission spectrum with Planck's formula. To check the performance of the apparatus, measurements on Fe_2O_3 (hematite) and NiO have been carried out.

KEY WORDS: emissivity; Fe_2O_3; laser heating; NiO; radiative properties.

1. INTRODUCTION

The solar technology research at the Paul Scherrer Institute is focused on the transformation and storage of solar energy. To provide chemical energy carriers, so called solar fuels, the thermochemical reduction of various metal oxides at very high temperatures ($T > 2000$ K) is investigated [1]. In this context, the spectral emissivity of hot surfaces is an important

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parameter necessary for both calculating the radiant heat transfer and allowing precise pyrometric temperature measurements. In addition, the knowledge of reflectivity and emissivity of materials used in the system, either as reactants of the solar chemical reactions or as construction materials of the reactor itself, plays a decisive role in the choice of the reactor design, its modelling, and in the estimation of the final performance of the entire process. In spite of their importance, radiative properties of the metal oxides used in the above mentioned thermochemical cycles, as well as many of the materials currently used in high temperature applications (e.g., alumina and zirconia), are known only at moderate temperatures or, at relatively high temperatures, for some discrete wavelengths [2]. In order to fill the void of missing necessary data, an apparatus for measuring the spectral reflectivity of condensed samples in the visible and near infrared range for high temperatures has been developed in our laboratory. In the following sections, the method used and the apparatus built will be described. Results obtained on Fe_2O_3 and NiO will be presented.

2. PRINCIPLE OF THE METHOD

2.1. Measurement Procedure and Data Analysis

The apparatus built allows the measurement of the spectral directional-hemispherical reflectivity ρ[4] as a function of temperature. The technique is based on the general scheme of the integrating sphere technique, where a comparative procedure is used [2]. For the measurements, the sample is placed in an integrating sphere and white light is focused on its surface. The light reflected from the sample and integrated by the sphere, ϕ_s, is detected by an ICCD camera. The same procedure is applied to a reference target of known reflectivity ρ_{ref}, the flux of reflected light measured being ϕ_{ref}. The two detected fluxes, ϕ_s and ϕ_{ref}, are compared and the reflectivity of the sample, ρ_s, is obtained from

$$\rho_s(\lambda, T) = \rho_{ref}(\lambda, T)\,\frac{\phi_s(\lambda, T)}{\phi_{ref}(\lambda, T)} \qquad (1)$$

where λ is the wavelength and T the temperature. From Eq. (1) follows that if the chosen reference material has a reflectivity equal to 1 in the investigated range of temperatures and wavelengths, the reflectivity of the sample is directly obtained from the measured fluxes.

[4] From now on, the spectral directional-hemispherical reflectivity, ρ, will be referred in the text simply as reflectivity.

Because the measurements are performed at high temperature, it must be taken into account that the thermal emission from the material is superimposed on the reflected light. Thus, for calculating the reflectivity, four spectra are taken: the spectrum of the hot sample with the white probing light focused on its surface ϕ_s^{light}, the thermal emission of the hot sample without the probing light ϕ_s^{hot}, the spectrum of the illuminated reference ϕ_{ref}^{light}, and its thermal emitted light, which, being the reference kept at room temperature, reduces to the background signal ϕ_{bg}. The reflectivity of the hot sample, is derived from

$$\rho_s = \frac{\phi_s^{light} - \phi_s^{hot}}{\phi_{ref}^{light} - \phi_{bg}} \tag{2}$$

where ρ_{ref} has been set equal to 1.

The apparatus is calibrated to an absolute scale and the temperature of the sample can be obtained by fitting the thermally emitted radiative energy to Planck's equation, the emissivity being known from the measured reflectivity as $\varepsilon = 1 - \rho$ (for opaque samples). For temperatures lower than 1200 K, the thermal emission is too weak for a reliable temperature fit, and therefore the surface temperature of the sample is estimated [3] from the temperature measured by a thermocouple on its rear side.

2.2. Experimental Setup

The apparatus is shown schematically in Fig. 1. The sample, a disk of 8mm diameter and ≈ 1 to 2 mm thickness, is located in the center of the integrating sphere on a revolving manipulator. It is placed on top of a small electric heater (Heat Wave/Spectra-Mat, Inc., E 292) with which sample temperatures up to 1200 K can be reached. The reference is mounted on the opposite side of the manipulator. Rotating the arm by 180° moves the sample or the reference in the measurement position. The manipulator, apart from serving as the sample holder, encloses the optical fiber used to collect the reflected light, the thermocouples, the leads for the electric heater, and the drains for the water cooling system.

The integrating sphere and the manipulator are coated with Spectralon, a Teflon-based Lambertian reflecting material with a reflectance close to unity in the visible [4]. Spectralon is also used for the reference. Three holes on the top of the sphere give access to the optical instrumentation. The hole on the left in Fig. 1 corresponds to the entrance port for the white probe light, the hole on the right for the laser, whereas the hole in the middle gives access to a video camera, used to align the system and monitor the sample during the experiments.

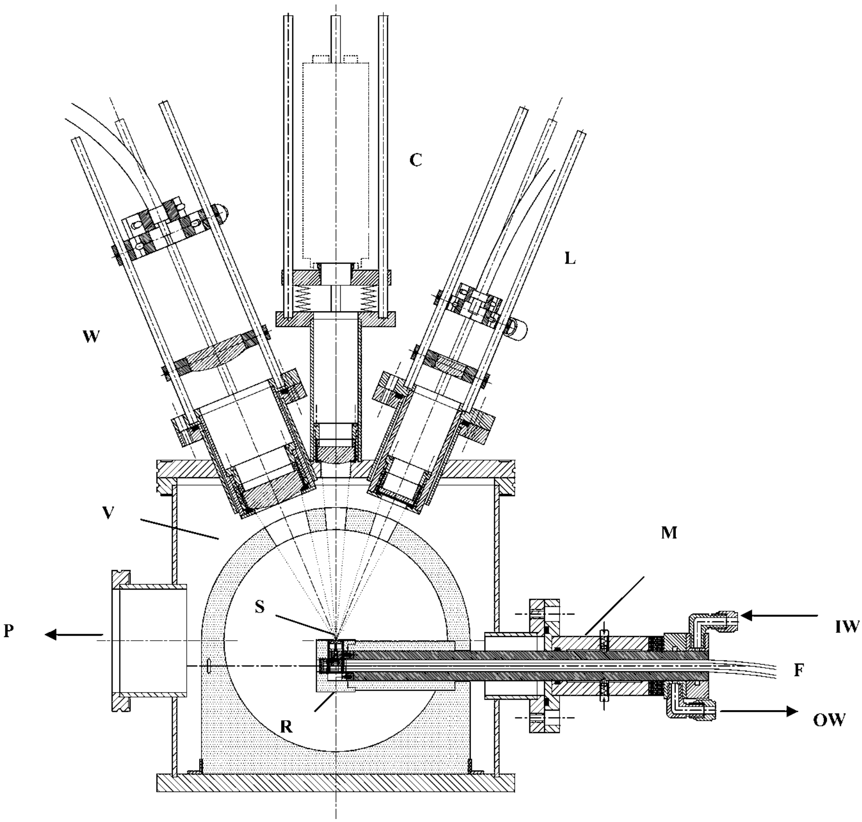

Fig. 1. Schematic of the apparatus for reflectivity measurements. S, sample; R, reference; M, rotatable manipulator; F, optical fiber; IW, inlet water cooling; OW, outlet water cooling; P, vacuum pump; V, vacuum chamber; W, white light, C, monitoring camera; L, laser.

The white light of a 250 W quartz-halogen lamp is focused on the sample in a spot of 3 mm diameter. The light reflected is collected by the integrating sphere, sent through an optical fiber to a spectrograph (ARC Spectra Pro 275; 300 $g \cdot mm^{-1}$) and detected with an intensified CCD-camera (La Vision, DynaMight; photocathode S 25) in the wavelength range 510 to 860 nm. All data are acquired and processed by a PC.

To heat the sample to temperatures above 1200 K, a flash lamp pumped dye laser operating at 596 nm (Candela, laser medium Rhodamine 6G) is used. The laser light is focused on the sample surface, and its spot overlaps the spot of the white light matching its size. With a pulse width of 300 μs, power densities up to 0.15 $MW \cdot cm^{-2}$ can be reached on the sample surface. In order to filter out the direct laser light, a notch-filter is placed at the entrance of the spectrograph. This causes an artifact appearing in all the recorded spectra at around 600 nm.

To suppress plasma generation, the integrating sphere is placed inside a cylindrical vacuum chamber. The chamber permits measurements carried out under controlled atmospheres or under a dynamic vacuum down to a pressure of 10^{-3} Pa.

3. REFLECTIVITY MEASUREMENTS

The reflectivity of hematite (Fluka, purity 99.9%) was measured at temperatures up to 1200 K. The samples, pellets of pressed powder of 8 mm in diameter and 0.9 mm in thickness, pressed at 62×10^6 Pa had a density of $3.00\ g \cdot cm^{-3}$. The measured reflectivity decreases with increasing the temperature. The plotted values in Fig. 2 are averages obtained from various experiments with different samples. The calculated standard deviation depends on wavelength and temperature, its average value being approximately 4% of the mean. Measurements carried out on the same sample show a reproducibility better than 1.5%.

The reflectivity of NiO (Merck, purity 90%) was measured for temperatures up to 1100 K. The samples, pellets of pressed powder of 8 mm in diameter and around 1.3 mm in thickness, prepared at 62×10^6 Pa have been sintered at 1573 K for 3 hours in air. After the treatment the samples had a

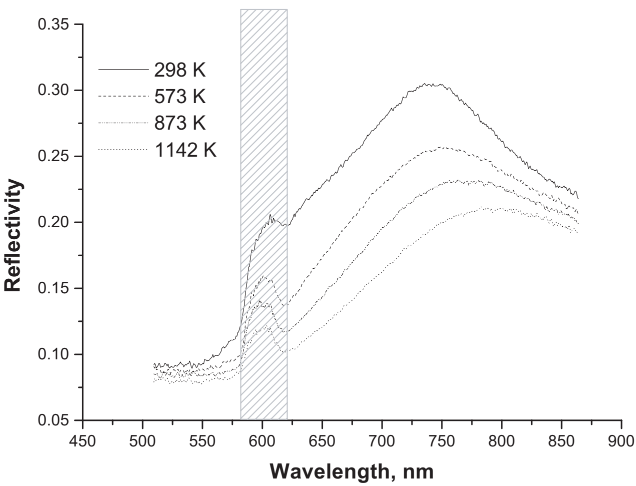

Fig. 2. Reflectivity of Fe_2O_3 as a function of wavelength for four different temperatures (hatched region: notch filter artifact).

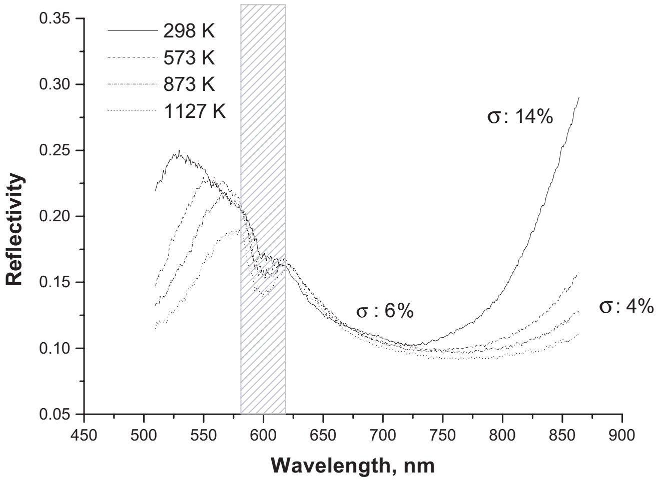

Fig. 3. Reflectivity of NiO as a function of wavelength for four different temperatures (hatched region: notch filter artifact).

density of 4.4 $g \cdot cm^{-3}$ and showed a greenish color. Again the measured reflectivity decreases monotonically with temperature. Figure 3 shows the values obtained as an average from different experiments. The calculated standard deviation varies between 4 and 6% of the mean for all the temperatures and wavelengths, apart for the room temperature values above 800 nm where it increases to 14%.

4. DISCUSSION

A comparison of the measured reflectivities for Fe_2O_3 and NiO with literature data was only possible at room temperature, since no data were found for elevated temperatures. In Fig. 4 the experimental values at room temperature for Fe_2O_3 are compared with literature data. The results are in good agreement in the range of 600 to 750 nm, while for lower and higher wavelengths the literature values are systematically lower. Because the tendency and the shape of the curves are in agreement with each other, the difference in the absolute values is attributed to the different morphology of the samples used in the experiments.

In Fig. 5 the experimental values of NiO at room temperature are compared with literature data. The agreement is excellent for values above 650 nm, while a systematic deviation can be shown at lower wavelengths. The discrepancy is attributed also in this case to the different morphology of the studied samples.

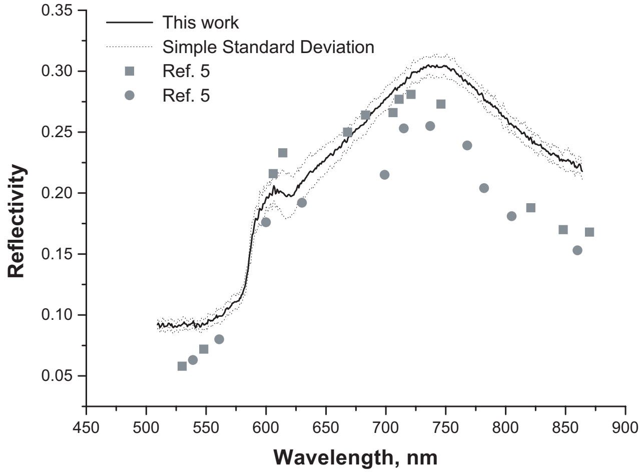

Fig. 4. Reflectivity of Fe_2O_3 as a function of wavelength at room temperature.

Measurements at temperatures above 1200 K using laser heating have been carried out for both the materials. For data collected during the laser pulse, however, even if the reflectivity itself could be obtained, a precise temperature determination of the sample surface temperature failed because of a broad-band emission from the laser superimposed to the spectra. Only

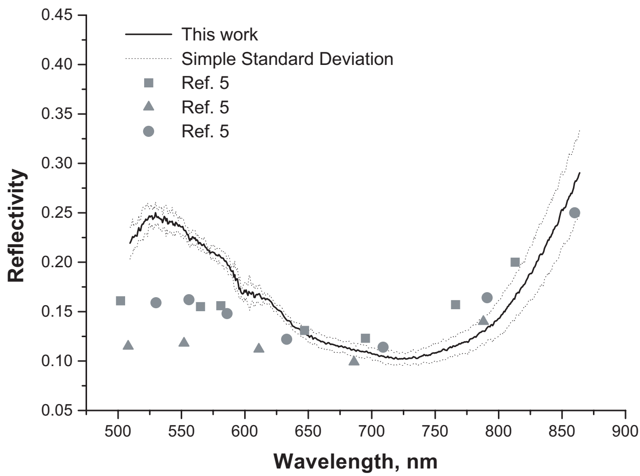

Fig. 5. Reflectivity of NiO as a function of wavelength at room temperature.

spectra recorded after the laser pulse were suitable for the temperature fit. Experiments by laser heating are currently in progress.

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