Journal of Engineering Physics and Thermophysics, Vol. 65, No. 2, 1993

SUBSECOND MEASUREMENTS OF OPTICAL PROPERTIES IN THE SPECTRAL RANGE 0.4-1.1 μm IN THE VICINITY OF HIGH-TEMPERATURE PHASE TRANSITIONS OF REFRACTORY OXIDES

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UDC 536.7

A new dynamic method is proposed for measuring the spectral hemispherical-directional reflection coefficients within the spectral range 0.4-1.1 μm in vicinity of high-temperature phase transformations of refractory oxides. Diffuse polychromatic irradiation of the tested sample makes it possible to exclude the effect of a sharp change of the indicatrix of reflection in the case of phase transformations and to obtain a large bulk of data for exact determination of the temperatures of phase transitions. The methodical error in determination of the spectral hemispherical-directional reflection coefficients does not exceed 2% within the investigated temperature range.

Introduction. The basic complexity of spectral reflectivity investigations in the zone of high-temperature phase transformations of refractory materials is related to a sharp change in the reflection mode at the transition point. For instance, when oxides are melted, the predominantly diffuse reflection is replaced by the predominantly specular one [1]. A change of the indicatrix of reflection at phase transitions complicates the problem of collecting the radiation reflected into a hemisphere, and therefore in the majority of cases an experimentalist tackles this problem with the aid of an integrating sphere. If in determining the spectral reflection coefficients in the vicinity of phase transitions a sample surface is subjected to directional illumination [2, 3, 4], determination of the hemispherical-directional reflection coefficient becomes problematic since a change of the reflection mode in phase transformations entails disturbance in the uniform illumination of the walls of the integrating sphere. But since uniformity of illuminating the sphere walls is the main condition in direct measurement of the hemispherical-directional reflection coefficient with the aid of the integrating sphere and the illumination itself enters into the formula for the reflection coefficient calculation, the method becomes incorrect and inapplicable in the vicinity of phase transformations.

We propose a new dynamic method for investigating the spectral hemispherical-directional reflection coefficient near high-temperature phase transitions of refractory materials. To avoid a sharp change of the indicatrix of reflection at phase transitions, we expose the sample to diffuse illumination.

1. Procedure and Experimental Setup. The indicatrix of reflection characterizes the angular distribution of radiation reflected from the investigated surface to a hemisphere at the prescribed angle of incidence. If instead of measuring the hemisphere illuminance at the directional incidence of the beam to a sample we apply the reverse principle, i.e., the hemispherical diffuse illumination of the sample and measurement of the radiant flux reflected from the sample in the prescribed direction, then we may obtain uniform light reflection from the sample and eliminate the effect of a sharp change of the indicatrix of reflection at phase transitions.

In this case, the Helmholtz reversibility property lies behind the method of measurement of the hemispherical-directional reflection coefficient, according to which [5]

$$\rho_\lambda(\theta,\ \psi,\ 2\pi) = \rho_\lambda(2\pi,\ \theta,\ \psi). \qquad (1)$$

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 65, No. 2, pp. 223-228, August, 1993. Original article submitted August 26, 1992.

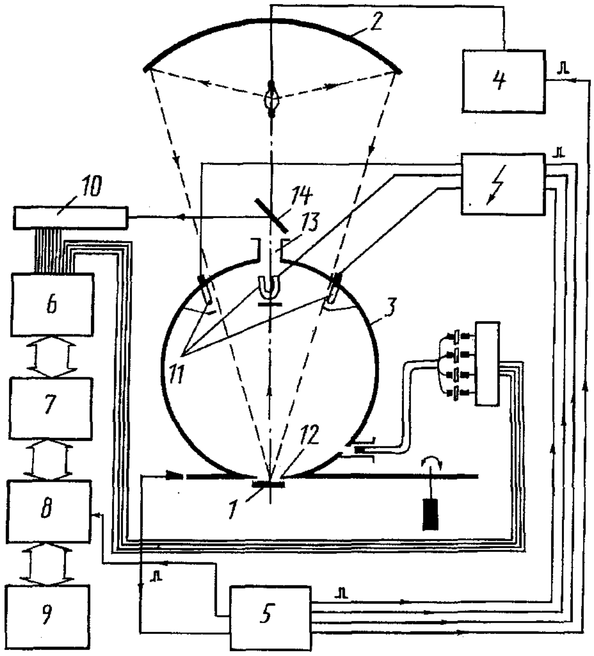

Fig. 1. Schematic of the experimental setup.

This means that the reflection coefficient of a substance irradiated at the angle (θ, ψ) and uniformly reflecting to the hemisphere is equal to that of the diffusely illuminated substance whose reflected energy is recorded in the direction (θ_r, ψ_r), with the angles (θ_r, ψ_r) and (θ, ψ) being equal.

The experimental setup consists of a system for heating the sample, a system for diffuse illumination of the sample, a systen of rapid suppression of the thermal radiation source, and a recording and experiment control system (see Fig. 1).

Sample 1 is placed in the focus of double optical furnace 2, which heats it to a temperature exceeding the melting point. Then the sample is quickly (for 20 sec) covered with integrating sphere 3, system 4 of synchronous suppression of optical furnaces actuates, and the sample is cooled at an initial rate of 2500 K/sec. Multichannel commutator 5 starts up the control and recording system, consisting of analog-to-digital converter 6, memory unit 7, processor 8, and printer 9, and thermograms of cooling of the sample are recorded with the aid of ten-wavelength pyrometer 10 within the spectral range 0.4-1.1 μm. The phase transition region of the sample recorded in the cooling thermograms is flashed by three lamps 11 positioned in the integrating sphere, which provides diffuse illumination of the sample through an outlet hole in sphere 12.

Light pulses reflected from the sample surface reach the optical system of the pyrometer through a hole in sphere 13 and tilting mirror 14.

The time interval between the flashes is provided by the multichannel commutator and may be regulated within wide limits.

The diameter of the area sighted by the pyrometer on the sample surface amounts to 1 mm at a distance of 1 m from the sample to the objective. The speed of pyrometer response is < 150 μsec; the range of the investigated temperatures is 1300-3000 K. The pyrometer was calibrated against standard temperature-calibrated lamps at a wavelength of 0.65 μm. Figure 2 is a three-dimensional representation of thermograms for 8 channels in the coordinates (L, λ, t), where L is the pyrometer signals, which are proportional to the luminance of the object; λ is the effective wavelength of the channel; t is the time from the moment of switching off the heater.

1.1. Determination of Reflection Coefficients. In measuring the spectral hemispherical-directional reflection coefficients, we have used reversibility property (1) and the relative method, according to which

$$\rho_\lambda(2\pi,\ \theta_r,\ \psi_r,\ T)=\frac{U^i_\lambda}{U^i_{6,\lambda}}\rho_{w,\lambda}(2\pi,\ \theta_r,\ \psi_r), \tag{2}$$

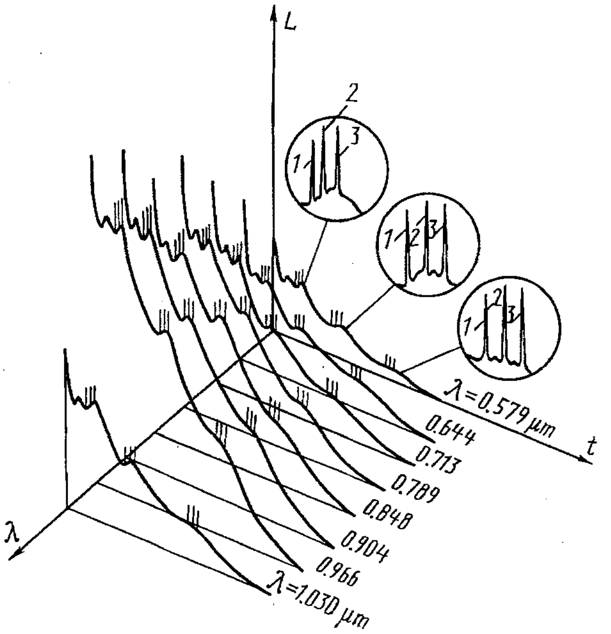

Fig. 2. Three-dimensional representation of the thermograms in the coordinates (L, λ, t): 1, 2, 3) numbers of the flash lamps connected in series. L, rel. units; λ, μm; t, msec.

where U_{λ}^{i}, $U_{w,\lambda}^{i}$ are the signals of the i-th photoreceiver for the sample and the standard; $\rho_{w\lambda}$ is the spectral reflection coefficient of the white standard. As the standard, we employed opal glass (the visible range) and fluoroplastic (the near IR range).

Diffuse illumination of the sample is ensured by optimal arrangement of the flash lamps in the integrating sphere coated with a 6-mm-thick compacted powder layer of fluoroplastic. Use of the fluoroplastic as a coating is due to the fact that according to the data of [6, 7] the compacted fluoroplastic possesses very good reflecting and scattering properties. As far as the coefficient of diffuse scattering, it exceeds all known well-reflecting coatings within the wavelength range 0.2-2.5 μm. To prevent direct incidence of the probing radiation on the sample, we used shutters.

1.2. Methodical Peculiar Features. On passing to the actual temperature, for determinating the spectral directional emissivity factor we used the Kirchhoff law, the opacity conditions for the sample surface, and the reversibility property:

$$\varepsilon_{\lambda}(\theta,\ \psi,\ T)=1-\rho_{\lambda}(\theta,\ \psi,\ 2\pi,\ T),\quad \rho_{\lambda}(\theta,\ \psi,\ 2\pi,\ T)=\rho_{\lambda}(2\pi,\ \theta,\ \psi,\ T),$$
$$T^{-1}-T_{\mathrm{b},\lambda}^{-1}=C_{2}^{-1}\lambda\ln\left[1-\rho_{\lambda}(2\pi,\ \theta,\ \psi,\ T)\right]. \tag{3}$$

The above relations are limited by (a) the hypothesis on local thermodynamic equilibrium and the assumption of the opacity condition for fulfilling the first and third relations; (b) the necessity of diffuse illumination of the surface for fulfilling the second relation.

Additional checking of these conditions led to the following conclusions:

1. The hypothesis on local thermodynamic equilibrium is entirely reasonable at the investigated cooling rates for the samples (2500 K/sec).

2. The degree of diffuse illumination of the samples is sufficiently high in the proposed method, and the observed deviations from the diffuse condition give a considerably smaller contribution to the total error as compared to other sources of methodical error. This is confirmed by the measured spectral reflection coefficients of materials with different modes of reflection of the tested surfaces (specular reflection in the case of polished aluminum and copper; diffuse reflection of freshly deposited magnesium oxide, fluoroplastic, and barium sulfide; combined specular-diffuse reflection of opal glass) and by their agreement with the available data on these materials within the limits of the adopted errors.

TABLE 1. High-Temperature Phase Transitions of Samarium Oxide

Reference	A $\rightleftarrows$ B	A $\rightleftarrows$ H	H $\rightleftarrows$ X	X $\rightleftarrows$ Melt
Foex, Traverse (1966) [11]	2103 K	2373 K	2523 K	2588 K
Lopato et al. (1974) [12]	2193 K	2403 K	2553 K	2613 K
Our data (1992)	2190±10 K	2275±10 K	2385±5 K	2440±5 K

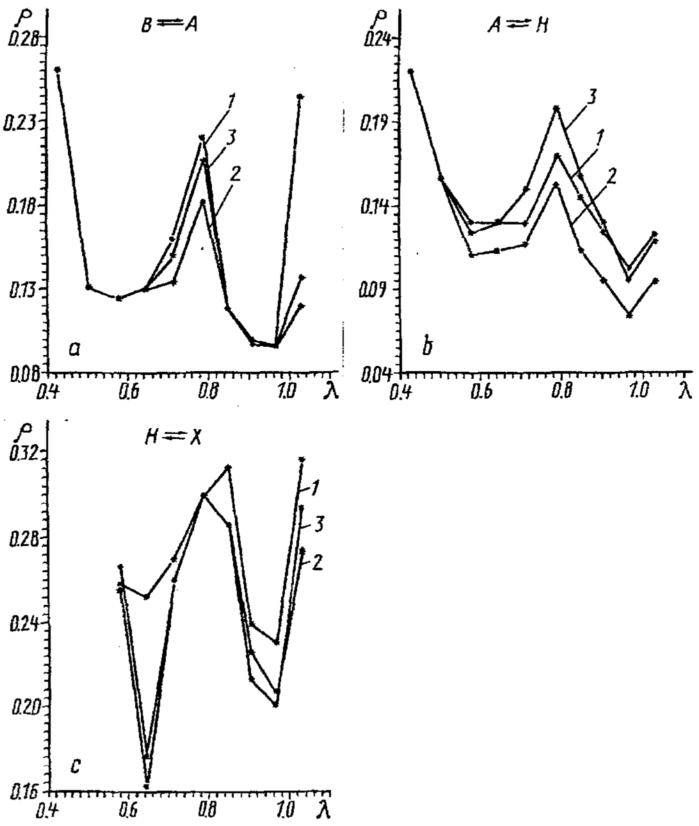

Fig. 3. Spectral dependence of the hemispherical-directional reflection coefficient of Sm_2O_3 in the region of high-temperature phase transitions: 1, 2, 3) sequence of flashes.

3. The opacity condition of the tested surface is the least well based assumption since its nonfulfillment may lead to considerable errors in determinating in the actual temperature of the sample. For instance, the opacity condition in the visible range is fulfilled not for all refractory oxides, especially if melt cooling is used. Despite this, in many investigations this method, in particular at a wavelength of 0.65 μm, is used in the open surface pyrometry [2, 3, 4]. But in our method the use of polychromatic illumination makes it possible to choose those wavelengths at which transparency of the samples is slight. For instance, for nonferrous rare-earth oxides it is desirable to use the opacity condition at those wavelengths that characterize the color of the investigated oxide.

1.3. Methodical Error. The main sources of errors in measurements of the spectral hemispherical-directional reflection coefficient by the proposed method are variations in the dimensions of the air gap between the outlet of the photometric sphere and the sample surface, which make the main contribution to the random component of the methodical error, as well as the uncertainty in the knowledge of the spectral reflection coefficient of the white standard, the error due to the presence of holes in the photometric sphere, and the deviation of the probing radiation from absolutely diffuse radiation, which make the main contribution to the systematic error of the method. Furthermore, in calculating the methodical error it is necessary to take into consideration additional error sources related to the accuracy of matching the reflection coefficients with the temperature and the wavelength.

Estimation of the enumerated contributions has shown that the total error of the method in measuring the spectral hemispherical-directional reflection coefficient in the investigated spectral (0.4-1.1 μm) and temperature (1300-2800 K) ranges does not exceed 2% at the confidence coefficient $P = 0.95$.

2. Preparation of Samples. As the subject of investigation, Sm_2O_3 was taken. The fraction of the main component in the tested material was not less than 99.9% of the total mass. From the powder, 10-mm-diameter tablets with a thickness of 4 mm were prepared using a cold compacting technique at the pressure $2 \cdot 10^8$ Pa. The tablets were placed in a focus of the optical furnace to make their surfaces reproducible. Then the system was calibrated and a run of ten check expriments was conducted in which the reproducibility of the experiment was evaluated, and the phase transition regions on thermograms were determined and then used for prescribing the control parameters of the experiment. It is worth noting that the suggested method requires utilization of high-purity samples (containing not more than 0.5% of foreign impurities) since in the case of oriented crystallization the impurities can gather at the center of the sample, to where a pyrometer is usually sighted, and lead to errors in measurements of the temperatures of phase changes. However these errors are avoided when pure samples are used.

3. Measurement Results. According to the literature data, samarium oxide undergoes three polymorphous transformations in the solid phase and a solid-liquid transition in a high-temperature region (>2000 K) [10, 11].

Table 1 lists the temperatures of the Sm_2O_3 phase transitions. Here A, B, H, X indicate hexagonal, monoclinic, cubic, and volume-centered cubic crystalline Sm_2O_3 modifications.

Figure 3 illustrates the spectral dependence of the reflection coefficient in the vicinity of the Sm_2O_3 phase transformations. It is established that at the point of a phase transition, regardless of the transition type, the reflection coefficient decreases within the entire spectral range investigated.

Use of polychromatic irradiation for probing purposes allows a large bulk of information to be obtained for accurately determining the temperatures of the phase transformations.

Good agreement of the actual temperatures calculated at the points of the phase transitions using the measured brightness temperatures and using the spectral emissivities at different wavelengths proves the reliability of the suggested method.

The results of measuring the spectral reflection coefficients in the vicinity of phase transformations of other refractory oxides will be reported in the next publications.

NOTATION

λ, effective wavelength; θ, polar angle of incidence; ψ, azimuthal angle of incidence; θ_r, polar angle of reflection; ψ_r, azimuthal angle of reflection; T, actual temperature, $T_{b,\lambda}$, brightness temperature; $\rho_{w,\lambda}$ spectral reflection coefficient of the standard; ε_λ, spectral emissivity of the sample; ρ_λ, spectral reflection coefficient.

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