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Melting Points, Spectral Reflectivity, and Emissivity of Semitransparent Ceramic Materials[1]

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A new method based on multiwavelength optical probing and multiwavelength pyroreflectometry of open sample surface to measure spectral optical properties of semitransparent ceramic materials at their melting points and to determine their true melting temperatures has been developed. With the method developed the spectral optical properties (reflectivity, emissivity, transmittance) of Nd_2O_3, Gd_2O_3, Er_2O_3, and Ho_2O_3 for seven wavelengths in the spectral range 0.4 to 1.1 μm at their melting points have been measured for the first time. It is shown that the method developed has a high precision in determining the true melting temperatures for semitransparent ceramic materials. In open surface pyrometry this method is used for the first time.

KEY WORDS: ceramics; emissivity; melting point; pyrometry; reflectivity; semitransparent materials.

1. INTRODUCTION

Some refractory oxide ceramics are related to the class of semitransparent volume scattering materials. In spite of the wide application of these materials in laser and solar technologies and advanced techniques, their thermal radiation properties at the melting point are poorly documented in the literature. This is due to the complexity of investigation of the semitransparent materials at high temperatures. The task becomes more difficult when advanced methods of measuring thermal radiation properties with single-side sample heating are used [1]. For example, in laser heating of some oxide ceramic materials their reflectivity and emissivity are not physical constants since due to the semitransparency of the oxides, these

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properties depend on the temperature distribution in surface layers and cannot be related to a definite temperature value [2].

Open surface pyrometry (without blackbody model) is often used to measure the temperature in these experiments. In this case the pyrometer is used to measure a temperature that is not the surface radiance temperature of the semitransparent sample due to the volume nature of its thermal emission. Therefore, the temperature measured by a pyrometer for semitransparent samples has been designated as the effective temperature [3]. So the authors [3] consider that a case-by-case approach must be made for every semitransparent ceramic sample, and the heating and measurement conditions must be considered on the same basis.

Our objective is to present a new method of measuring thermal radiation properties at the melting point of semitransparent ceramic materials and their true melting temperatures on the basis of open sample surface pyrometry. The method developed does not need an individual approach for every material being studied.

2. METHOD

2.1. Opaque Materials

In our earlier publication [4] a method for measuring spectral reflectivity and emissivity of opaque materials near their high-temperature phase transformations was developed and described in detail. Here, we propose to extend the capabilities of the method for measuring thermal radiation properties of semitransparent ceramic materials at their melting points. A description of the method is as follows (see Fig. 1).

The sample placed at the focal zone of an imaging furnace is heated to temperatures above its melting point. Then the sample is rapidly covered by the integrating sphere and the sample is allowed to cool. A multichannel commutator starts the recording system and turns on the flash-lamps at desired times. The flash-lamps placed into an integrating sphere produce a diffuse irradiation of the cooling sample at the moment of the phase transition of interest through the lower aperture in the sphere wall.

The phase transition is manifested by a peak in the radiance temperature-versus-time function at different wavelengths and by a plateau in the true temperature-versus-time function (Fig. 2). The peak is probed by the pulse light of the flash-lamps. The reflected portions of the polychromatic light incident on the sample and temperature signals are measured by means of a multiwavelength high speed micropyrometer that operates in the spectral range 0.4 to 1.1 μm. If the opacity assumption holds for the sample surface, then the method enables one to measure spectral reflectivity

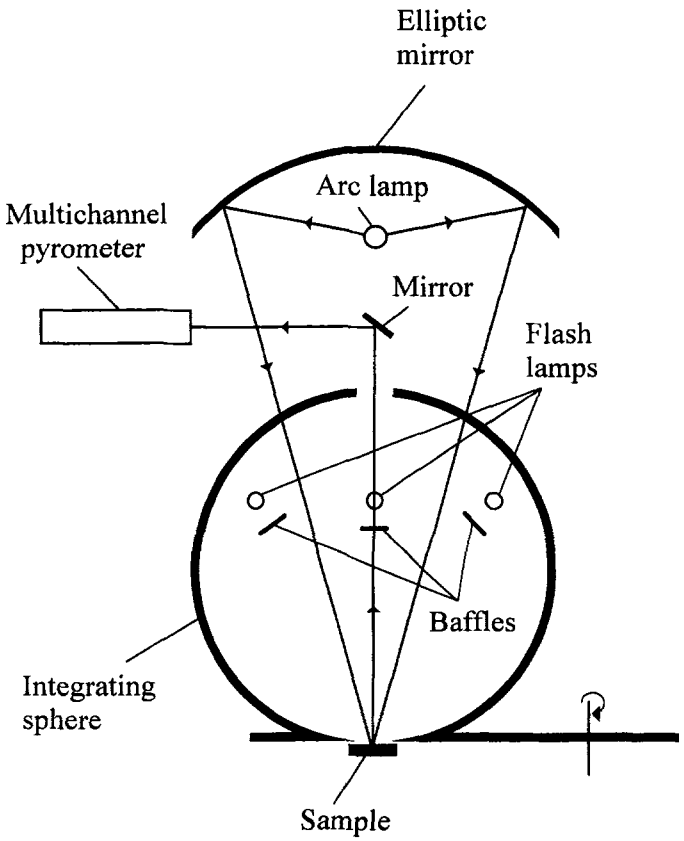

Fig. 1. Schematic diagram of the experimental setup.

and emissivity of refractory materials at their high-temperature phase transitions including melting.

2.2. Semitransparent Materials

In order to extend the capabilities of the method to semitransparent materials, we do not make the assumption that the sample surface is opaque for all wavelengths. Multiwavelength pulse light probing the sample surface heated by a concentrated light flux with simultaneous application of multiwavelength pyroreflectometry enables one to measure the spectral reflectivity, emissivity, and radiance temperature at different wavelengths. Then the true temperature of the sample surface is calculated.

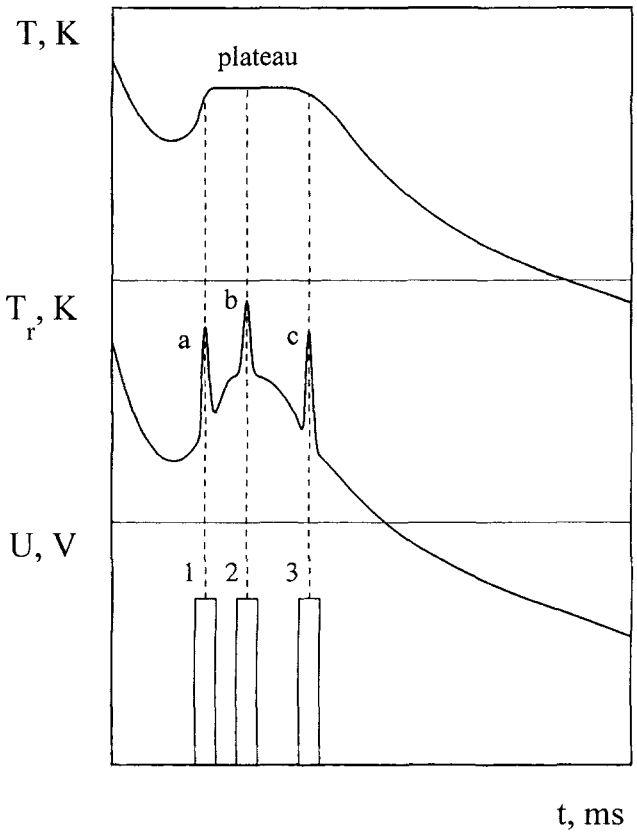

Fig. 2. Typical behavior of radiance T_r and true temperature T-versus-time function during sample cooling near the phase transition point. (1)–(3) Master pulses to start flash-lamps; (a)–(c) the reflected portions of the pulse light of flash-lamps incident on the sample at different times near the phase transition.

At the phase transition point all the N true temperatures have equal values if the sample surface is opaque (here N is the number of pyrometer channels). If the sample is semitransparent, then the true temperatures determined with opaque surface assumption at N wavelengths have different values and it is a very difficult task to obtain the melting temperature.

We have found that the effective temperatures at the melting point of the semitransparent ceramics increase with wavelength from 0.4 to 1.1 μm. This means that absorptance increases with increasing wavelength. If the opaque surface assumption holds for the wavelengths of 0.848, 0.904, and 0.966 μm, the calculation of true temperature gives the same values for the

melting point of the semitransparent ceramic material. Thus, the measured spectral range 0.4 to 1.1 μm is divided into the opaque and transparent regions. We can write the following equations for the transparent region:

$$\rho_\lambda^* + \tau_\lambda^* + \varepsilon_\lambda^* = 1 \tag{1}$$

$$T^{-1} - T_{\mathrm{ef},i}^{-1} = \lambda_i C_2^{-1} \ln[1 - \rho_{\lambda,i}^* - \tau_{\lambda,i}^*], \qquad i = 1, 2, \ldots, k \tag{2}$$

For the opaque region,

$$\rho_\lambda + \varepsilon_\lambda = 1 \tag{3}$$

$$T^{-1} - T_{\mathrm{r},j}^{-1} = \lambda_j C_2^{-1} \ln[1 - \rho_{\lambda,j}], \qquad j = k+1, \ldots, N \tag{4}$$

In the above equations, k is the number of channels in the transparent region, $\rho_{\lambda,i}^*$ is the effective spectral directional-hemispherical reflectance at the ith channel for the semitransparent sample, $\tau_{\lambda,i}^*$ is the effective spectral directional hemispherical transmittance, ε_λ^* is the effective spectral directional emittance, ε_λ is the spectral directional emissivity, $T_{\mathrm{ef},i}$ is the effective temperature of the semitransparent sample, T is the true sample surface temperature, λ_i is the wavelength at the ith channel of a multiwavelength pyrometer, $\rho_{\lambda,j}$ is the spectral directional-hemispherical reflectivity of the sample at the jth channel, $T_{\mathrm{r},j}$ is the radiance temperature of the sample surface at the jth channel, and C_2 is the second constant in Planck's distribution.

Multiwavelength optical probing of the sample surface and using a multiwavelength pyrometer for temperature and reflectivity measurements at different wavelengths give sufficient information for solving these equations. Here $T_{\mathrm{ef},i}$, $\rho_{\lambda,i}^*$ $(i = 1, 2, \ldots, k)$ and $\rho_{\lambda,j}$, $T_{\mathrm{r},j}$ $(j = k+1, \ldots, N)$ are measured, and T and $\tau_{\lambda,i}^*$ are determined from this set of equations.

3. RESULTS

The materials used in this investigation were Nd_2O_3, Er_2O_3, Gd_2O_3, and Ho_2O_3. The purity of each of these oxides was greater than 99.95%. Reflectivity and emissivity measurements were performed in the liquid state of these materials at their melting points. Sources of uncertainty in reflectivity and emissivity measurements were presented in our earlier publication [4]. The overall uncertainty in spectral optical properties measured by this method does not exceed $\pm 2\%$. The uncertainty in determining the true melting temperatures is not more than ± 10 K.

Measured spectral optical properties for Nd_2O_3 at its melting point are summarized in Table I. It is shown that Nd_2O_3 is transparent at 0.579

Table I. Measured Spectral Optical Properties of Nd_2O_3 at Its Melting Point ($T_m = 2564 \pm 10$ K)

	λ (μm)						
	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.25	0.25	0.20	0.18	0.18	0.16	0.14
$\tau(\lambda)$	0.31	0.29	0	0	0	0	0
$\varepsilon(\lambda)$	0.44	0.46	0.80	0.82	0.82	0.84	0.86
T_r (K)	2365	2352	2480	2497	2489	2493	2497
T_m (K)	2565	2561	2567	2567	2563	2563	2562

Table II. Measured Spectral Optical Properties of Gd_2O_3 at Its Melting Point ($T_m = 2666 \pm 10$ K)

	λ (μm)						
	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.196	0.200	0.192	0.220	0.126	0.120	0.100
$\tau(\lambda)$	0.351	0.317	0.068	0	0	0	0
$\varepsilon(\lambda)$	0.453	0.483	0.740	0.780	0.874	0.880	0.900
T_r (K)	2457	2453	2565	2572	2605	2610	2620
T_m (K)	2666	2666	2667	2665	2660	2666	2669

Table III. Measured Spectral Optical Properties of Er_2O_3 at Its Melting Point ($T_m = 2686 \pm 10$ K)

	λ (μm)						
	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.190	0.190	0.187	0.185	0.166	0.132	0.130
$\tau(\lambda)$	0.410	0.395	0.093	0.055	0	0	0
$\varepsilon(\lambda)$	0.400	0.415	0.720	0.760	0.834	0.868	0.870
T_r (K)	2445	2430	2573	2582	2617	2620	2620
T_m (K)	2687	2687	2685	2686	2692	2682	2685

Table IV. Measured Spectral Optical Properties of Ho_2O_3 at Its Melting Point ($T_m = 2664 \pm 10$ K)

	λ (μm)						
	0.579	0.644	0.713	0.789	0.848	0.904	0.966
$\rho(\lambda)$	0.220	0.220	0.220	0.219	0.210	0.180	0.150
$\tau(\lambda)$	0.390	0.370	0.120	0.026	0	0	0
$\varepsilon(\lambda)$	0.390	0.410	0.660	0.755	0.790	0.820	0.850
T_r (K)	2419	2409	2525	2560	2572	2575	2590
T_m (K)	2663	2665	2663	2665	2667	2660	2665

and 0.644 μm and opaque from 0.713 to 0.966 μm. Spectral optical properties of Gd_2O_3 at its melting point are presented in Table II. Here the transparent region is widened to 0.713 μm and the opaque region covers 0.789 to 0.966 μm. Measured spectral optical properties for Er_2O_3 and Ho_2O_3 at their melting points are given in Tables III and IV, respectively. In all the tables, the true melting temperatures are calculated for different wavelengths and the recommended melting temperatures (T_m) are given. The data on spectral optical properties of these oxides that account for their semitransparency at the melting point have been obtained for the first time.

4. DISCUSSION

To estimate the reliability of the method developed, the true melting temperatures of the oxides determined from this study are compared with available literature data. Comparisons are given in Table V. It is shown that our results for the melting temperatures of the ceramics investigated are in good agreement with the results of Foex [5] and Lopato et al. [6]. The values of the melting temperatures for all these refractory oxides obtained by Noguchi and Mizuno [7] are much lower than those obtained by other investigators. Noguchi and Mizuno measured melting temperatures on the open sample surface heated at the focal zone of a solar furnace. In order to determine the true melting temperature, they measured simultaneously the radiance temperature and spectral reflectivity at 0.65 μm. To obtain the spectral emissivity, Noguchi and Mizuno used the opaque surface assumption at 0.65 μm. As mentioned above (Tables I to IV), this assumption does not hold at 0.65 μm for these oxide ceramic materials at their melting points. Noguchi and Mizuno measured only the specular component of the reflectivity at the melting point instead of the directional-hemispherical reflectivity. These incorrect assumptions of the experiment led to the lower values of the melting temperatures.

Table V. Melting Temperatures (K) of Semitransparent Ceramics from the Literature

Reference	Nd_2O_3	Gd_2O_3	Er_2O_3	Ho_2O_3	Note
Foex (1965) [5]	2583 ± 10	2668 ± 10	2673 ± 10	2669 ± 10	An absolute blackbody model was used
Noguchi and Mizuno (1967) [7]	2506 ± 20	2603 ± 20	2617 ± 20	2603 ± 20	Open surface; only the specular component of reflectivity for an opaque body was measured
Lopato et al. (1974) [6]	2593 ± 25	2653 ± 25	2663 ± 25	2663 ± 25	An absolute blackbody model was used
Bober et al. (1980) [2]	2540 ± 25	—	—	—	Open surface; the diffuse component of reflectivity for an opaque body was measured
Present work	2564 ± 10	2666 ± 10	2686 ± 10	2664 ± 10	Open surface; the semitransparent nature of these materials was taken into account for the first time

Bober et al. [1] measured the melting temperature for Nd_2O_3 with an integrating-sphere laser reflectometer. They used the opaque surface assumption at 0.63 μm for an open sample surface (flat disk) at the melting point of Nd_2O_3. It can be seen from Table I that Nd_2O_3 is transparent up to 0.644 μm, so the opaque surface assumption at 0.63 μm accepted in Ref. 1 breaks down for Nd_2O_3 at its melting point.

As mentioned above the agreement of our results with the values obtained by Foex [5] and by Lopato et al. [6] is very good, although our method differs from theirs. Both Foex [5] and Lopato et al. [6] used the model of an absolute blackbody in a solar furnace to measure the melting temperatures of these refractory oxides. Measurements were performed on a thick melt layer occurring inside the rotating blackbody. Such experimental conditions enable one to create the optical thick layer of the melt and to measure properly the true melting temperatures of these semitransparent materials. Comparisons of our results with the results obtained by quite different methods confirm the reliability of our method developed for measuring spectral optical properties of semitransparent ceramic materials at their melting points.

5. CONCLUSION

A new method based on multiwavelength optical probing and multiwavelength pyroreflectometry of an open sample surface to measure the

spectral optical properties of semitransparent ceramic materials at their melting points and to determine their true melting temperatures has been developed. The main features of this method are as follows: (a) diffuse multiwavelength probing the open sample surface at the melting point with the use of a multiwavelength pyroreflectometer for simultaneous reflectivity and temperature measurements at different wavelengths; (b) finding the transparent and opaque regions for each semitransparent material at its melting point; and (c) determining the spectral optical properties and true temperatures at different wavelengths at the melting point for semitransparent materials. Spectral optical properties (reflectivity, emissivity, transmittance) of Nd_2O_3, Gd_2O_3, Er_2O_3, and Ho_2O_3 for seven wavelengths in the spectral range 0.4 to 1.1 μm at their melting points have been measured for the first time.

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