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Radiative Properties of Uranium Dioxide Near Its Melting Point[1]

T. P. Salikhov,[2,3] V. V. Kan,[2] and C. Ronchi[4]

A new technique for measuring radiative properties of nuclear fuel materials at high temperatures has been developed. The technique is based on pulse diffuse optical probing of the sample surface and on pyroreflectometry used in measuring radiative properties of refractory materials during laser heating or cooling. Pulse diffuse optical probing of the sample has been realized for the first time in subsecond pyrometry of the open surface heated by laser radiation. Such a procedure of sample irradiation during sample laser heating or cooling enables reflectivity and emissivity measurements near high temperature phase transitions to be performed in spite of possible sharp changes of the reflection indicatrix at phase transitions in the investigated material. With the method developed in this study, the spectral emissivity and reflectivity of uranium dioxide near its premelting and melting points have been measured. It has been found that condensation of the vapor plume formed above the sample during laser heating influenced the melting and boiling temperatures of uranium dioxide. The first-order phase transitions in uranium dioxide, such as solid–vapor–solid and liquid–vapor–liquid, have been observed in uranium dioxide for the first time during laser heating. Also, new data on the spectral emissivity of uranium dioxide at a wavelength of 0.644 μm and in the temperature range of 2000 to 4200 K are presented.

KEY WORDS: emissivity; laser heating; melting; pyrometry; spectral reflectivity; uranium dioxide.

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[2] Physical Technical Institute, Mavlyanova 2B, 700084 Tashkent, Uzbekistan.

[3] To whom correspondence should be addressed.

[4] European Commission, Joint Research Centre, European Institute for Transuranium Elements, Postfach 2340, D-76010 Karlsruhe, Germany.

1. INTRODUCTION

Melting in uranium dioxide is a very complicated phenomenon. There is not sufficient clarity in understanding this matter up to now. On the other hand, radiative properties of materials are very sensitive to structural transformations in materials. Thus, investigations of the radiative properties of uranium dioxide in the neighborhood of its melting point and the study of the kinetics of radiative properties during melting could provide an understanding of the physical mechanism of this interesting phenomenon. The objective of this work is to investigate the behavior of the radiative properties of uranium dioxide near its melting point and other transformations occurring in uranium dioxide at high temperatures. This task is very complicated since a sharp change in the surface reflection indicatrix takes place at the melting point of refractory materials. Most of the traditional methods for radiative property measurements at high temperatures are based on reflectometry. However, they can be applied only to materials with a fixed reference surface (diffuse or specular reflection surface) and do not take into account possible changes in the reflection indicatrix during heating, cooling, or phase transitions. Therefore, a new method based on a subsecond optical technique for measuring the radiative properties of refractory materials near their phase transitions and at very high temperatures has been developed.

2. EXPERIMENTAL METHOD

The experimental setup is shown in Fig. 1. A flat sample is located in the center of an integrating sphere of 180-mm diameter. The internal sphere wall is coated with 6-mm porous fluorocarbon, which has ideal reflection and diffuse properties in the 0.3- to 2.5-μm range (according to data of Eckerle et al. [1]). The sphere is provided with two holes, for the powerful laser beam input and for the detection of the sample radiance, by means of a high-speed pyrometer operating at a wavelength of 0.644 μm. The hermetic sphere can support internal pressures of inert gas up to 4 bar to reduce sample evaporation at high temperatures.

By means of a focused CO_2 laser beam of 1000-W power, the sample can be heated to temperatures above 4000 K over a period of 10 to 200 ms. The baffles placed near the sample divide the sphere into upper and lower parts. In the upper part are located three pulse flash lamps provided with high-voltage power supplies, whose light produces an almost perfectly diffuse irradiation of the sample surface. The reflectivity of the sample, heated by the CO_2 laser radiation, is probed by the pulse radiation of the flash lamps. The light of one flash lamp, after multiple reflection in the sphere,

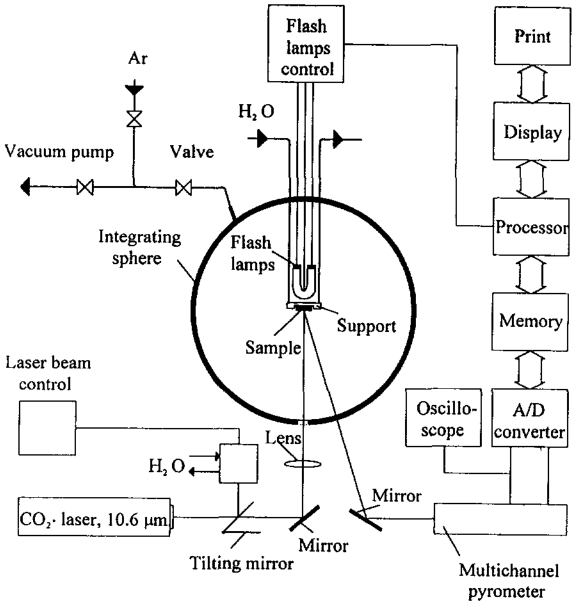


Fig. 1. Experimental setup.

produces a diffuse irradiation of the heated sample surface, while the radiation reflected from the sample surface is recorded by a high-speed pyrometer. The pulse reflection signals, in excess of the background of the thermal radiation of the sample, are used to calculate the spectral hemispherical directional reflectivity according to the expression

$$\rho_\lambda(2\pi, \Theta, \varphi, T) = \frac{U_i}{U_{s,i}} \rho_{s,\lambda} \tag{1}$$

where U_i and $U_{s,i}$ are, respectively, the pulse signals from the pyrometer for the sample and for the standard; $\rho_{s,\lambda}$ is the spectral reflectivity of a standard with well-known reflectivity; and Θ and φ are, respectively, the radial and azimuthal angles determined by the direction of observation of the sample radiance.

To obtain the spectral directional hemispherical reflectivity, Helmholtz's reciprocity principle is used in the following form:

$$\rho_\lambda(2\pi, \Theta, \varphi, T) = \rho_\lambda(\Theta, \varphi, 2\pi, T) \tag{2}$$

which is valid for the case of diffuse irradiation of the sample surface.

The spectral directional emissivity is determined from Kirchhoff's law (for opaque surfaces),

$$\varepsilon_\lambda(\Theta, \varphi, T) = 1 - \rho_\lambda(\Theta, \varphi, 2\pi, T) \tag{3}$$

This expression is valid under laser heating conditions if local thermal equilibrium is effectively present.

It should be noted that a pyrometer provides detection of not only the pulse reflection signals but also the radiance temperature of the sample surface at the same wavelength. Therefore, in the determination of the true temperature of the sample surface, direct information on the real emissivity can be used, enabling high accuracy of the true temperature to be obtained from the equation

$$T^{-1} - T_r^{-1} = \lambda C_2^{-1} \ln[1 - \rho_\lambda(2\pi, \Theta, \varphi, T)] \tag{4}$$

where C_2 is the second Planck's radiation constant; T_r and T are, respectively, the radiance and true temperatures; and λ is the wavelength.

The pulse diffuse optical probing of a sample surface heated by a powerful laser beam for reflectivity measurements at high temperatures has been realized for the first time in application of a subsecond optical technique. Such a procedure of sample irradiation during sample laser heating or cooling enables reflectivity and emissivity measurements near high-temperature phase transitions to be performed in spite of possible sharp changes of the reflection indicatrix at phase transitions in the investigated material. Also, the technique permits observations of the kinetics of the reflectivity and emissivity behavior during phase transitions in high temperature materials.

3. RESULTS

The samples of UO_2 (with ^{235}U-depleted uranium) were obtained from the Institute for Transuranium Elements, Karlsruhe, Germany, in the form of sintered pellets of 97% theoretical density. A disk of 9-mm diameter and 2-mm thickness was placed in the center of an integrating sphere of 180 mm diameter with high diffuse reflectance. After initial evacuation of the sphere, a valve was opened, and the sphere was filled with pure inert gas (argon) at a pressure of 2.5 bar. Then, with a focused CO_2 laser beam (10.6 μm), the sample was heated to approximately 3000 K. The heated surface area was 1 mm in diameter. Heating continued until the input power was balanced by the total heat losses; at this stage, the laser was switched off. The cooling curve was recorded by a high speed micropyrometer at a wavelength of

0.644 μm. The viewing spot of the pyrometer on the sample surface was 0.5 mm.

The calibration of the pyrometer has been performed with a tungsten band lamp at 0.644 μm. The pyrometer was designed in such a way that its analogue and logarithmic converter yielded an output signal which, in accordance with Wien's law, was linear in temperature. Therefore, the calibration procedure could be carried out with the two-point method up to 4500 K. After calibration, the absolute values of the output signal of the pyrometer became equal to the values of the radiance temperature.

Measurements of the spectral optical properties of uranium dioxide have been made during the cooling stage. Pulse diffuse probing was performed by flash lamps placed in the integrating sphere and switched on at various temperatures. The time intervals between the operation of flash lamps and the time delay of the start of the first lamp after the laser was turned off were fixed with a multichannel commutator.

In order to obtain reliable experimental data on spectral optical properties, reproducible cooling curves had first to be obtained. Yet numerous experiments have shown that several factors may influence the results. For example, two radiance peaks were found on the cooling curve if the starting temperature (i.e., the maximum temperature achieved when the laser is switched off) was above 3100 K and there was only one peak if the starting temperature was below 3100 K. The temperatures of both peaks change depending on the pressure of the gas, the gas composition, the starting temperature, and the residence time of the sample at the starting temperature. Furthermore, the form of the cooling curve and of the reflectivity peaks depends on other factors such as sample size, heated area, temperature gradients, etc. All of these parameters had to be optimized and kept constant in order to perform an effective analysis of the data. The experiments have been performed under the following experimental conditions: for all the experiments, the heated area on the sample surface was approximately 1 mm in diameter and the inert gas was pure argon at either 2.5 or 3.5 bar. The starting temperature was a variable parameter of the experiment.

Figure 2 shows the cooling curves as a function of the starting temperature that was varied from 3070 to 3330 K (here it is a radiance temperature). Two radiance peaks were found on the cooling curves at temperatures that increased with increasing starting temperature, while the temperature of the second peak increased more rapidly than the first one. For a starting temperature of approximately 3330 K, the two peaks merge together, and this behavior is no longer affected by the starting temperature.

The method of this study can be used to carry out accurate measurements of spectral reflectivity and emissivity during this transition. Figure 3

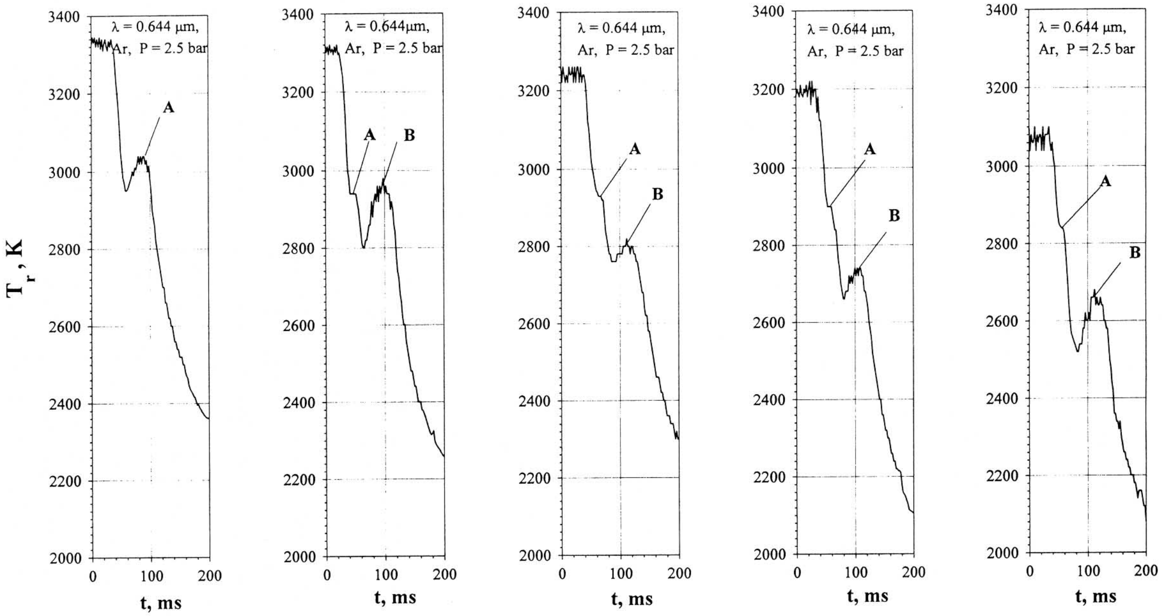


Fig. 2. Cooling curves of sample initially heated to different starting temperatures. Cooling curves are presented as time dependence of radiance temperature at $\lambda = 0.644\ \mu$m. (A) Melting; (B) premelting transition.

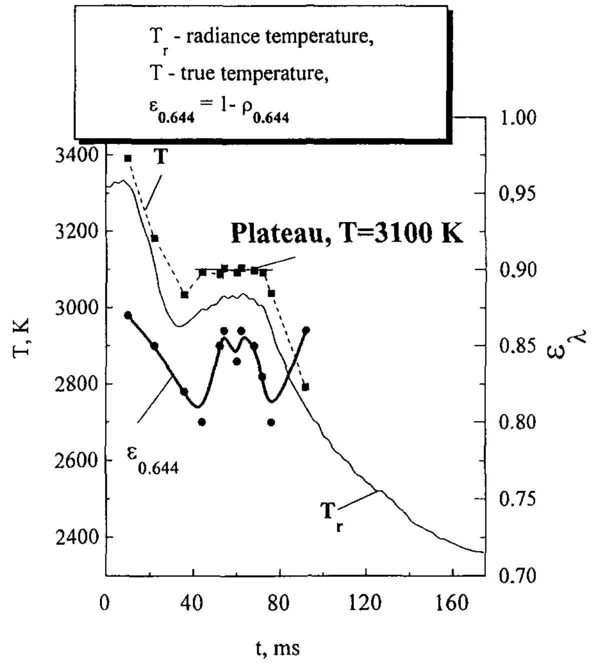


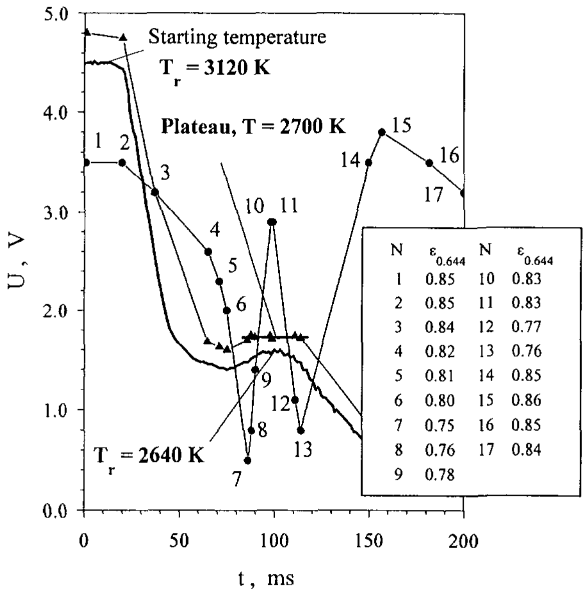
Fig. 3. Spectral emissivity ε_λ and radiance temperature T_r at a wavelength of 0.644 μm and the true temperature T in the vicinity of the melting point of stoichiometric uranium dioxide as a function of time.

shows the behavior of the spectral reflectivity and emissivity at 0.644 μm in the process of this transformation. The complicated form of these curves reveals the kinetics of this transition. Interestingly, it is found that the calculation of the true temperature from the data of radiance temperature and spectral emissivity near the transition gives the plateau on the true temperature curve as a function of time. The plateau temperature corresponds to a value of 3100 ± 20 K. From literature data [2, 3], the melting point of stoichiometric uranium dioxide is in the range 3110 to 3140 K; therefore, this peak is likely produced by the liquid–solid transition in stoichiometric uranium dioxide.

Concerning the second peak on the cooling curves, it is to be noted that a class of diatomic compounds which crystallize in the face-centered cubic fluorite lattice exhibit a premelting transition near $0.85T_m$. The existence of such a transition in UO_2 was first qualitatively predicted by Bredig [4] in 1969 and experimentally confirmed by Ronchi et al. [5] in 1993. This transition was observed at 2670 K [5] in stoichiometric UO_2, while in hypostoichiometric uranium dioxide (UO_{2-x}), the premelting transition was observed at a temperature increasing with x up to a maximum of 2950 K. On the other hand, no such transition was detected in hyperstoichiometric uranium dioxide (UO_{2+x}).

Figure 4 shows the measurements of spectral reflectivity and emissivity at $\lambda = 0.644\,\mu m$ near the second phase transition for a starting temperature of 3120 K. The cooling curve corresponding to these experiments is also shown. In spite of the complex form of the time dependence of the spectral reflectivity and emissivity near the second phase transition, some interesting results have been obtained. Careful measurements of the spectral reflectivity and emissivity near the second phase transition enable one to plot the dependence of the true temperature on time. It can be seen that the time dependence of the true temperature has a plateau with characteristic features of a first-order phase transition. The average temperature of the plateau is 2700 K, and this value of the transition temperature is in agreement with that measured by Ronchi et al. [5] for the stoichiometric uranium dioxide.

From reflectivity and emissivity measurements near other peaks on the cooling curves at different starting temperatures, the true temperatures of



N	$\varepsilon_{0.644}$	N	$\varepsilon_{0.644}$
1	0.85	10	0.83
2	0.85	11	0.83
3	0.84	12	0.77
4	0.82	13	0.76
5	0.81	14	0.85
6	0.80	15	0.86
7	0.75	16	0.85
8	0.76	17	0.84
9	0.78		

Fig. 4. Spectral emissivity ε_λ and radiance temperature T_r at a wavelength of $0.644\,\mu m$ and the true temperature T near the premelting transition of UO_2 as a function of time.

these transitions can be determined and a diagram of "moving" melting and premelting points is shown as a function of the starting temperature in Fig. 5. It can be seen that the positions of these points depend on the starting temperature, and the premelting point "moves" more rapidly than the melting point in increasing the starting temperature. The "meeting" of these points occurs at a temperature of 3100 K, which, as mentioned above, is in agreement with the melting temperature of uranium dioxide reported in the literature. Thus, a premelting phenomenon is observed in uranium dioxide under certain experimental conditions. In these cases, the premelting transition decreases the melting temperature of uranium dioxide and influences the melting process. In the present work, the premelting phenomenon was observed in the temperature range of 2700 to 3100 K in an atmosphere of inert gas (argon) at a pressure of 2.5 bar. In another study [5] the premelting transition in uranium dioxide was observed in an atmosphere of inert gas (argon, helium) and in a reducing environment (inert gas +3% hydrogen) at pressures of 2, 25, 40, 50, 75, and 100 bar over the temperature range of 2670 to 2950 K. Also, the premelting transition was detected in thorium

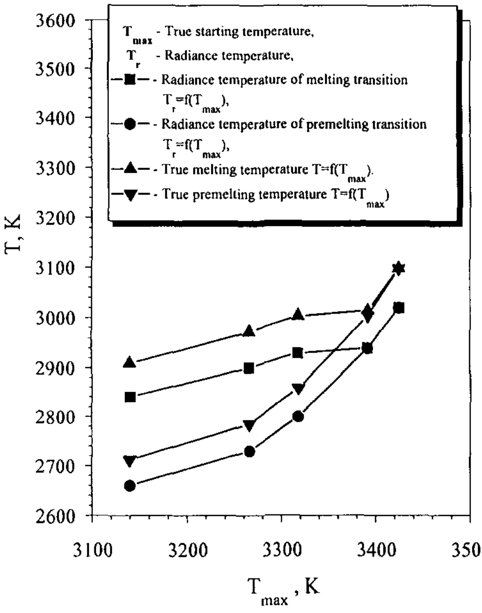


Fig. 5. Melting and premelting temperatures of UO_2 as a function of starting temperature. The true temperatures of melting and premelting points were calculated from the data on radiance temperature and spectral emissivity at these points.

dioxide at 25-bar argon and 25-bar oxygen atmospheres [6]. Thus, the premelting transitions in uranium and thorium dioxides were observed at various experimental conditions. It is important to understand the nature of this physical phenomenon.

As mentioned above, the experimental parameter that influenced the temperature of this transition has been determined. This parameter is the starting temperature (the maximum temperature of the sample at a given laser power density). On increasing the starting temperature, the premelting point "moves" on the temperature scale from 2700 K to the melting point of uranium dioxide (Fig. 5). The starting temperature was increased to the boiling temperature of uranium dioxide at 3.5 bar. An unexpected result was obtained. Figure 6 shows the cooling curves at a wavelength of 0.644 μm on increasing the starting temperature to 3500 K (radiance temperature) at a pressure of 3.5 bar. It can be seen that, in this case, there are two peaks again on the cooling curve; the first one is large and the second is small. Reflectivity and emissivity measurements enabled true temperatures of these transitions to be determined. Using the data on spectral reflectivity and emissivity measured in the vicinity of these transitions, one

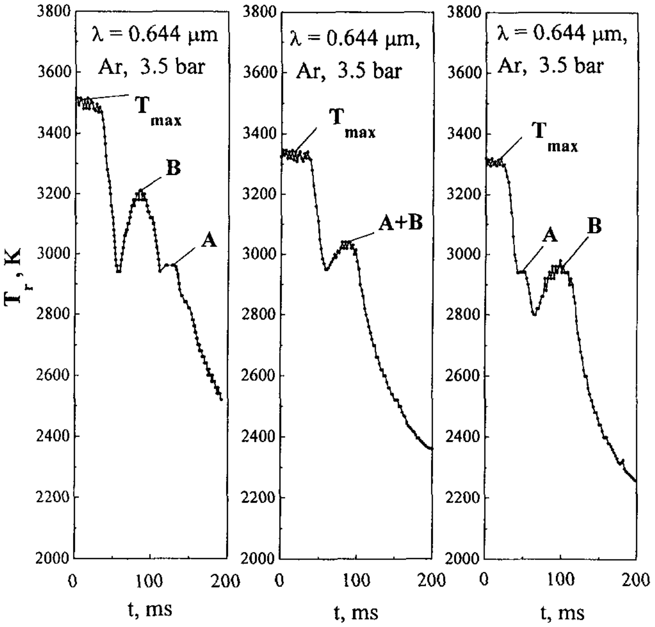


Fig. 6. Phase transformations in uranium dioxide on cooling curves at different radiance starting temperatures. (A) Melting; (B) premelting transition.

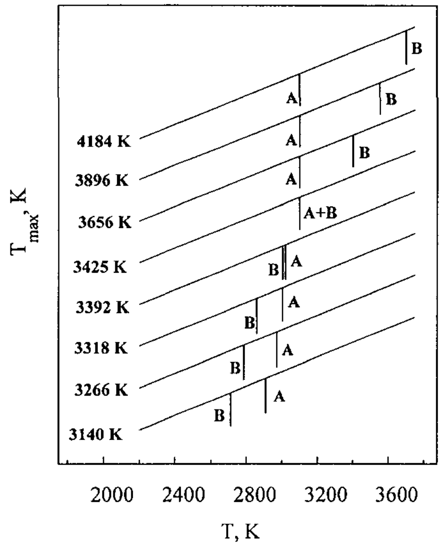


Fig. 7. The positions of melting and premelting points of uranium dioxide on the temperature scale at different true starting temperatures. The true temperatures of melting and premelting points were calculated from the data on radiance temperature and spectral emissivity at these points. T_{max}, true starting temperature; T, true temperature. (A) Melting; (B) premelting transition.

can plot the diagram of "movement" of these transformation points with increasing the starting temperature on the true temperatures scale (Fig. 7). It can be seen that the position of one of the transformation points is at a constant temperature of 3100 K independent of increases in the starting temperature, while the second point approaches the boiling temperature of uranium dioxide at a pressure of 3.5 bar (see Fig. 8). The boiling temperature of uranium dioxide at a pressure of 3.5 bar is about 4200 K [7].

Hence, the transformation point that is constant at 3100 K with increases in the starting temperature is the melting point of uranium dioxide. The temperature of the second transition depends on the starting temperature and approaches the boiling temperature of uranium dioxide at a given pressure. Also, in Fig. 6, it is observed that the transformation energy of this transition is larger than the heat of melting. On the basis of these observations, it is concluded that the nature of this transition is connected with the vapor phase of uranium dioxide.

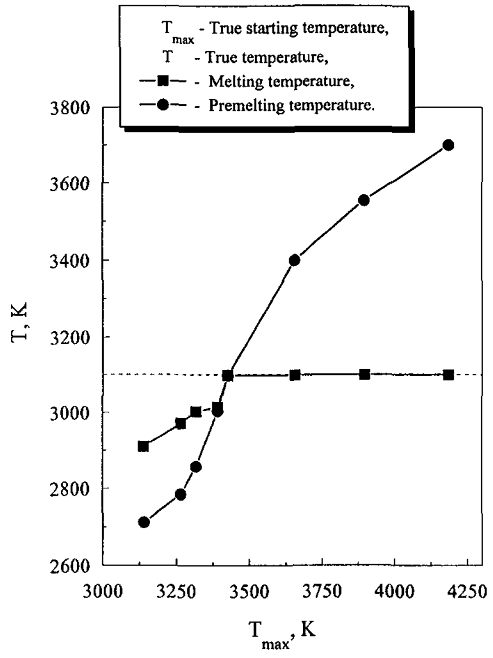


Fig. 8. Phase transition temperatures of UO_2 as a function of true starting temperature. The true temperatures of melting and premelting points were calculated from the data on radiance temperature and spectral emissivity at these points. T_{max}, true starting temperature.

Figure 9 shows the spectral emissivity of uranium dioxide at a wavelength of 0.644 μm and at pressures of 2.5 and 3.5 bar. It can be seen that the emissivity at 3.5 bar is lower over the investigated temperature interval than that at 2.5 bar. This effect is likely related to an increase of the specular component of the spectral reflectivity due to high temperature condensation of the vapor plume above the sample at a pressure of 3.5 bar.

4. SUMMARY

A new method for measuring the radiative properties of refractory materials near their high temperature phase transitions has been developed. The pulse diffuse optical probing of the sample to measure radiative properties of materials at high temperatures using a high-power laser beam was realized in a subsecond optical experiment for the first time. This

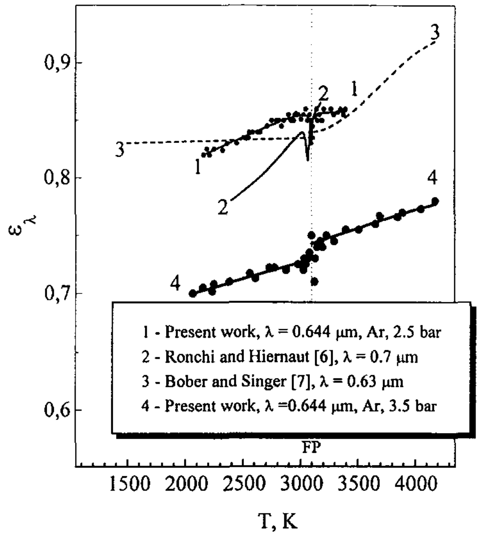


Fig. 9. Spectral emissivity of uranium dioxide as a function of temperature for a wavelength of 0.644 μm and for pressures of 2.5 and 3.5 bar. FP, freezing point.

procedure can be used to perform reflectivity and emissivity measurements near high temperature phase transitions in refractory materials with high precision in spite of significant changes in the reflection indicatrix during phase transitions.

Measurements of the spectral reflectivity and emissivity of uranium dioxide in the temperature interval of 2000 to 4200 K at a wavelength of 0.644 μm and at pressures of 2.5 and 3.5 bar have been performed. Two phase transitions in uranium dioxide in the temperature range investigated have been detected. Reflectivity and emissivity measurements near these transitions enabled the true temperatures to be obtained. These measurements enhance the understanding of the nature of these transitions in uranium dioxide. The experimental conditions under which the melting and premelting transitions occurred in uranium dioxide have been established. The second transition detected in the solid phase as a premelting transition was observed in the liquid phase of uranium dioxide as a threshold liquid–liquid transition. It was interesting that the temperature of this transition approached the boiling temperature of uranium dioxide at a given pressure on increasing the sample heating or cooling rate. On the basis of the experimental results, the following observations can be made.

(1) The vapor plume formed above the sample of uranium dioxide during laser heating influenced the melting and boiling of uranium dioxide under laser heating conditions.

(2) The condensation of the vapor plume in solid uranium dioxide was observed on the cooling curves as a premelting transition. This threshold transition is likely accompanied with a disorder in the fluorite structure of uranium dioxide before melting (according to the measurements, this transition is a first-order transition).

(3) The condensation of the vapor plume above the sample in the liquid state of uranium dioxide below its boiling temperature has been observed on the cooling curves for the first time. Such liquid–vapor–liquid transitions can be considered as a preboiling transition in uranium dioxide.

(4) The true temperatures of the premelting and preboiling transitions in uranium dioxide depend on the sample heating or its cooling rate. On increasing the heating rate, the preboiling temperature increases to approach the boiling temperature of uranium dioxide at a given pressure. The premelting and preboiling transitions in uranium dioxide have the same nature in relation to the threshold transformation of the vapor plume above the sample under laser heating conditions.

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